Sour oil and gas management

3.3.1 Introduction

Petroleum streams containing hydrogen sulphide, H_2S, in amounts greater than a few ppm are referred to as 'sour', a term whose origin goes back to the earliest days of the oil and gas industry, when the oil was tasted to verify whether or not it contained this compound. Hydrogen sulphide is a colourless, highly toxic and dense gas (density 1.39 g/l at 25°C and 1 bar; boiling point −60°C) which is readily soluble in hydrocarbons. It is characterized by a foul odour, detectable at 1 ppm, but tends to rapidly saturate the human olfactory system, making it particularly pernicious. The 8 h exposure limit is 10 ppm, and exposure to 600 ppm rapidly provokes respiratory disturbance and death.

Not surprisingly, sour petroleum resources have always posed special problems to operators. If in the past, a highly sour resource (containing several mole% or more of H_2S in the associated gas) might have been considered unattractive for development relative to other assets, today operators are developing fields containing as much as 30% H_2S. The interest for these resources reflects several intersecting trends, including the diminishing availability of easy-to-produce conventional oil resources, increased natural gas (NG) prices in North America, and the opening of Russia, Central Asia and the Middle East to international operators. Their sour petroleum resources, in fact, have historically characterized these geographical regions and international oil and gas companies must be ready to face the challenges of highly sour production in exchange for the opportunity to operate in these rich petroleum provinces.

Hence, the development of sour oil and gas resources is rapidly emerging as a major industrial and technological theme. The problems posed by sour reservoirs include, in the first place, health and safety environment (HSE) issues, which accompany all operations, from the exploration phase through to field abandonment. In fact, the high toxicity of H_2S requires special operating procedures to ensure worker safety during drilling and in production operations. The usual by-product of processing sour oil and gas is elemental sulphur, a bright yellow solid that melts at 120°C, which also must be disposed of correctly, so as to avoid impact on the area surrounding the site of production.

The presence of H_2S, moreover, impacts negatively upon the economic value of an asset, with the need to employ special materials for all fluid streams containing H_2S and humidity; the unit cost of corrosion-resistant metal alloys is as much as ten times greater than that of the carbon steel that would be employed in a sweet oil development. The processes used for NG sweetening also add considerably to capital and operational expenditure; for a remote gas field, the economic limit for gas sweetening using present technologies may be reached for NG containing c. 15 mol% H_2S (see below).

The conventional technology train for the treatment of a sour gas stream is shown in **Fig. 1 A**. This consists of a sweetening step, where the H_2S is removed from the gas, followed by the Sulphur Recovery Unit (SRU). Central to the SRU is the Claus plant, in which the H_2S is converted to elemental sulphur. The gaseous effluent from the Claus plant still contains 2-5% of the total sulphur, which must be further processed in a TGU (Tail Gas Unit) to meet emissions standards for SO_2. Present technologies can be pushed to recover as much as 99.9% of the total sulphur separated from the NG. Where high total volumes of H_2S and/or high concentrations must be treated, new solutions are being sought in order to reduce development costs (**Fig. 1 B**).

Fig. 1. Conventional processing scheme for large volumes of sour gas (A) and a scheme of an innovative process for bulk sweetening with re-injection of acid gas (B).
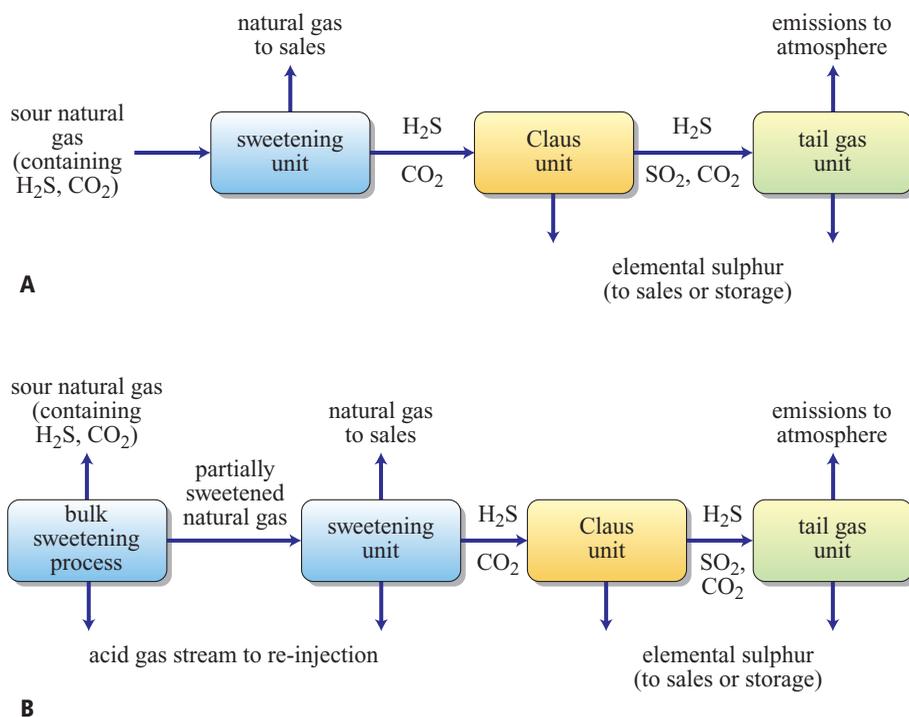
One of the most important developments, which originated in North America and is only now beginning to be applied internationally, employs re-injection of the separated acid gas stream into the reservoir or a suitable, sufficiently deep saline aquifer. In this way, the costs associated with the Claus plant and the TGU are eliminated and the production of elemental sulphur is avoided. At Karachaganak, Eni as joint operator has adopted a variant on this process: the H_2S removed from that part of the associated gas stream utilized for energy requirements and for gas export is mixed with the remaining raw gas and re-injected into the upper part of the reservoir. The c. 500 bar injection pressure constitutes the world record for this type of operation.

Another major focus of industrial R&D regards the development of new, low-cost processes capable of effecting a partial, or bulk, removal of H_2S from highly sour gas streams. Such processes would be installed upstream of a traditional sweetening plant, reducing the volume of H_2S entering the latter, and appear particularly promising where they can be combined with acid gas re-injection (see Fig. 1B again). Many view the development of bulk separation technology as a prerequisite for the economic development of highly sour gas reservoirs, and the major oil companies are active in this area.

The sulphur that emerges from the SRU unit is another source of problems for the operator, particularly in remote geographical locations. Though constituting one of the principal feedstocks of modern society (annual consumption is about 60 million tons), there is a chronic glut of sulphur on the world market. Sulphur produced in remote locations is stranded, and must be stored; this is done by forming large, million-ton blocks of solid, elemental sulphur. The prospect of long-term sulphur storage is driving a search for new storage technologies, or permanent disposal solutions, capable of reducing the long-term environmental and economic liabilities associated with block storage. Interest continues also in the development of new commercial uses for sulphur (see below).

A further word must be said about smaller volume operations (H_2S 1-10 t/d) such as those found in Italy and elsewhere, where H_2S is removed and converted to sulphur via a redox process. The consolidated redox technology has been used for a long time, but the more tons of H_2S removed, the higher the costs of the technology. It is difficult to operate optimally, produces a foul odour, and supplies sulphur of low quality that must be disposed of rather than sold. Research for improved processing options, therefore, continues in this area as well.

3.3.2 Origin of H_2S in oil and gas accumulations

The ability to predict the geological H_2S risk during exploration operations would help both to prioritize potential exploration targets better and to ensure the safety of drilling personnel. Today, this is possible only

to a limited extent, and in areas where considerable knowledge of the subsurface has already been gained through petroleum exploration and development. Reliable prediction of the geological H_2S risk requires detailed knowledge of the mechanisms governing H_2S generation and its migration and accumulation in petroleum-filled structures.

A number of chemical and biological pathways that can lead to the formation of H_2S have been identified (**Table 1**). Of these, the most widespread and important are believed to be Biological Sulphate Reduction (BSR) and Thermal Sulphate Reduction (TSR) (Machel, 2001). BSR is a process mediated by Sulphate Reducing Bacteria (SRB) which are active under strictly anaerobic conditions. These microorganisms metabolize hydrocarbons by employing sulphate ions present in the brine as the electron acceptor (oxidant) in a process which is fast on the geological timescale and most frequently is controlled by the limited availability or diffusion rate of sulphate or another nutrient. The conditions favourable for BSR are believed to include: temperature between 40 and 80°C, the presence of dissolved sulphate ions, and low-to-moderate brine salinity. BSR of crude oil is believed to involve the oxidation of linear saturated hydrocarbons and alkylbenzenes. The H_2S produced inhibits BSR activity above approximately 5 mol% of H_2S in the

hydrocarbon phase, which defines the upper limit on the concentration of H_2S that can be produced by this process; because of the existence of pathways leading to the spontaneous removal of H_2S (see below), rarely does BSR lead to H_2S concentrations in excess of 1-2%.

While the considerations above refer to the petroleum quality in a reservoir prior to its development; BSR can, under favourable conditions, take place on the shorter timescale of oil production operations. In fact, operators in the North Sea and the Gulf of Mexico are all too familiar with the phenomenon of reservoir souring, in which sulphate ions in the injected seawater are used by SRB, probably introduced together with the seawater, to metabolize the water-soluble hydrocarbons. This can lead, in extreme cases, to the generation of several thousand ppm H_2S in the produced fluids, creating tremendous problems for the operator. In fact, serious corrosion problems and expensive platform retrofitting can be the result if the reservoir development plan has been based on the expectation of a sweet petroleum stream. A similar problem can be encountered when producing reservoirs containing sulphate-rich brines from reservoirs too hot for BSR. Once the produced fluids cool to below 80°C, SRB microbial activity becomes a risk and can generate troublesome levels of H_2S in the surface facilities and transport lines.

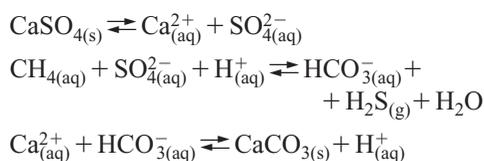**Table 1.** Main sources of H_2S in petroleum accumulations

ORIGIN OF H_2S	H_2S GENERATION MECHANISM	MAIN CHARACTERISTICS
Biological sulphate reduction (BSR)	$Petroleum + CaSO_{4(s)} \rightarrow CaCO_{3(s)} + H_2S + H_2O +$ contaminated petroleum and bitumen	Maximum T: c. 80°C, inhibited by high levels of salinity Rarely produces concentrations of H_2S in petroleum above a few mole percent
Degradation of organic sulphur compounds	Hydrolysis of organic sulphur compounds	Generation of H_2S limited by the sulphur content of petroleum of less than a few mole percent
Reaction with elemental sulphur	$4S + CH_{4(aq)} + 2H_2O \rightarrow CO_{2(g)} + 4H_2S_{(g)}$	Elemental sulphur is present almost exclusively as traces in petroleum reservoirs
Volcanic seepage	The H_2S, generated in the deep subsurface, migrates into the reservoir along deep fractures or faults.	Restricted to areas of volcanic activity; rarely associated with hydrocarbon accumulations
Thermal sulphate reduction (TSR)	$Petroleum + CaSO_{4(s)} \rightarrow CaCO_{3(s)} + H_2S + H_2O +$ contaminated petroleum and bitumen	Minimum T: 120-140°C Requires the presence of anhydrites May generate percentages of H_2S up to 95 %

Present understanding of these phenomena is incomplete, and research efforts continue to investigate the factors which govern the reservoir and surface souring processes (Burger *et al.*, 2005).
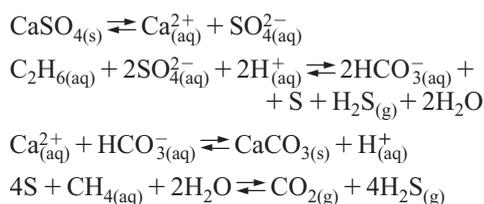
As noted above, TSR is the dominant mechanism responsible for the generation of high concentrations of H_2S in petroleum reservoirs, and has been implicated in the formation of NG reservoirs containing above 95 mol% H_2S. The presently limited understanding of this process can be attributed both to the complexity of the reactions involved and to the difficulty of reproducing the high temperature, pressure conditions and long time-scale of TSR processes in the laboratory. Nevertheless, through a combination of laboratory and field case studies, the general picture of this process has been developed (Machel, 2001; Cross *et al.*, 2004).

TSR involves the reaction of hydrocarbon compounds with sulphate minerals (anhydrites), such as evaporitic beds or other mixed lithologies, in the presence of brine. These reactions proceed on a geological timescale and modification of the petroleum accumulation may be only partial. The minimum temperature at which this process becomes important is estimated by various authors to lie between 120 and 140°C. Petroleum quality, the sulphate dissolution rate and brine availability are believed to influence the rate of TSR, while pH, the presence of H_2S and other minerals are thought to catalyze the process. Deposition of the solid $CaCO_3$ by-product of reaction may inhibit complete reaction of the available sulphate minerals. The chemical transformations generally invoked are indicated below for methane and higher saturated hydrocarbons.

In the case of methane, the following reactions occur:

$$CaSO_{4(s)} \rightleftharpoons Ca^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$
$$CH_{4(aq)} + SO^{2-}_{4(aq)} + H^+_{(aq)} \rightleftharpoons HCO^-_{3(aq)} + \\ + H_2S_{(g)} + H_2O$$
$$Ca^{2+}_{(aq)} + HCO^-_{3(aq)} \rightleftharpoons CaCO_{3(s)} + H^+_{(aq)}$$

In the case of ethane and higher alkanes, however, the reactions are as follows:

$$CaSO_{4(s)} \rightleftharpoons Ca^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$
$$C_2H_{6(aq)} + 2SO^{2-}_{4(aq)} + 2H^+_{(aq)} \rightleftharpoons 2HCO^-_{3(aq)} + \\ + S + H_2S_{(g)} + 2H_2O$$
$$Ca^{2+}_{(aq)} + HCO^-_{3(aq)} \rightleftharpoons CaCO_{3(s)} + H^+_{(aq)}$$
$$4S + CH_{4(aq)} + 2H_2O \rightleftharpoons CO_{2(g)} + 4H_2S_{(g)}$$

As indicated for the higher alkanes, elemental sulphur is a product of the TSR reaction. Although it can further react with CH_4 to generate H_2S, it can also be chemically incorporated into other components of the petroleum, as further discussed below, although small but significant amounts may remain in the reservoir as elemental sulphur. Other routes to sulphur production include the following:

$$CaSO_4 + 3H_2S \rightarrow CaO + 3H_2O + 1/2S_8$$

TSR processes take place under conditions of temperature in which thermal maturation occurs, and contribute to the change in the oil quality. The saturated hydrocarbon compounds present in petroleum are preferentially consumed by TSR reactions, with methane being the least reactive of these. TSR consequently results in a relative increase in methane and in the aromatic components of the crude at the lower range of temperature for TSR. Nevertheless, the correlation of TSR with API gravity is weak because benzothiophenes and heavier aromatic sulphur compounds may be formed as the result of the reaction of the elemental sulphur by-product with hydrocarbons, offsetting the consumption of heavier hydrocarbons. The increase in the percentage of methane may favour precipitation of the asphaltenic component, with negative consequences for reservoir quality. In advanced stages and at a higher temperature, TSR favours the formation of dry natural gas, with an H_2S content of 95 mol% or even higher. Under these conditions significant amounts of elemental sulphur may also be present in the gas phase.

The amount of H_2S found within a reservoir is determined not only by the amount of H_2S generated by TSR reactions, but also by the presence of pathways capable of removing it from the oil during migration or within the reservoir. The presence of iron or other transition metal ions in the brines or mineral phases with which the H_2S comes into contact can scavenge a considerable amount of H_2S through the formation of metal sulphides (e.g. pyrite). Common iron minerals include siderite ($FeCO_3$) and magnetite (Fe_3O_4), and the clay phase chlorite; other clay phases may incorporate iron ions as well (Aagard *et al.*, 2001). Thus, in general, clay-rich porous media tend to be less prone to high H_2S accumulations. For the same reason, carbonate rocks containing anhydrites are the best candidates for high H_2S accumulations. Another pathway for H_2S removal, dissolution into the brine phase, can be important where the aquifer is hydrodynamically active.

The distribution of H_2S within a reservoir can be quite heterogeneous and cases of extreme, systematic variability across a structure are known (Al-Eid *et al.*, 2001). Several mechanisms can bring about this phenomenon. One is the migration of H_2S into a reservoir successive to hydrocarbon charging, in which case the slow homogenization of the H_2S may be

incomplete. A heterogeneous distribution of H_2S also can be produced where there are hydraulically isolated compartments within the reservoir, or where clays and other H_2S scavenging minerals are unevenly distributed within the structure.

