AADE-18-FTCE-034

Lab-Scale Real-Time Mud pH and EC Monitoring System while Drilling in Hydrogen Sulfide Formations

Ethar H. K. Alkamil, Missouri University of S&T, University of Basrah; Ahmed K. Abbas, Iraqi Drilling Company, Missouri University of S&T; Ralph Flori, Missouri University of S&T

Abstract

Safely drilling boreholes through hydrogen sulfide bearing formations presents a significant challenge for the oil and gas industry. In this era of increased concern for personal safety and environmental factors, the industry needs additional tools and methods for handling this deadly and corrosive gas. In this work, we describe a monitoring system for drilling mud pH and electrical conductivity (EC) as indicators of H_2S and adjusts mud pH to neutralize free H_2S.

This paper describes a lab-scale flow loop drilling system with real-time monitoring and treatment systems for mud H_2S contamination control. The system combines a lab-scale flow loop with a pipe representing the wellbore with a set of sensors that mimic the rig mud logger. The sensors detect the influx of H_2S by continuously measuring drilling fluid pH and electric conductivity (EC) as the fluid circulates. When the H_2S is indicated by a significant change in EC accompanied by decreasing pH, an automatic mud treatment system activates to restore and maintain a targeted mud pH value.

The system demonstrates a reliable response to mud property changes with 0.1 error pH units. The lab-scale facility treats the contaminated circulated fluids to control the degree of acidity or alkalinity in drilling fluids. It significantly improves a drilling operator's ability to monitor the influx of H_2S and to quickly and safely initiate appropriate treatment.

Introduction

It has been estimated that roughly 19 TCF of natural gas exists in the US in reservoirs which are contaminated with hydrogen sulfide (H_2S). Safely drilling boreholes through hydrogen sulfide bearing formations poses a critical challenge for the US oil and gas industry [1, 2]. Furthermore, in addition to the acute rig-site safety issues with H_2S, this gas also has a long-term detrimental effects as it is a major environmental pollutant from oil and gas production and processing [3]. Thus, early identification of the presence of low levels of H_2S in a drilling fluid stream can lead to greater personnel safety and lessened environmental impacts [4].

Hydrogen sulfide is a colorless gas with an offensive odor (rotten eggs) at very low concentrations and a sweetish taste. It is soluble in water, alcohol, oils, and many other solvents. It has a specific gravity of 1.19. It is considered a weak acid; it is toxic to humans and corrosive to metals. Hydrogen sulfide can be dangerous to personnel on the surface as it is extremely toxic to human and even animal life, and it is extremely corrosive to most metals as it can cause cracking of drill pipe and tubular goods, and destruction of testing tools and wire lines [5].

Moreover, the hydrogen sulfide content of reservoir fluids has an important impact on the economic value of the produced hydrocarbons and production operations [6, 7]. When hydrogen sulfide enters the borehole during drilling, completion or testing for hydrocarbons, it creates several serious problems. These problems are encountered regardless of the source of the hydrogen sulfide [8]. Unsolved issues regarding hydrogen sulfide persist in the oil field; thus, opportunities remain for better and more robust detection and treatment systems.

Hydrogen sulfide is indicated by a decrease in pH and changes in fluid properties. The objective of this work is to describe a lab-scale monitoring system for drilling mud pH and electrical conductivity (EC) as indicators of H_2S, and the system adjusts mud pH automatically to neutralize free H_2S.

Drilling Crew Protection

Hydrogen sulfide is an extremely flammable toxic gas. It's heavier than air and it forms explosive mixtures with oxygen or air. It burns with a blue flame, producing sulphur dioxide (SO_2), which is also a toxic gas that can have harmful effects on health and the environment [9].

The oil and gas industry and governmental agencies have set acceptable limits for working in areas with H_2S exposure, such as with drilling operations. The most broadly accepted guideline at present states that, for individuals in good general health and with no history of physiological complications, the acceptable 8-hr the time-weighted average for continual exposure to H_2S shall not exceed 20 ppm [10].

