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SULFUR

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Elemental sulfur is essential to human existence. Without sulfur there would be no human life. Sulfur and its derivatives are intimately related to formation of protein and amino-acids in plants, animals and humans. In addition to allowing humans to thrive, sulfur is a cornerstone of agricultural, industrial, feedstuff, preservative processes and medicinal applications. Sulfur's pre-eminence commenced in antiquity as our predecessors recognized the element's myriad unique characteristics. Incipient chemistry in the Middle Ages brought further recognition, followed by a crucial role in industrial chemistry from the 18th century forward. Today, in addition to traditional uses, sulfur and its derivatives are being examined for applications in super-efficient electric storage batteries, as a superconductor and as a component for solar-based electrical generation.

Sulfur's millennia-old negative public perception is justifiably linked to odorous and deadly compounds from volcanoes: hydrogen sulfide (H_2S) along with sulfur dioxide (SO_2) and trioxide (SO_3), to name few. Being the alchemists' "stone that burns" to create the foregoing compounds, and more, added to its mystery. In modern times, its negative persona is mostly linked to airborne pollution from power generation, fuels and industrial processes. The last 50 years' notoriety focused on the dramatic visual impact of acid rain and its resultant environmental degradation. Acid rain's link to deforestation, new-found understanding of respiratory illnesses tied to sulfur dioxide mist and legislated removal from fuels are but a few of the negative headlines associated with sulfur and its compounds. While justified, such pollution controls are now not exclusive to sulfur. Society is focused on mitigating the impact of human activities on the entire biosphere, be it eliminating dust generated by farmers at planting, converting sewer plant effluents into potable water, reducing all stack gas emissions and sequestering carbon dioxide, not just sulfur compounds. Unfortunately, many in society continue to view sulfur as a malignant substance rather than appreciating its essential role in human life: healthy food, medicine, green energy, construction materials, essential to innumerable chemical reactions and beneficial products, a natural fungicide and pest repellent, saving lives by providing the mercaptam-derived rotten-egg odor in otherwise odorless natural gas, medicinal salve, and an organically certified material. Sulfur's role as an essential fourth plant nutrient is now recognized to be required in all types of cultivation — conventional and organic. The Sulphur Institute (TSI) calls sulfur "an advantaged element" for its myriad uses. TSI represents an excellent resource for furthering readers' knowledge of this element from uses, transportation and safety (sulphurinstitute.org).

Sulfur was historically obtained from volcanic deposits, which limited availability. *Fire and Brimstone: The History of Melting Louisiana's Sulphur* (D. Davis and R. Detro, Louisiana Geological Survey,1992) may be consulted for further information. Its Latin name translates to "the stone that burns." Thus, sulfur's association with Hades, Satan and the origin of its English appellation — brimstone. In addition to the foregoing resource, the author recommends an excellent online resource for further information regarding this multifaceted element, *Materials Flow of Sulfur* (J. Ober, USGS 2002, http://pubs.usgs.gov/of/2002/of02-298/).

Sicily, a center of volcanic activity, was the focus of European sulfur availability from the pre-Christian era until the first decade of the 20th Century. Sulfur's essential role in gunpowder manufacture made many Sicilians extremely wealthy. The early 20th Century brought an indisputable paradigm shift to the industry. Herman Frasch developed a process to melt sulfur entrained in limestone deposits with superheated water, lifting molten sulfur to the surface with compressed air rather than pumps dependent on mechanical integrity and requiring periodic replacement. Frasch deposits are often associated with salt dome geologic structures prevalent in Gulf of Mexico oil fields. Almost overnight, this technology converted sulfur extraction from a labor-intensive gathering and purification process employing many persons to an industrial operation limited only by the size of equipment, deposits and makeup water due to geological losses. The Frasch method of hydraulic mining with superheated water upended the Sicilian sulfur monopoly at the dawn of the chemical century. From 1905, when the island provided 95 percent of global supply, it fell to 50 percent by 1913 (Louisiana Geological Survey), as World War I's demand for gunpowder boomed. The advent of Frasch sulfur shifted production across the Atlantic, where deposits were ideally suited to the new technology. The U.S. Gulf Coast, eventually including output in coastal Mexico and Pecos County in West Texas, became the center of the Frasch sulfur industry until the late 1990s. Then, just as Frasch sulfur rapidly eliminated the Sicilian production monopoly, recovered sulfur from EPA-mandated hydrocarbon purification disrupted the Frasch monopoly. U.S. natural gas prices, Frasch's essential raw material needed to heat injected process water, concurrently went from $0.25/MMBTU in the mid-1970s to more than $10/MMBTU by the early 1990. The combined impact forced all U.S. mines to close.

