LOGGING OPERATIONS IN SOUR GAS WELLS

JAMES G. CONNELL and ROBERT M. SHAPIRO
Schlumberger Well Services

INTRODUCTION

Formidable technical and operational problems arise in the course of drilling, testing, and producing wells which contain appreciable amounts of hydrogen sulfide. Though not the worst of such problems, wireline operations are certainly rendered more difficult and dangerous.

Logging equipment is designed to perform properly in the high temperatures and pressures found in oil and gas wells. The presence of hydrogen sulfide has thrust forward a new hostile-environment problem. The troubles are twofold: the threat of personnel overexposure, and the deterioration of metal components which are exposed to H_2S.

Industrial plants have long known of the dangers to personnel who are exposed to hydrogen sulfide. Steps were taken to learn the procedures necessary for personnel safety. These procedures were then adapted for use by our logging crews, and have been effective in that no case of hydrogen-sulfide poisoning has been reported.

The downhole problem created by the presence of hydrogen sulfide is harder to correct. The solution to the problem was evidently either to protect vulnerable steels from contact with the gas, or to use other materials which were not vulnerable. Both measures have been successfully applied. Protective coatings are good enough to permit the use of standard cables and downhole tools in cases of low H_2S concentration, but special H_2S-resistant cables are needed for severe conditions. In no case, however, should sour-gas logging operations be looked upon as routine.

H_2S-resistant pressure-control equipment is also available. Pressures to 15,000 psi can be controlled.

PERSONNEL SAFETY

Crewmen must understand the physiological effects of hydrogen sulfide. This is a continuing educational process; new people must be indoctrinated, and older ones reminded of the dangers involved.

Physical and Chemical Characteristics

Hydrogen sulfide is a colorless, flammable gas having an offensive odor and a sweetish taste. It is highly toxic; in fact, almost as deadly as hydrogen cyanide, and between five and six times more dangerous than carbon monoxide. Another hazardous feature of H_2S is that it is heavier than air (its density is 1.19), thus tending to collect in low places. Moreover, the gas is highly explosive in mixtures of 5 to 27% (50 to 270 thousand ppm) with air.

The odor of rotten eggs has been regarded by many as an indicator of H_2S. However, the sense of smell is unreliable as a warning device for this insidious gas, for two reasons:

1. The rotten-egg odor is lost after two to fifteen minutes of exposure, to concentrations as low as 0.010 to 0.015% by volume (100-150 ppm) of the gas.
2. Exposure to higher concentrations can dull the sense of smell completely in less than a minute, and can produce a false sense of security.

Toxicity

The effects of the toxicity of the gas are shown in Table 1. A tolerance to the gas is never acquired. One sniff of a sufficiently high concentration of H_2S

can cause acute poisoning.

Treatment

There is no known antidote for H_2S poisoning; however, prompt first aid may save many lives. Victims should be removed to fresh air immediately by rescuers protected by demand-type breathing apparatus. Artificial respiration should be supplemented by the administration of dilute oxygen if breathing is slow, labored, or otherwise impaired. Artificial respiration should always be administered if breathing has stopped. Even though breathing is paralyzed, the heart may continue beating for ten minutes after the attack. In all cases, victims of H_2S poisoning should have a doctor's care as soon as possible after exposure.

Detection and Protection

Since the odor is unreliable as a danger signal, other means of detection must be used when H_2S may be present. Logging companies must depend largely on well operators for detecting and measuring the strength of any H_2S contamination that may happen. However,the logging crews have a hand-held H_2S monitor available, which displays discoloration of a length of the detector tube, according to the strength of the gas.

Workers in an area where the presence of H_2S is known or suspected must have ready access to breathing apparatus. This apparatus should be of the demand-air type, using a back-carried supply of air. Though cumbersome, such self-contained units allow the user much greater mobility than the alternative type, which supplies air from a large stationary tank to the user via a hose. The portable units carry a 30-minute supply of air. They are meant for evacuation or rescue use, and are not to be used in the routine performance of work.

Respirators, gas masks, etc., which do not supply their own air, give little or no protection from H_2S.

