Safer Sulfur Transport

Controlling skin - effect, heat-traced liquid sulfur pipelines with fiber optics

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SAFETY, ENVIRONMENTAL, AND operational concerns associated with transporting liquid sulfur by truck over public roadways are causing sulfur producers to review alternatives in an effort to determine a better transportation method. This article presents one such alternative to sulfur trucking—a pipeline transport employing a skin-effect, heat-traced (SEHT) system monitored and controlled by fiber-optic technology—and reviews engineering aspects of the technologies.

Sulfur Properties

Sulfur is an element with characteristics that cause it to vary significantly with changes in temperature. In particular, Figure 1 depicts the variation of sulfur viscosity with temperature. Sulfur is a solid at ambient temperatures and exists in two crystalline forms, rhombic and monoclinic, and an amorphous form. Both crystalline forms consist of eight-member rings, but for each crystalline form the arrangement of the rings and the interatomic distances differ. Amorphous sulfur is formed when liquid sulfur

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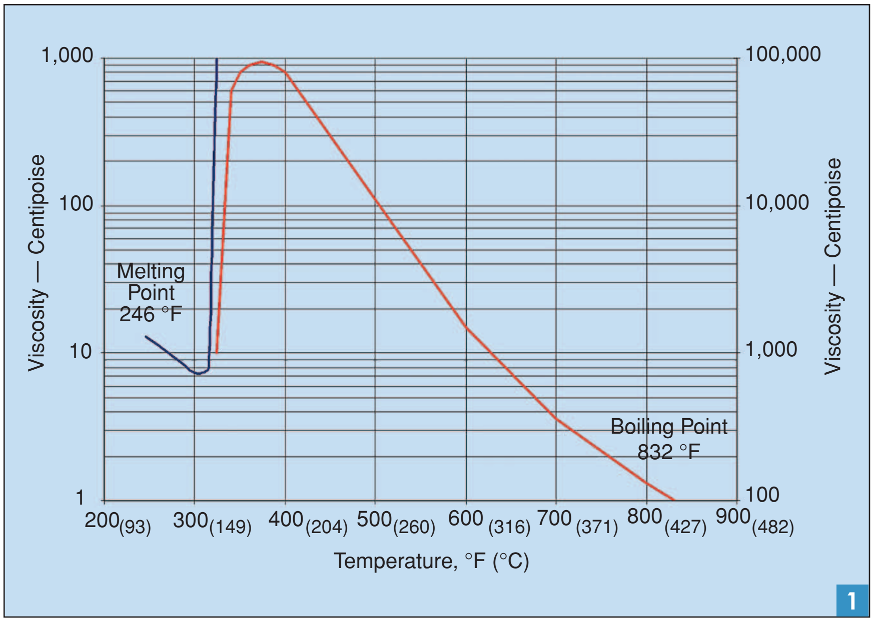
which has been heated to elevated temperatures is allowed to cool rapidly. Amorphous sulfur slowly changes to the rhombic crystalline form at ambient temperatures.

Rhombic sulfur is the stable form of the element at room temperature. If rhombic sulfur is heated to about 95 °C, it changes into monoclinic crystals, with the absorption of 3.0 kcal/kg of energy. Above 95 °C and up to its melting point, monoclinic sulfur becomes the more dominant structural form. The melting points of solid sulfur range from 113 °C for rhombic sulfur to 119 °C for amorphous sulfur. Pure crystals of monoclinic sulfur melt at 115 °C. The heat of fusion for sulfur is 9.2 kcal/kg. When melted, sulfur becomes a brownish-yellow transparent liquid, the molecular structure of which also consists of eight-member rings.



Sulfur viscosity graph [1].

Liquid sulfur becomes more fluid with rising temperature up to a temperature of about 160 °C. At this point, liquid sulfur undergoes a change, turning dark reddish brown. The formation of long-chain sulfur polymers in conjunction with the eight-member sulfur rings produces a dramatic increase in its viscosity, rendering the pumping of sulfur impossible.

