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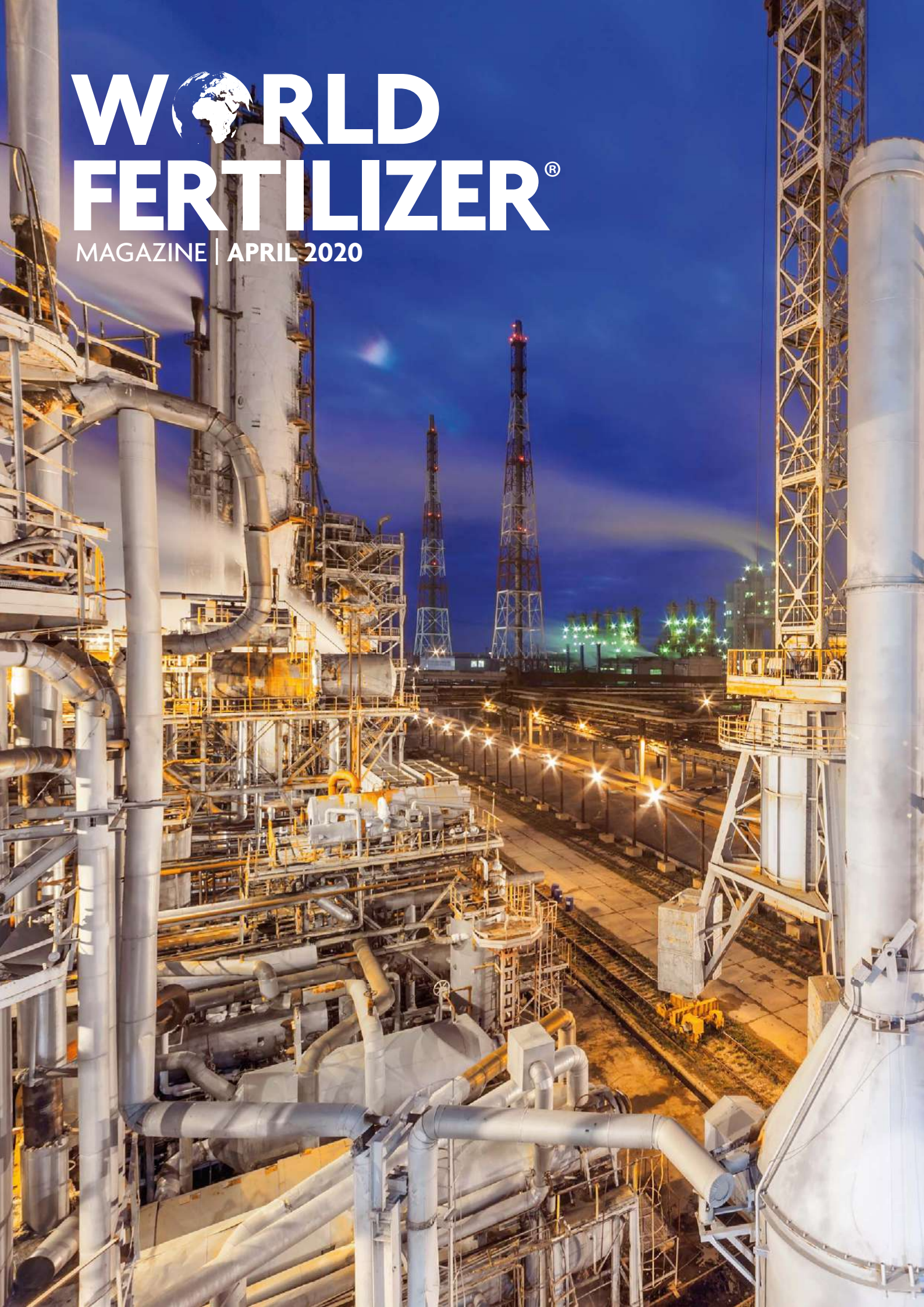

Scaling up Saudi sulfur

AK Tyagi, Nuberg EPC, India, looks at the production of sulfur and provides a case study on a plant installation in Saudi Arabia.

Sulfuric acid (H_2SO_4) is the most common chemical used for reducing pH during water treatment. A colourless, odourless, and oily liquid, it is also exceptionally corrosive due to its strong acidic nature. In the 17th century, sulfuric acid was first produced by Johann Glauber, who burnt sulfur together with saltpetre (potassium nitrate, KNO_3), in the presence of steam. In various grades the acid is used in the manufacture of fertilizers, pigments, dyes, drugs, explosives, detergents, and inorganic salts and acids, as well as in petroleum refining and metallurgical processes.