General Safety Considerations

The well operator has the responsibility of informing all service companies prior to a job, if the presence of H_2S is anticipated. The concentration should also be given, if known.

- Each member of the wireline crew should be schooled in first aid, especially the techniques of artificial respiration.
- Safety equipment should be checked to be sure all equipment is functional before leaving shop.
- At the lease, the physical layout should be noted by the wireline company personnel.
- The wireline unit should be spotted upwind whenever possible.
- An on-the-job safety meeting should be held with the well operator to discuss normal and emergency procedures.

THE LOGGING CABLE

The introduction of the steel-armored cable to the wireline industry was a significant event. This development paved the way for great strides in the evaluation and completion of wells.

At about the same time, the Pincher Creek and Jumping Pound sour-gas fields were being discovered in Canada. Since that time, the occurrence of H_2S in association with natural gas has steadily increased. A substantial proportion of the producing wells in the United States are now making H_2S in measurable quantities.

The effect of H_2S on armored logging cables quickly became apparent. Cables began failing in the hole or after being retrieved, chiefly through embrittlement of the armor wires. Recognizing that H_2S was the culprit, a study was begun to determine the nature of the problem and to seek a solution. ("Logging cable" is used in this paper as a generic term, to include both multi-and monoconductor cables of all sizes.)

Research Program

Objectives of the research program were to:

1. Find suitable chemical inhibitors to increase the life of cables in corrosive or embrittling environments
2. Provide predictions of the maximum safe exposure time for cables, with and without inhibiting agents, in a given corrosive and embrittling medium
3. Recommend materials more resistant to embrittlement than those in use.

"Embrittlement" is a descriptive term meaning "reduction of ductility". Ductility is the inelastic yielding of a material under stress, before failure occurs; but extreme hydrogen embrittlement causes failures in steel before the yield point is reached.

Studies were made to determine the causes of metal deterioration and failure modes. Four types of deterioration were recognized:

1. General corrosion
2. Pitting corrosion
3. Stress corrosion cracking
4. Hydrogen embrittlement

Source causes of the deteriorations are as follows:

1. *General Corrosion* - General corrosion is an electrochemical reaction, commonly termed tarnishing, rusting, or corroding. It requires that two metals having a difference of potential in the Galvanic Series be electrically in contact through an electrolyte, with a metallic return path for the current. The more "noble" of the metals becomes a cathode, and is protected, while the less noble becomes an anode, and is consumed by a process of ion transfer (electrolysis).

A simplified equation of this action is:

$$H_2S + Fe^{++} + H_2O \rightarrow FeS + 2H^+$$

where Fe (iron) is the consumed anode, and the FeS (Ferrous Sulfide) is the cathode.

Note that if moisture (H_2O) is not present, H_2S is noncorrosive. Even though the water does not enter actively into the reaction, it is needed to ionize the H_2S.

2. *Pitting Corrosion* - Pitting corrosion is corrosion of the type described above, but on local sites. In H_2S, iron sulfide is often formed, thus creating an insulated or passive area at each site. Then, metal loss is predominantly around the black sulfide patches.

General corrosion and pitting corrosion are thus quite similar.

3. *Stress Corrosion Cracking* - In early studies, "stress corrosion cracking" was defined as the conversion of metal to sulfides by anodic reaction along grain boundaries or other paths of weakness, causing failure at abnormally low loading. There is considerable disagreement as to whether this is a distinct process or merely the result of stress intensification due to corrosion along minimum-area boundaries. The term is retained here to describe this generally familiar phenomenon.

4. *Hydrogen Embrittlement* - The cause of embrittlement in steel is the absorption of atomic hydrogen. The embrittlement results from changes in bulk properties of the metal when hydrogen atoms formed at the surface diffuse into the crystalline structure of the steel. The source of the hydrogen, in this context, is the corrosion reaction in (1) above.