Liquid sulfur is normally delivered into the pipeline at 140–145 °C. The pipeline SEHT system maintains the sulfur at an average fluid temperature of 135–140 °C over the entire length of the pipeline. The minimum required sulfur delivery temperature is 124 °C. Therefore, a safe margin of 11–16 °C is provided during normal operation. At the upper end of the pipeline maintenance temperature range, a minimum safety margin of 20 °C is provided to remain well below any viscosity changes observed in sulfur at 160 °C.

As sulfur cools and changes from liquid to solid, it contracts by about 10% of its original volume. This is due to changes that occur in the arrangement of the octagonal rings and the interatomic distances during the transition of state. If sulfur solidifies inside the pipeline, it will gravitate to the sag bends as it contracts; as a result, there will be some empty sections in the pipeline.

During remelting operations, with even heating applied over the length of the pipeline, the expanding liquid will once again fill the voids created. The remelt operation must be carefully controlled. If a section of pipe is remelted against adjacent solid sections, there could be an overpressure condition that could lead to pipe rupture. To limit overheating of empty pipe sections, a fiber-optic temperature sensing system could be employed to monitor the heating process over the entire length of the pipeline to ensure the pipeline or its insulation is not damaged during this process.

Safety and Risk Evaluations

H_2S Behavior and Removal (Degasification) from Liquid Sulfur

Typically, sulfur produced by the Claus reaction contains 250–300 ppmwt of hydrogen sulfide (H_2S). More H_2S appears to be present at higher temperatures than at lower temperatures. This anomaly of physical adsorption is attributed to the formation of hydrogen polysulfides (H_2S_x) under the Claus reaction conditions. H_2S_x is a weakly bound polymeric sulfur compound formed by the equilibrium reaction between sulfur and H_2S

$$H_2S + (X - 1)S \leftrightarrow H_2S_x.$$

This reaction proceeds to the right with increasing temperature conditions.

During storage or transport of the sulfur, the H_2S_x compounds will decompose (via procession of the above equation) as equilibrium is achieved at the operating temperature. This results in formation of dissolved H_2S in the liquid sulfur, which will pass to the gaseous phase.

The purposes of sulfur H_2S removal processes (degasification) are to release dissolved H_2S and accelerate the decomposition of hydrogen polysulphides. In addition to the operating temperature, the rate of degasification is influenced by the residence time, the amount of agitation, and the use of certain catalysts. To meet the generally accepted guideline of 10 ppmwt total H_2S for sulfur transport, sulfur degasification processes employ a combination of residence time, agitation, and sometimes catalysts to remove H_2S. The net result is a sulfur product with a H_2S concentration of 10 ppmwt or less suitable for transport.

Sulfur Leak Detection

The most effective way to detect leaks is with the sulfur pipeline's flow meters. If significant leaks exist, the totalized meter readings will detect them. When spilled onto soil, molten sulfur will solidify prior to any significant movement into the soil. Its relative insolubility prevents transport downward to groundwater underlying any potential spill site. Traces of H_2S, if present in the spilled material, represent the only aqueous phase contaminant likely to be detected in affected groundwater. Degasification of the sulfur to 10 ppmwt or less H_2S greatly reduces the risk that H_2S will be present.

Operating Sulfur Pipelines

There are several operating sulfur pipelines, some of which have been in operation for over 25 years. The majority of these pipelines are aboveground installations of less than 3 km in length and utilize a SEHT system to maintain the sulfur at the required operating temperature.

