Prior to 1960, Alberta’s production of elemental sulfur was minimal. Then came sour natural gas. By 2006 production had escalated to approximately 7 million tpy of elemental sulfur. Sour gas is now accompanied by heavy oil and oil sands (up to 5% sulfur by weight) as sources of recovered sulfur and Alberta’s huge stockpiles of the commodity continue to grow. Europe’s increasingly stringent environmental standards for sulfur content in fuels will probably be emulated by the rest of the world. Less sulfur in fuels also means stockpiles are not quickly depleted. Increases in stockpiled sulfur should have resulted in Paul Crawford, Enersul LP, Canada, asks, has the environmental impact of recovered elemental sulfur improved?
in significant increases in fugitive emissions had it not been for a parallel improvement in emission suppression technologies and safety standards; legislated as well as industry initiated. Has the environmental impact of sulfur handling been reduced over the past 25 years?

Sulfur recovery refers to the conversion of hydrogen sulfide (H\textsubscript{2}S) to elemental sulfur. Hydrogen sulfide is recovered by means of a sulfur recovery unit (SRU), which converts the gas into liquid elemental sulfur. Elemental sulfur is recovered from the processing of sour natural gas (which has high H\textsubscript{2}S content) from the refining of crude oil and, most importantly for this presentation, the upgrading of bitumen into synthetic crude oil (SCO).

Sulfur emissions can take various chemical forms such as H\textsubscript{2}S, sulfur dioxide (SO\textsubscript{2}) and the yellow substance itself: elemental sulfur. Enersul is actively engaged in both the elemental and degassing aspects of the sulfur forming and handling industry. This article addresses the environmental impact of elemental sulfur and hydrogen sulfide as a byproduct of sour gas refining.

Liquid and/or solid sulfur can be stored, formed and handled at different points downstream from the SRU. Proper forming, storage, handling and remelting methods are required to ensure minimal environmental impact.

Forming, storage and handling of sulfur all have potential for the release of sulfur based emissions, as illustrated in Figure 1. Both the hot liquid sulfur from the SRU and the formed sulfur particles, which may be formed for ease of transportation, handling and storage, can be sources of emissions. In the case of molten sulfur, vapour and residual traces of H\textsubscript{2}S from which the sulfur is recovered can become fugitive emissions. Degassing will be addressed later in the article. When the sulfur is solidified into various forms, inherent friability can lead to the formation of sulfur dust or even particulate which may be inhaled. These emissions, apart from their direct impact on biological systems, are especially sensitive to oxidation by bacteria. Oxidation forms acidic byproducts, which dissolve in water and can adversely affect the environment. These are the emissions that will be addressed.

**Sulfur forming**

Many different processes produce bulk solid sulfur. The degrees of mechanical strength and friability (the ease with which dust forms) of the formed sulfur depend on the process used to form the sulfur.

The singular most important impact of formed sulfur on the environment is the amount of dust, or fines, in the form and the additional amount of dust, which results from subsequent handling. Sulfur particles or dust with maximum dimensions not exceeding 0.3 mm are generally considered fines.

**Crushed bulk**

This is not intentionally formed sulfur but the result of breaking block sulfur, which had been poured as a solid block for storage. This early form of elemental sulfur was very irregular in shape and size as well as being very dusty (Figure 2).

Shell Canada’s Jumping Pound sulfur plant officially opened in June 1952. Upon startup it produced 32 tpd of sulfur initially poured into a vat. As the material hardened, higher sheet metal walls were added until a giant, yellow, 4000 t block had been created. Impossible to ship, the block was blown apart by dynamite, piled into trucks and hauled to the railhead.

Crushed bulk contains many fines, which become airborne during handling. The quantity of fines will vary between 20 - 35 wt%.

**Slate**

Slating became common in the 1960s and was one of the first intentionally manufactured forms of sulfur. Enersul’s first
slating plant began operations at Shell's Waterton facility in 1970. Liquid sulfur is poured onto a slowly moving belt (Figure 3) and the sulfur on the belt is cooled with water and down draft air fans, which also serve to help spread the sulfur across the belt (the fans blow fugitive emitted hydrogen sulfide away; see degassing). As the sulfur cools it solidifies into sheets, which vary in thickness between 3 - 5 mm. The sheets are then broken into smaller pieces called slate and sent to storage by a conveyor.