Generally, from concentrations of 1 ppm, H_2S is detectable by the human nose (rotten eggs odor). Meanwhile, 5 ppm is considered as the maximum continuous working exposure limit (8 hours a day or 40 hours per week). 10 ppm is considered as the short time exposure limit (maximum of 4 exposures a day of less than 15 minutes each) and the concentration above which respiratory protection is required [9]. However, at concentrations approaching 100 ppm, H_2S suppresses the sense of smell in a matter of minutes and can cause burning in the eyes and throat as shown in Table 1 [10]. The sense of smell cannot, therefore, be relied upon for H_2S detection. At 500 ppm, H_2S can affect reasoning and balance and cause respiratory disturbances in 2 to 15 minutes. Finally, exposure to 1,000-ppm concentrations can be fatal in minutes.

Table 1. Effect of H_2S

Concentration	Reaction
100 ppm	Coughing, eye imitation, loss of smell after 2-5 mins.
200 ppm	Marked eye and respiratory tract imitation after 1 hr exposure.
500 ppm	Loss of consciousness and possibly death in 30 min to 1 hr.
700 ppm	Rapid unconsciousness, cessation of breathing, and death.
1000 ppm	Unconsciousness with early cessation of breathing and death in a few minutes even if removed to fresh at once.

Methodology

pH is a measure of the acidity or “basicity” of an aqueous solution and ranges from a scale of 0 to 14. Distilled water is said to be neutral, with a pH close to 7.0 at 77 °F. Solutions with a pH greater than 7 are basic or alkaline, while solutions with pH less than 7 are said to be acidic. Since the scale (0 to 14) is logarithmic, each number represents a 10 fold change in the pH of the water. For example, a solution with a pH of 7 is 10 times more acidic than one with a pH of 8 as shown in Table 2.

One method for mitigating the effect of H_2S gas is alkaline control, which involves the use of caustic or lime to maintain the mud pH at a level sufficiently high so that the partial pressure of hydrogen sulfide relative to the mud at the wellhead is reduced to a safe level. When carefully monitored, alkaline control in principle can minimize danger to personnel by controlling the evolution of hydrogen sulfide from the mud [11, 12].

In water-base muds, the three sulfide species, H_2S and HS^- and S^{-2} ions, are in dynamic equilibrium with water and H^+ and OH^- ions. The percent distribution among the three sulfide species depends on pH. H_2S is dominant at low pH, the HS^- ion is dominant at mid-range pH and S^2 ions dominate at high pH. In this equilibrium situation, sulfide ions revert to H_2S if pH falls.

Depending upon the pH factor of the mud, sulfides will exist in one of three different forms [13]. Refer back to Figure 1, maintaining a high pH (not lower than 10) can neutralize hydrogen sulfide by converting H_2S to HS^- and the S^{-2} sulfide ions, which are solubilized [14].

Table 2. pH levels showing the range from acidic to basic with neutral at pH 7

pH of Common Substances		
pH	[H 3 O +], M	Example
0	1	Battery acid, 1 M sulfuric acid
1	0.1	Stomach acid, 0.1 M hydrochloric acid
2	1 × 10 −2	Lemon juice
3	1 × 10 −3	Vinegar
4	1 × 10 −4	Soft drink
5	1 × 10 −5	Rain water
6	1 × 10 −6	Milk
7	1 × 10 −7	Pure water
8	1 × 10 −8	Baking soda, NaHCO 3
9	1 × 10 −9	Washing soda, Na 2 CO 3
10	1 × 10 −10	Milk of magnesia, Mg(OH) 2
11	1 × 10 −11	Aqueous household ammonia, NH 3
12	1 × 10 −12	Limewater, Ca(OH) 2
13	1 × 10 −13	Drano, 0.1 M NaOH
14	1 × 10 −14	Drano, 1.0 M NaOH

Following the detection of soluble sulfides, the fluid should be immediately treated with an applicable scavenger. Safe, successful drilling of hydrogen sulfide bearing formations requires good drilling practices, extra attention to pH values, and proper drilling fluid formulation. Most government regulations require that a minimum pH level of 10 be maintained at all times in an H_2S environment [15, 16].