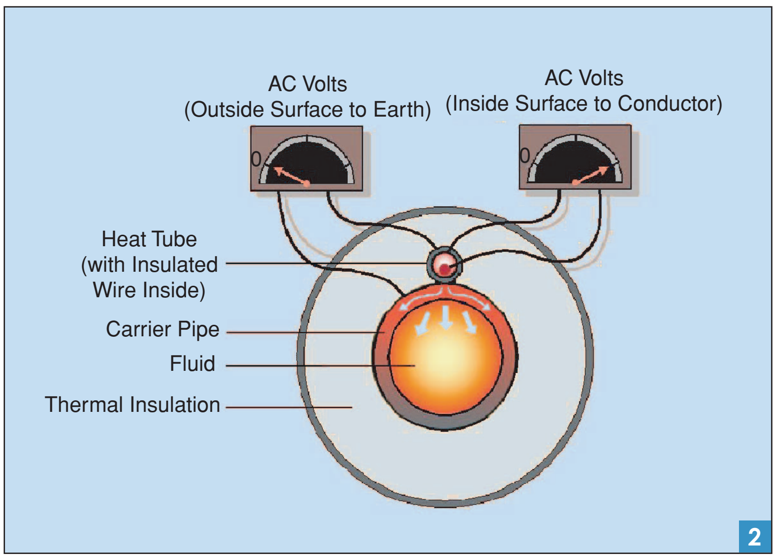
The longest sulfur pipeline currently in operation is a 200-mm-diameter, 41-km-long water-heated buried pipeline in Alberta, Canada. This pipeline utilizes a hot water heating system and is installed underground. Another long sulfur pipeline is a 150-mm-diameter, 33-km-long pipeline in Carter Creek, Wyoming. This pipeline is installed aboveground with SEHT. It has operated since its commissioning in 1983. A 250-mm-diameter, 24-km-long pipeline in Jubail, Saudi Arabia, using SEHT was commissioned in 1983.

It is widely accepted by plant owners and pipeline operators that an SEHT system is cost-effective, reliable, and safe for long sulfur pipelines.

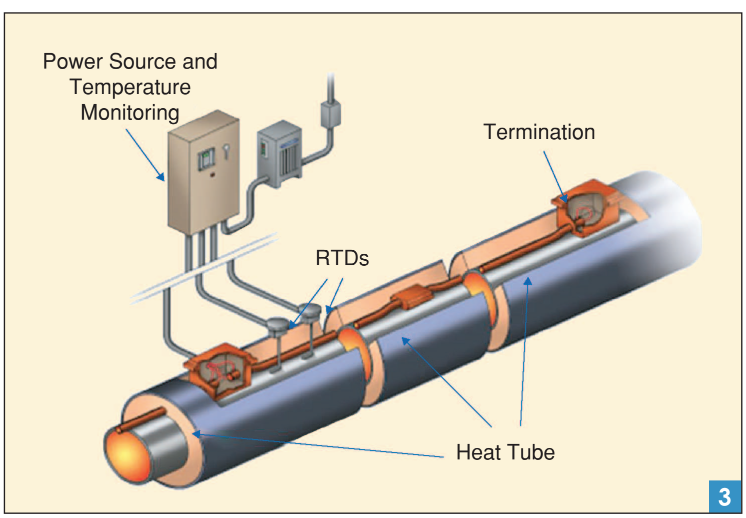
SEHT for Pipelines

Skin Effect System Fundamentals

Skin effect heating is a series circuit electrical heating technology based on two well-established phenomena in electrical theory—"skin effect" and "proximity effect." The current density in a conductor carrying alternating current is not uniform over the cross section of the conductor, but rather is greater near the surface, thereby displaying a phenomenon known as "skin effect." The effective current-carrying cross section of the conductor is therefore reduced and, thus, its effective resistance is increased. Skin effect in a conductor is brought about by the self-induced electromotive force set up by the variations in the internal flux in a conductor and has a greater effect at higher frequencies of the ac source.



Cross section of pipe with skin effect heating.



Skin effect system configuration.