Mandated removal of sulfur from motor fuels created a surge of supply which needed to be removed from refinery and gas plant sites. Refineries faced added investment, operating and disposal cost for what was viewed as a waste product. Faced with a disposal emergency, oil companies went to consumers of Frasch sulfur and offered recovered sulfur at "whatever price was needed to keep it moving from the refinery." The magnitude of change and its continuing evolution can be appreciated by legally mandated change in the sulfur content of diesel fuel going from 6-4 percent to 0.15 percent from the 1980s through 1990s. This paradigm shift led to the demise of U.S. and Mexican Frasch output by 2001. Today, Frasch mining is limited to Poland. A 2015 attempt to reopen Iraq's Mishraq Mine was stymied by armed conflict. Another legislated surge of sulfur from refineries will commence in 2020 as marine bunker fuels face reductions under International Maritime Organization (IMO) regulations from the same range of 4-6 percent S to 0.5 percent.

In summary, recovered sulfur obtained from removing sulfur from natural gas and sulfur compounds present in hydrocarbon-derived fuels, is a "nondiscretionary waste process." Thus, sulfur must be disposed of continuously, regardless of demand; whenever output exceeds use it must be disposed of, regardless of the cost to do so. In contrast, Frasch mining operations closely balanced supply with demand through inventory and production management.

Global sulfur producers face two further disruptive supply-related events and one disruptive consumption restructuring as we look at future developments.

The first is a global reduction in the sulfur content of marine (ship) fuels from approximately 3 percent to 0.5 percent S, estimated to increase refinery sulfur output by more than 5 Mt (5.5 million st) (Ralph Grimmer; Stillwater Associates; TSI Annual Sulphur Symposium, April 2018). The requirement will commence in 2020 as marine bunker fuels face sulfur-content restrictions under International Maritime Organization (IMO) regulations.

The second is rapidly expanding sulfur recovery from gas processing activities in the Arab Gulf, Kazakhstan and proximate country production. As an example, Abu Dhabi has increased its sulfur output since 2013 from less than 2 Mt (2.2 million st) to 8 Mt (8.8 million st). Projects, plans and expectations are for another four million tons to be generated by 2022, growing thereafter. This rise is being supported

Table 1

Elemental sulfur production and demand (Mt).

	2014	2015	2017	2022
World production	59.3	62.0	66.9	75.0
World demand	61.4	61.8	63.0	66.0
Balance	-2.1	0.2	3.9	9.0
Sources: IFA, Integer Research and Con-Sul Inc.				

Table 2

Principal regions of elemental sulfur production and forecast (Mt/a).

	2015	2018	2022	Change
Middle East	13.4	21.7	25.0	11.6
FSU	10.3	12.6	14.0	3.7
East Asia	10.0	11.9	12.0	2.0
North America	14.1	13.6	14.0	(0.1)
West Europe	3.8	3.9	3.0	(0.8)
Other	7.7	7.7	7.0	(0.7)
Total	59.3	71.4	75.0	15.7
Sources: IFA, Integer Research and Con-Sul Inc.				

by internal and external demand for gas as exports of liquefied natural gas, increasingly a global fuel of choice.

The demand disruption has just been announced as the world's leading sulfur consumer, OCP of Morocco, and the leading producer (Abu Dhabi's ADNOC national oil company with 8 Mt/a (8.8 million stpy) of sulfur output have inked an agreement to produce a unified phosphate fertilizer production joint venture to use sulfur production within Abu Dhabi.

Table 1 is used to illustrate global sulfur output, demand and balance.

Care should be taken when evaluating this potential excess supply balance. Such high indicated volumes have traditionally led to price declines and stockpiling of uneconomically available sulfur which reduces the balance to more reasonable levels. The indicated volume will lead to price competition in producers' efforts of disposal. That, in turn will cause suppliers to limit losses by ceasing shipments to markets as has occurred in the past in Canada and Caspian nations. Thus, the real practical surplus for 2022 should only reach 2-3Mt/a (2.2 million to 3.3 million stpy).

The Middle East now leads all producing regions. Abu Dhabi's Habshan and Shah gas fields, and others, have propelled the region into first place. Greater sulfur output is expected in coming years as sour gas fields in Saudi Arabia, Kazakhstan, Kyrgyzstan, Turkmenistan, Abu Dhabi, Iran, Qatar and others initiate startups, more sour crudes are refined and China continues aggressive oil and gas development. A note of caution regarding the forecasts, however: in this region, one almost always encounters delays. High temperature, pressure and hydrogen sulfide content create huge technical and operating challenges. Gas fields are deep and hot, with a very high content of hydrogen sulfide. An example, the Kashagan field in Kazakhstan, has now just re-started production and sales, compared to a 2002 forecasted startup announced in 1990-1992. The third startup attempt, mentioned in last year's issue worked possibly adding 1 Mt (1.1 million st) to 2019 supply. ■