Compared to crushed bulk, slating reduced the amount of fines generated during storage, handling and transportation to approximately 4 - 7 wt%. This was a considerable improvement but a small start in the effort to reduce environmental emissions. Slate is irregularly shaped with many sharp edges, which break every time the material is handled, creating more fines (Figure 4).

Air prill

Increasing pressure during the 1970s to be ever more environmentally conscious kept the sulfur forming and handling industry working toward improving elemental sulfur forms. Air prilling, originally from Poland, came on the scene.

With the air prill process, liquid sulfur is sprayed from the top of a tower against an upward flow of air. The air cools the sulfur droplets into hard sulfur pellets or prills. The process dramatically reduced the amount of fines in the formed product. The air prill was one of the first forms of sulfur to be classed as a Premium Product by the Sulphur Development Institute of Canada (SUDIC). And although the process was a great leap forward for the industry, the upward flow of air carried sulfur emissions from the top of the tower into the atmosphere, creating a new type of emission.

WetPrill™

The WetPrill™ sulfur forming process has been a staple in Enersul's Canadian operations since 1978.

In the WetPrill™ process, molten sulfur is pumped onto perforated trays, which direct the sulfur in narrow streams into an agitated water bath. Pellets or prills form as the sulfur comes in contact with the water. This produces generally spherical and, in modern modifications, more uniformly sized pellets.

The fines content amounts to approximately 0.2 wt% with a moisture content of the formed product of 1.7 - 2.5 wt%. The friability of the end product is significantly less than slate but does not meet SUDIC Premium Product specifications. The forming facility is not expensive and is well suited to the smaller tonnages associated with lower sulfur throughput operations.

Pastillation

The basic principle of this technology involves a continuously running steel belt, which is cooled from the underside by water sprayed through nozzles. Pastillation is used for making pastilles from many other liquids, not merely sulfur. A feeding system specially developed for sulfur deposits a regular array of liquid sulfur in the form of droplets onto the steel belt. The drops are cooled by the water along the length of the belt and are discharged in the form of solid hemispherical pastilles on to a conveyor system. Care must be taken during operation to ensure the droplets do not coalesce before solidifying, and temperature control is important. The product can meet SUDIC Premium Product specifications and is suited to smaller throughput tonnages with its typical 6 - 12 tph capacity.

GX™ granulating process

The first two GX™ granulation plants were built by Enersul in 1979. GX™ granulation is a size enlargement process in which liquid sulfur is sprayed onto a core or seed of solid sulfur inside a rotating drum and cooled to a solid state before the next coat of liquid sulfur is applied. Temperature and spray nozzle control are important.

Through repeated applications of liquid sulfur, the seed increases in volume and weight. This eliminates the inherent shrinkage of sulfur during the solidification stage, as with the air prill, WetPrill™ and pastillation, and ensures the process provides a spherical, dry granule completely free of voids. GX™ is ‘solid through and through’ and resistant to breaking down into fines and dust. The reduced impact on the environment as well as health and safety are significant.

The fines amount to approximately 0.5 wt% and the moisture content of the formed product is 0.5 wt%. Particulate sulfur emissions are less than 50 mg/kg stack effluent.

Premium Product

The SUDIC Premium Product specifications introduced in the late 1970s were likely the most significant step forward in the long struggle to improve the properties of formed solid elemental sulfur and to meet the ever more stringent demands for a more environmentally safe and friendly product. Research for improvements continues but useful and cost attractive as the other types of
forming may be, the best way to reduce environmental impact is to install a sulfur forming process that meets SUDIC Premium Product specifications. The industry has come a long way in improving the storage, handling and transportation aspects of formed, solid elemental sulfur and the associated challenges of fugitive emissions. The SUDIC premium product specification for formed sulfur is shown in Appendix 1. GX™ product exceeds SUDIC specification for premium product quality, is designed for throughput tonnages of 15 and 50 tph, and allows for multiple unit configurations.