Heat is generated on the inner surface of a ferromagnetic heat tube by I^2R loss of the return current flow and by hysterisis and eddy currents induced by the alternating magnetic field around the insulated conductor that is attached to the pipeline. Additionally, a small amount of heat is produced by the I^2R loss in the insulated conductor. The thermally rated, electrically insulated wire is installed inside the heat tube and connected to it at the end termination. An ac voltage source is connected between the heat tube and insulated wire. The inductive interaction between the current in the insulated conductor and the return current in the heat tube causes the current in the heat tube to concentrate on the inner surface of the heat tube. Figure 2 shows a cross section of SEHT pipe. The current concentration in the inner surface of the heat tube is so complete that there is virtually no measurable voltage on the outer wall of the heat tube. There is no current flowing on the outer surface of the heat tube, keeping it safe and groundable. The heat tube is attached to the process pipe, allowing the heat to be transferred to the process pipe. The attachment method of the heat tube to the pipe will have an impact on the heat transfer. See Figures 2 and 3 for a skin-effect heating system configuration.

Skin-effect heating systems are inherently safe, with no electrical potential on the outside of the carrier pipe or heat tube. Useful heat is transferred directly to the carrier pipe at very low temperature differentials.

Since the heat tube is uniformly applied to the carrier pipe, temperature variations along the line are minimal. The heating element is a piece of pipe and therefore is difficult to damage in the field. Should the conductor wire become damaged, pull boxes built into the system allow for easy removal and replacement of the wire.

Heating System Design Considerations

Temperature Maintenance

The primary objective of the heat tracing system is to compensate for the heat loss from the pipeline to the atmosphere. Liquid sulfur, for optimum viscosity, is maintained at 135–145 °C. In general, skin-effect heating circuits are designed to operate well below their maximum capacity at normal operating mode, which thereby extends the life expectancy of the overall system. It is customary to install skin-effect heating systems with a design safety margin of 25–40%.

Redundancy

The critical nature of sulfur pipelines often mandates heating systems with 100% redundancy for normal temperature maintenance applications to ensure uninterrupted operation. These requirements often result in multiple heating circuit designs with 100% spare capacity. An optimum design for a 100% redundant skin-effect heating system is achieved by carefully selecting a thermal insulation system with multiple heat tubes.

Remelt Considerations

One of the critical aspects of the system performance criteria for a sulfur pipeline is the ability to remelt solidified sulfur in the pipeline. Under adverse conditions, there is a possibility that power to the skin-effect system could be cut off. If a prolonged power outage occurs, the downtime may be long enough to result in sulfur solidification inside the pipeline. Liquid sulfur shrinks in volume by approximately 10% as it changes from liquid to solid. The reduction in volume will create voids at various locations and packed sulfur in other locations.

The remelt process could lead to

- hot spots (overheating) at these voids and
- excessive pressure generated by melting sulfur (expansion) that could burst the pipe.

Past research and experience has shown that the reheat process must allow sulfur molecules that have traveled to the packed areas to reverse their path so that they may return to the void areas without restriction. This process requires the application of the maximum available power from the skin-effect heat management system to create a melted sulfur stream on the inside top of the pipe. By placing the heat tube or tubes near the 12 o'clock position, the reheat process is most efficiently accomplished as the heat transferred to the sulfur naturally creates a gradual stream creation.

The use of fiber-optic temperature monitoring and control systems offers incredible insight into the temperature profile of the pipeline, especially during remelt conditions.

Thermal Insulation

As in any heat tracing application, the quality and selection of proper thermal insulation systems plays a vital role in the satisfactory performance of the heat-traced pipeline. In the case of sulfur pipelines, this is particularly critical as localized thermal insulation failure could result in a pipeline blockage.

The ideal thermal insulation system for the sulfur pipelines utilizes a composite insulation system, preferably prefabricated. A composite insulation system with an inner layer featuring high-temperature rigid insulation material such as expanded perlite or high-density mineral wool is often the preferred choice. The outer layer will often consist of closed-cell high-density foam insulation with high exposure temperature capabilities. The outer jacket serves to protect the underlying insulating material from the external environment and to reduce or prevent the intrusion of water into the insulating material. Common outer jacket materials are sheet metal (aluminum or galvanized steel), high-density polyethylene (HDPE), or hypalon. HDPE and hypalon jacket systems use adhesives and fusion welds to prevent water intrusion.