Two major hypotheses have been advanced to explain the mechanism of hydrogen embrittlement:

a. *Pressure Hypothesis* - Atomic hydrogen diffusing through the metal lattice combines at the surface of internal voids to form molecular hydrogen gas, the pressure of which acts to push the metal apart from within.

b. *Internal Adsorption* - Hydrogen atoms diffusing through the lattice are adsorbed on the surface of embryonic cracks (dislocation pile-ups), thereby reducing the energy required to create the new surface for transforming the pile-up into a crack.

A recently revised definition in the "Drilling Manual" states the following: " . . . hydrogen embrittlement is a phenomenon that causes a normally ductile material to fail in a brittle manner. It occurs when materials are under stress in an environment capable of forming atomic hydrogen. Hydrogen-induced delayed brittle failure is a form of hydrogen embrittlement that is characterized by sudden, sometimes catastrophic, failure at relatively low stresses, often under static conditions, after having withstood much higher stresses and dynamic conditions for a considerable period of time. Hydrogen sulfide embrittlement, as a special case of hydrogen embrittlement, is the principal cause of hydrogen-induced delayed brittle failure of the drill stem assembly. Hydrogen sulfide embrittlement is often referred to as a stress corrosion cracking, sulfide stress cracking, sulfide embrittlement, or hydrogen embrittlement."

The NACE (National Association of Corrosion Engineers) defines stress corrosion cracking and hydrogen embrittlement occurring in an H_2S environment as "sulfide stress cracking" or SSC. This term (SSC) will be used in this paper.

Research Testing and Results

The standard logging cable is produced from "Improved Plow Steel", a high-carbon grade (AISI-1075), heat-treated and cold-worked to a strength of

250,000 psi and above. It is zinc coated. Under simulated downhole conditions of temperature, pressure, and H_2S environment, several observations were made, the more important of which were:

1. Improved plow steel is susceptible to sulfide stress cracking (SSC) and will fail at stresses less than 15 percent of the ultimate tensile strength of 250,000 psi.
2. Susceptibility to SSC increases with rising temperatures until a maximum is reached at 77°F and then declines as temperatures continue to rise.

Testing of film-forming inhibitors, which would retard both corrosion and embrittlement of the logging cable, was undertaken. Specifications were:

1. The material should adsorb strongly on metal surfaces and resist erosive effects of the cable motion through fluid.
2. When the protective film is broken, it should be self-healing.
3. It must possess controlled solubility and dispersibility.
4. And it should display no adverse side effects.

Both organic and inorganic inhibitors were tested. Both types were found to be effective in low concentrations of H_2S (less than 2 percent).

Testing was undertaken to determine the metallic components (armor and conductors) needed in the construction of a "hydrogen-sulfide-proof" cable. An initial step was to select those materials believed resistive or immune to attack. Some of these were discarded because of high cost, undesirable properties, or procurement difficulties; e.g., gold beryllium, tantalum.

Results of the Test

1. Multiphase MP35N, an alloy of nickel, cobalt chromium, and molybdenum, was selected for fabrication of the armor.
2. Nickel-clad copper (ASTM B-355), Class 10) was selected as the conductor material.

Monoconductor cables were fabricated in 0.20-in. diameters and then subjected to mechanical properties testing and sulfide stress cracking tests. Mechanical properties were equivalent to or better than the 0.20-in. standard cable, and no sulfide stress cracking occurred.

Results from tests for predicting the maximum safe exposure time for standard cable in varying H_2S concentrations, inhibited and uninhibited, were not encouraging. Time of exposure and the conditions under which the H_2S exists are the largest variables. If the H_2S is dry, the cable will not be affected, but the addition of a small amount of water will create the condition needed for SSC.

It was also found that a cable may suffer loss of ductility in H_2S environment but subsequently may recover from this condition to a large degree. This is possible only if irreversible damage (in the form of embryonic cracking) has not occurred. The hydrogen atoms that have entered the steel will rediffuse to atmosphere when the external concentration drops below that within the metal, except when molecular hydrogen (H_2) has formed. Again, many variables enter into this, such as time in contact with H_2S, concentration of H_2S, and stresses.

