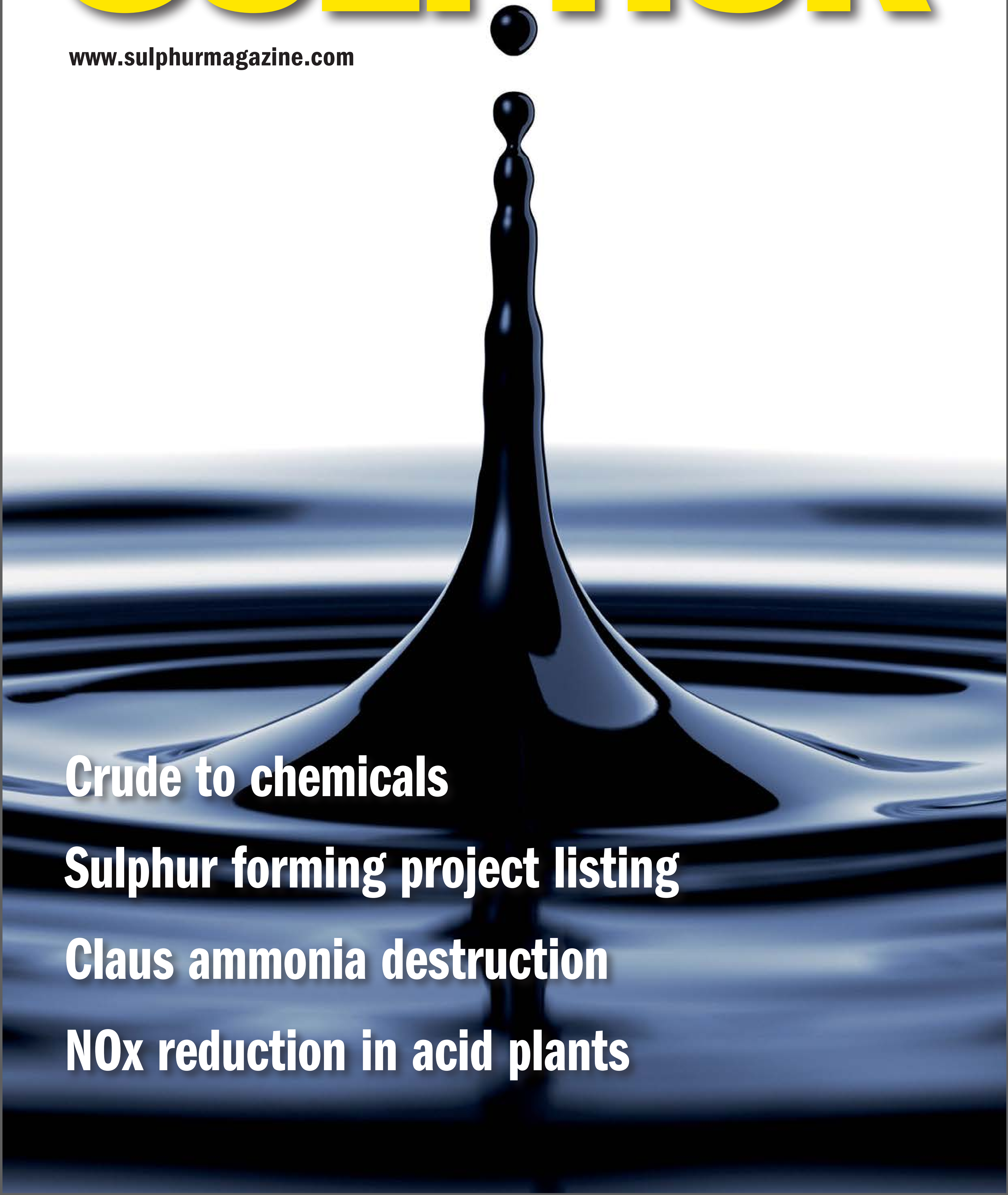
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48

Number 395

July | August 2021

SULPHUR

www.sulphurmagazine.com



Crude to chemicals

Sulphur forming project listing

Claus ammonia destruction

NOx reduction in acid plants

1 47
2 48
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46

Temperature measurement in sulphur recovery

Temperature monitoring and measurement of the Claus thermal reactor in sulphur recovery units is one of the most challenging applications in the oil and gas industry. Recently, market interest in unpurged thermocouples has increased with the introduction of new unpurged thermocouple designs utilising alternative thermowell materials such as monocrystalline sapphire.

DELTA CONTROLS CORPORATION

Purged vs unpurged thermocouples in Claus thermal reactors

T. Keys, M. McCallister, and M. Coady

Temperature measurement in the main reactor of the sulphur recovery unit (SRU) is not only a primary process variable, but also critical for the overall safety and reliability of the reactor. Recently, many legacy reactors with limited to no temperature instrumentation may be required to handle more throughput than originally designed. In addition, many reactors are adding supplemental oxygen resulting in increased operating temperatures. With higher reactor operating temperatures, the importance of temperature monitoring is greatly increased. As standard process temperatures rise through the use of oxygen enrichment and reach maximum capabilities of the refractory, it is and will be increasingly important to have accurate and reliable temperature indication.