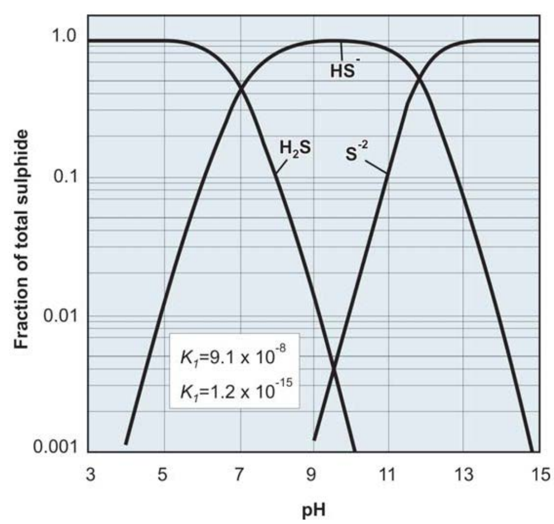

Figure 1. Ionization chart for the distribution of sulfides [14]

Lab Facility Setup

The test rig facility in Figure 2 used in this work is a small scale well model which is designed to act as a mud circulation system. The well model provides a way to simulate the influx of different formation fluids while drilling. Mainly the test rig consists of the following parts:

Figure 2. Lab-scaled Mud Circulation System

a) Mud Circulation System

The mud circulation system consists of two mud tanks with 60 gallons total capacity, a variable flowrate pump, a supercharged pump, pressure gauge, and electrical and manual valves. The rig model has about 15ft of PVC pipe with a diameter of 3/4inch. The open hole is modeled by a 30 inch high and 4inch diameter PVC pipe.

b) Influx Simulation System

To simulate an influx situation, a fluid injection pump is attached to the aforementioned designed wellbore. This injects pressurized fluid into the bottom of the annulus when activated by a manually operated valve.

c) Monitoring System

pH and EC sensors are installed to monitor the acidity and conductivity of the mud out of the well. The rig sensors are connected to a PC interface controller card, as shown in Figure 3. A controller is used to monitor and control the rig model during experiments and to process data.

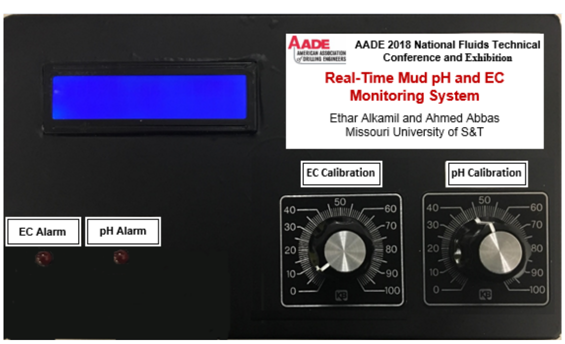

Figure 3. Real-Time pH/EC Monitoring Simulator

d) pH Treatment Unit

The pH treatment unit consists of a barrel filled with concentrated caustic soda (with 14 pH) and a manually operated valve.

Sensors/Monitoring System Installation

The real-time mud contamination monitoring system shown in Figure 4 consists of a PC interface kit with a MATLAB graphic user interface (GUI). The kit monitors two contimnation indicators, one for electric conductivity (EC) and the other for mud pH (acidity or alkalinity).

Influx of H_2S is indicated by a sudden increase in mud electrical conductivity (EC). This system detects that sudden change in EC and triggers an alarm. The mud engineer can then determine if the EC change is due to H_2S and if so, activate the mud pH treatment system. This system will then restore and maintain a targeted mud pH value. Alternatively, if drilling in an area where H_2S is likely, the system can be left “on” continuously, where any sudden increase in EC is assumed to be due to H_2S and pH treatment will be initiated automatically.