Pipe Supports and Anchors

In general, pipe supports and pipe anchors are major sources of localized heat loss that adversely affects the thermal balance of a heated pipeline. With high-temperature applications, the design and selection of pipe supports, pipe anchors, and other structural material play an important role in ensuring trouble-free operation. Temperature-sensitive liquids such as sulfur demand a homogenous temperature along the entire length of the pipeline to achieve the desired performance. A localized heat sink could result in plugged lines and loss of production.

Temperature Sensing and Control

The power control system of a skin-effect heating system requires a closed-loop temperature control where the carrier pipe temperature is continuously monitored and compared to the reference set-point temperature. As the pipe cools below the set point, the electrical tracing system is energized and the heat energy is replaced. Application of power to the heating circuit is done by means of a contactor or circuit breaker. The typical installation will include a primary medium voltage circuit breaker (or fused isolation switch, as appropriate), transformer, and a separate secondary contactor being used for the actual on-off control of the heater power. The secondary controller will normally be a fused vacuum contactor. The contactor is controlled by an input from the temperature control system. Typical control modes are:

- ***Automatic maintain mode***: In this case, the average of sensor temperatures is used to switch the tracing on or off to maintain a preset pipeline temperature.
- ***Manual on-off mode***: A remote input is used to manually switch the tracing on or off. This mode should only be used in conjunction with the high-limit mode below.
- ***High-limit mode***: High-temperature alarm settings are used to switch the tracing off in the event that the temperature sensors detect high temperature. This mode is provided principally to protect against damage to the skin-effect heater resulting from excessively high temperatures.

- *Reheat mode*: Maximum power output settings are used to deliver the maximum amount of heat possible from the heating system in the event that operator-initiated remelt of the solidified sulfur is desired.

In addition to the conventional control system used in the past, this article advocates the implementation of technologically advanced optical fiber technology to monitor and control sulfur pipelines.

Optical Fiber Technology for Measurements

Industrialization of fiber-optic sensing technology has been technically difficult and expensive. Fiber-optic sensors were used in an EPRI study to measure transformer-winding temperatures in the early 1980 timeframe. These early fiber-optic temperature sensors utilized a phosphor component with a resulting fluorescence that was temperature dependent. The early fiber-optic systems worked well for point measuring needs and were utilized commercially in semiconductor manufacturing equipment, medical applications, and some microwave and high-voltage applications.

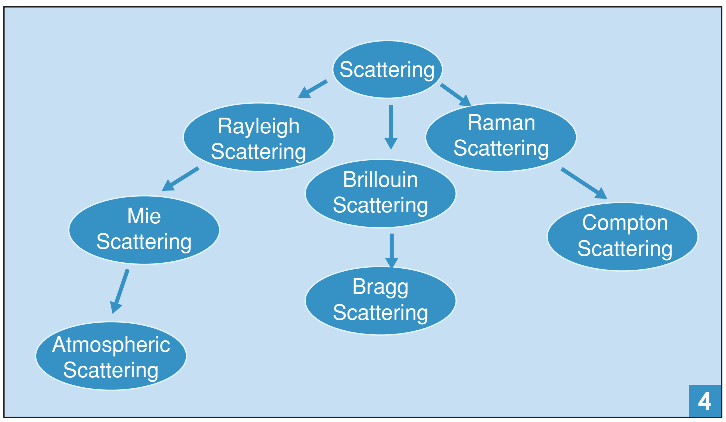
As the technology developed, the need for distributed temperature measurement systems grew, leading to reductions in the cost of electronic time domain reflectometry equipment. However, most systems measured both strain and temperature, making it difficult to decouple the two effects.

For many years, industrial end users have had a well-founded reluctance to install distributed fiber-optic systems of any kind. This reluctance has arisen from concerns about both the fragility of the fiber and the difficulty associated with repairing the fibers when they are mechanically damaged. The recent widespread deployment of fiber-optic cable in the 1990s for telecommunications, data, and instrumentation applications has greatly enhanced both the cable ruggedness and experience level with installations and repair techniques. A wide variety of cable types and terminations are readily available for most applications.