Fugitive dust
Sulfur is a brittle material and can easily degrade during handling giving rise to fine dust, which can be hazardous because it is easily airborne. Airborne dust can cause fires and explosions as well as health and environmental problems. When processing formed sulfur, fugitive dust emissions can be a problem at conveyor transfer points, when loading formed sulfur to a stockpile or railcar, truck or ship or even to a sulfur bagging line.

Fine sulfur dust dispersed in air in sufficient concentrations and in the presence of an ignition source is a potential dust explosion hazard. Because of its low electrical conductivity, static electricity built up by movement of the material itself can cause spark discharge and explosions. The explosive limits of sulfur dust in air are: lower, 35 g/m$^3$ and upper, 1400 g/m$^3$.

Sulfur dust resulting from sulfur storage and handling has the potential to acidify soils in areas surrounding sulfur forming and handling facilities. Dust can also contaminate the surface and groundwater if it comes into contact with any surface runoff water.

Sulfur forming systems that produce premium product significantly reduce fugitive dust, particularly when compared with the earlier crushed bulk and slate. Additional mitigation measures have been implemented throughout the years and further the prevention of fugitive sulfur dust issues during handling and loading of formed sulfur. These measures include dust suppression, proper material handling and storage.

Debates continue among regulatory authorities as to the hazard classification of formed solid elemental sulfur (IMO, bulk cargo code) but product improvements during the last 25 years have made storage, handling and transportation of this essential commodity easier, safer and more environmentally friendly.

Dust suppression system (DSS)
Successful though the improvements to the formed product have been in reducing fugitive dust emissions, many of the storage, handling and transportation systems still in use can be hard on such a friable product as solid sulfur. Hence the need for DSS. Care must be taken in both the selection and application of DSS agents; end users demand a very high standard of purity in their elemental sulfur (99.90%+). The commodity is increasingly applied in elemental form as a soil amendment and lack of product purity would be harmful to not only the soil but could also have unknown, potentially damaging impact on crops of all kinds. Compatible DSS is therefore essential.

A dust suppression system can be installed at conveyor transfer points and at load out stations. Enersul’s DSS uses a combination of water, compressed air and a surfactant mixed together in a (proprietary) foam generator. The foam is applied to the formed sulfur at the abovementioned points and helps suppress dust. To ensure compliance with the SUDIC premium product specifications, the foam adds a maximum 0.5% moisture by weight to the formed product.

Materials handling
Conveyors fitted with belt cleaners eliminate not only the carry back of residual sulfur but also continued degradation of the product, which ordinarily produces undesirable
fugitive emissions. Transfer points properly designed with a minimal drop distance will reduce rough handling and the potential formation of fines. Handling systems should also be designed to minimise the number of conveyors and conveyor transfer points. Covering the conveyors can also minimise the release of fines to the environment.

Grounded telescoping spouts have been developed to prevent damage by directing the sulfur close to the stockpile, railcar, truck, ship or bag. The spout minimises the height from which the sulfur falls exposed to the wind and other elements and this helps reduce the emission of fugitive dust. Grounding the spout minimises static charge.

**Storage**

Indoor storage of formed sulfur shields the commodity from winds, reduces fugitive dust emissions and protects stockpiles from contamination. Expensive though this refinement may be (Figure 5), it is the preferred modern method of storing formed product awaiting delivery to end users. In the past, storage of formed sulfur in an enclosed space was not advised because of the danger of dust explosions, but improvements in product friability as well as such product handling equipment as stacker/reclaimers have minimised dust formation. If indoor storage cannot be provided, a location shielded from prevailing winds should be selected. Erecting windbreaks can be considered if no natural formations or barriers are present, but consideration should be given to the potential disturbing effects of eddy currents and down draughts, which can pick up fines and render them airborne.