Sulphur isotopic analyses on H_2S, organic sulphur components of the oil and reservoir mineral phases (e.g. anhydrites and pyrite), when used in conjunction with other information, constitute a particularly powerful tool for determining the likely origin of the H_2S within a structure. The isotopic parameter $\delta^{34}S$ is defined according to:

$$\delta^{34}S = \left[\frac{(^{34}S/^{32}S)_{sample}}{(^{34}S/^{32}S)_{standard}} - 1 \right] \cdot 1.000$$

where $\delta^{34}S$ is assigned a value of zero in the standard, which is troilite found in the Diablo Canyon meteorite. In fact, where TSR operates, the value of $\delta^{34}S$ for H_2S should be very similar to that of the anhydrite source, and in fact can be used to identify that source. In several cases, sulphur isotopic data have been used, together with other geological information, to infer the minimum temperature for onset of TSR in the petroleum system (Manzano *et al.*, 1997). Whereas the $\delta^{34}S$ parameter of the organic sulphur compounds in an oil not subjected to TSR will have the same value as the source rock, sulphur incorporated chemically into the petroleum following TSR should tend toward the same $\delta^{34}S$ value as the H_2S. The BSR pathway for H_2S generation, on the other hand, is characterized by a large isotopic fractionation between sulphate and sulphide.

3.3.3 H$_2$S removal in small volume plants

Desulphurizing hydrocarbons to remove H_2S in excess of the required specifications is one of the most expensive aspects of the treatment of acid gas streams. Being a highly toxic gas, H_2S must not only be removed from the hydrocarbon stream with efficiencies close to 100%, but also turned into a less hazardous species, usually elemental sulphur, with additional costs (*Gas* […], 1994). In large treatment plants which remove dozens of tons of H_2S a day or more, Claus processes are normally used. For smaller volumes the Claus process is uneconomic, and H_2S transformation makes use of other, generally less effective, conversion systems. In these instances, the technological options available are essentially of two types: non-regenerated sorbents and redox processes (Kensell and Leppin, 1996; Quinlan, 1996). One of the most effective parameters for the selection of the optimal process is the plant's capacity in terms of

removed sulphur. **Fig. 2** shows an estimate of the cost of treating an NG stream as plant capacity varies. In addition to showing the rapid rise in the cost of treating the gas as the H_2S content increases, the diagram highlights the need to use different desulphurization technologies depending on the quantity of H_2S to be removed.

To remove a few dozen to several hundred kg of H_2S per day from acid gaseous hydrocarbon streams, non-regenerated chemical sorbents are generally used (Foral and Al-Ubaidi, 1995). The acid gas comes into contact with solid or liquid chemicals which react with the H_2S to produce a spent stream which must be disposed of. The sorbent may form the packing in an absorption column, as in the Sulfatreat and Iron Sponge technologies, or, for liquid reagents, a washing column may be used; alternatively, the reagent, usually a triazine or less commonly an amine, may be injected directly into the acid gas stream inside the gas pipeline. Injection into the pipeline requires small and simple equipment (a liquid/gas mixer at the entrance to the pipeline and a separator at the exit) but, due to the cost of the chemicals, it is not viable for volumes above a few dozen kg of sulphur per day. In general, the use of non-regenerated solid or liquid sorbents makes it possible to reach the required quality specifications for gas with low capital costs. However, operating costs are high, up to or over 15 euro per kg of sulphur produced. These costs are considered acceptable if the quantity of sulphur to be removed is small, but become unsustainable when tons of sulphur per day must be removed from the gas streams.

Regenerable reagents have been developed since the 1940s, but large numbers of desulphurization processes based on regenerable reagents have been available to the oil industry only since the 1970s. Most of these processes are based on reversible oxide reduction in the liquid phase; they are therefore known
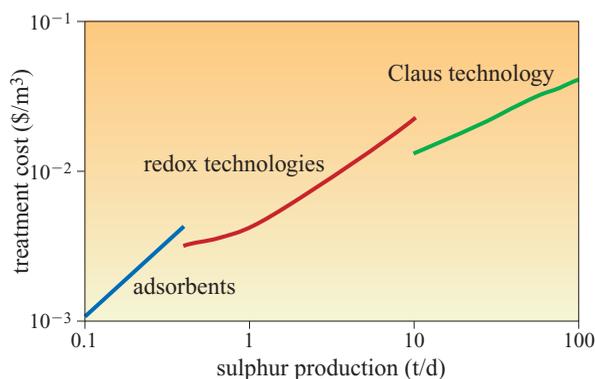

Fig. 2. Desulphurization costs for a natural gas production facility (capacity = 10^6 Sm^3/d).

collectively as 'liquid phase redox processes'. Redox processes (Connock, 1996) can be used for production volumes lying in the range of a few hundred kg of sulphur per day up to the lower economic limit of amine/Claus processes, about several dozen tons of sulphur per day.

Fig. 3 shows the typical scheme of a redox process. In the absorption stage, the acid gas comes into contact with the absorbent solution; the H_2S reacts chemically with the solution and the sweetened gas exits the reactor. In most cases, the solution contains a reagent which oxidizes the H_2S to sulphur; in others, oxidation occurs at a later stage. After the oxidation of the absorbed H_2S, the partially spent circulating solution is sent to the regeneration stage, where its oxidization capacity is regenerated with air through oxidation reactions which are generally catalyzed. A separation stage, either before or after regeneration, recovers the sulphur produced in the form of a concentrated suspension. After the replacement of the circulating solution to re-establish the original composition and volume, it is returned to the absorption reactor for a new cycle.

One of the first redox processes developed was the Stretford process (Keene, 1989). Based on the absorption of H_2S in an alkaline solution followed by oxidation to sulphur with the redox pair $(VO_2^-)/(V_4O_2^{2-})$, the Stretford process covered a significant portion of the redox desulphurization market for many years. For environmental and safety reasons, the presence of vanadium in the redox solution led to the abandonment of the construction of new facilities in favour of safer and more environmentally-acceptable processes based, for example, on the redox pair Fe^{2+}/Fe^{3+}. Liquid phase redox processes using solutions of iron salts are prevalent in the desulphurization capacity range between 0.5 and 20 t/d of sulphur. Hundreds of plants have been built with the LO-CAT (Merichem GTP,
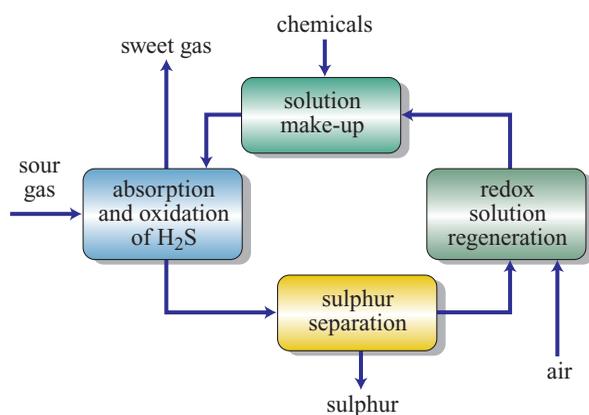
ARI, Wheelabrator, US Filter and others) and Sulferox (Dow Chemical) technologies (Mamrosh and Allen, 1994, Nalg, 1995).

Despite the commercial success of these plants, redox desulphurization processes continue to present high costs and various operating problems. High capital expenditure is required for the materials necessary to resist chemical attack by the oxidizing solutions; the reactors must therefore often be built of stainless steel. Operating costs are high mainly due to the costs of the chemicals, which contribute to desulphurization costs to the tune of several hundred euro, and in some cases over a thousand euro, per ton of sulphur produced. Furthermore, operating problems encountered include the tendency to form stable foams, to deposit sulphur in the transport lines, and the production of sulphur which does not meet commercial specifications, and must be disposed of, for example, by landfilling. These limitations become even more significant for high-pressure applications or offshore platforms.

The response to the problems presented by commercial redox processes has been the development of new processes which aim to simplify redox chemistry, reduce operating costs and make plant management less problematic (Quinlan *et al*., 1997). Some of these new processes use organic solvents to avoid the problems associated with the presence of sulphur dispersed in aqueous streams. Examples include the Crystasulf process developed by Radian International and Hysulf process developed by Marathon Oil. In other processes, like Thiopaq, originally developed by Paques, and later in collaboration with Shell Global Solution, a basic aqueous solution is used to sweeten the acid gas. This prevents elemental sulphur from being formed in the absorption reactor; instead, sulphur forms during the regeneration phase, presenting less serious operating problems, especially for pressurized applications. The Thiopaq process belongs to the family of redox processes which use biological reactors (Anders and Webb, 1995). In Thiopaq plants, the regeneration of the absorbent solution occurs in a bioreactor where the sulphide deriving from the absorption of the H_2S into the basic solution is oxidized by aerobic micro-organisms to sulphur and in part to sulphate minerals. The alkalinity used for absorption, which would otherwise render the process uneconomic, is thus regenerated. The Desulfeen process, developed by EniTecnologie (Gianna *et al*., 2004) also employs a biological reactor, in this case for the regeneration of the absorption solution. In the Desulfeen process, based on the redox pair Fe^{2+}/Fe^{3+}, the circulating solution, acidified with sulphuric acid, is regenerated in a bioreactor containing *Thiobacillus ferrooxidans*

Fig. 3. Diagram of the workings of redox processes.

bacteria. This choice, made possible by using strains of *Thiobacillus ferrooxidans* able to reoxidize iron under acid pH conditions, entails a series of operating and economic benefits: less foam, better separability of sulphur, the low cost of the chemicals and higher quality of the sulphur produced.

As an alternative to liquid phase redox processes, some suppliers are developing technologies based on thermal processes adapted to small volumes, which make use of the fastest H_2S oxidation kinetics obtainable at relatively high temperatures. An example is the direct oxidation process offered by Sulfatreat, in which the acid gas is sweetened by oxidizing the H_2S with air, mixed with the gas in stoichiometric quantities in a catalytic reactor. The percentages of H_2S removed (around 90%) are far from those obtainable with non-regenerable sorbents or liquid phase redox processes, many of which allow acid hydrocarbon streams to be desulphurized to H_2S concentrations below 1 ppm vol. However, the advantages are significant: the absence of circulating solutions, the multi-year life of the catalyst and the production of extremely pure liquid sulphur.

Many new low-volume desulphurization technologies have been developed to the pilot/demonstration plant scale, and in some cases have been used in industrial plants. However, despite the availability of numerous new processes (those mentioned are only a few of those discussed in the specialized literature), the commercial scene continues to be dominated by conventional processes. This situation may change in the near future; under pressure from environmental regulations on sulphur emissions, a growing fraction of acid hydrocarbon streams in the petroleum industry are destined to be desulphurized, creating a significant increase in the demand for desulphurization capacity in the interval suited to redox processes. It is likely that in a cost-conscious market such as that for gas treatment, the increase in demand may pave the way for the emergence of more innovative processes.

3.3.4 High volume sour gas treatment processes

Sour petroleum streams and large total H_2S volumes to process constitute special challenges for oil and gas operators, on account of the high capital and operating costs of the consolidated technologies, and the need to manage the large volumes of elemental sulphur produced, particularly in remote locations. In Canada, the Middle East and Central Asia facilities are operating which treat sour gas streams containing

as much as 30% H_2S, and total amounts as high as several thousand tonnes of H_2S per day.

Sour gas sweetening

The pipeline specification for NG generally requires an H_2S level of 5 ppm or less. The upgrading, or 'sweetening', of a sour natural gas is accomplished using processes which selectively remove the H_2S from the NG, with high hydrocarbon recovery. The acid gas thus removed, which may also contain significant amounts of CO_2, COS, CS_2 and mercaptans, is sent to a SRU (e.g. Claus plant) or, increasingly, to re-injection (see Section 3.3.5).

The main processes used for NG sweetening are based on selective absorption using solvents, although adsorption using molecular sieves is also used for some intensive purification processes. The chief characteristics of the consolidated processes are discussed briefly in this section (for a more detailed treatment, see Chapter 3.2). These and other processes are the object of industrial R&D activities, pursued with the aim of reducing the cost of producing highly sour (H_2S 10-30 mol% or higher) petroleum resources. As mentioned above (see Section 3.3.1), most efforts are currently focussed on the bulk sweetening of highly sour NG upstream of the final sweetening plant, and envision re-injection into the reservoir or another deep geological structure, rather than Claus processing, of the acid gas separated.

Consolidated sweetening processes

Absorption processes

The selectivity of solvent-based sweetening processes for sour natural gas relies on either a chemical or physical affinity. Chemical solvents react with the acid gas components to form loosely-bonded chemical complexes. On heating at reduced pressure, these complexes dissociate and release the acid gas from the solvent. Physical solvents absorb acid gases by dissolution. After absorption, the acid gases may be released from the solvent by reducing the pressure, thermal stripping, or a combination of both. Recently, blends of physical and chemical solvents have been developed which combine some of the advantages of both; these are also commonly regenerated by thermal stripping. In each case, the regenerated solvent is recycled to the absorber, while the acid gas stream flows to the SRU. The choice of solvent is based on the gas composition, expected sweet gas specifications, requirements of the SRU, etc. For a list of the major solvent families and the blends presently in use for NG sweetening, see Chapter 3.2.
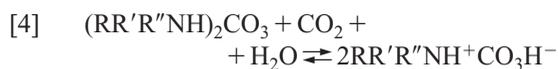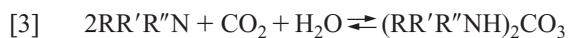
The most widely used chemical solvents for the removal of acid gases from NG streams are alkanolamines (referred to generally as amine solvents), employed as aqueous solutions. These chemical solvent processes are particularly applicable when acid gas partial pressures are low and/or low levels of acid gas are desired in the residue gas. Because of the low hydrocarbon solubility in the aqueous solution, these processes are particularly effective for treating gases rich in heavier hydrocarbons. Some alkanolamines can be used to selectively remove H_2S in the presence of CO_2.

The basic chemical processes involved in H_2S capture by amines are illustrated below:

[1] $2RR'R''N + H_2S \rightleftharpoons (RR'R''NH)_2S$

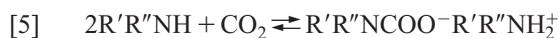[2] $(RR'R''NH)_2S + H_2S \rightleftharpoons 2RR'R''NH^+ HS^-$
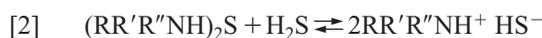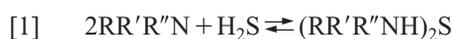
where R denotes an alkanol group and R′ and R″ can be either alkyl or alkanol groups, hydrogen, or a mixture of the two depending on whether the amine is primary, secondary or tertiary. Alkanolamines also react with carbon dioxide in two ways:

• formation of carbonate and bicarbonate

[3] $2RR'R''N + CO_2 + H_2O \rightleftharpoons (RR'R''NH)_2CO_3$

[4] $(RR'R''NH)_2CO_3 + CO_2 +$
$\qquad\qquad + H_2O \rightleftharpoons 2RR'R''NH^+CO_3H^-$

• formation of carbamate

[5] $2R'R''NH + CO_2 \rightleftharpoons R'R''NCOO^-R'R''NH_2^+$

While reactions [1] and [2] are fast, [3] and [4] are slow.

Amine chemical structure has an important impact on reactivity with H_2S and CO_2, and can be used to enhance selectivity for H_2S. Sterically hindered amines are the most basic and have the fastest reaction rates with H_2S, but are less prone to carbamate formation (carbamate formation is entirely excluded with tertiary amines). Benefits of selective H_2S removal include the need for reduced solution flow rates, higher H_2S concentrations in the separated acid gas and smaller amine regeneration units. In many industrial applications, removal of H_2S from the gas stream is the only objective of the process, such as in streams with low ratios of H_2S to CO_2 (as in Claus plants for the treatment of tail gas), and in NG with a CO_2 content at or below the sales gas specification.

The basic process for amine scrubbing involves contacting the gas (at elevated pressure) with the solvent counter-currently in a packed or trayed absorption column (**Fig. 4**). A significant portion of the co-absorbed hydrocarbons is recovered by reducing the pressure of the rich amine in a flash drum. Finally, the chemical solvent is regenerated, after heat exchange and filtration, in a distillation column which operates at, or near, 1 bar.

Processes using physical solvents are based on physical absorption of the acid gases and employ a process scheme resembling that for the amine solvents (see Fig. 4 again), with the addition of a series of flash units between the absorption and regeneration columns. Physical solvent processes are favoured where the partial pressure of the acid gas in the feed is high (greater than c. 345 kPa), heavy hydrocarbon content is low and selective removal of H_2S is desired. Some follow-up treatment or blending is generally required to achieve pipeline specifications for H_2S. The interest in these processes derives from the low energy requirements for regeneration, which is achieved by multi-stage flashing at low pressures, by stripping with inert gas at low temperature or by heating and stripping with steam or solvent vapours.

Physical solvents generally can remove COS, CS_2, and mercaptans as well as H_2S while, in certain instances, simultaneously dehydrating the gas. The absorption step is operated at, or lower than, ambient temperature in order to enhance the solubility of the acid gases. The solvents are relatively non-corrosive, so carbon steel can be used in the plants. However, the physical solvents also absorb heavy hydrocarbons from the gas stream, resulting in high hydrocarbon content in the acid gas stream as well as possibly significant hydrocarbon losses. On the main physical absorption processes, see Chapter 3.2.