SRU temperature measurement technologies

There are currently two technologies suitable for reliable temperature monitoring in the main reactor: infrared pyrometers and thermocouples. It is recommended to use both technologies for maximised reliability.

Pyrometers designed for sulphur recovery are specifically engineered for the optical characteristics of the reactor and high temperature environment. Thermocouples suitable for sulphur recovery are designed utilising special materials and protection mechanisms to provide accuracy and reliability at the extreme process temperatures. These thermocouples utilise a series of alumina ceramic thermowells and noble metal type thermocouple elements. Thermocouples in sulphur recovery utilise purged or unpurged technology with purged designs offering the highest reliability track record. Recent research and development efforts by Delta Controls Corporation have resulted in a highly reliable unpurged alternative.

Table 1: **Chart of thermocouple temperature ranges**

Type	Composition	Temperature Range
B	Pt-30% Rh versus Pt-6% Rh	0°C to +1,820°C
E	Ni-Cr alloy versus a Cu-Ni alloy	-270°C to +1,000°C
J	Fe versus a Cu-Ni alloy	-210°C to +1,200°C
K	Ni-Cr alloy versus Ni-Al alloy	-270°C to +1,372°C
N	Ni-Cr-Si alloy versus Ni-Si-Mg alloy	-270°C to +1,300°C
R	Pt-13% Rh versus Pt	-50°C to +176°C
S	Pt-10% Rh versus Pt	-50°C to +1,768°C
T	Cu versus a Cu-Ni alloy	-270°C to +400°C

Source: NIST

SRU thermocouple challenges

Thermocouples, both purged and unpurged, are presented with numerous individual challenges in the sulphur recovery environment, and when presented together compound to create significant reliability challenges. Proven thermocouple designs utilise a series of alumina ceramic thermowells and noble metal thermocouple elements.

The high temperatures permit only a few thermocouple types to fall in the readable range (see Table. 1). Also many metals commonly used on thermocouple sheaths, or thermowells, are not suitable due to melting temperatures below +3,000°F (+1,649°C). In addition to high temperatures, the process is highly corrosive with process gases hydrogen sulphide, sulphur dioxide, and other sulphur species present. Noble metal thermocouple types such as B, R, and S may be subjected to a multitude of detrimental effects, including hydrogen embrittlement, platinum oxide sublimation (see Fig. 1), and other degradation reactions. These reactions lead to signal degradation or, ultimately, failure.

An alumina thermowell does not provide complete protection from the process gases. The porosity of the aluminium oxide at operating temperatures allows small amounts of process gases to diffuse through the thermowell, particularly at operating temperatures. If these gases are allowed to accumulate inside the thermowell, they will corrode, contaminate, or otherwise degrade the thermocouple within a few weeks.

Purged thermocouple technology

The proven method of protecting thermocouple elements is to purge the thermowell with an inert gas, usually nitrogen, in order to sweep away any process gases that diffuse through the primary thermowell (see Fig. 2). The gas is piped to the upper chamber of the thermocouple where it then travels down the holes of the element support where the thermocouple wires are positioned. The gas envelops the sensing junction at the end of the support. Any diffused process gas is mixed with the nitrogen, then directed to the outlet. Due to the slow rate of process gas diffusion through the thermowell, a purge flow of approximately 11 L/h is sufficient to provide protection without significantly cooling the thermocouple.

Disadvantages of purged thermocouple technology

Purged thermocouple designs, when properly installed and maintained, are the proven solution for reliable temperature indication from turnaround to turnaround. However, purged thermocouples are not without compromise. Installing and maintaining the purge system will require additional costs and complexity that may be considered a disadvantage. The purge gas system also introduces additional potential failure modes for the thermocouple as the purge gas must remain free of contaminants such as moisture or hydrocarbons that may damage the thermocouple elements. The system requires periodic maintenance to verify correct pressure and flow settings as well as functionality.