Recommended Field Practices

1. Experience indicates that there are no really safe operating conditions for an unprotected standard cable in hydrogen-sulfide environment. However, in wells having H_2S concentrations up to 2 percent by volume (or 500 ppm in mud), standard cables have been used with success. These cables were protected with inhibitors, and exposure times were kept to four hours or less.

2. Standard cables should not be run in wells with H_2S concentrations of over 2 percent by volume (500 ppm in mud). Complete failure of the cable can occur in the hole, on being retrieved, or on the spooling drum.

3. The 0.20-in. MP35N monoconductor cable can be used in any concentration of H_2S. Its principal use is in cased holes or producing wells, in which the H_2S concentration cannot be controlled.

4. In drilling wells, operators are encouraged to use H_2S scavengers in the mud system to decrease or remove the H_2S present. Also, operators are requested to maintain high-pH systems, which tend to reduce the effect of H_2S on standard cables. So far, no multiconductor logging cables have been made of the H_2S-resistant materials, since

drilling wells will normally permit the use of inhibited standard cables.

5. When requesting logging services for wells with H_2S, the operator should inform the logging company:

a. What fluids are in the well
b. What percent H_2S is in the mud
c. What other corrosive agents are present; e.g., acid, CO_2.

Having this information, the logging company can decide whether a trip into the well is feasible, and, if so, can begin preparing their people and equipment for the job.

6. The displacement technique has been used in servicing many producing wells in which H_2S was present. This involves filling the tubing volume with inhibited condensate or oil, thus displacing the original tubing fluid into the formations through the perforated interval. The standard cable can then be used safely, if properly inhibited and if the time of exposure is held within limits.

7. Standard logging cables that have been run in wells with H_2S should be checked for possible embrittlement before being used again. One method is to use an iron-sulfide-detecting solution on the cable. The presence of iron sulfide suggests the possibility of permanent damage. The next test is made by wrapping an armor wire strand several times around its own diameter. If the armor wire breaks, it indicates a ductility less than that required for new armor. If either or both tests indicate possible SSC damage, the cable should be checked by cable and/or rope-socket strength tests before being used again.

PRESSURE CONTROL

Because of the economic importance of operating in a sour gas environment, it became necessary to learn the successful use of materials in these conditions. A task group, known as NACE T-1F, was formed by the oil and gas companies to accomplish this. They produced a document offering guidelines to oilfield manufacturers in an effort to improve the reliability of pressure-control equipment. This document, NACE 1F166, is updated as new information is obtained.

Surface pressure-control equipment being used in the 1950's did not meet the NACE 1F166 specifications. At that time steps were taken to devise techniques that would allow the present equipment to be used safely on wells having low pressures and low H_2S concentrations. Designing was begun of equipment to handle the more extreme conditions of pressure and concentration.

Use of Standard Pressure-Control Equipment

Three techniques were developed which permitted the use of existing equipment:

1. All internal parts of blowout preventers, risers, wellhead adapters, and stuffing boxes are bathed with a solution of inhibitor before rigup.
2. The pressure-control equipment is rigged up to the well, which is filled with fluid. The riser and blowout preventer are then filled with an inhibitor whose density is less than that of the well fluid. The well is opened, and inhibitor floats on well fluid, thus giving continuous coating action.
3. After the pressure-control equipment is rigged up and the well is opened, a continuous stream of inhibitor is fed into the pressure-control system, to replace any losses.

Under low pressures (less than 5000 psi) and low concentrations of H_2S (less than 2 percent by volume) these techniques proved feasible. They are still used today with pressure-control equipment which is not rated H_2S resistant. However, careful consideration and planning must precede this usage. It must be remembered that the pressure-control equipment, during normal use, is near the temperature of highest susceptibility (77°F) to H_2S embrittlement. Pressure-control equipment that is not rated H_2S resistant should not be used where concentrations of H_2S are expected to exceed two percent by volume (500 ppm) or where pressures exceed 5000 psi. After exposure to low H_2S concentration, the equipment should not be used again for several days. This time period allows the equipment to return to a nearly normal state as the atomic hydrogen diffuses out. If this is not done, a future operating stress may exceed the critical level for the amount of hydrogen remaining, causing premature failure.