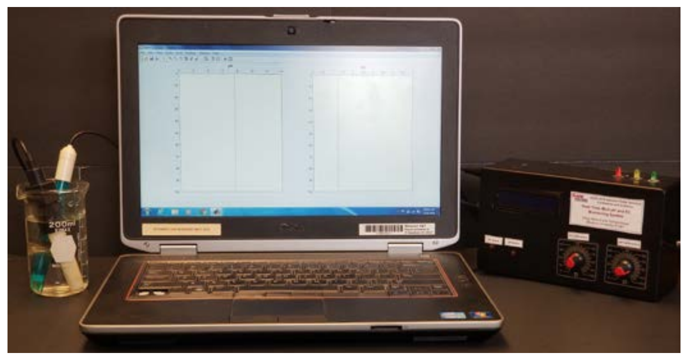

Figure 4. Real-Time pH/EC Monitoring System

System Testing and Calibration

The system has been extensively tested to ensure that it reliably and correctly measures pH and EC in the circulating drilling fluid. Secondly, if the fluid alkalinity changes significantly, the valve of the caustic barrel will be controlled to neutralize the circulation pH level. These responses will be tested and calibrated using the pH calibration meter (with 0.1 error) shown in Figure 5.

Figure 5. pH calibration meter

Table 3. Measured pH and EC response to caustic treatment of the influx event

Treatment Steps	Caustic Soda volume (mL)	Elapsed Time (Sec.)	EC (µS/cm)	pH
1	10	60	75.2	9.12
2	20	115	74.4	9.24
3	40	174	72.5	9.41
4	50	234	72.1	9.48
5	60	292	71.6	9.55
6	70	354	70.8	9.61
7	80	409	70.4	9.67
8	90	468	70.01	9.72
9	100	526	69.4	9.77
10	120	586	68.8	9.87
11	140	645	67.81	9.95
12	150	712	65.01	10.01

Results and Discussion

The circulation system was filled with a prepared drilling mud with 10.01 pH. The two tanks have a capacity of 42 liters, the piping capacity is 1 liter, and the 4 inch pipe (which represents the wellbore) has a 1.6 liter capacity. When 1 liter of citric acid with 4.07 pH is added to the bottom of the wellbore through the injection system to simulate the influx event, the EC and pH alarm systems are both triggered as shown in Figure 6. The monitoring system shows that the EC sensor responses to the injected fluid faster than the pH one in 36 seconds as shown in Figure 6-a,b.

One feature of the proposed Real-Time pH/EC Monitoring System in Figure 4 is that it displays three colors of alerts (see Figure 6-a) indicating levels of circulation fluid acidity: green, yellow, and red. Colors and numerical values are displayed on the computer screen, but dedicated colored LED's are also included to be more visible to the driller and drill crew who aren't looking at the screen. So, before the acid injection, the green LED is ON. After injecting a significant level of acid (mimicking H_2S intrusion), thus producing deviation from the acceptable sensor value, the red LED alarm light is triggered. After sufficient treatment with caustic soda liquid to neutralize the circulation system acidity (at pH 9.8), the yellow LED activates. It remains ON until the circulation system pH reaches the desired value to safely suppress H_2S (at pH 10), at which time the green LED is activated.

Table 3 summarizes the pH measurements in the lab-scaled circulation system at successive injection times during the pumping of caustic into the borehole (cleanup phase), along with the corresponding resistivity measurement as measured by the electric conductivity sensor.