One of the most recent developments in natural gas sweetening technology is the use of hybrid solvents which employ a mixture of chemical and physical solvents in order to combine the favourable characteristics of each (e.g. selectivity for CO_2 or mercaptans), and may be tailored to the needs of the specific application. As an example, the mixtures of sulpholane with diisopropanolamine (DIPA) or methyldiethanolamine (MDEA) employ the physical solvent sulpholane in an aqueous medium, and make it possible to remove H_2S, CO_2, COS, CS_2, mercaptans and polysulphides. DIPA is used where complete removal of H_2S, CO_2 and COS is desired while MDEA is preferred for the selective removal of H_2S in the presence of CO_2, with partial removal of COS. The main advantages reside in the low energy requirements, high acid gas loadings and low corrosivity of the solvent. The disadvantages are those typical of physical and chemical solvents: co-absorption of heavy hydrocarbons in the NG stream and the need to regenerate the chemical solvent for gas streams containing CO_2.

Fig. 4. Simplified process scheme for acid gas removal by amine scrubbing.
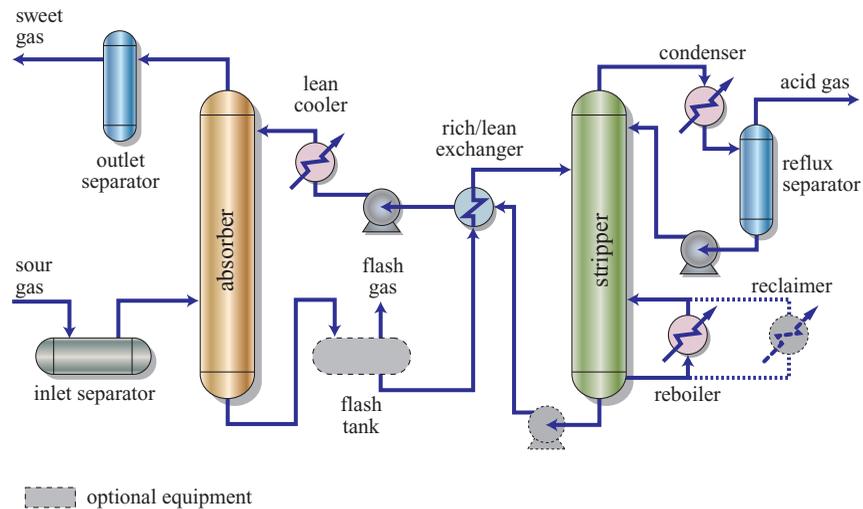
Adsorption processes

Adsorption processes employing 13X and 5A molecular sieves have been used for a variety of applications where very high gas purity is required. This technology provides simultaneous water and acid gas removal down to very low water contents (0.1 ppm vol). Large-pore molecular sieves such as 13X also provide separation of mercaptans. In the presence of CO_2, however, 13X molecular sieves tend to catalyze the formation of COS by reaction between H_2S and CO_2. Commercial units with a capacity up to $6 \cdot 10^6$ Sm^3/d (standard m^3 per day) are in operation. These units may have two or three adsorber beds, and the molecular sieves are regenerated thermally. Traces of glycol, glycol degradation products or oil can poison the molecular sieve.

Bulk sweetening processes

The movement of the industry towards re-injection of acid gases as a means of reducing the volume of elemental sulphur produced in petroleum operations has important implications for NG sweetening processes. Where moderate H_2S volumes are treated, it may be convenient to employ conventional sweetening processes with the treated gas exiting at pipeline specification and the separated acid gas stream sent to re-injection. For very large volume operations, however, the industry is exploring the development of partial, or bulk sweetening processes to be installed ahead of a final, conventional sweetening process (**Fig. 5**). The underlying concept of this research is that it may be possible to develop bulk sweetening processes capable of removing a large part (50-95%) of the H_2S at a much lower unit cost than the conventional processes.

This technology may be the key to the economic development of highly sour gas

resources in the Middle East and Central Asia, which would otherwise have treatment costs approaching the commercial value of the sweetened NG. To illustrate this point, **Table 2** reports an estimate of the total costs for sweetening an NG (c. 7 million m^3/d) containing 19 mol% of

Table 2. Costs per unit of gas treated with conventional technology (amine sweetening, Claus, TGU, sulphur storage) for an associated gas containing 19% of H_2S

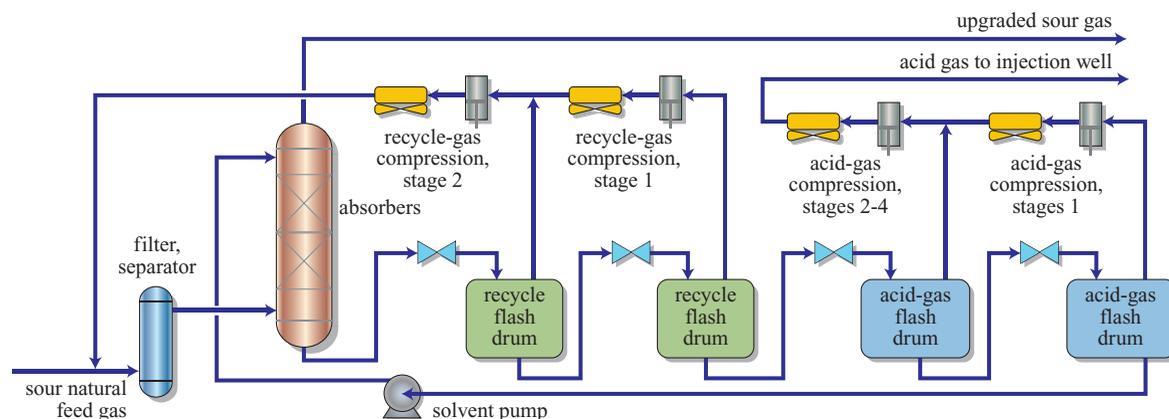|	DOLLARS/MBTU	DOLLARS/T OF SULPHUR
Materials	0.001	0.118
Facilities	0.19	24.82
Sulphur storage	0.06	8.00
TOTAL, GROSS VARIABLE COSTS	0.25	32.93
Credit-by-products (steam)	0.11	14.40
TOTAL, NET VARIABLE COSTS	0.14	18.53
Fixed costs	0.10	12.59
TOTAL COSTS	0.24	31.12
Depreciation (10%/y)	0.22	29.35
PRODUCTION COSTS	0.46	60.47
Profits (15%/y)	0.34	44.03
RECOVERED PRODUCTION COSTS	0.80	104.50

Fig. 5. Schematic of the Kwoen bulk gas sweetening process (Palla *et al.*, 2004b).

H$_2$S, assuming the use of conventional technology (amine sweetening, Claus processing, tail gas cleanup and sulphur storage) and a remote location. The treatment cost, c. 0.80 dollars/MBtu gas treated, is equal to, or greater than, the market value of the NG itself for many remote locations. Thus we can say that today, an approximate cut-off for the economic viability of a remote sour gas reservoir is around 15% H$_2$S or less. A similar conclusion has been reached by Lallemand and Minkkinen (2002). Although the future market value for remote gas is hard to predict, this analysis serves to underscore the economic burden of traditional sour gas processing on the development of such resources, and to identify the economic 'prize' that would be associated with a breakthrough in the treatment of such resources.

Bulk sweetening processes also represent a solution for incrementing the total NG throughput of an existing treatment plant without the need to add extra SRU capacity. The first example of a large bulk sweetening process, based on the Morphysorb process at the Kwoen gas plant in Northeastern British Columbia, Canada was built

Table 3. Bulk gas sweetening at the Kwoen plant

VAPOUR	ACID GAS FEED	TREATED ACID GAS	ACID GAS
Flow rate (10^6 Sm^3/d)	8.49	7.53	0.96
Pressure (MPa)	7.45	7.38	6.97*
Temperature (°C)	17	13	49
COMPOSITION (% mol)			
CO$_2$	8.60	7.21	19.60
H$_2$S	13.54	5.33	78.71
CH$_4$	77.26	86.81	1.47
C$_2$H$_6$	0.21	0.23	0.09
C$_3$H$_8$	0.02	0.02	0.02
COS	0.02	0.02	0.05
CH$_3$SH	0.01	0.00	0.04
N$_2$	0.34	0.38	0.00
H$_2$O	0.01	0.00	0.04

* After compression

Table 4. Proposed processes for the bulk sweetening of acid gas

PROCESS	PHYSICAL BASIS
Sprex	Cryogenic distillation of H_2S
Membrane separation	Use of selective membranes for the separation of H_2S
Absorption by hydrocarbons	Absorption of H_2S with a physical solvent
Morphysorb	Absorption of H_2S with a physical solvent
Separation with hydrates	Selective formation of H_2S hydrates and their separation from the natural gas

for precisely this purpose (Palla *et al*., 2004a, 2004b). This process employs a physical solvent, comprised of a mixture of *N*-formylmorpholine and *N*-acetylmorpholine, which displays strong selectivity for H_2S over CO_2 and lower hydrocarbon losses to acid gas than other physical solvents. It also possesses good chemical and thermal stability and is environmentally compatible. The Kwoen gas plant initiated operation in 2002 and is designed for bulk H_2S removal and disposal of more than 875 t/d of sulphur through the injection of the separated and liquefied acid gas into a depleted gas reservoir. The plant reduces the H_2S content of the NG stream from 13.5% to 5.3% mol, which allows the centralized gas gathering and upgrading plant to realize its full gas production capacity without the need for additional sulphur recovery capacity. **Table 3** shows the properties and compositions of the gas streams entering and exiting the Kwoen gas plant. The process, illustrated in Fig. 5, was realized with a series of simple flash-regeneration stages in place of a regeneration column so as to minimize energy requirements and capital cost. The gas is absorbed by a Morphysorb solution in two parallel packed columns. The acid gas final flash drums operate at 0.45 MPa and 0.18 MPa respectively. The acid gas that flows from the final flash drum is compressed to a final discharge pressure of 7.6 MPa. The compressor aftercooler liquefies the acid gas prior to its entering a 14 km, 6-inch (15.24 cm) diameter pipeline which carries it to the injection well.

Again in this sector, several innovative physical processes are being studied as a basis for the bulk separation of H_2S from highly sour NG streams (**Table 4**). The general characteristics desired in such a system, where the acid gas is destined for re-injection, can be identified as follows: the bulk removal process should produce the acid gas at elevated pressure, and preferably cold and dry, in order to reduce the cost of compressing it to the formation pressure; it should also require minimal energy input for gas regeneration, as surplus heat energy from the Claus unit is not available in this scenario. However, compared with a commercial gas development project, in a bulk sweetening process methane recovery efficiency will be less of a performance constraint. This is true in remote locations (such as Tengiz, Kashagan), where some of the acid gas by-product of oil production is destined for re-injection.

The Sprex process

A scheme for bulk H_2S removal has been proposed by the Institut Français du Pétrole (IFP), and Total (Lallemand and Minkkinen, 2002). The overall process incorporates an H_2S bulk removal step upstream of a chemical solvent treatment (using activated MDEA) and is intended for use in conjunction with acid gas re-injection into a disposal reservoir. Bulk removal is accomplished in the Sprex contactor through a low temperature distillation of H_2S from methane carried out at elevated pressure (c. 100 bar). Mercaptans are not removed, and as there are significant losses of higher hydrocarbons with the H_2S stream, the most interesting applications are for the treatment of lean natural gases (C_{3+} <1.0%). One of the main advantages of this process is that the H_2S-rich stream from the bulk separation step is obtained as a liquid, which reduces the cost of compression for re-injection. All water contained in the inlet raw gas will be dissolved in this liquid stream, which will also contain some of the incoming hydrocarbons. A simplified Sprex process flow diagram is depicted in **Fig. 6**.

The dried gas leaving the Sprex contactor is cooled through a gas-gas heat exchange, gas-condensate heat exchange, and then through a refrigerated chiller before being passed to a Low Temperature Separator (LTS) drum at line pressure. Fluid composition and the LTS temperature largely determine H_2S removal performance. The higher the acid gas content of the inlet gas, the higher the pre-extraction performance. **Table 5** reports the material balance calculated for an NG stream containing 34% mol H_2S with the LTS operating at $-30°C$. A pilot plant-scale test of the project is being readied for start-up near Pau, France at the time of writing. The economic assessment reported in **Table 6** shows that, for highly sour gas streams, the Sprex process can significantly reduce CAPEX (CAPital

Fig. 6. The Sprex process for bulk H_2S removal (Lallemand and Minkinnen, 2002).
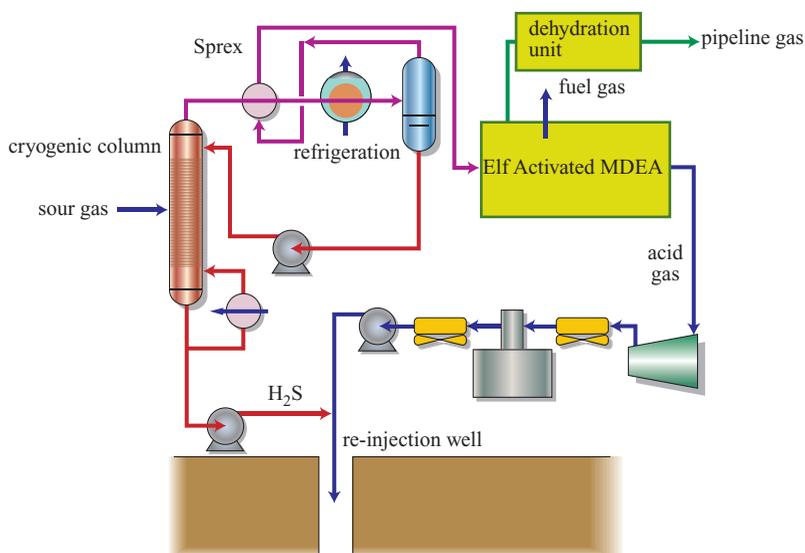
EXpenditure) and power consumption compared to conventional sweetening processes.

H_2S absorption by field hydrocarbons
Eni is currently exploring a simple and inexpensive process for bulk separation, in which the removal of H_2S is performed by absorption with hydrocarbon fractions available at the well site (e.g. virgin naphtha or stabilized crude oil). This application is aimed at remote oil production operations with large volumes of associated gas, where there is very limited market value for the light hydrocarbons.

Process simulation studies suggest the possibility of achieving methane recoveries as high as 95% from an NG containing 14% H_2S and 4% CO_2, with a product gas containing 0.4% mol H_2S. The chemical stability of the hydrocarbon solvent offers the possibility of effecting desorption at high temperature, producing the H_2S-rich disposal stream at high pressure (10-15 bar), which reduces the compression ratio required for acid gas re-injection. It should be possible to further enhance methane recovery, though at the expense of an increase in the treatment scheme complexity (e.g. by employing intermediate desorption

Table 5. Predicted performance of the Sprex process (Lallemand and Minkkinen, 2002)

COMPOSITION OF ACID GAS (pressure, 70 bar)	% VOL
H_2S	35.0
CO_2	7.5
Methane	56.5
Ethane	0.6
Propane and heavier hydrocarbons	0.4
Water	Saturated
SPECIFICATIONS OF TREATED GAS	
H_2S content (ppm vol)	4
CO_2 content (ppm vol)	2
WASTE GAS	
Re-injection pressure (bar)	150

Table 6. Economic comparison of the Sprex process and the MDEA sweetening process for a natural gas with an H_2S content of 35% (Lallemand and Minkkinen, 2002)

CAPEX (BASE 100 FOR CONVENTIONAL TREATMENT)	WITHOUT SPREX	WITH SPREX
Sprex unit	0	23
Compression MDEA and acid gas + facilities	100	57
Total for process units	100	80
ENERGY REQUIREMENTS (MW)		
Electricity (motors, pumps and compressors)	52	29
Heat energy (low pressure steam)	46	34

and a partial recycle of gas to the absorption column). The overall process is similar to that for other physical solvents. A pilot-scale plant for testing this process has been in operation near Milazzo, Italy since early 2005.

The loss of heavier hydrocarbons with the H_2S stream favours use of the process in remote locations where the market value of these products is the lowest. A comparison of the CAPEX and OPEX (OPerating EXpenditure) costs estimated for a conventional plant (for example amine, Claus, TGU) and the same process with an upstream bulk separation step (with the acid gas recovered re-injected into the reservoir) shows that this process offers considerable potential economic advantages. The composition of the gas treated is the same as that in Table 3 whereas a geographically and logistically remote site were assumed in the cost estimate exercise.

Separation of H_2S via hydrate formation

Another physical property, based on the different tendency of H_2S and NG to form clathrate hydrates, has also been proposed as the basis for effecting bulk sweetening of sour gas. In fact, hydrate formation with H_2S is significantly favoured thermodynamically compared to methane (CO_2 is intermediate between the two); the onset for H_2S hydrate formation is only 3 bar at 10°C, whereas methane forms hydrates at this temperature only above 70 bar. In a multi-component system the gas concentrations in the gas and solid phases tend to be enriched or reduced in the components present in the starting mixture.