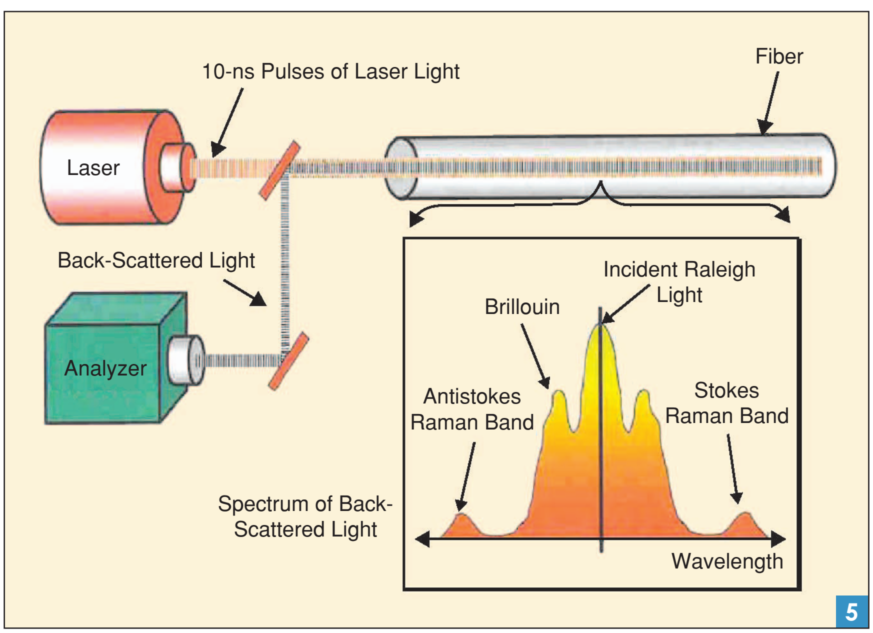
Fiber-optic temperature monitoring has particular advantages over thermister- and thermocouple-based systems, as fiber-optic systems are very robust and unaffected by electrical noise. In addition, fiber-optic monitoring facilitates the measurement of average temperatures at 1-m intervals over the length of the fiber along the entire length of the pipeline. This substantially reduces the potential impact of localized temperature variations in the pipeline.

Figure 4 shows a light scattering phenomena tree. Note that each branch bears the name of the discoverer, many of whom were Nobel Prize winners. Each branch is a viable physical phenomenon that is temperature dependent to varying degrees and that can be observed and measured in fiber-optic systems. The different types of scattering are all temperature dependent, with amplitude, frequency, and some light wave interference being the criteria. Depending on the implementation, some of these scattering measurement techniques can lend themselves best to "point" or "distributed" sensing. For the purposes of this article, it is not necessary to understand each physical mechanism but rather only that there are many different methods by which to obtain the temperature information from a fiber-optic system.

Figure 5 shows the back-scattered light spectrum for various vendors' equipment. For distributed temperature measurement, a pulse laser is coupled to an optical fiber through a directional coupler. The light is backscattered as the pulse propagates through the fiber owing to changes in density and composition as well as molecular and bulk vibrations. In a homogeneous fiber, the intensity of the



Light scattering phenomena tree.



Back-scattered light spectrum.

backscattered light decays exponentially with time. Because the velocity of light propagation in the optical fiber is well known, the distance can be determined from the attenuation of the intensity of the backscattered light. Thus, the temperature and distance can be resolved simultaneously.