Unpurged thermocouple technology

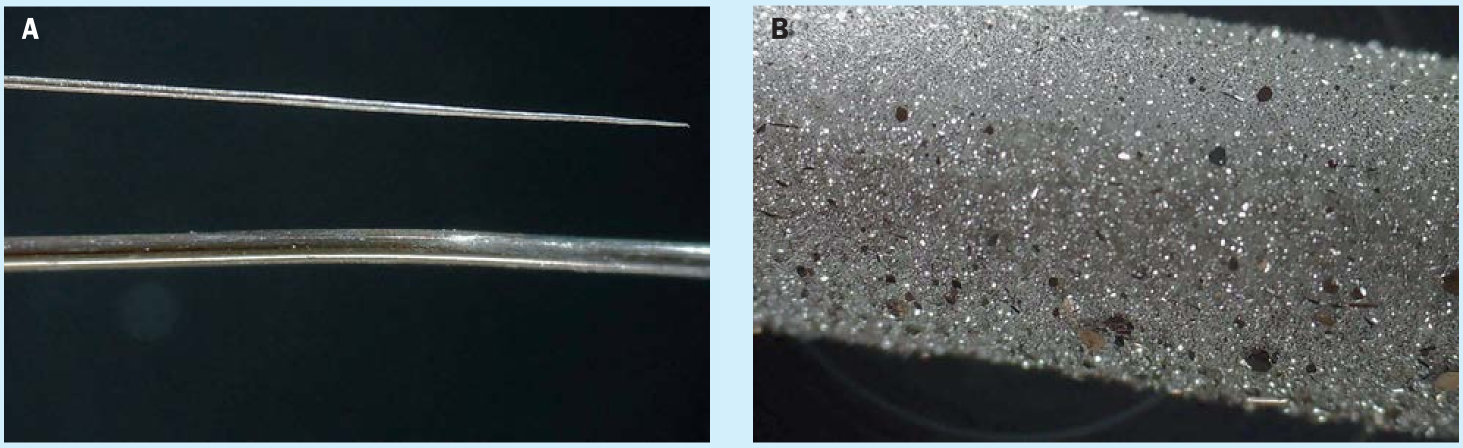
Plants may attempt to reduce operational and capital expenditure costs by installing unpurged thermocouples that are unsuitable for the challenges of the reactor environment. Most of these attempts result in a failed thermocouple after a relatively short time resulting in the main reactor losing critical temperature indication and introducing associated safety concerns.

Recently, market interest in unpurged thermocouples has increased with the introduction of additional unpurged thermocouple designs utilising alternative thermowell materials such as monocrystalline sapphire. Sapphire is grown from a single crystal, rather than slip cast or recrystallised like alumina resulting in a molecular monocrystalline crystal lattice structure that is uniform throughout the thermowell. Traditional high purity alumina ceramic has a higher molecular porosity that can allow process gases to diffuse through the ceramic at the high operating temperatures in the main reactor. Sapphire is compositionally identical to high purity alumina as both are composed of aluminium oxide, Al_2O_3. However, the monocrystalline structure of sapphire is not porous at high temperature and therefore the diffusion of process gases through its crystalline matrix is much slower than through alumina ceramic. While monocrystalline structures are absent of grain boundaries, it is unlikely that process gas diffusion is completely prevented.

The utilisation of a sapphire thermowell in an unpurged thermocouple design exclusively is not sufficient for long term reliability of the instrument. The seals that surround the thermowell are critical to the prevention of process gas diffusion into the assembly. Even the most effective seals will not have a zero leakage rate. While contaminants may be impeded by the sapphire thermowell, the seals surrounding the thermowell are subject to trace amounts of leakage. The trace contaminants can accumulate inside the thermocouple assembly eventually causing degradation of the thermocouple elements.

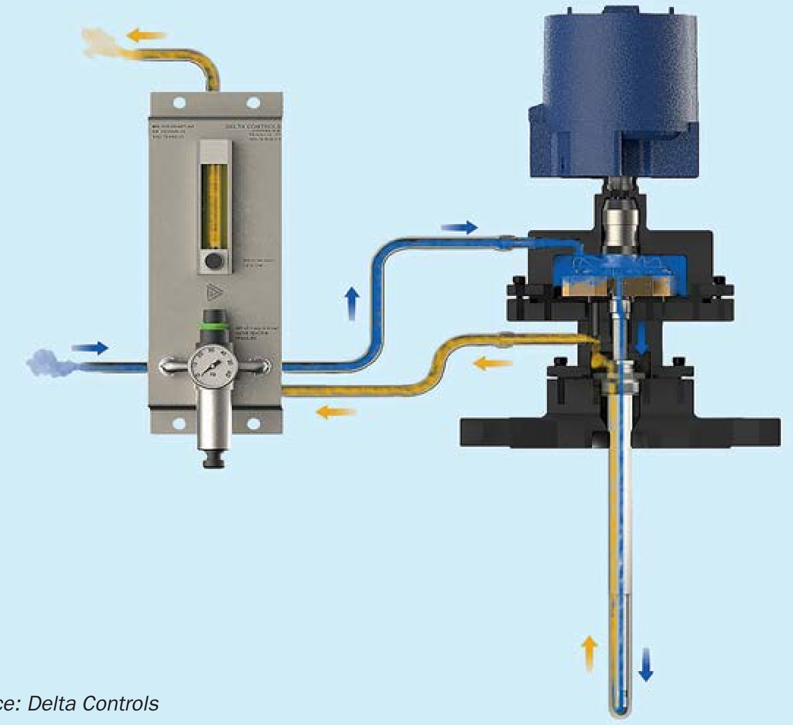
The Delta Controls Model HTV thermocouple (Fig. 3) reliably addresses the seal leakage problem by implementing a newly developed, patent-pending seal