A thermodynamic study showed that the most relevant variable for the yield of the sweetening process (defined as the ratio between Py and Qz, being Q the molar amount of feed gas, P the molar amount of equilibrium gas, z the molar concentration of CH_4 in the feed gas and y the molar concentration of CH_4 in the equilibrium gas) is the amount of water. Predicted equilibrium compositions of a humid sour

gas stream as a function of T, P and water content are reported in **Table 7**.

A schematic flow diagram of a process for gas sweetening via hydrate formation is shown in **Fig. 7**. The process involves the following steps: *a*) pressurization, if required, of the feed gas mixture using an adiabatic compressor to the set pressure (higher than hydrate formation pressure); *b*) precooling of the pressurized feed gas to a given temperature by heat exchange with the purified NG stream from the hydrate formation unit; *c*) cooling of the feed gas to the set temperature (lower than hydrate formation temperature) using an ethylene glycol solution stream; *d*) hydrate formation in a high pressure unit kept at constant temperature with a second ethylene glycol solution stream; *e*) hydrate dissociation in a dissociation unit by heating with a stream of hot water (seawater or produced water) of a highly-concentrated H_2S gas stream; *f*) the water necessary for hydrate formation is supplied by a recycling stream from the hydrate dissociation unit.

Potential benefits of hydrate separation reside in the possibility of treating associated gas containing a high level of H_2S without the need for special solvents or substrates (solid catalyst, membranes, etc.). The only requirements are water, pressure (20-50 bar) and cooling/heating systems (0-50°C); the energy needed for sustaining the process (heating/cooling cycles) can be obtained by combusting part of the sweetened natural gas. The process should also be capable of providing the acid gas stream at moderately elevated pressure to facilitate re-injection.

Gas permeation: membrane processes

In membrane separation processes a high pressure gaseous mixture is passed over a thin layer of dense material (the membrane) where the dissolution of each component into the membrane is based on solubility and partial pressure. Diffusion across the membrane

Table 7. Yields of the hydrate sweetening process for a binary mixture with an H_2S/CH_4 ratio of (15/85)% mol

	Yield (% mol)					
	10 MPa, 10°C		4 MPa, 4°C		4 MPa, 1°C	
Water (% wt)	Methane recovered	H_2S (%) in treated gas	Methane recovered	H_2S (%) in treated gas	Methane recovered	H_2S (%) in treated gas
10	99.29	13.91	99.49	13.74	99.51	13.72
50	90.12	6.85	91.50	5.81	91.54	5.63
70	67.36	2.90	69.26	2.15	69.05	2.00
85	1.29	1.00	5.24	0.72	4.59	0.68

Fig. 7. Process for gas sweetening via selected formation of H$_2$S hydrates.
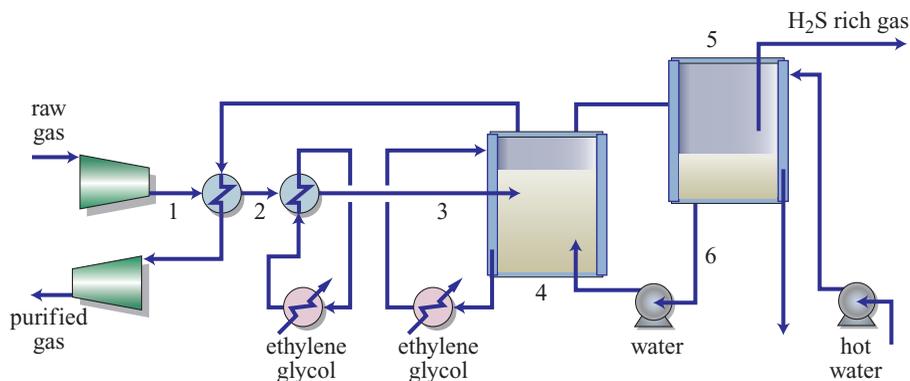
produces two streams: the permeate, enriched in the most permeable gases, and the retentate or product, which is that part of the feed that has not crossed the membrane (**Fig. 8 A**).

Increasing the partial pressure of the component to be removed from the feed gas (by increasing its molar fraction or the absolute pressure of the feed gas, or by decreasing its molar fraction or the absolute pressure in the permeate side) reduces the membrane area required for separation. Commercial membranes for acid gas separation are composed of either cellulose acetate or polyimide polymer. The spiral wound membrane geometry, which consists of a stack of flat sheets of membrane alternated with porous spacers wrapped around a perforated collecting pipe (**Fig. 8 B**), is preferred as it allows for the highest partial pressures. The feed gas flows in the axial direction, parallel to the central pipe, while the permeate stream flows radially towards it. The membranes can operate at pressures up to 130 bar and temperatures from 30-90°C. The membrane modules are usually arranged inside pressure vessels containing 1-8 modules.

Gas permeation is increasingly being applied by upstream operators for CO$_2$ removal from NG, with capacities up to $7 \cdot 10^6$ Sm^3/d being installed and volumes up to $14 \cdot 10^6$ Sm^3/d under development or construction. However, no commercial applications for H$_2$S removal have been set up and operational experience is limited to gas streams with a low H$_2$S content.

The separation of H$_2$S from NG by permeation using current membrane materials is characterized by a trade-off between residual H$_2$S in the treated NG and the loss of hydrocarbons with the acid gas permeate. This has blocked commercial development of membrane separation in traditional gas processing schemes. For bulk separation processes, however, this trade-off may be less significant, and industry efforts are presently

underway to evaluate the potential benefits of this technology. Membrane processes, in fact, possess some important intrinsic advantages: they are environmentally safe, have lower energy requirements and are simple to operate, as there are no moving parts, adjustments or solvents. These characteristics make the application of membrane systems particularly attractive for remote or inaccessible locations. The modular nature of membrane separation allows incremental additions to capacity.

H$_2$S treatment

Today, H$_2$S treatment processes all lead to the generation of elemental sulphur. Large scale sulphur recovery operations (>20 t/d of S) treat H$_2$S as furnished from the sweetening plant and convert it to elemental sulphur through the Claus process, which accomplishes the following overall transformation:

$$H_2S + 1/2O_2 \rightarrow H_2O + S$$
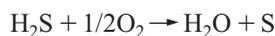
This reaction is carried out in three or more separate stages in a large and complex plant.

As the regulations on emissions from oil and gas operations have tightened, processes capturing as much as 99.9% of the total sulphur present in NG have been developed. Large scale H$_2$S processing plants represent a significant capital expense and, together with the tail gas units needed to clean the off-gas to specifications, can triple the cost of a gas-sweetening unit. For this reason, efforts continue to improve the economic as well as the environmental performance of these processes.

This section examines the Claus process and its major variants, which continue to dominate sulphur recovery, and the processes employed for tail gas clean-up (see also Chapter 3.2). Finally, alternative processes and major modifications of the Claus process which are presently the object of R&D are discussed.
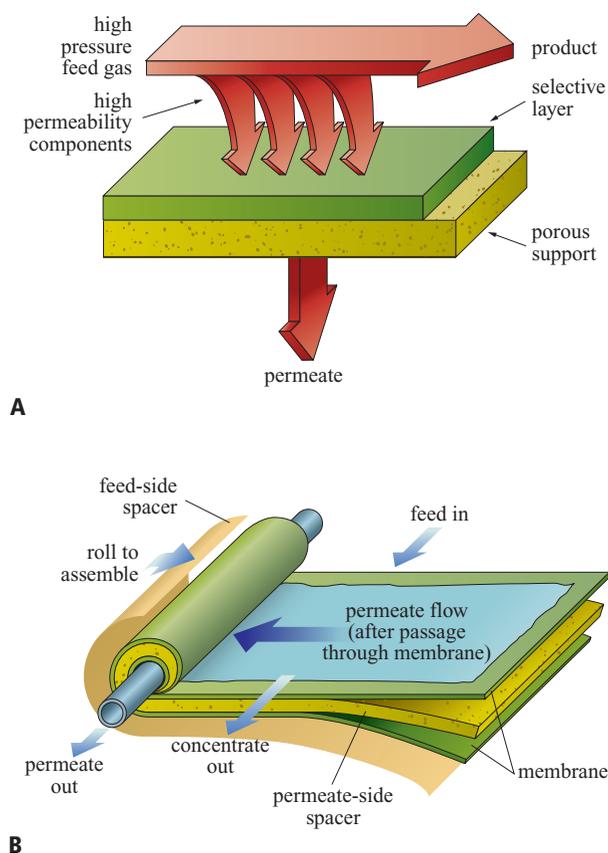
Fig. 8. Membrane-based separation of gas mixtures (A) and the spiral wound geometry (B) commonly used for NG treating.

The Claus process and its modifications

The best-known and most widespread process for the treatment of acid gases is the Claus process, which converts H_2S into liquid elemental sulphur. Claus plants treat gas streams containing 15-80% mol H_2S, up to several % mol hydrocarbons, with the remainder comprised of CO_2, water vapour and other trace compounds such as COS and CS_2.

The Claus process, first conceived in 1883, comprises two steps, the first of which is the oxidation of one third of the H_2S to SO_2 in a furnace, and the second is the reaction of SO_2 with the remaining H_2S (the Claus reaction) to form elemental sulphur and H_2O (GPSA, 1998):

$$H_2S + 3/2O_2 \rightarrow SO_2 + H_2O$$
$$2H_2S + SO_2 \rightleftharpoons (3/x)S_x + 2H_2O$$
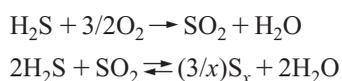
This reaction is endothermic at high temperature and exothermic at lower temperature ($+10$ Kcal/mol SO_2 at 800°C and -25 Kcal/mol SO_2 at 100°C) on account of association equilibria involving sulphur in

the vapour phase, which can be represented as follows (the stoichiometry coefficients are omitted):

$$S_8 \rightleftharpoons S_7 \rightleftharpoons S_6 \rightleftharpoons S_5 \rightleftharpoons S_4 \rightleftharpoons S_3 \rightleftharpoons S_2$$
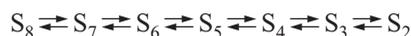
These equilibria are shifted to the left at low temperature and to the right at higher temperature (above 800°C, only S_2 is present). The equilibrium conversion to sulphur in the Claus reaction as a function of temperature is reported in **Fig. 9**, which is characterized by a minimum around 600°C.

In practice, the Claus reaction is carried out in several separate stages. In the first, at a temperature between 980 and 1,370°C and in the absence of catalyst, one-third of the H_2S together with any hydrocarbons and other combustible substances are burned in air in a furnace. In these conditions, the oxidation of H_2S to SO_2 takes place, followed by the slower reaction between H_2S e SO_2 to yield sulphur and water. This stage generates the major part of the heat of reaction, which is recovered for various uses within the plant (e.g. for regeneration of the solvent in the sweetening unit); conversion to sulphur is about 70%. Two or more catalytic stages are generally installed downstream of the furnace to boost sulphur recovery. These generally operate below 370°C and provide a maximum sulphur recovery of 97-98%. Higher recoveries are achieved and sulphur (SO_2) emissions requirements are satisfied only through the use of expensive tail gas processing units (TGU).

The main advantages of the Claus process include the production of high quality sulphur, the possibility to convert COS, destroy NH_3 and HCN, and the production of large amounts of heat in the form of steam. On the other hand, the Claus process places strict requirements on the incoming acid gas characteristics (a minimum of 15% mol H_2S in the gas stream, limited hydrocarbon content, etc.). The push to achieve ever-greater levels of sulphur recovery has led to an increase in the number of catalytic conversion stages and to the addition of tail gas treatment units of increasing sophistication, increasing the cost and complexity of the Claus process.

There are two principal variants of the Claus process: straight-through and split flow. The first is employed where the concentration of H_2S is greater than 50%, and oxidizes only part of the H_2S in the incoming stream. The second is generally employed for lower H_2S concentrations, and splits the incoming acid gas stream into two parts (1/3 and 2/3), the smaller of which is fully oxidized before being combined with the non-oxidized portion.

Fig. 9. H_2S conversion
to elemental sulphur
as a function
of temperature for:
an acid gas
containing 3.5% mol
hydrocarbons (in red);
a refinery
acid gas stream
(c. 7% mol hydrocarbons,
1% mol mercaptans)
(in blue);
pure H_2S (in green)
(GPSA, 1998).
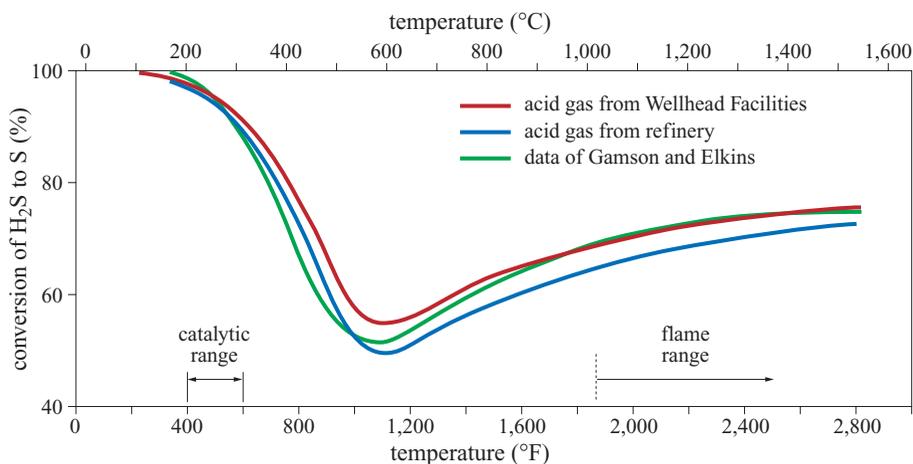
A schematic diagram of the Claus process in the straight-through configuration, comprised of three catalytic stages is reported in **Fig. 10**. The principal phases of the process are:
- Combustion (in a deficiency of air) of c. one third of the H_2S present in the acid gas stream, of the hydrocarbons and any other combustible substances. The furnace operates at 20-100 kPa greater than the atmospheric pressure.
- Cooling of the combustion products with the recovery of heat and production of steam (10-35 bar, 185-245°C). The mean temperature of the effluent gas is generally 315-370°C.
- Condensation and recovery of sulphur from the furnace effluent and the effluent from the catalytic converters, with production of low-pressure steam (3.4-4.8 bar). The effluent gas temperature from the first condensers is c. 177°C, and 127-149°C from the final condenser.
- The gas exiting from the condensers must be reheated to above the dew point of sulphur to avoid condensation in the successive converter.
- The catalytic converters (generally employing an allumina catalyst) promote the reaction between H_2S and SO_2 at the low temperatures downstream of the furnace.

A new variant on the Claus process employs oxygen-enriched air. The reduced volume of the air employed leads to more economic plant dimensions for large-scale operations, and can also be used to enhance existing plant capacity. Oxygen enrichment is generally kept below 28% to avoid the need for special materials, but some plants are operating with 60% oxygen-enriched air. Though the application of this variant is most convenient in refinery operations which can justify the cost of an oxygen plant or have access to other sources of oxygen, even stand-alone upstream operations may have favourable economics for very large-scale acid gas plants (e.g. 2,000 t/d of S).

Tail gas treatment

The steadily increasing sulphur content of produced oil and NG and growing environmental pressure have pushed oil and gas producers and refiners to adopt technologies offering very high levels of sulphur recovery. Typical sulphur recoveries for a two-stage Claus plant are usually 90-96%, increasing to 95-98% with the addition of a third stage. Other tail gas unit (TGU), technologies are required to achieve recoveries of 99% or higher, of which two general types exist: H_2S recycle and subdewpoint (see also Chapter 3.2).
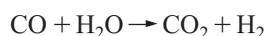
H_2S recycling processes

In these processes the oxidized sulphur compounds exiting from the Claus plant are reconverted to H_2S and recycled. The general layout of one of these, the Shell Claus Offgas Treating (SCOT) process, is shown in **Fig. 11**.

The typical composition of the tail gas entering the tail gas treatment plant (TGU) is as follows: COS, 200-5,000 ppm vol; CS_2, 200-5,000 ppm vol; H_2S, 0.3-5% vol; SO_2, 0.15-0.75% vol; S_{vap}, saturated at the operating T and P.

The SCOT process is comprised of two main sections: the reactor, where hydrolysis and hydrogenation reactions are carried out (see below), and the absorption section.

The hydrolysis reactions are as follows:

$$COS + H_2O \rightarrow CO_2 + H_2S$$
$$CS_2 + 2H_2O \rightarrow CO_2 + 2H_2S$$
$$CO + H_2O \rightarrow CO_2 + H_2$$

The following hydrogenation reactions also take place:

$$SO_2 + 3H_2 \rightarrow 2H_2O + H_2S$$
$$S_n + nH_2 \rightarrow nH_2S$$

Fig. 10. Example of three-stage Claus plant: straight-through operating with acid gas-fueled inline burners for reheating (GPSA, 1998).