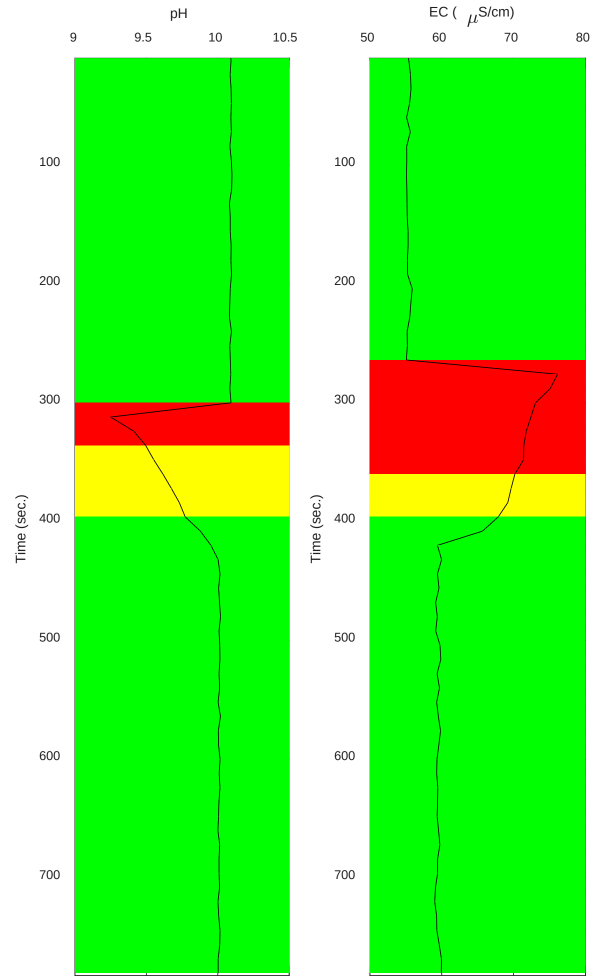

Figure 6. Real-Time pH/EC Monitoring PC Interfaced Simulator, (a) pH sensor response, (b) EC sensor response

Figure 7 illustrates the real time fluid pH response to the amount of caustic soda added to the circulation system. The treatment system should ideally slow the flow of caustic as the pH level approaches 10.

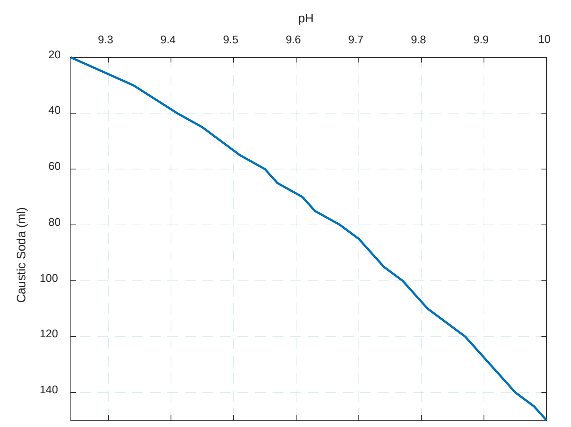

Figure 7. Circulation System pH Treatment Response

Conclusions

The presence of H_2S in hydrogen sulfide bearing formations introduces significant risks due to its extreme toxicity and its corrosive effects on drilling rig equipment. To ensure protection of drilling operation personnel, a real-time pH/EC monitoring system has been developed including three different levels of alerts while simulating H_2S influx. The absolute accuracy of the circulation system fluid pH measurement is 0.1 pH units.

The system demonstrates a reliable response to mud property changes. The new facility provides a suite of additives designed to control the degree of acidity or alkalinity in drilling fluids. It significantly improves a drilling operator's ability to monitor the influx of H_2S and to quickly and safely initiate appropriate treatment.

Finally, this project demonstrates a robust method for reducing risks to drilling personnel, to rig equipment, and to the environment while drilling in areas with H_2S dangers.

Acknowledgments

We would like to express our appreciation to the Iraqi Ministry of Higher Education and Scientific Research (MOHESR)-University of Basrah for sponsoring Ethar Alkamil to finish this work. Our appreciation is extended to the Higher Committee for Education Development in Iraq (HCED) for sponsoring Ahmed Abbas to finish this work. We also want to thank Geosciences, Geological and Petroleum Engineering Department in University of Missouri for Science and Technology for providing the facilities to do this project.