Hydrogen-Sulfide-Resistant Pressure-Control Equipment

Laboratory testing proved that SSC failures could be precluded by means of designs which permit the use of relatively low-yield-point and low-hardness steels. Materials which meet these requirements are low-alloy steels (AISI 4130 to 4140) which have been heat treated to control ductility and hardness.

Three types of H_2S-resistant pressure-control equipment have been built to our specifications.

They are classified by working pressure ratings: 5000; 10,000; and 15,000 psi.

All three are quite heavy. For example, the dual-ram preventer of the 15,000-psi equipment weighs 1000 lb, and an 8-ft section of riser comes to 350 lb.

Before going to the field, this equipment was tested extensively, and passed all tests. It has since been used in H_2S concentrations up to 40 percent by volume, and pressures up to 15,000 psi, without serious problems.

Recommended Field Practices

1. Because of the danger to personnel, pressure control in an H_2S environment must allow little or no loss of H_2S gas at the surface. A grease-injection-type system is thus recommended.

2. When there is less than two percent H_2S by volume and less than 5000 psi pressure, non-H_2S-resistant pressure-control equipment can be used with proper precautionary measures.

3. Hydrogen-sulfide-resistant pressure-control equipment should be used whenever possible if H_2S is present. It should be used without exception when H_2S concentrations exceed two percent by volume (500 ppm), or when pressures exceed 5000 psi.

4. When requesting pressure control equipment for an H_2S well, the operator should inform the logging company:

   a. What percent H_2S is present
   b. What pressure is to be expected
   c. What control is desired; i.e., H_2S-resistant or not; pressure ratings.

5. At the location, the operator and logging company personnel should determine a plan of action for the job, verify the suitability of all wellhead connections and valves, and agree upon emergency procedures.

OTHER ASPECTS OF SOUR-GAS LOGGING

The effects of H_2S concentrations on downhole tools have not been mentioned. The material and design systems used in our downhole tools reduce the vulnerability of equipment to SSC damage except in certain cases. These exceptions are:

1. Centralizer arms
2. Coil springs, as used in calipers and centralizers
3. Pressure vessels, as used with the formation tester tool.

Centralizer arms must be fabricated of hardened steel to prevent excessive wear. They are also in a state of continual stress. Both factors make them highly susceptible to SSC. The use of special inert-metal-plated arms, plus treatment with inhibitors before entering the well, has greatly reduced the incidence of SSC failures.

Coil springs used in contact with well fluids are likewise susceptible to SSC, and are treated similarly to provide protection.

The sample chambers of standard formation tester tools are subject to potentially dangerous weakening in the presence of H_2S, either in the mud system or in the formation fluids being sampled. When the presence of H_2S is considered a possibility, special H_2S-resistant sample chambers must be used.

A troublesome side effect has been encountered in the Permian Basin, where sour gas wells are often drilled with brine water as the drilling fluid. Well operators resorted to the generous use of filming-amine inhibitors, which protected the drill string, and also the logging cable and downhole tools. Some types of tools, such as dipmeters, rely on small electrodes in electrical contact with the mud, to make their measurements. Sometimes the inhibiting action of the filming amines was so efficient that it effectively insulated these metal electrodes, thus incapacitating the tool. One solution has been to discontinue use of the inhibitor for several days prior to logging.

This phenomenon has been reported only where unweighted brine water was used for drilling.

Logging operations can be successfully performed in sour-gas environments, providing that suitable measures are taken to protect personnel and equipment.

Logging company personnel must recognize the inherent dangers associated with hydrogen sulfide, and be prepared to operate safely.

By the judicious use of H_2S scavengers in the mud systems and inhibiting agents on the cables, standard logging cables can be protected from low concentrations of hydrogen sulfide (less than two percent by volume), for limited periods. Displacement techniques have been used successfully in cased holes, to control the H_2S concentrations during logging operations.

Monocables have been developed that are resistant to hydrogen sulfide. These should be used whenever possible in low concentrations of H_2S, and always when concentrations are greater than two percent by volume.