The gases exiting the Claus plant are heated to c. 300°C, mixed with a reducing gas containing H_2, and then passed over a fixed bed reactor containing a Co/Mo catalyst where the oxidized sulphur species are converted to H_2S. The gas leaving the reactor at 320-340°C is cooled in two steps to 40°C. The cooled gases are sent to an absorption column where a chemical solvent (e.g. MDEA) is used to capture H_2S and CO_2. The off-gas typically contains ≤ 150 ppm of H_2S and can be sent to the incinerator. The acid gases are recovered from the rich solvent in a stripping column and recycled to the Claus unit.

Subdewpoint processes

These processes operate at temperatures below the dewpoint of elemental sulphur, thereby ensuring a high conversion of H_2S and SO_2 to sulphur. The Sulfreen process is a typical example of a low temperature, dry bed Claus process. It consists of two or more reactors, a blower for regeneration, a gas heater and a separator. The catalytic beds are comprised of an activated allumina, which acts simultaneously as adsorbent and catalyst. At the reaction temperature (120-140°C) H_2S and SO_2 are almost completely converted to sulphur. This remains

adsorbed onto the catalytic bed, which must be regenerated periodically at 300°C using gas from the Claus furnace. Two or more reactors are therefore required for continuous operation. A Claus plant with three catalytic beds and a Sulfreen unit can achieve 99.5% sulphur recovery; in a further refinement, COS, CS_2 and H_2S can be converted to sulphur in a hydrolysis unit installed ahead of the Sulfreen reactor.

The highest total sulphur recoveries are presently obtained with the Clauspol process, in which the Claus reaction proceeds to completion in a non-volatile organic solvent. This is accomplished by sending the tail gas from the Claus unit to the bottom of a filled reactor where it flows upwards against a countercurrent solvent flow. The H_2S and SO_2 are absorbed by the solvent which contains a catalyst. The sulphur produced by the Claus reaction is only partially soluble in the solvent and is recovered as a liquid phase at the bottom of the reactor. The newest version of the Clauspol process maintains the solvent below the sulphur saturation limit, to reduce sulphur in the off-gas to less than 50 ppm vol. The 'desaturation loop' is comprised of three heat exchangers and a separator. In this configuration a combined Claus/Clauspol process can achieve conversions of
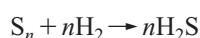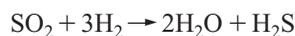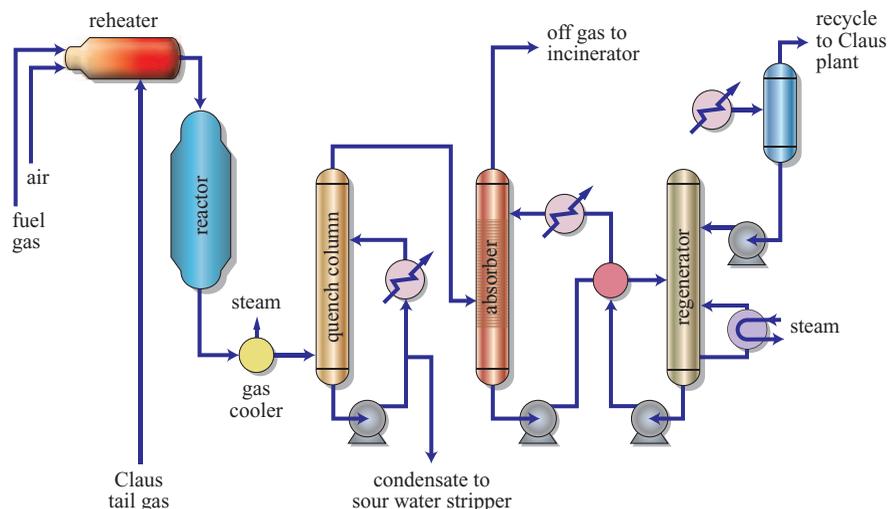
Fig. 11. Basic design of the SCOT process.

over 99.9% by utilizing a high performance TiO_2 catalyst in the Claus process to ensure conversion of CO_2 and CS_2.

Innovative processes for H_2S treatment

The increasing cost and complexity of the existing Claus and TGU processes have encouraged a continued search for new H_2S treatment and emissions control technologies and processes. Of particular interest are catalytic partial oxidation processes in short contact time reactors, which offer the possibility of achieving significant reductions in the dimensions of the reactors and reducing the total number of stages compared to the Claus process. Secondly, efforts continue on the development of treatment processes capable of recovering significant amounts of H_2 from H_2S.

Short contact-time Claus reactor

The sulphur partial oxidation catalysis process currently under study by ConocoPhillips (Allison *et al*., 2003) carries out the transformation of H_2S to sulphur in the presence of air in a compact reactor. The results achieved thus far suggest that the current level of performance of the Claus process can be achieved with the elimination of one or more catalytic beds. The reduction in number and size of the stages may lead to capital expenditure savings up of to 50% compared to a conventional Claus process. The reactor temperature lies in the range from 700-1,500°C and the catalyst used, covered by a patent, is a mixture of Pt/Rh catalyst containing a lanthanide metal supported on zirconia or α-allumina. Laboratory tests have been carried out with gas

streams containing from 20 to 100% H_2S. Residence time in the catalytic bed is in the order of 10-50 ms, and reactor dimensions are 10% or less of those of a Claus furnace. Operating conditions and the results of laboratory tests are reported in **Table 8**.

The sulphur yield (75%) can be compared with that of a conventional Claus furnace (55-65%). Laboratory testing indicates that the process can stand both significant (greater than two-fold) variations in the gas flow rate and ample variation in the ratio air/H_2S (from 1.7-2.7) without significant impact on the H_2S conversion rate and yield of sulphur.

A pilot scale plant (1 t/d of sulphur produced) comprised of two identical reactors has been realized at the ConocoPhillips Ponca City refinery (Oklahoma, USA), which has provided a gas

Table 8. Partial catalytic oxidation of sulphur: conditions and results of laboratory tests (Allison *et al*., 2003).
GHSV=Gas Hourly Space Velocity

H_2S conversion (%)	83
Selectivity for sulphur (%)	90
Sulphur yield (%)	75
SO_2 yield (%)	8
H_2 yield (%)	10
air/H_2S	2.1
GHSV (h^{-1})	265,000

Table 9. Oxidation of H_2S in the gas phase in a quartz reactor* (Clark *et al*., 2004)

T (°C)**	CONTACT TIME (ms)	YIELD (mol/100 mol of reagent)		CONVERSION (%)	
		H_2	SO_2	H_2S	O_2
200	180	0.0	0.1	1.2	2.7
400	127	0.1	0.3	21.6	43.4
600	98	5.9	6.7	41.9	100
700***	88	6.4	6.5	43	100
	44	7.4	6.0	46.8	100
	24	7.8	5.4	48.3	100

*   Feed: 79.9% of H_2S, 20.3% of O_2
**   Temperature of external furnace
***   Results of the thermodynamic calculation at 700°C: yield of H_2, 0.50 mol; yield of SO_2, 1.17 mol; H_2S conversion, 47.8%; O_2 conversion, 100%

stream containing 80-88% H_2S, 1-2% hydrocarbons and ammonia, with the balance made up by CO_2. The focus of current studies is to increase the yield of sulphur to over 94%, which would make it possible to eliminate the need for post-reactor catalytic stages entirely.

Thermal dissociation of H_2S to sulphur and H_2

Hydrogen production from H_2S, favoured thermodynamically, is certainly among the most attractive hypothetical alternatives to the Claus process currently under study. Notwithstanding numerous efforts in this area, it has not yet been possible to identify a process that captures this potential. Studies conducted by Alberta Sulphur Research (ASR) during the 1990s identified the thermodynamic limitations to the transformation of H_2S to H_2 and sulphur via a thermal-cracking route (Clark *et al*., 2003). Among the principal problems identified were the inability to find a favourable temperature for the catalytic Claus converters; above 325°C, the H_2 produced reacts with SO_2 in the presence of the catalyst, whereas the conversion of H_2S was insufficient at lower temperatures. Another limitation identified regards the difficulty of separating H_2 from the effluent stream. All the evaluations carried out indicate that thermal dissociation of H_2S to sulphur and hydrogen via the process studied is not economically attractive.

ASR is presently exploring partial catalytic oxidation in a short contact time reactor as a means for achieving the non-equilibrium conversion of H_2S to H_2 and sulphur. The thermodynamics for three alternative pathways for the reaction of H_2S with oxygen are reported below:

[1] $H_2S + 1/2 O_2 \rightarrow H_2O + 1/8 S_8$
$$(-208.7 \text{ kJ/mol})$$

[2] $H_2S + 3/2 O_2 \rightarrow H_2O + SO_2$
$$(-518.2 \text{ kJ/mol})$$

[3] $2 H_2S + 1/2 O_2 \rightarrow H_2 + H_2O + S_2$
$$(-72.1 \text{ kJ/mol})$$
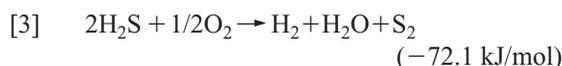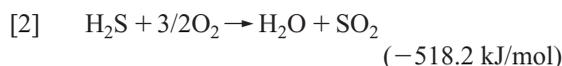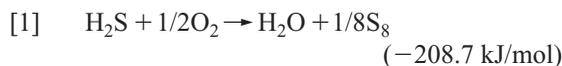
Assuming that oxidation of H_2S proceeds via a radical pathway, the reaction pathway reported below has been suggested as a possible route to H_2 and S_2, provided that the competing oxidation to SO_2 can be avoided (Clark *et al.*, 2004). This result would require catalytic conditions with the efficient removal of heat.

Results for the uncatalyzed conversion of H_2S in the presence of O_2 over a range of temperatures and contact times are reported in **Table 9**. Small amounts of H_2 are detected above 600°C, the yield increasing at shorter contact times. These results suggest that the reaction is within the kinetic regime and that H_2 is not the result of thermal dissociation at this temperature. On the other hand, the significant amounts of SO_2 formed are contrary to the predictions of the reaction scheme reported below and the equilibrium prediction at 700°C.
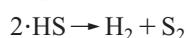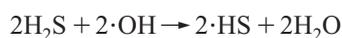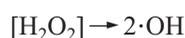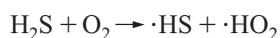
$$H_2S + O_2 \rightarrow \cdot HS + \cdot HO_2$$
$$H_2S + \cdot HO_2 \rightarrow \cdot HS + [H_2O_2]$$
$$[H_2O_2] \rightarrow 2 \cdot OH$$
$$2 H_2S + 2 \cdot OH \rightarrow 2 \cdot HS + 2 H_2O$$
$$2 \cdot HS \rightarrow H_2 + S_2$$

Table 10. Catalytic oxidation of H_2S over α- and γ-allumina* (Clark *et al.*, 2004)

T (°C)**	CONTACT TIME (ms)	YIELD (mol/100 mol of reagent)		CONVERSION OF H_2S (%)	SELECTIVITY FOR H_2 (%)
		H_2	SO_2		
α-allumina					
300	6.3	0.5	0.1	51.6	1.1
400	8.7	4.2	0.2	55.1	9.6
500	7.6	5.8	1.2	56.6	12.9
γ-allumina					
200	18.5	7.1	0.0	60.5	14.6
300	15.3	7.8	0.0	61.9	15.7
400***	13.0	9.2	0.2	62.2	18.6

*   Feed: 79.9% of H_2S, 20.3% of O_2
**   Temperature of external furnace
*** After 4 h: yield of H_2, 10.7 mol; yield of SO_2, 0.02 mol; conversion of H_2S, 64.6%; selectivity for H_2, 20.8%

To depress the undesired reactions leading to SO_2 formation, the possibility of using α- and γ-allumina catalysts was examined (**Table 10**). These un-doped catalysts significantly reduced SO_2 formation, with γ-allumina proving particularly effective in catalyzing the partial oxidation of H_2S to H_2 at 400°C, while limiting SO_2 formation to a very low level (0.25% conversion to SO_2). The selectivity improved at still lower external furnace temperatures, with no SO_2 detectable in the product stream. H_2 selectivity was also examined as a function of the H_2S/O_2 ratio in the feed between 200 and 600°C. Below 500°C, a maximum in the selectivity for H_2S was found for an H_2S/O_2 ratio of 4, which agrees with the stoichiometric requirement for the formal reaction [3] shown above. **Fig. 12** summarizes the observations on the factors controlling H_2 selectivity in the partial oxidation of H_2S and relates these to the presumed chemical steps underlying the process.

The Gas Technology Institute (GTI) has explored high temperature, non-catalytic routes for the decomposition of H_2S to sulphur and H_2 (Slimane *et al.*, 2002). As reported in **Fig. 13**, H_2S decomposition to H_2 and sulphur is disfavoured thermodynamically until a very high temperature, sulphur conversion reaching 50% only above 1,350°C. In the process studied by GTI, the energy required for the transformation is furnished by the oxidation of part of the H_2S. The partial oxidation and decomposition of the H_2S take place within a porous medium where temperatures in the order of 1,400°C are reached. The process is complex, with the reaction front advancing progressively within the reactor. Periodic inversion of the direction of flow, as shown in **Fig. 14**, has been proposed as a means to confine the reaction. Published reports on laboratory-scale tests claim H_2 yields of up to nearly 20% (**Fig. 15**). The major part of the H_2 contained in the H_2S should be converted to H_2O (not reported), while the production of SO_2 should be comparable to that obtained with the Claus process. How to recover the H_2 generated from the high temperature reaction gas remains an open problem.

3.3.5 Sour gas re-injection

Acid gas re-injection is attracting much attention as an environmentally-sound and cost-effective approach that can avoid the cost of traditional H_2S processing and the problems of handling the elemental sulphur product, particularly for very sour NG streams. In this process, the acid gases separated are compressed and injected into the disposal reservoir through a special well, in a manner similar to the disposal of produced water (**Fig. 16**). The disposal zone can be either a hydrocarbon reservoir (the producing reservoir itself or a nearby, depleted one) or a saline aquifer. In operations where a part of the sour associated gas is destined for re-injection, this can be enriched
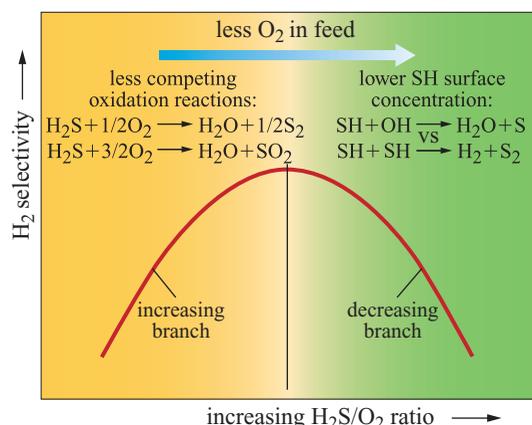
Fig. 12. Controlling factors for H_2 selectivity in partial oxidation of H_2S (Clark *et al.*, 2004).
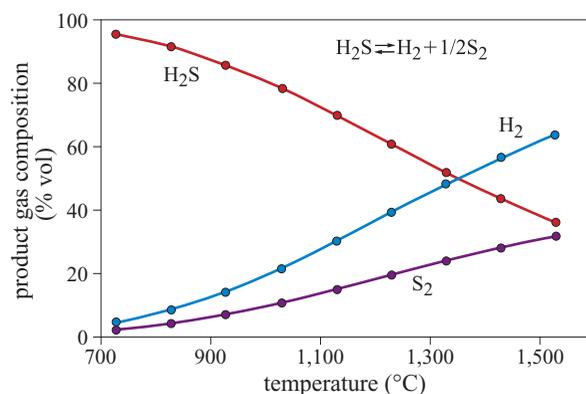

Fig. 13. Thermal equilibrium for H_2S decomposition to H_2 and sulphur versus temperature (Slimane *et al.*, 2002).
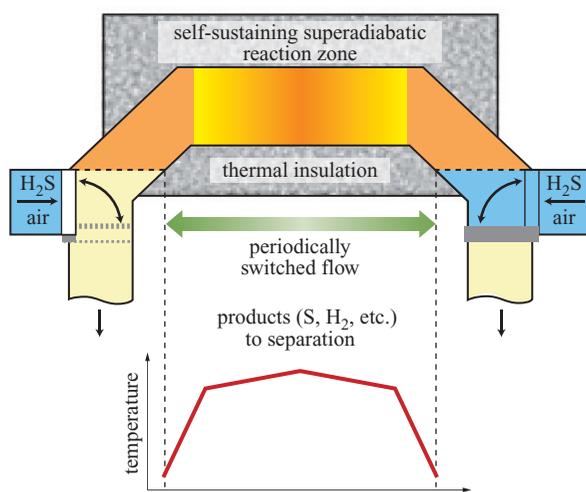

Fig. 14. Conceptual scheme for a superadiabatic reactor for H_2S decomposition (Slimane *et al.*, 2002).
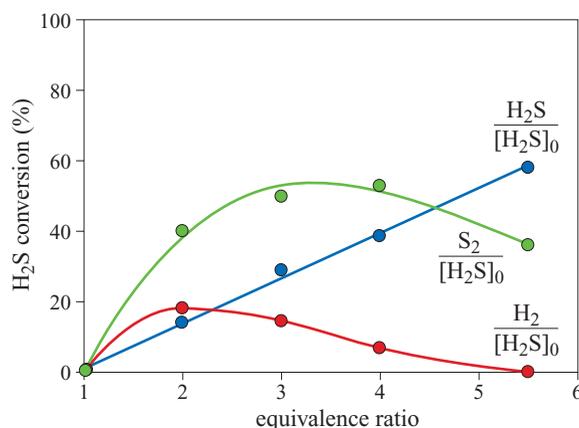

Fig. 15. Experimental results on H_2S conversion; equivalence ratio is defined as the molar ratio of O_2 supplied to the O_2 that is stoichiometrically required to burn all the H_2S (Slimane *et al.*, 2002).

with H_2S separated from the sales gas. One of the potential benefits of injecting H_2S and acid/sour gas into the reservoir is that the excellent solubility characteristics of H_2S favour oil recovery (Thibeau *et. al.*, 2003). The downside of such a miscible flood scheme, of course, is the risk of early breakthrough of highly sour gas to the producer wells, and the inevitable build-up of acid gas within the reservoir which will lead, late in the production life, to acid gas recycling.