The Brillouin scattering has higher amplitude, but it varies as a combination of both stress and temperature. In early stages it was considered hard to separate the two effects. The Raman scattering has lower amplitude, so stress is not a factor when the Stokes bands are used to null out this effect. Employing a fiber loop and taking measurements from each end, the system can eliminate fiber attenuation, providing a more accurate temperature measurement. Recent advances in fiber-optic temperature sensing technology takes advantage of stimulated Brillouin interaction as opposed to spontaneous Brillouin scattering. Several different techniques have been developed to ensure excellent signal-to-noise ratio. The substantial Rayleigh noise normally associated with distributed sensing is virtually eliminated since the level of the detected signals is much greater. The temperature information is contained in the local Brillouin frequency shift (not in the intensity of the scattered light), which guarantees low noise and greater long-term stability. Improved front-end electronics have been developed to resolve the previously difficult and expensive "weak" signal information for temperature resolution on high-length fibers. Theoretical analysis and data have proven that spontaneous Raman- and Brillouin-based fiber-optic distributed temperature sensors offer extended ranges (up to 60 km) with high temperature accuracy.

Fiber-Optic Temperature Sensors for Sulfur Lines

Installation and Operation

Distributed fiber-optic temperature sensors contribute significant operational advantages to the operation of long sulfur transfer lines. Currently, there are many vendors providing distributed fiber-optic system cables capable of sensing distributed temperature over many kilometers. Many of these installations are downhole applications where fiber optics are used for control and optimization of steam flood operations. It is also used for monitoring of paraffin and hydrate control in the case of production wells.

Equipment required for fiber-optic temperature measurement consists of a laser pulse transmitting unit, a backscattering light recording unit, a portable computer for data recording and analysis, and the fiber-optic cable itself. Placement of the fiber-optic cable in a skin-effect-based heating installation is an interesting issue. There are different schools of thought on determining the placement of the optic fiber on a sulfur pipeline with skin-effect heating. Thermal time constants, temperature maintenance versus heat-up requirements, and protection from overheating of the skin-effect heating power cable inside the heat tube all play a part in the location of the distributed temperature sensor.

Placement of the sensor within the heat tube would allow the measurement of the temperature of the heat tube and the power cable. This positioning of the sensor also enables the direct measurement of the power cable temperature when maximum power is being applied to melt out the solid sulfur. Since the limiting temperature of the power cable is critical to reliable operation, direct measurement has a distinct advantage. Care must be taken, however, not to protect the fiber with any ferromagnetic or metallic sheath as this would cause the sheath to act as part of the skin-effect heating system. An all-polymer electrical insulating and mechanical protection system is required.

Placement of the fiber on the outer surface of the heat tube is another possibility. This still provides good coupling to the heat tube for monitoring the temperature of the power cable, but does not monitor the sulfur pipe itself. Protection of the fiber cable can be provided by a stainless steel sheath with the fiber loosely inserted into the sheath. Placement of the fiber optic on the transfer pipeline would give a good estimate of the sulfur temperature. However, it would not monitor the heat tube and skin-effect power cable.

A fourth possibility exists. Since the fiber is a distributed temperature system, the fiber can be "snaked" over different parts of the system, allowing periodic checking of the outside of the heat tube, pipe supports, and the bulk of the cable monitoring the main transfer pipe. With this type of system, a "mapping" of locations with tags on the temperature output aids in the interpretation of the temperature results.

In any case, the method of installing the optical fiber on the pipeline should be chosen to allow maximum flexibility. The preferred method shall protect the fiber from mechanical stress/damage and guarantee trouble-free installation.

Sourcing of fiber-optic temperature measurement systems is becoming easier since there are commercial systems available that have been specifically designed for the oil and gas industry. One vendor has over two million feet of distributed temperature sensors installed predominately in steam assisted, gravity drain (SAGD) heavy oil formations all over the world. Vendors are happy to quote installation as well as product supply.

Conclusions

The combination of skin-effect heating and a distributed temperature sensing fiber-optic system represents a significant advancement in pipeline heating control design. Both skin-effect heating and distributed fiber-optic systems with proven industrial track records are commercially available. These technologies are well suited for sulfur line heat tracing applications, particularly long transmission pipelines. As the cost of the fiber-optic systems become more affordable, this new and reliable technology will become increasingly attractive and prevalent in the industry.

Reference

[1] *Engineering Data Book*, 11th ed. (FPS version). Gas Processors Suppliers Assoc., Tulsa, Oklahoma, 1991.

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