Standard pressure-control equipment can be used on wells having low concentrations of H_2S and pressures less than 5000 psi, if special precautions are taken.

Pressure-control equipment that is hydrogen-sulfide resistant has been developed and, when possible, should be used on wells where low concentrations of H_2S occur. It should always be used where concentrations of H_2S are greater than two percent by volume or where pressures are in excess of 5000 psi. The maximum working pressure is 15,000 psi.

Performing wireline services in the presence of hydrogen sulfide represents a specialized area of operation, but when conducted by trained and informed crews using tested equipment and techniques, this important capability is quite feasible in all present-day sour-gas fields.

BIBLIOGRAPHY

1. Garwood, George L.: Equipment Selection for Sour Gas Condensate Wells. *The Drilling Contractor*, Mar.-Apr., 1974, p. 40.
2. The Killer - H_2S. The Workmen's Compensation Board, Alberta, Canada.
3. Unpublished Research Memorandum: Hydrogen Embrittlement - Study Program I. G.L. Simard and F. Bernstein, Schlumberger-Doll Research Center, 1960.
4. Townsend, H.E., Jr.: Hydrogen Sulfide Stress Corrosion Cracking of High Strength

TABLE I

Toxicity of hydrogen sulfide to men

H_2S %	0-2 Min	2-15 Min	15-30 Min	30 Min-1 Hr	1-4 Hr	4-8 Hr	8-48 Hr
0.005 0.010 50-100 ppm				Mild conjunctivitis respiratory tract irritation.			
0.010 0.015 100-150 ppm		Coughing; Irritation of eyes; loss of sense of smell.	Disturbed respiration; pain in eyes; sleepiness.	Throat irritation.	Salivation and muscous discharge; sharp pain in eyes; coughing.	Increased symptoms.*	Hemorrhage and death.*
0.015 0.020 150-200 ppm		Loss of sense of smell.	Throat and eye irritation.	Throat and eye irritation.	Difficult breathing; blurred vision; light shy.	Serious irritating effect.*	Hemorrhage and death.*
0.025 0.035 250-350 ppm		Irritation of eyes; loss of sense of smell.	Irritation of eyes.	Painful secretion of tears; weariness.	Light shy; nasal catarrh; pain in eyes; difficult breathing; conjunctivitis.	Hemorrhage and death.*	
0.35 0.045 350-450 ppm		Irritation of eyes; loss of sense of smell.	Difficult respiration; coughing; irritation of eyes.	Increased irritation of eyes and nasal tract; dull pain in head; weariness; light shy.	Dizziness; weakness; increased irritation; death.		
0.050 0.060 500-600 ppm	Coughing; collapse and unconsciousness.*	Respiratory disturbances; irritation of eyes; collapse.*	Serious eye irritation; light shy; palpitation of heart; a few cases of death.	Severe pain in eyes and head; dizziness; tremities; great weakness and death.*			
0.060 0.070 0.080 0.10 0.15 600-1,500 ppm	Collapse;* unconsciousness;* death.	Collapse,* unconsciousness ; * death.					

*Data secured from experiments on dogs which have a susceptibility similar to men.

Source: National Safety Council data sheet D-chem. 16

Steel Wire. *Corrosion* - NACE Vol. 28, No. 2, Feb. 1972, pp. 39-45.

5. Report of NACE Unit Committee T-1F on Metallurgy of Oil Field Equipment, prepared by Task Group T-1F1 on "Sulfide Cracking Resistant Metallic Materials for Valves for Production", Materials-Protection and Performance, Vol. 12, No. 3, Mar. 1973.
6. Samuels, Alvin: New Material Treats H_2S in Drilling, Completion Fluids. *Oil and Gas Jour.*, Apr. 29, 1974, pp. 71-74.
7. Patton, Charles C.: Corrosion Fatigue Causes Bulk of Drill-String Failures. *Oil and Gas Jour.*, July 29, 1974, pp. 163-168.

ACKNOWLEDGMENT

The authors thank Mr. Tyler Hamby, of Shell Oil Company, for his invaluable contributions.