Acid gas re-injection technology was developed in North America where over 60 operations are active at the present time, approximately two-thirds located in Alberta, Canada. Overall, it is estimated that a total of 750,000 t of H_2S and 635,000 t of CO_2 are disposed of each year in Western Canada alone. One of the largest facilities, the Kwoen project (see Section 3.3.4), re-injects over 860 t/d of H_2S.

To date, acid gas re-injection processes in North America have employed relatively shallow aquifers or depleted gas reservoirs requiring relatively low pressures for injection (<100 bar; Wichert and Royan, 1997). One of the major issues for the extension of this process to other regions of the world is the much higher injection pressures that will be required (Miwa *et al.*, 2002). One of the most important raw gas injection plants yet built is in the oil-processing centre of the sour (c. 3-4% of H_2S) giant Karachaganak condensate field, in the north-west of Kazakhstan. This facility disposes of 6.4 billion cubic metres of sour gas per year at pressures of c. 500 bar by re-injection into the reservoir. A similar solution is under evaluation for the Tengiz and Kashagan fields, which contain

up to 20% mol of H_2S in the associated gas and have even higher static pressures. Work by equipment manufacturers is underway to ensure that the compressor capacity required for such injection schemes will be available to the development projects.

Properties of acid gas mixtures

The acid gas stream recovered from NG and sent to the compressor for re-injection consists mainly of H_2S, CO_2 and a small amount of hydrocarbons. Where conventional chemical solvents are used for separation, the gas mixture coming from the regeneration column will also be saturated with water; for example, the water content is c. 65 g/Sm^3 at 35-50 kPa and 50°C. The physical properties of this mixture which are relevant to the design of the compression and injection schemes include: *a*) vapour/liquid phase behaviour; *b*) water content at saturation in the vapour, liquid and dense phases; *c*) conditions for hydrate formation; *d*) the density of the vapour, liquid and dense phases; *e*) heat capacity over a broad range of pressure and temperature. While these properties are available for pure H_2S and CO_2, equations of state or other means must be used to estimate the properties of their mixtures, particularly under high-pressure conditions, for which there is little operational experience.

Two important concerns for acid gas systems are the increased potential for corrosion and the propensity to form hydrates at elevated pressures. The corrosion risk can be controlled by avoiding the formation of a free water phase in the system, while hydrate formation can be avoided by operating so that the water pressure is maintained below the thermodynamic threshold. Depending on the acid gas composition and injection conditions, chilling, glycol dehydration, desiccants and/or

interstage cooling during acid gas compression can be used to remove water.

Fig. 17 reports the saturation water content versus pressure for different compositions of H_2S and CO_2 at 49°C (Caroll and Maddocks, 1999). The water content decreases with increasing pressure and below about 4 MPa is insensitive to the acid gas composition. For mixtures containing 50% or more H_2S, a jump in water content is observed in correspondence with the formation of a liquid H_2S phase, which has a greater water-holding capacity than the gas phase. For 1/1 and 3/1 H_2S/CO_2 mixtures, there is a range of pressures over which three phases exist (note that CO_2 does not liquefy at this temperature).

Hydrates are solid clathrate complexes of water incorporating guest molecules, which form at elevated pressure and at temperatures greater than 0°C. As seen above (v. Section 3.3.4), H_2S is a strong hydrate former and can form hydrates at pressures as low as 3 bar. Hydrate formation must be avoided at all points in the re-injection system, from the compressor to the well bore. **Fig. 18** reports the pressure and temperature conditions for hydrate formation of H_2S and other pure compounds (the hydrates are stable to the left of and below the lines drawn on the graph). For acid gas injection, the compression cycles must be designed to avoid crossing both the phase envelope and the hydrate region, as shown in **Fig. 19**. Hydrocarbon contents greater than 5% will decrease the ability of the acid gas mixture to hold water at high pressures. Hydrocarbons also reduce the bubble point temperature, meaning that a lower temperature will be required to convert the acid gas mixture to a liquid phase at a given pressure.

Acid gas compression and injection facilities

The ultimate pressure to which the acid gas must be compressed for injection depends on the rate of injection, the length and size of the

Fig. 16. Schematic illustrating process of managing acid gas production via re-injection (Royan and Wichert, 1995).
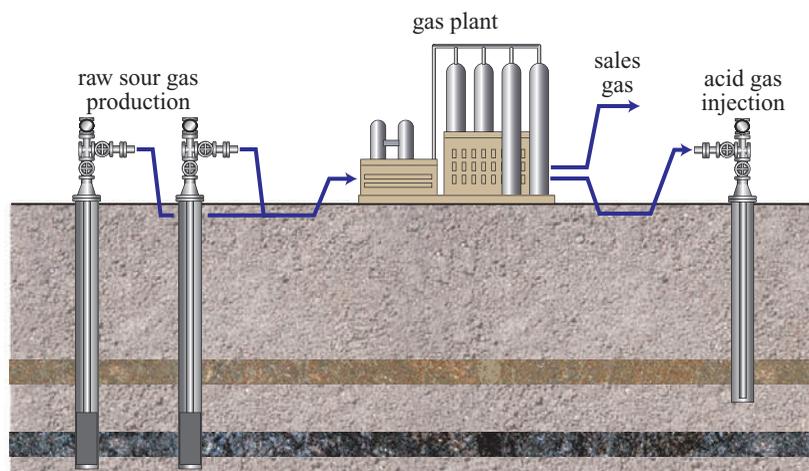
injection line, the diameter of the well tubing, the pressure of the reservoir, the permeability of the zone and the depth of the zone. Provided that the acid gas mixture contains little hydrocarbon, liquefaction can be achieved under moderate conditions (e.g. 6 MPa at 20°C for a methane content below 3%). The density of the acid gas mixture under these conditions will lie in the range between 0.6 and 0.8 g/l. The hydrostatic head in the well bore, due to the density of the acid gas in the liquid and dense states, will contribute to determining the injection pressure into the reservoir.

A wellhead injection pressure of 6 to 9 MPa can be achieved by a four-stage compressor, with a compression ratio between 2.2 and 2.9 per stage. Although large-scale compressors are available for sour gases, there is still a need to demonstrate the potential for using large centrifugal multistage acid gas compressors at discharge pressures of 8-10 MPa, followed by pumping to higher pressures.

The total power requirement to compress acid gas from 0.1 MPa to about 9.6 MPa is about 7.94 kW for 1,000 m^3/d. Were it possible to recover the acid gas from the sweetening unit at a higher pressure, there would be considerable savings in energy requirements; providing the acid gas stream at 1.2 MPa would, in fact, halve the number of compression stages. Meriting particular interest, therefore, are those processes for bulk separation in which the solvent is regenerated at moderate pressure.

One of the main concerns for re-injection operations is that the compression section will be sensitive to any changes in the composition of the acid gas coming from the sour NG treating section.
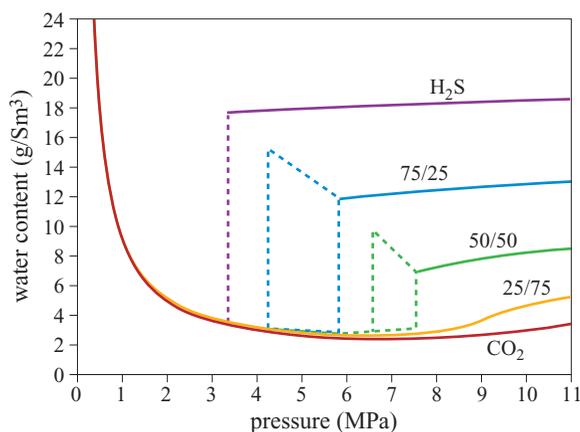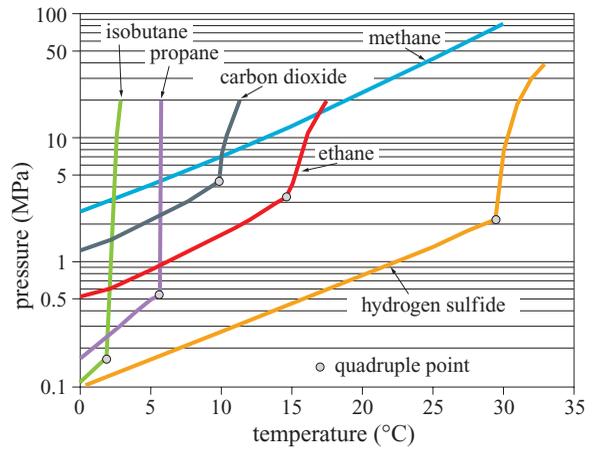

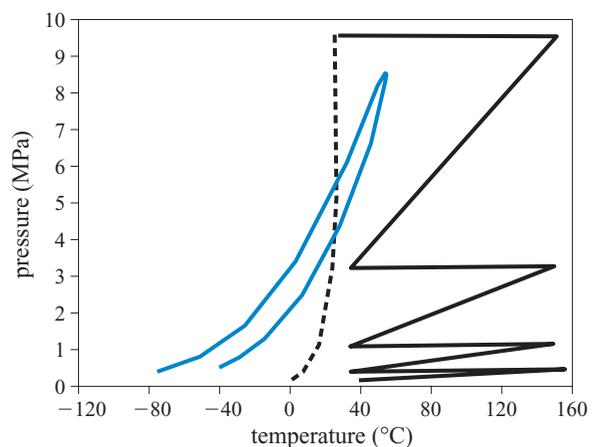**Fig. 18.** Thermodynamic conditions for hydrate formation with pure compounds.

Fig. 19. Four-stage acid gas compression showing pressure rise and temperature variations for a mixture containing 49% of H_2S, 49% of CO_2 and 2% of CH_4. The phase envelope for the liquid drop-out phase is shown by the blue line, while the phase boundary for the formation of hydrates is shown by the broken line.

For every application, the capital costs, life cycle operating costs, and life cycle energy efficiency must be considered to select the optimum design.

Acid gas behaviour in the reservoir

The possibility of employing acid gas injection to manage produced H_2S depends, of course, on the availability of a suitable reservoir or saline aquifer to receive it. A disposal zone must provide adequate injectivity and capacity and guarantee containment of the acid gas over a time-scale that can be measured in hundreds or thousands of years. Major properties that must be evaluated to

Fig. 17. Water content of acid gas at 49°C (dashed areas denote three-phase regions) (Caroll and Maddocks, 1999).

ensure disposal zone suitability include: *a*) extension of the cap rock, and cap rock impermeability and resistance to acid gas over time; *b*) isolation of the disposal reservoir from other producing reservoirs or aquifers; *c*) distance of migration of the acid gas over a long time scale; *d*) response of the disposal zone minerals and fluids to the mixture injected.

The well materials and cement used for completion and abandonment must provide suitable, long-term resistance to the acid gas mixture in order to ensure against leakage upwards from the well path to higher formations or to the surface. This aspect of acid gas re-injection merits further study, particularly as regards cement integrity around the well bore. Standard Class G well cements have been shown to be unsuitable for use in injection wells, while resin-based blends and latex blends have been found to have acceptable resistance, at least in one specific case (Whatley, 2000).

Where the injection zone is a depleted oil or gas reservoir that previously contained a significant amount of H_2S, the uncertainties associated with the cap rock (areal extension, sealing capability and compatibility with H_2S) and the response of reservoir minerals to H_2S injection may be small. In general, the final pressure of the disposal reservoir is kept below the original pressure in order to reduce the risk of migration of the injected gas out of the target formation. On the other hand, where a saline aquifer is the geological formation destined for injection, a full suite of geological and geochemical studies may be appropriate, including studies on the long-term migration of the acid gas from the point of injection (Whatley, 2000).

The response of minerals and fluids present in the disposal zone to the acid gas is an issue that should be evaluated with experimental studies. Formation of insoluble phases (mineral precipitates or hydrocarbon solid drop-out) in the near well bore region, resulting from a mixture of the acid gas components with the oil or brine phase, could compromise well injectivity. On the other hand, mineral phase dissolution in the acid gas mixture could structurally compromise the well bore, leading to possible collapse, or open up pathways for migration of the acid gas upwards and out of the target zone.

Although many studies are generally run prior to, and during, an injection project to test materials and rock behaviour, another key issue that must always be considered is storage site monitoring. Proper actions must be programmed not only over the injection period (tens of years), but also on a longer time scale.

Case study: Kwoen

At the Kwoen site in British Columbia (see Section 3.3.4), acid gas from the final flash drum is compressed to 1,350 psi ($\approx$9 MPa) and liquefied in a compressor aftercooler. Liquid pumps operating at 2,125 psi ($\approx$14 MPa) send the acid gas through a 14 km, 6-in (15.24 cm) diameter pipeline to the injection site where the acid gas liquid flows down the injection well tubing to a depth of 2,630 m. The injection reservoir (a depleted gas field) is a naturally fractured carbonate, tight matrix; the reservoir pressure at the start of injection is 600 psi ($\approx$4 MPa). Currently, one injection well disposing of 860 t/d of sulphur is in operation, but there are plans to add a second injection well later.

3.3.6 Sulphur storage and disposal

The preceding paragraphs described the technologies used by the oil industry to desulphurize petroleum products, leading to the production of large amounts of H_2S. Despite growing interest in re-injection into underground formations, most H_2S is transformed into sulphur, a non-hazardous substance and an essential raw material for industry. The production of sulphur from H_2S has increased over the years, paralleling the growth of demand for energy; this has gradually made the petroleum industry one of the main sources of supply for this element on the world markets.

Production of sulphur from petroleum

World sulphur consumption, in elemental form or as an alloy, reached an historic peak of 63 million tons in 2003 (Stone, 2003). For decades, the main problem linked to the supply of this raw material was to ensure the necessary transportation logistics from production sites to the industries using it. Technological advances and concerns about the environment and safety have led to the modification over the years of transportation systems for elemental sulphur. Questionable practices from an environmental point of view, such as the transportation of large blocks of solid material, have been eliminated in favour of safer systems such as transportation in tablet or granular form or as liquid sulphur.

During some periods of low demand, the logistical issue was complicated by the concomitant need to temporarily store large quantities of elemental sulphur. During the 1980s, millions of tons of elemental sulphur from the desulphurization of hydrocarbons were stored, awaiting the right

market conditions for sale. However, the accumulation of unsold products was a temporary phenomenon, due to the capacity of the system to balance supply and demand in a relatively short time. Up until the late 1990s, in fact, a large part of sulphur production came from mining. When the demand for sulphur lagged behind production and the surplus became substantial, the drop in prices forced part of the sulphur originating from mines out of the market; some sulphur mines closed and the balance was re-established. This regulation mechanism between demand and supply worked efficiently for many years, up to the point when mining production practically disappeared, definitively removing the only tool for rebalancing the market available to operators.

Currently, over 90% of worldwide elemental sulphur production derives, as an unavoidable by-product, from the oil industry's hydrocarbon desulphurization plants. The market for industrial by-products, by their very nature, cannot use demand and supply regulation mechanisms effectively, and the accumulation of excess production is often the only way of preventing the collapse of the market. Recently, due to the availability of increasingly large quantities of sulphur from the oil industry, there has been a structural imbalance in worldwide sulphur production, with an excess in the order of 2-3 million tons per year (Kitto, 2002).

It is extremely hard to predict if and when growth in demand will be able to absorb excess production and rebalance the market. Sulphur production continues to increase, driven by the growth in energy requirements and the tendency to progressively lower the maximum permitted concentration of sulphur in fuels. On the demand side, factors such as the growth in world population, the rapid development of emerging countries, especially China and India, the economic recovery of the ex-Soviet countries and other, equally complex, phenomena will be important for rebalancing the relations between production and consumption.