Nomenclature

EC =*Electrical conductivity*
H_2S = *Hydrogen sulfide*
HSE = *Health, safety, environmental*
NaCl = *Sodium chloride*
S^{-2} , HS^{-} = *Sulfide ions*
SO2 = *Sulphur dioxide*

References

1. Carnegie, A. J. G., Raghuraman, B., Xian, C., Stewart, L., Gustavson, G., Ruefer, S., … Dawoud, A. "Applications of Real-Time Downhole pH Measurements." International Petroleum Technology Conference, (2005). doi:10.2523/IPTC-10883-MS.
2. Raghuraman, B., O'Keefe, M. D., Eriksen, K. O., Tau, L. A., Vikane, O., Gustavson, G., & Indo, K. "Real-Time Downhole pH Measurement Using Optical Spectroscopy." Society of Petroleum Engineers, (2007). doi:10.2118/93057-PA.
3. Carnegie, A. J. G., Raghuraman, B., Xian, C., Stewart, L., Gustavson, G., Ruefer, S., … Dawoud, A. "Applications of Real-Time Downhole pH Measurements." International Petroleum Technology Conference, (2005). doi:10.2523/IPTC-10883-MS.
4. Duffy, P., Woods, G., Walsh, J., Kane, M. "Online Real-Time Water Quality Monitoring and Control System." ICCT, Orlando, USA, (2010).
5. Saasen, A., Omland, T. H., Ekrene, S., Brévière, J., Villard, E., Kaageson-Loe, N., … Meeten, G. "Automatic Measurement of Drilling Fluid and Drill-Cuttings Properties." Society of Petroleum Engineers, (2009). doi:10.2118/112687-PA.
6. Richards, L., Magnone, D., Dongen. B., Ballentine, C., Polya, D. "Use of lithium tracers to quantify drilling fluid contamination for groundwater monitoring in Southeast Asia." Applied Geochemistry, (2015). Volume 63, Pages 190-202, ISSN 0883-2927, https://doi.org/10.1016/j.apgeochem.2015.08.013.
7. Promsawat, T., Kummool, S., Pongswatd, S., and Julsereewong, A. "Real-time monitoring and reporting alarm system for pH measurement in wet scrubbers." 16th International Conference on Control, Automation and Systems (ICCAS), Gyeongju, pp. 353-358, (2016). doi: 10.1109/ICCAS.2016.7832343.
8. Mathews, S., Raghuraman, G., Rosiere, B., Wei, W., Colacelli, S., and Rehman, A."Laboratory Measurement of pH of Live Waters at High Temperatures and Pressures." Society of Petroleum Engineers, (2009). doi:10.2118/121695-MS.
9. Dagtas, B., Garnier, F., and Noble, G. "Management of H2S Risk in Total ABK". Society of Petroleum Engineers, (2006). doi:10.2118/98504-MS.
10. Abel, W. "Planning, training, equipment all crucial in H2S blowout." Oil & Gas Journal, (1995) United States.
11. Wendt, P. "Generalized Theory for Evolution and Dispersion of H2S from Alkaline Muds." Society of Petroleum Engineers Journal, 23(02), 365-376, (1983) doi:10.2118/10176-pa.
12. Phelan, P., Khouri, A., and Wahed, H. "H2S Measurement Using Wireless Technology." Society of Petroleum Engineers, (2014). doi:10.2118/171720-MS.
13. Wendt, P. "Effectiveness of H2S Scavenging by Ironite Sponge at High pH." Society of Petroleum Engineers, (1987). doi:10.2118/16282-MS.
14. KMC Oil tools, Drilling Fluid Engineering Manual, Version 1, Kuala- Lumpur. Section 12, pp. 1-12, Section 11b, pp 26-30, (2006).
15. Carter, R., and Adams, J. "Hydrogen Sulphide in the Drilling Industry." SPE Journal, Symp. On Deep Drilling and Production, Texas, Pp 125-128, (1979).
16. Al Moajil, A., Khaldi, M., Hamzaoui, B., Al-Rustum, A., and Al-Badairy, H. "Formation Damage Assessment of High pH and Salinity Completion Fluids in Gas Wells." Society of Petroleum Engineers, (2017). doi:10.2118/188266-MS.