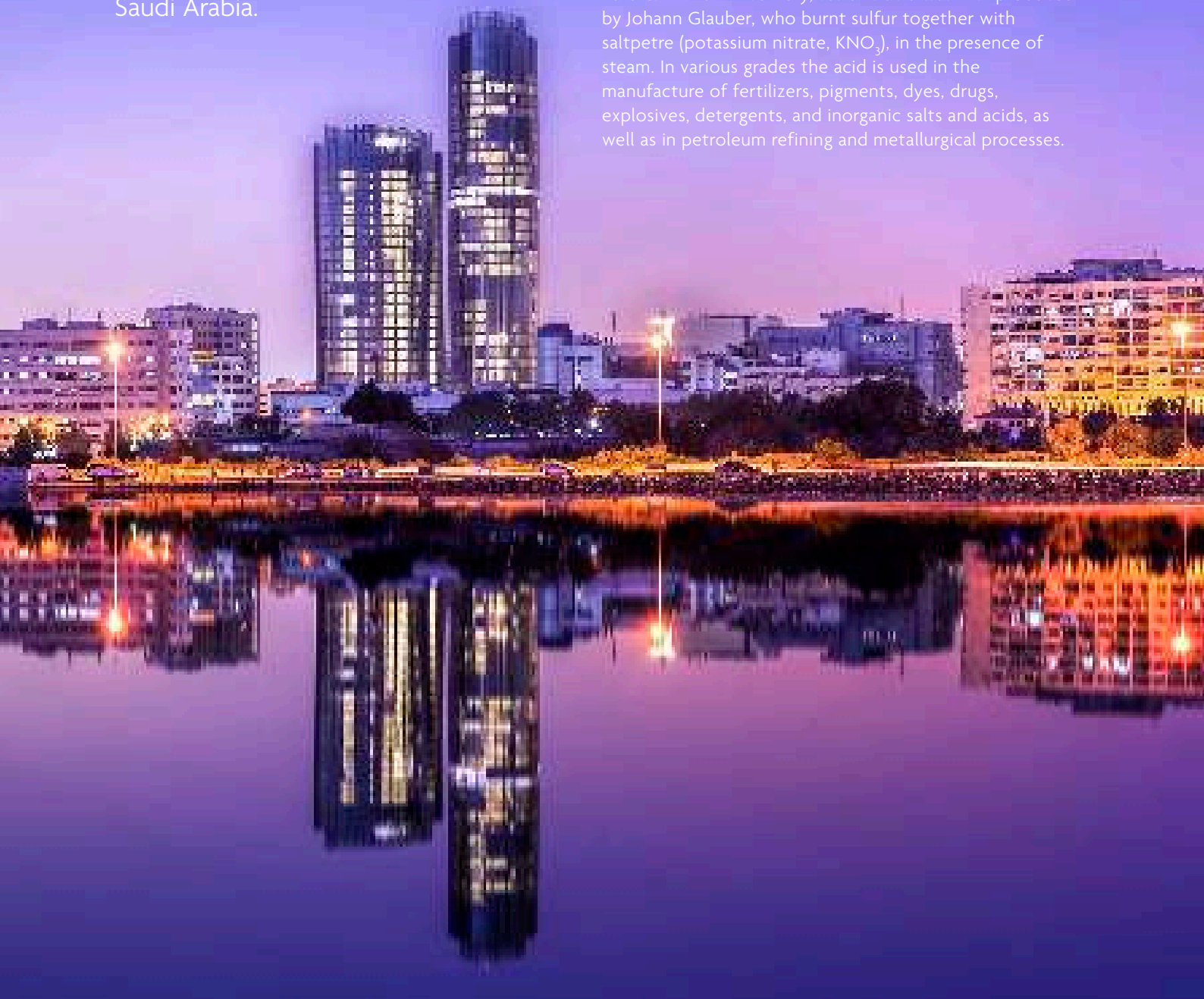

Figure 1. View of the entire Addar plant.

Figure 2. Sulfolane plant building and pressure vessels.

Figure 3. The Addar sulfuric acid plant.

Table 1. Annual production of sulfuric acid

Region	Mass (t)
World	231 million
China	74 million
US	37 million
India	16 million
Russia	14 million
Morocco	7 million

Manufacturing of sulfuric acid

In keeping with the general evolution of technology, gradual upgrading of the manufacturing of sulfuric acid has also taken place over time. There are two major processes used for the production of sulfuric acid: the lead chamber process and the contact process. However, the processes vary considerably from each other. A few basics that govern the manufacturing of the element are:

- Extraction of the pure element in the form of sulfur from its ore.
- Conversion of sulfur into sulfur dioxide (SO_2) in the presence of oxygen (O_2).
- Transformation of sulfur dioxide into sulfur trioxide (SO_3).
- Conversion of sulfur trioxide into sulfuric acid.