**Sulfur blocking**

Enersul has been involved with the pouring of many millions of t of excess recovered sulfur production to block. The record of commercial elemental sulfur supply and demand over the last 25 years has shown increasing production and cyclical demand. As a result, significant amounts of sulfur remain in storage for sometimes long periods of time.

Sulfur blocking consists of transporting liquid sulfur via an insulated and usually heated pipeline from the SRU to a storage site where it is poured to a block. In the past, many producers and oil sands mining companies were reluctant to move sulfur to market because of low prices for the commodity and/or lack of transportation infrastructure; they opted instead to pour the sulfur to block (Figure 6).

These blocks, while common to the oil and gas industry, were looked upon as an unwanted byproduct of oil and gas production. In the mid 1970s, and again until recently, declining sulfur markets led to the development of sulfur stocks in the form of huge blocks in many locations around the world.

Blocks are not a long term solution and one of the main environmental issues is production of sulfur dioxide as the sulfur reacts with air. Sulfur dioxide is a component of sulfuric acid; an emission challenge of significance. Sulfuric acid can lower the pH of soil and groundwater, thereby creating an environmental problem.

When the first blocks were poured, little effort was made to prepare the sites. Producers simply graded the soil and poured the liquid sulfur. Today, advancements include construction of an asphalt base, plastic liner around the rim of the block area and provisions for collecting and treating surface water runoff. Enersul have seen significant improvement, but cleaning up old mistakes remains important.

Another important environmental issue in sulfur handling is H₂S and SOₓ, which can be present in the sulfur, delivered from the SRU. These gases are released during solidification and thereafter thus adding to emissions. Degassing liquid sulfur before it is poured to block has substantially reduced the amount of these dissolved gases to less than 10 ppm. Emissions are effectively reduced upon solidification in the block and upon remelting during recovery.

Another noteworthy issue is the erosion, which occurs mainly at the sides of the blocks. Rain and freezing/thawing conditions can sometimes lead to block walls breaking down and the subsequent risk of dust being spread into the environment (Figure 7). The practice of stepping the block walls to avoid uncushioned collapse from high elevations has been developed to protect employees from injury.

**Liquid sulfur degassing**

Residual H₂S is usually present in liquid sulfur downstream of the SRU. When the gas exceeds 30 ppm it presents a danger to persons in the area. A number of technologies have been developed to address this serious and odorous environmental issue.

Liquid sulfur degassing involves three key steps:

- Hydrogen polysulfide (HₓSₓ) decomposition; much dissolved H₂S is present in the polysulfide form and must be decomposed in order for degassing to be effective.
- H₂S removal for the liquid sulfur to the gas/vapour headspace.
- Removal of the H₂S from the headspace.

Many degassing systems have been developed over the last 20 years.

**Shell Catalytic (1987)**

The Shell Catalytic system is a patented process for reducing the hydrogen sulfide and hydrogen polysulfide content of liquid sulfur by passing liquid sulfur through a bed of catalyst material comprised of at least one inorganic metal sulfide.

**Enersul HySpec™ (1995)**

The HySpec™ process uses patented gas/liquid contactors inside a series of separate reactor cells with a select catalyst to aid in the rapid decomposition of hydrogen polysulfides. The catalyst is subsequently removed by the process, which ensures optimum solid sulfur resistance to breakage in downstream forming and handling.

Data illustrating the performance of two existing HySpec™ plants and a test plant is summarised in Table 1. The catalyst addition rate of less than 5 ppm(w) was sufficient to achieve degassing. The consumption amounts to only a few litres per day. The catalyst consumption
depends on the sulfur temperature and is dictated by the volatility property of the catalyst rather than loss of catalytic property.

Goar Allison D’GAASS (1997)

Degassing by means of the D’GAASS process takes place outside the sulfur pit in a pressurised vertical vessel, which places unprocessed sulfur in counter current contact with pressurised process air. The hydrogen sulfide is oxidised to sulfur and water so there is no need for disposal of the removed H₂S. The unprocessed sulfur is pumped to the vessel and placed in intimate contact with air across special fixed vessel internals.