While awaiting the recovery of world demand for sulphur, some oil companies are forced to store enormous quantities of sulphur on their production sites. This has created a new management issue, which arises more from the awareness that the sulphur will probably remain in its elemental form for a long time than from the amounts of unsold sulphur. This is an unusual situation, since sulphur has always been managed as an intermediate destined for transformation into something else at a later point. The need to store sulphur for long

periods poses completely new problems, the most pressing of which is to ensure that the environmental impact of large amounts of elemental sulphur concentrated in relatively small areas is kept under control.

There are two possible solutions. The first considers sulphur a valuable material which should be stored until the market allows it to be sold. This line of action involves developing technologies for the construction of sulphur storage facilities, safe for people and the environment, which allow it to be recovered when required by the market. The second solution considers excess sulphur as waste to be disposed of; this premise underlies more or less definitive disposal technologies, deriving in part from traditional technologies and systems applied to industrial waste.

Sulphur storage facilities and environmental issues

The sulphur industry uses storage facilities of all types and sizes. However, when large quantities of sulphur are to be stored for a long time, the only technology used is the construction of enormous parallelepipeds of solid material. The storage of liquid or solid sulphur in other physical forms (granules, tablets, flakes) is part of the logistical chain needed to transport the material to market; in general, the time required is kept as short as possible. For long-term storage, needed for surplus production, the only way of storing the material is in the form of blocks, each containing hundreds of thousands of tons of sulphur (Rutland, 1998). During the 1980s in Canada, the leading producer of this element, up to twenty million tons were stored at one time in this form.

The technology used to build storage facilities is based on the solidification of liquid sulphur from the recovery plant, usually a Claus plant, in blocks several hundred metres long and between 10 and 20 m tall (greater heights would lead to the risk of collapse, as the material's mechanical resistance would be exceeded). From production to the storage facility, the sulphur is transported in a liquid state through pipelines, which are often thermally insulated and, if necessary, heated. To avoid the sulphur solidifying in the transport lines, the distance between the sulphur production facility and the storage site must be as short as possible: usually the storage area is no more than a few dozen kilometres away.

The surface of the area used for storage should be as large as possible. This is because sulphur is not a good heat conductor and solidifies slowly; it must therefore be poured in thin layers to give each layer the time needed for it to cool completely

before the next layer is poured. The preparation of the area destined for storage generally involves covering the ground with a layer to isolate it from the sulphur. A layer of asphalt may be used, but this solution is expensive; on most occasions low-cost solutions are used, such as a sheet of plastic, generally high density polyethylene or PVC, placed on the ground, which is suitably prepared before the construction of the block. The construction technique involves enclosing the area destined to host the sulphur block with mobile metal sheeting set around the whole perimeter. Liquid sulphur is then poured into the area limited by the panels from a distribution tower equipped with mobile arms through which the liquid is poured over the confined space to a depth of about 10-15 cm, then it is allowed to cool. To obtain a uniform layer, the mobile arms are moved during pouring to different areas of the block, so as to cover the whole surface.

As it solidifies, the sulphur contracts and takes on a residual porosity which, depending on the thickness of the layer and the cooling conditions, is in the order of a few percent. After solidification, the layer of sulphur is allowed to cool further to permit the transposition from the allotropic β form, which the sulphur takes on immediately after solidification, to the α form, thermodynamically stable below 90ºC. During this transition the solid contracts further, with a 5.6% reduction in volume, and acquires its definitive density. The empty spaces produced by contraction may be partially filled as later layers are poured, improving the compactness of the material. However, the sulphur block inevitably fractures diffusely following the contraction in volume. After the entire volume enclosed by the metal panels has been filled, the panels are dismantled and moved to a higher level to allow further layers of sulphur to be poured, and so forth until the whole block has been formed. To prolong cooling times, two blocks may be built simultaneously, pouring the sulphur alternately into one or the other. It is normal practice to contain the sides with metal panels to improve the block's stability.

The accumulation of large amounts of elemental sulphur in small areas causes concerns about potential risks for the environment and for people. The first effect is the visual impact on the landscape, especially significant if the site is near towns; there is also the risk of significant sulphur loss to the surrounding environment. Sulphur loss may occur by various mechanisms; a small quantity of H_2S and SO_2 is present in the liquid sulphur sent for storage, and these gases may be released both during solidification and

subsequently by diffusion from the mass of solidified sulphur. Special degasification treatments for the liquid sulphur lower the presence of these toxic gases to a few tens of ppm before it is sent for storage, thus significantly reducing the problem. A second mechanism of sulphur leakage from storage facilities into the environment is the formation of sulphur powder on exposed surfaces due to erosion (**Fig. 20**) and evaporation. Although not quantified, these phenomena may generate large amounts of sulphur powder, which can be transported by the wind over long distances. The elemental sulphur released into the environment in the dispersed form is relatively rapidly incorporated into natural biological cycles by oxidation, mainly biological, to sulphuric acid. Oxidation is the product of the metabolic activity of thiobacilli, extremophile autotrophic bacteria capable of using the oxidation of sulphur as a source of metabolic energy. This natural process in the sulphur cycle is usually beneficial for the environment, but may represent a risk when the generation of sulphuric acid produced by the bacteria exceeds the capacity of the receptor system to block the acidity produced. If this occurs, the pH tends to decrease, sometimes reaching levels far more acidic than natural ones. In these cases, it is necessary to intervene by supplying basic substances such as lime, calcareous rocks, etc. to return the system's pH to its original values.

The production of sulphuric acid in excess of the capacity of the soil to absorb it is what generally occurs around sulphur storage facilities, on the blocks and in their immediate vicinity. The block itself and the sulphur powders released from it are an abundant source of sulphur for the ubiquitous thiobacilli, whose activity leads to the rapid acidification of the meteoric waters coming into contact with the sulphur. This is probably the most significant environmental issue. Given its low pH, the surface water from the storage site must be collected and neutralized before it can be released into water courses. In addition to its costs, this phenomenon leads in the short term to a management problem and in the long term to a responsibility for the owner of the sulphur. For the large blocks of sulphur at some industrial facilities, the cost of treating surface water may be extremely high (in the order of millions of dollars per year).

Although there is no reliable data on the actual impact on the environment in the vicinity of sulphur storage facilities, the pressure exerted by public authorities in favour of environmentally-friendly technologies is leading to the

Fig. 20. Erosion
of the side
of a sulphur block
(by courtesy
of the Author).

abandonment of current storage practices.
Recently, the demand for new sulphur storage
facilities has increased, driven by some petroleum
production sites destined to generate large
quantities of sulphur remote from potential
markets. It is easy to predict that the increase in
capacity must be met with innovative technologies
able to guarantee a high level of safety for the
environment and for people. The problem is
complex and expensive, and is perceived as a
potential obstacle to production. If the technologies
traditionally used to store hazardous industrial
waste were applied to sulphur storage, the costs
would be far higher than those of current systems.
It is thus imperative to identify innovative low-cost
sulphur storage systems which are environmentally
safe and wholly acceptable to the population and
public authorities.

New solutions for sulphur storage

The solutions under study for the construction
of environmentally safer sulphur storage facilities
are based on the peculiarity of the environmental
risk associated with the presence of large quantities
of elemental sulphur, almost entirely due to the
biological process of sulphur oxidation by
thiobacilli. One possible solution is being tested at
Fort McMurray-Athabasca (Alberta, Canada),
where enormous quantities of sulphur are produced
from oil sands by the Athabasca Oil Sands Project
(AOSP). The technology tested by Alberta Sulphur
Research (Clark, 1998), in collaboration with
Syncrude, involves burying the blocks of sulphur
at a depth which will ensure a low and constant
temperature throughout the year. If, as in some
parts of northern Canada, the mean temperature is
below that needed for the survival and
reproduction of thiobacilli ($>5^{\circ}C$), the oxidation of
sulphur is in practice completely inhibited,
eliminating the risk of the acidification of waters
and soils. In more temperate zones, however, this
solution cannot be applied.

A different solution has been developed by Eni.
The approach adopted involves exploiting a natural
property of the thiobacilli in order to reduce the risk
of acidifying surface waters at sulphur storage
facilities. It has been discovered that these bacteria,
though able to oxidize sulphur under all the
conditions present in different natural habitats, are
highly sensitive to environments which are both
acidic and have high ionic strength; in practice, in
environments with high ionic strength, the thiobacilli
stop growing as soon as the pH reaches acidic values.
The solution proposed (Crescenzi *et al*., 2005) is
based on the inhibiting action exerted by high ionic
strength environments on thiobacilli, and involves
passivizing the surface of the sulphur blocks by
treating them with non-organic salts to inhibit

biological oxidation. Subsequently, the blocks are covered with a layer of soil that, in addition to protecting the block from erosion, also have the function of absorbing any emissions of H_2S and SO_2. Compared to the burial of the blocks described above, this approach is applicable everywhere and probably less expensive, since it makes it possible to inhibit the activity of thiobacilli at all temperatures, and does not require the use of pits.

Underground disposal

To solve the problem of surplus production definitively, as an alternative to surface storage facilities, disposing of sulphur in underground structures has been suggested, as in the disposal of some other industrial waste products. Two possible technologies have been proposed for sulphur disposal. The first uses injection under hydraulic fracturing conditions and involves the preparation, starting with the liquid sulphur from the Claus unit, of a sulphur and water slurry which is then pumped under pressure into the geological structure destined to receive it (Cobianco *et al.*, 2005). Although not yet developed on an industrial scale, this solution makes use of knowledge and equipment which are already known and widely used in the oil industry, for example in the disposal of drilling debris. Preliminary estimates suggest that this technology is economically advantageous when compared with the costs and environmental liabilities (in other words the costs of the environmental rehabilitation of an industrial site) associated with the construction and maintenance over several decades of sulphur storage facilities. The sulphur thus disposed of would only be partially recoverable, however, so that this solution is aimed primarily at disposing of production when very long storage times are predicted. In these cases, the environmental liabilities associated with open-air storage may be heavier than the commercial value of the sulphur. The other disposal route proposed for sulphur makes use of an underground cavern created in a salt formation (Pickren, 2003). This cavern may already exist, or be created by water leaching in accordance with conventional mining practices. In the latter case, however, large amounts of water are needed, many times the volume of the cavern to be created; this water, saturated in salt, must then be disposed of. The sulphur is pumped into the underground caverns in liquid form or as a water slurry. Despite its higher costs, the latter option is considered preferable since the sulphur, when injected into underground caverns above its melting point, may remain liquid for a considerable time (several years), generating greater risks than storage in the form of slurry. By using the Frash-type recovery techniques

adopted in mines, the sulphur disposed of in salt formations can technically be recovered in case of market demand. There are no known industrial applications.

It is possible that sulphur will continue to be produced in quantities higher than industrial capacity. The R&D efforts being made by oil companies lead one to hope that in the near future solutions suited to different production contexts will become available and that, when necessary, sulphur will be stored for considerable periods without damaging the environment or endangering the general public.

3.3.7 The sulphur market and new uses

The closure of the large sulphur mines over the past decade has led worldwide elemental sulphur production to practically coincide with that deriving from the desulphurization of hydrocarbons. The oil industry, which has in practice become the main source of this form of sulphur, has few options available for controlling the amounts which it is forced to produce. Without recourse to the large-scale re-injection of H_2S, the production of sulphur by upstream petroleum activities is destined to increase, as is that from downstream activities, given that all forecasts indicate greater recourse in the future to sour reservoirs to meet increasing demand for energy.

Generally speaking, the sulphur produced by the oil industry represents an economic resource which partially offsets production costs. However, it becomes a problem when the price of sulphur and the distance from end users makes transportation uneconomic, forcing companies to maintain large stores of unsold material. This aspect of the management of sulphur produced by the desulphurization of hydrocarbons is the object of much attention from oil companies. A second aspect of 'enforced' sulphur production relates to the effects of the relationship between demand and supply on the world market. Forecasts predict that growing enforced production capacity will consolidate a situation of glut in the sulphur market. Increasing the world demand for sulphur has thus become an objective, pursued by creating new opportunities in traditional markets or promoting the development of new sectors capable of absorbing at least a part of the excess sulphur.

World sulphur production

Sulphur is an essential raw material for a series of transformation industries which consume more than 60 million tons per year worldwide to produce

essential commodities for economic development such as fertilizers, paints, non-ferrous metals, etc.

This important raw material is available on the markets in different forms. Elemental sulphur is the most important commercially, which is now derived almost entirely from the oil industry as a by-product of fossil fuel production (see above). Another major source of sulphur is pyrites, iron sulphide-based minerals. In the worldwide production of sulphuric acid, pyrites contribute about 8% of sulphur consumption, especially in developing countries. The remainder of the industrial demand for sulphur is met by other sources, largely the production of non-ferrous metals. **Table 11** shows the percentage contribution of each source of supply, from the total of about 64 million tons of sulphur consumed by industry in 2001.

Sulphur consumptions

Sulphur is mainly used to make fertilizers. The availability of sulphur is therefore an essential condition for the development of industrial agriculture and for meeting the food requirements of populations. Other industries essential for economic development also depend heavily on the availability of this raw material, and for many years sulphur consumption was one of the most reliable indicators for measuring the degree of development of industrialized countries. This correlation does not hold true today, but sulphur continues to be a vital material for the development of emerging countries undergoing strong economic growth, such as China and India. **Fig. 21** shows the differentiation of sulphur consumption in the forms which are commercially important worldwide. Observing consumption patterns during the modern period, it is easy to see that it tends to grow in parallel with the increase in gross domestic product, confirming the central and irreplaceable role of sulphur in industrial development. However, for some years, despite its abundance and low cost, technological changes have tended to minimize consumption wherever possible. The reasons for this lie in a greater sensitivity to environmental issues, leading to the lowering of emissions of sulphur oxides

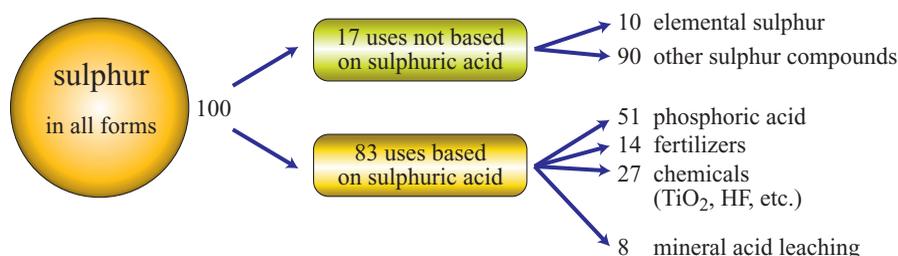**Table 11.** Distribution of world sulphur production among different sources as recorded in 2001

SOURCES OF SULPHUR IN ALL FORMS	%
Elemental sulphur recovered from the desulphurization of fuels	64
Sulphur from pyrites	8
Elemental sulphur from mines	2
Other sources (for example, production of non-ferrous metals)	26

into the atmosphere, due to their fundamental role in the generation of acid rain, and to a drastic decrease in waste production. The industrial use of sulphur, in particular as sulphuric acid, almost always creates large amounts of industrial waste; in the production of phosphate fertilizers, for example, each kg of sulphur used generates 3 to 5 kg of phosphogypsum to be disposed of. When it is economically viable, therefore, efforts are made to adopt technologies which keep the use of sulphur to a minimum. Hitherto, this trend has not altered the speed of growth of world sulphur consumption but in the future, concern for environmental issues may lead to a significant decrease in the use of this material in some production sectors, contributing to even greater imbalances in the ratio of largely enforced production to consumption.

Non-conventional uses of sulphur

Even during periods of low availability, far from today's glut, sulphur has always been a material available at low cost and with a high degree of purity. The potential for finding new uses for elemental sulphur has received constant attention from operators, leading to the development of applications in the most diverse fields, such as lighting, electrical accumulators, slow-release fertilizers, adhesives and foams. However, the amounts needed for these uses are relatively modest compared to those required for

Fig. 21. Consumption of all types of sulphur in the different sectors of use.

sulphur in all forms 100

17 uses not based on sulphuric acid
- 10 elemental sulphur
- 90 other sulphur compounds

83 uses based on sulphuric acid
- 51 phosphoric acid
- 14 fertilizers
- 27 chemicals (TiO_2, HF, etc.)
- 8 mineral acid leaching

conventional uses. During the periods of abundant supply which have occurred since the 1970s, interest in developing new uses for sulphur has increased in those industrial sectors which are theoretically able to generate a consumption of millions of tons per year, in other words so as to absorb a significant proportion of world production. This possibility is basically linked to its use in two sectors: in agriculture to supply sulphur to crops and in construction materials, such as sulphur asphalt for the construction of roads and sulphur cement for the production of concrete. These non-conventional uses will be examined separately below; finally, an interesting new proposal for using sulphur in the energy production sector is noted.