Fig. 1: **Effects of platinum oxide sublimation. The thermocouple element thins to a needle point and platinum deposits up the ceramic element support as crystals. A) Mass loss thinning as a result of platinum oxidation. The bottom wire has full cross section remaining. B) Platinum crystals deposited on a ceramic element support.**



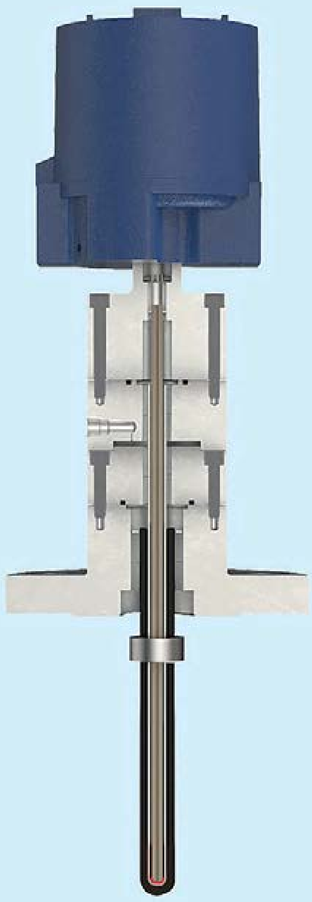
Source: Delta Controls

Fig. 2: **Operation of a purged thermocouple**



Source: Delta Controls

Fig. 3: **Unpurged thermocouple**



Source: Delta Controls

mechanism designated as QSeal™. The design utilises a series of protection mechanisms to prevent process gas diffusion, gas accumulation, and seal leakage from compromising the temperature indication. The issues are first addressed with careful selection of advanced seal materials that minimise diffusion through the seal structure. Secondly, a high compression wedge seal design mechanically reduces contaminant bypass around the seal. Finally, and most importantly, the seal system design prevents any contaminants that bypass the primary seals from accumulating within the thermocouple assembly to concentrations higher than the ambient atmosphere. Secondary seals, which are exposed to a nearly ambient atmosphere, isolate the open end of the sapphire thermowell; therefore, contaminant leakage through secondary seals is negligible. Multiple redundant seals, in addition to the primary and secondary seals, ensure process containment is maintained in the event of thermowell breakage.

Disadvantages of unpurged thermocouple technology

While thermocouples utilising a sapphire thermowell have been in high temperature applications for many years, the designs have only recently been evaluated for use in sulphur recovery thermal reactors. Due to the recent implementation of this technology, it is unproven in terms of reliability and longevity in sulphur recovery service.

The absence of grain boundaries in monocrystalline sapphire can slow the diffusion of process gases through the thermowell, but it is unknown whether the diffusion rate is sufficiently minimised to prevent thermocouple deterioration for the targeted five to seven years between turnarounds. Another potential concern is the effect of the atmosphere contained within the thermocouple assembly will have on the longevity of the device. A number of deleterious reactions are known to occur with platinum at high temperatures. These reactions are not a problem in a purged thermocouple, where the purge gas is constantly replacing the atmosphere within the thermocouple assembly with inert nitrogen. How problematic contained atmosphere is remains to be seen.

Trials are underway, but an insufficient number of sapphire protected thermocouples have been installed long enough to clearly demonstrate turnaround to turnaround reliability. Until the technology has matured and demonstrated reliability, it is recommended that sapphire protected thermocouples only be installed in addition to other proven temperature measurement technologies such as purged thermocouples or pyrometers.

In conclusion, unpurged sapphire thermocouples show promise as an alternative to purged thermocouples; however, overcoming the associated application challenges in sulphur recovery service require more than changing the thermowell material. Careful attention must be paid to the seal materials, seal design, and overall architecture of the thermocouple assembly to assure safety, longevity, and reliability.

Unpurged sapphire thermocouples have only been used in SRUs for a relatively short time. It will be 5 to 10 years before enough field data has been collected to evaluate whether unpurged sapphire thermocouples are as reliable as purged thermocouples in SRUs.

The Claus thermal reactor is a challenging environment for the long term reliability of all temperature indicating devices. It is imperative that an accurate temperature measurement be continuously reliable for efficient and safe operation. Low reliability thermocouple design consequences include not only financial costs, but also potential loss of safety critical SIS indication while in operation and increased down time of the SRU. As proven in hundreds of worldwide installations for nearly 50 years, a properly designed and installed purged thermocouple reliably serves this purpose.