Lead chamber process

The lead chamber process was first designed in 1746 by John Roebuck of Birmingham, UK. The process has its origin in the early preparation of sulfuric acid by the oxidation of sulfur dioxide with nitric acid, but produces sulfuric acid by oxidising sulfur dioxide with moist air using gaseous nitrogen oxides as catalysts. The reaction takes place primarily in a series of large, box-like chambers of sheet lead that give the process its name. It is an outdated process for the production of sulfuric acid, but still continues to be practiced in a few parts of the world. The summary of the process is described by the equation below:

$$2SO_2 + O_2 \rightarrow 2SO_3$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$

During the process, hot sulfur dioxide is passed into the lead chamber and then washed using nitrous vitriol. Sulfur dioxide is then oxidised into sulfur trioxide. Next, it is dissolved in acid wash leading to the formation of glover acid, which is 78% sulfuric acid. In the mean time, a mixture of gases, such as oxygen, nitrogen, nitrogen oxides, sulfur dioxide and steam, are passed from a glover tower through the lead chamber where they react with water to produce sulfuric acid.

Contact process

The contact process is another method currently used for the production of sulfuric acid in the high concentrations required for industrial purposes. Formerly, platinum was used as a catalyst for the reaction, but as its reaction led to arsenic impurities in the sulfur feedstock, vanadium oxide is now preferred over platinum.

The contact process consists of five major steps:

Production of sulfur dioxide from sulfur

This can be achieved by burning sulfur in an excess of oxygen to obtain a mixture of sulfur dioxide gas and oxygen:

$$S + O_2 \rightarrow SO_2$$

Or, by heating sulfide ores such as pyrites in an excess of oxygen:

$$4FeS + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

Purification of sulfur dioxide

This removes dust particles, oxides of iron and arsenic. The purification unit includes a series of stages:

- Dusting tower: the mixture of sulfur dioxide and excess of air contains several impurities that must be removed or risk a loss of efficiency from the catalyst. The sulfur dioxide is mixed with an excess of air and is passed through a purifier in which electric charges attract the solid particles that are removed.
- Washing tower: in this stage, sulfur dioxide is washed completely to rinse away any soluble contaminants.
- Drying tower: the gas is dried by a spray of concentrated sulfuric acid for further purification.
- Arsenic purifier: the gaseous mixture is directed into the arsenic purifier to remove arsenic oxide. Once the sulfuric dioxide is completely purified, it can be converted into sulfuric trioxide.

Converting sulfur dioxide into sulfur trioxide

This is carried out to manufacture industrial sulfuric acid, so the contact process of sulfur trioxide production has to be economically efficient. To convert sulfur dioxide to sulfur trioxide, sulfur dioxide is mixed with oxygen and the mixture is passed over a catalyst of vanadium oxide (V_2O_5) at a temperature as high as 450°C and at a pressure of 2 atm. The mixture of sulfur dioxide and oxygen forms sulfur trioxide. At standard conditions, the equilibrium is positioned to the left and the amount of sulfur trioxide produced is relatively small. In order to improve the yield of sulfur trioxide, the reaction is carried out at 450°C and 2 atm using catalysts compounds such as V_2O_5.

$$2SO_2 + O_2 \leftrightarrow 2SO_3$$

Conversion of SO_3 to oleum

In this step of the contact process, concentrated sulfuric acid is used to dissolve the sulfur trioxide which produces the oleum. Sulfur trioxide is cooled in a heat exchanger and is then absorbed in concentrated sulfuric acid in another tower to provide oleum with disulfuric acid ($H_2S_2O_7$):

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7 \text{ – oleum}$$

Dilution of oleum to sulfuric acid

In this final step of the contact process, dilution of oleum is achieved by reacting it with water, and as a result, concentrated sulfuric acid (98% H_2SO_4) is produced:

$$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$$

Annual global production of sulfuric acid

The global sulfuric acid market was valued at US$9.35 billion in 2015 and is projected to reach US$11.10 billion by 2021, at a compound annual growth rate (CAGR) of 2.87% between 2016 – 2021. The sulfuric acid market size was 244.26 million t in 2015 and is expected to reach US$83 billion by 2022. Fertilizer consumption is highest in China and India, followed by the US. Based on calculations from the Food and Agriculture Organization of the United Nations (FAO), the caloric requirement is expected to double in the next 25 years, with the global population touching 8 billion. Sulfur production is expected to increase by approximately 27% between 2016 – 2021. In these respective studies, 2015 has been speculated as the base year and 2021 as the forecast year to estimate the market size of sulfuric acid. Prime drivers include an increase in the production of nutrient-rich food crops and steady and sustainable demand for sulfuric acid due to its diversified applications.