The use of sulphur as a fertilizer

The most promising sector in terms of potential market size is that of sulphur-based fertilizers to meet the demands for agricultural use (Boswell and Friendsen, 1993). Sulphur, which is an important component of plants, is removed from fields in significant quantities with every harvest. If it is not replaced, its absence limits yields and lowers the quality of the produce (Messick and Fan, 1999). In fact, the lack of sulphur is not a common condition in agricultural soils. Sulphur has always entered the soil in abundance together with phosphate and nitrogen fertilizers, which contain sulphates, and in meteoric waters in the form of sulphuric acid deriving from the sulphur oxides present in the air. Modern cultivation practices tend to use concentrated fertilizers without sulphates, and regulations on atmospheric pollution have drastically decreased emissions of SO_2 and consequently the presence of sulphuric acid in atmospheric precipitation. The result is a gradual depletion of sulphur in cultivated lands, which promises to give rise to massive world demand for elemental sulphur in the future. Although recorded on numerous occasions in many parts of the world (Graziano, 1995), the sulphur deficit has not yet stimulated a significant market for elemental sulphur in the fertilizer sector. The reasons for this are not clear; it depends largely on the reluctance of farmers to introduce new cultivation practices, but lack of investment by the fertilizer industry may also play a part.

Use of sulphur in the construction industry

Whilst awaiting the expected entry of elemental sulphur into common agricultural fertilization practices, the construction materials sector, in which sulphur is present as sulphur asphalt and sulphur cement, remains the only market potentially able to increase the demand for sulphur sufficiently to reduce the gap between production and consumption. Sulphur asphalt and sulphur cement are binding materials which have been known for decades (Petrossi *et al*., 1972; McBee, 1981). Sulphur asphalt is a substitute for the asphalt used for road surfacing. Sulphur cement is used to make concrete in place of hydraulic Portland cements. The commercial interest in these uses for sulphur has experienced ups and downs over the years, depending on fluctuations in sulphur prices, but R&D activities have been constant, creating products of ever-increasing quality. Both sulphur asphalt and sulphur cement have been developed commercially and occupy market niches which, however, have not yet reached the size required to significantly increase industrial demand for elemental sulphur. The impression shared by operators is that the limitations, which in the past have hindered the large-scale development of the sulphur market in construction materials, have not yet been overcome and, even under conditions of production surplus, prevent the growth in demand for these products.

Sulphur asphalt

Sulphur was first used to improve the properties of asphalt during the 19th century, but only during the 1970s did the availability of low-cost sulphur and the high cost of bitumen lead to an effective drive to develop a market for sulphur asphalt (Rennie, 1977). Sulphur asphalt is generally prepared by mixing hot liquid sulphur and bitumen. In the blends, sulphur exists in three different forms: one part chemically bonded to the hydrocarbon molecules, one part dissolved in the bitumen, and the remainder in the form of small crystalline sulphur particles dispersed in the bituminous mass. The part which reacts is generally small, since the reaction between sulphur and hydrocarbons is slow at the blending temperature. The solubility of sulphur in bitumen depends on its composition and temperature; for a typical commercial bitumen at 140ºC one can expect a solubility of around 20%, so that as a general rule, the crystalline part accounts for 20% in weight of the mass of the sulphur present. The sulphur present in the blend modifies the original properties of the bitumen (Bencowitz and Boe, 1938; Akili, 1984). For example, viscosity decreases as sulphur content increases, as does the resistance to penetration. The properties of the bituminous concretes formulated with sulphur asphalt, however, do not change significantly up to sulphur concentrations of 15% in volume (around

30% in weight). With higher concentrations, greater rigidity and a more limited application temperature interval are observed. For these reasons, in practice, the highest possible concentration is 35% in volume in the absence of plasticizers.

Since its first introduction over a century ago, sulphur asphalt has been tested numerous times for the construction of road surfaces. Hundreds of kilometres of road were built with increasingly perfected materials during the 1970s and 1980s, especially in North America (Prince, 1978); the results have rarely been negative. In the great majority of cases, the quality and durability have been deemed similar to, or better than, conventional roads. The economic competitiveness of sulphur asphalt is usually also guaranteed during periods of availability of low-cost sulphur. However, there is one characteristic which hinders the large-scale use of sulphur asphalt. In field tests, the emission of unacceptable amounts of sulphur gases, consisting mainly of H_2S and SO_2, during the application of sulphur asphalt has been recorded on numerous occasions. Based on the published evidence (Prince, 1978) collected by experts in this sector, it appears that significant amounts of these gases may be produced during the heating and application while hot of the sulphur asphalt, due in part to the reaction of sulphur with hydrocarbons. Only a careful control of the temperature of the materials to keep the sulphur asphalt below the limit temperature of 150ºC can contain this phenomenon.

Understandably, the danger of toxic emissions represents a significant obstacle to the use of a new bitumen. In construction sites, it is difficult to control the temperature during operations to prepare and apply the road surface with great accuracy. The products available today on the markets are better from this point of view than those in the past; it is therefore probable that perfecting the materials will make it possible to prepare formulations which are thermally more stable, thus overcoming this significant limitation on the development of the sulphur asphalt market.

Sulphur cement

The binding properties of liquid sulphur have been known from the earliest times. In the modern era, systematic attempts to use sulphur to formulate concrete date from the beginning of the 20th century; however, these were abandoned due to the low resistance and durability of the products. The turning point came in the early 1970s (Sullivan *et al.*, 1975), when additives capable of overcoming the structural defects produced by the solidification process were combined with the sulphur; during the transition from the liquid to the solid state this led to a loss of over 10% in volume. Over the years, an incredible number of products, both organic and mineral, have been used to this end: olefins, dicyclopentadiene, styrene, phosphorus, black carbon, vegetable oils, crude oils are only some of the additives tested to improve sulphur's binding properties. The sulphur cement currently available on the market possesses excellent properties, without doubt better than those of Portland cement (*Sulphur* […], 1994). The concretes formulated with sulphur cement, as well as having better mechanical properties than those of hydraulic cements, also have the chemical inertia of sulphur, making sulphur cement highly competitive for applications in aggressive or corrosive environments, e.g. in chemical plants, in marine environments or where toxic and hazardous waste products are rendered inert (Darnell, 1996). **Table 12** shows some of the mechanical properties of a typical sulphur concrete, compared with those of the hydraulic equivalent made with Portland cement.

Table 12. Comparison between the properties of sulphur concrete and conventional concrete

	Sulphur concrete	Portland concrete
Resistance to compression (MPa)	45-70	20-35
Resistance to bending (MPa)	6-10	3-4
Modulus of rupture (MPa)	9-13	535
Thermal expansion ($°C^{-1}$)	14-15	12
Elastic modulus ($10^3 \cdot MPa$)	30-40	30
Humidity absorption %	<0.10	0.3-3.0
Chemical resistance	high	low

The consumption of sulphur cement has increased since the 1980s, when the first commercially competitive products appeared on the market. At the end of the 1990s, the volume of the world market had reached 35,000 t/yr. The high cost and greater complexity of its use compared to Portland cement represent the main limitations hindering its development in a wider market. The cost of producing sulphur concrete is in fact two or three times that of an identical volume of hydraulic concrete. This high cost is in part linked to the higher cost of the raw material and in part to greater manufacturing costs, given the need to operate at temperatures above the melting point of sulphur (119oC). Despite its excellent properties, therefore, it is unlikely that sulphur cement will replace Portland cement for common uses. In difficult environments, however, its better qualities of resistance and durability seem sufficient to allow the progressive affirmation of this material.

Use of sulphur as a fuel

Sulphur's calorific value is 2,160 kcal/kg; although this is far lower than that of fossil fuels, it is high enough to hypothesize a thermal use to produce energy, if it is impossible to sell. This way of monetizing sulphur has been proposed by Alberta Sulphur Research. The thermal monetization of sulphur is necessarily accompanied by the production of twice the mass of SO_2, to be disposed of by injecting it into underground reservoirs in liquid form. This proposal has aroused the interest of some oil companies, which have examined its technical feasibility and economic and environmental sustainability. No pilot-scale testing activities are currently known. One important doubt concerns the behaviour of the SO_2 in the rock formation destined to receive it, since contact with water generates a strongly acidic solution. An interesting hypothesis is the possibility of injecting the SO_2 into a sour reservoir; in this case the Claus reaction between SO_2 and H_2S inside the reservoir would lead to the formation of sulphur. Despite doubts regarding the actual potential for energy monetization, it is probable that, as long as the sulphur glut lasts, this scheme to produce energy from an unusable residue without emitting greenhouse gases will attract the attention of operators.

References

AAGARD P. *et al.* (2001) *H2S-controlling reactions in clastic hydrocarbon reservoirs from the Norwegian Shelf and US Gulf Coast*, in: *Proceedings of the 10th International symposium on water-rock interaction*, Villasimius (Italy), 10-15 July, v.I, 129-132.

AKILI W. (1984) *Modification of sand-asphalt by the addition of sulphur*, in: *Sulphur '84. Proceedings of the international conference*, Calgary (Canada), 3-6 June, 617-628.

AL-EID M. *et al.* (2001) *Investigation of H2S migration in the Marjan complex*, «SPE Reservoir Evaluation & Engineering», 4, 509-515.

ALLISON J.D. *et al.* (2003) *Partial oxidation of hydrogen sulfide to elemental sulfur: a Claus alternative*, in: *Sulphur 2003. Proceedings of the international conference*, Banff (Canada), 2-5 November.

ANDERS B., WEBB E.C. (1995) *Treatment of H2S containing gases: a review of microbiological alternatives*, «Enzyme and Microbial Technology», 17, 2-10.

BENCOWITZ I., BOE E.S. (1938) *Effect of sulphur upon some properties of asphalts*, in: *Proceedings of the American Society for Testing Materials annual meeting*, 39, Part II, 539.

BOSWELL C.C., FRIENDSEN D.K. (1993) *Elemental sulfur fertilizers and their use on crops and pastures*, «Nutrient Cycling in Agroecosystems», 35, 127-149.

BURGER E.D. *et al.* (2005) *A mechanistic model to evaluate reservoir souring in the Ekofisk Field*, in: *Proceedings of the International symposium on oilfield chemistry*, Houston (TX), 2-4 February, SPE 93297.

CAROLL J.J., MADDOCKS J.R. (1999) *Design considerations for acid gas injection*, in: *Proceedings of the Laurance Reid gas conditioning conference*, Norman (OK), February.

CLARK P.D. (1998) *Improved strategies for blocking and underground storage of elemental sulphur*, «ASRL Quarterly Bulletin», 35, 16-37.

CLARK P.D. *et al.* (2003) *High temperature cracking of H2S to hydrogen in ceramic reactor systems*, «ASRL Quarterly Bulletin»,126, 3-61.

CLARK P.D. *et al.* (2004) *Production of H2 from catalytic partial oxidation of H2S in a short-contact-time reactor*, «Catalysis Communications», 5, 743-747.

COBIANCO S. *et al.* (2005) *Permanent disposal of sulphur: an environmental and economically sound strategy for the future?*, in: *Proceedings of the 7th Offshore Mediterranean conference*, Ravenna (Italy), 16-18 March.

CONNOCK L. (1996) *A better understanding of LRSR processes*, «Sulphur», January-February, 42-52.

CRESCENZI F. *et al.* (2005) Italian Patent EA6453 to Eni, EniTecnologie.

CROSS M.M. *et al.* (2004) *Thermochemical Sulphate Reduction (TSR): experimental determination of reaction kinetics and implications of the observed reaction rates for petroleum reservoirs*, «Organic Geochemistry», 35, 393-404.

DARNELL G.R. (1996) *Sulphur polymer cement a final waste form for radioactive and hazardous wastes*, American Society for Testing Materials special technical publication, STP 1240, 272-281.

FORAL A.J., AL-UBAIDI B.H. (1995) *Evaluation of H2S scavenger technologies*, Gas Research Institute, Report GRI-94/0197.

Gas processes '94. A special report (1994), «Hydrocarbon Processing», 73, 67-116.

GIANNA R. *et al.* (2004) Patent WO2004056454 to EniTecnologie.

GPSA (Gas Processors Suppliers Association) (1998) *Sulfur recovery*, in: *Engineering data book*, Tulsa (OK), GPSA, 2v.; v.II, section 21.

GRAZIANO P.L. (1995) *Preventing iron chlorosis in fruit trees using elemental sulphur*, «Sulphur in Agriculture», 19, 63-66.

KEENE D.E. (1989) *British Gas Stretford Process: the basis of good process design and operations*, in: *Proceedings of the Gas Research Institute liquid redox sulphur recovery conference*, Austin (TX), 7-9 May, 72-115.

KENSELL W., LEPPIN D. (1996) *Review of the H₂S direct oxidation processes*, in: *Proceedings of the 7th Gas Research Institute sulphur recovery conference*, Austin (TX), 24-27 September 1995, 81-100.

KITTO M. (2002) *The sulphur market: developments and trends*, «Sulphur», July, 18-23.

LALLEMAND F., MINKKINEN A. (2002) *Processes combine to assist acid-gas handling, reinjection*, «Oil & Gas Journal», 21 January.

MCBEE W.C. (1981) *Modified sulphur concrete technology*, in: *Proceedings of Sulphur '81: an international conference*, Calgary (Canada), 367-388.

MACHEL H.G. (2001) *Bacterial and thermochemical sulfate reduction in diagenetic settings-old and new insights*, «Sedimentary Geology», 140, 143-175.

MAMROSH D.L., ALLEN M.C. (1994) *Status of sulferox technology and recent developments*, in: *Proceedings of the 6th Gas Research Institute sulphur recovery conference*, Austin (TX), 15-17 May, 51-65.

MANZANO B.K. *et al.* (1997) *The influence of thermochemical sulphate reduction on hydrocarbon composition in Nisku reservoirs, Brazeau river area, Alberta, Canada*, «Organic Geochemistry», 27, 507-521.

MESSICK D.L., FAN M.X. (1999) *Plant nutrient sulphur gains global momentum*, «Sulphur», 260, 26-33.

MIWA M. *et al.* (2002) *Sour gas injection project*, in: *Proceedings of the Abu Dhabi International petroleum exhibition and conference*, Abu Dhabi, 13-16 October, SPE 78547.

NALG G.J. (1995) *ARI-LO-CAT/ARI LO-CAT II. Application and process technology update*, in: *Proceedings of the 7th Gas Research Institute sulphur recovery conference*, Austin (TX), 24-27 September, 29-37.

PALLA N. *et al.* (2004a) *Morphysorb process proves feasible in first commercial plant*, «Oil & Gas Journal», 5 July, 54-59.

PALLA N. *et al.* (2004b) *Duke Energy installs first Morphysorb unit at Kwoen gas plant*, «Oil & Gas Journal», 12 July, 52-57.

PETROSSI U. *et al.* (1972) *Reactions and technological properties of sulphur treated asphalt*, «Industrial and Engineering Chemistry. Product Research and Development», 11, 214-219.

PICKREN R.A. (2003) US Patent 6582025 to Crescent Technology.

PRINCE S.M. (1978) *Construction and performance of sulphur-asphalt road in Texas*, «Advances in Chemistry Series», 165, 161-171.

QUINLAN M.P. (1996) *Evaluation of selected emerging sulphur recovery processes*, «GasTips», 3, 26-35.

QUINLAN M.P. *et al.* (1997) *Evaluation of selected emerging offshore sulphur recovery processes*, in: *Proceedings of the Gas Processors Association annual convention*, San Antonio (TX), 10-12 March, 183-190.

RENNIE W.J. (1977) *Sulphur asphalts. The Pronk 51/A emulsion binder system*, Calgary (Canada), SUDIC.

ROYAN T., WICHERT E. (1995) *Sulphur disposal by acid gas injection*, in: *Proceedings of the Acid gas Canadian gas processors association meeting*, Calgary (Canada), 20 September.

RUTLAND C. (1998) *The right way. The old practice of pouring sulphur to poorly prepared or unprepared ground can have serious and costly future ramifications reports*, «Sulphur», 256, 41-44.

SLIMANE R.B. *et al.* (2002) *Production of hydrogen by superadiabatic decomposition of hydrogen sulfide*, in: *Proceedings of the US Department of Energy Hydrogen program review meeting*, Golden (CO), 6-10 May, NREL/CP-610-32405.

STONE K. (2003) *Sulphur. Mineral and metal commodity reviews*, in: *Canadian minerals yearbook*, 52, 1-6.

SULLIVAN T.A. *et al.* (1975) *Sulphur in coating and structural materials*, «Advances in Chemistry Series», 140, 55-74.

Sulphur polymer cement concrete (1994), Washington (D.C.), The Sulphur Institute, 58.

THIBEAU S. *et al.* (2003) *Simulation of sour gas injection into low permeability oil reservoirs*, in: *Proceedings of the Society of Petroleum Engineers annual technical conference and exhibition*, Denver (CO), 5-8 October, SPE 84362.

WHATLEY L. (2000) *Acid-gas injection proves economic for West Texas gas plant*, «Oil & Gas Journal», 98, 58-61.

WICHERT E., ROYAN T. (1997) *Acid gas injection eliminates sulfur recovery expense*, «Oil & Gas Journal», 95, 63-72.

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