A stream of liquid sulfur containing polysulfides as well as hydrogen sulfide and a stream of an oxidising gas are introduced into a vessel and mixed. The streams are passed through the vessel at a pressure of at least 40 psig at a certain temperature and for a residence time sufficient to remove substantially all the polysulfides and hydrogen sulfide from the liquid sulfur.

Comparisons

The last quarter century has seen advancements in the sulfur industry, changes which have led to a great reduction in the negative environmental impact of elemental sulfur forming and handling. For example, if Alberta’s current production of sulfur was in the form of crushed bulk, 1.5 - 2.5 million t would be fines (20 - 35 wt% of today’s sulfur production). These fines that would become airborne during handling and could easily cause explosions, health and environmental problems.

If the 7 million tpy of production was produced as slate, 0.25 - 0.50 million t would be fines.

Formed sulfur meeting SUDIC’s Premium Product standard would result in only 0.035 million t having a chance to become airborne. This figure could be further reduced with dust suppressant and proper material handling. These numbers represent impressive improvements.

Those who advocate environmental responsibility may not be satisfied, but the sulfur handling industry cannot be labelled asleep at the wheel as far as sulfur based emissions are concerned.

Conclusions

The environmental impact of element sulfur forming and handling has improved markedly over the last 50 years. Forming solid sulfur and transporting it to the end user can be achieved with minimal environmental impact by using best available practices. Dangerous H₂S and SO₂ can now be removed from liquid sulfur. Sulfur can now be formed into Premium Product, which significantly reduces the fines produced during handling. Proper material handling techniques and technologies further mitigate potential damage.

Sulfur blocks present a greater challenge, old blocks poured on soil in particular. Some blocks are more than 40 years old and need to be recovered in order to not damage the environment any more than they already have. Given seemingly increasing pressure from the public stakeholder to protect the environment, regulations and standards in the future are likely to become nothing if not more stringent. The oil and gas industry in the province will not be immune. The industry has come a long way since sour gas, but between increasing sulfur production, unpredictable markets and cleaning up past mistakes one cannot ignore the need for continued effort.

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Appendix 1

<table>
<thead>
<tr>
<th>Property</th>
<th>SUDIC Premium Product specification for sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shape and size</td>
<td>Generally spherical between 2 and 6 mm</td>
</tr>
<tr>
<td>Size distribution</td>
<td>Less than 5% to be retained on a No. 1/4 US screen (6.3 mm)</td>
</tr>
<tr>
<td></td>
<td>Minimum of 75% to pass through a No. 3-1/2 US screen (5.6 mm)</td>
</tr>
<tr>
<td></td>
<td>Minimum of 75% to be retained on a No. 7 US screen (2.8 mm)</td>
</tr>
<tr>
<td></td>
<td>Less than 2% to pass through a No.16 US screen (1.00 mm)</td>
</tr>
<tr>
<td></td>
<td>Less than 0.5% to pass through a No.50 US screen (0.30 mm)</td>
</tr>
<tr>
<td>Moisture content</td>
<td>Less than 0.5 wt% moisture (bulk average) as produced</td>
</tr>
<tr>
<td>Friability performance</td>
<td>Less than 1% of fines (-50 mesh material) generated under standard stress level I Friability test</td>
</tr>
<tr>
<td></td>
<td>Less than 2% of fines generated under standard stress level II test</td>
</tr>
<tr>
<td>Bulk density</td>
<td>Not less than 1040 Kg/m³ loose 1200 kg/m³ agitated (vibrated)</td>
</tr>
<tr>
<td>Compaction</td>
<td>Fines generated after under direct shear test under static loading of 165 kPa (approximatley 15 m of stock pile) not to exceed 0.5% fines by weight</td>
</tr>
<tr>
<td></td>
<td>Fines generated after under direct shear test under dynamic loading of 165 kPa (approximately 15 m of stock pile) not to exceed 0.5% fines by weight</td>
</tr>
<tr>
<td>Angle of repose</td>
<td>Not less than 25°</td>
</tr>
<tr>
<td>Other</td>
<td>Chemical composition must not be altered from feedstock</td>
</tr>
</tbody>
</table>

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