Production of sulfuric acid in India

India, being one of the major producers of sulfuric acid in the world, is characterised by a growing agriculture sector and increasing metal processing activities, along with a rising consciousness about wastewater treatment; each of these factors drive the sulfuric acid market in India. According to a study, the Indian sulfuric acid market is projected to exhibit a CAGR of 3.35% between 2016 – 2025, on account of increasing fertilizer production in the country. Moreover, growing demand and consumption of sulfuric acid can be attributed to the country's rapid population growth, and is slowly driving demand for infrastructure, food crops and various base metals in the country. Sulfuric acid is prepared for use as the most crucial raw material and main element in the agricultural sector, with applications in production of fertilizers and pH balance.

Case study: sulfuric acid plant in Saudi Arabia

Addar Chemicals Co., based in Jubail, Saudi Arabia, contracted Nuberg EPC for the construction of a new sulfuric acid and sulfolane acid plant in Jubail. The latter was Saudi Arabia's first greenfield sulfolane manufacturing plant and has a capacity of 6000 tpd. The sulfuric acid plant has a capacity of 80 tpd.

The scope of the project included process, technology know-how, detailed engineering, design, procurement, manufacture and supply of plant equipment as well as erection, construction, project management, commissioning, and start-up of the plant. The company followed local regulations and standards as prescribed by the Royal Commission for Jubail and Yanbu (RCJY) and the Saudi Standards, Metrology and Quality Organisation (SASO).

Managing the process planning of both the plants at the same time as well as at the same location was the main challenge. Allocation of different sets of resources and personnel between both plants would risk the project going considerably over budget. To tackle this challenge, the planning team put their full focus on the sulfuric acid plant first and then, after the completion of that plant, moved on to the allotment process of resources and staff in the sulfolane acid plant's planning stages. This kept costs low and helped to deliver the project within budget.

Personnel management was again a challenge given linguistic differences; however this issue was soon resolved, with a total staff in peak time of 250 – 350. Due to visa restrictions, the exiting of staff in a month at the time of ongoing construction resulted in delays in executing

the project. Despite these challenges, the sulfuric acid plant was completed on time.

Equipment/machinery

The scope of the project included the engineering, procurement and construction (EPC) and lumpsum turnkey of the sulfuric acid plant. An overview of some of the key equipment and machinery for the project is presented below.

Detailed engineering package

Details about each individual component and process were also stated with accompanying documents. This section covered key engineering design features, such as:

- Process engineering: design basis, process flow diagram equipment list, process datasheet and line list.
- Piping engineering: design basis, piping layout, isometrics and bill of material.
- Rotary and static equipment: transformer, diesel generator set, uninterrupted power supply, battery charger and bus duct.
- Electrical and instrumental engineering: design basis, single line diagram, load list, cabling and earthing layout.
- Mechanical engineering: design basis, general arrangement equipment – static, design calculation, technical specification of rotator equipment.
- Fire and safety equipments: fire water pump, fire fighting systems (sprinkler system and extinguishers), fire alarm detection – heat detector, smoke detector, call point, very early smoke detection apparatus system.
- 3D simulation and software: Cadwork software was used to create a 3D model of the sulfuric acid plant, allowing it to be seen in in real time virtually, detect any issues and also provide a detailed knowledge of different disciplines on a single 3D model.

Project management

Some of the major key factors in the project management processes for Addar included the following:

- Close monitoring of critical activities to ensure compliance.
- The use of bar charts and a critical path method (CPM) to indicate every activity of the project.
- Coordination with clients and vendors during the detailed engineering.
- Procurement and delivery progress control.
- Preparation of monthly progress reports with comments on compliance or deviations.

Conclusion

The sulfuric acid plant in Jubail was commissioned in November 2018 and executed by the company in Saudi Arabia. The plant produces sulfuric acid (98%), which is used for, among other purposes, the manufacture of ammonium sulfate and super phosphate of lime. In tandem with an increasing demand for organic chemicals the sulfuric acid industry has grown, with approximately 70% of today's sulfuric acid production used for making fertilizers. WF

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