

The History of the Contact Sulfuric Acid Process

By

Leonard J. Friedman & Samantha J. Friedman

Acid Engineering & Consulting, Inc.

Boca Raton, Florida

Introduction

Sulfuric acid was known as early as the Eighth Century, used in the Tenth Century, and first mention in the literature by Valentinus in the latter half of the Fifteenth. Sulfuric acid is manufactured by burning sulfur or some other metallic sulfide in oxygen or air followed by the oxidation of sulfur dioxide (SO₂) with air or oxygen to sulfur trioxide (SO₃), and the combination of the sulfur trioxide with water to form sulfuric acid (H₂SO₄). Two general groups of processes are used to produce sulfuric acid: the nitration or “Chamber/Tower” process; and the catalytic or “Contact” process.

Chamber Process

In the nitration or Chamber process (introduced in 1746), nitrogen compounds are used to enhance the gas phase oxidation reaction of sulfur dioxide with oxygen. The reactions are complex with the formation of the intermediate nitrosylsulfuric acid (HOSO₂ONO or HSO₃.NO₂ or SO₅NH), followed by the decomposition of nitrosylsulfuric acid by water to form sulfuric acid and nitrogen oxide (NO). The nitrogen oxide is regenerated by oxygen or air to nitrogen dioxide (NO₂), and the combination of nitrogen compounds (NO & NO₂ or N₂O₃) is recycled to the sulfur dioxide oxidation step. Large lead chambers, some as large as 500,000 ft³ each, were used for the oxidation step to facilitate the removal of the heat of reaction (hence the process name “Chamber” process). In later years packed towers replaced the lead chambers, and the process was renamed the “Tower” process. Gay-Lussac and Glover towers

were used to react the nitrosylsulfuric acid produced in the Chambers or Towers with water and regenerate the nitrogen compounds. Product acid from the Glover tower is 60 Baume (77.67%) sulfuric acid. The acid could be concentrated by heating to 66 Baume (93.19%). In the 1980's the Tower process was offered by Ciba-Geigy as a route to reduce sulfur dioxide emissions from power station stack gas. Note: Today nitrosylsulfuric acid is formed in a contact acid plant by the reaction of sulfur dioxide with nitrogen oxides formed in the furnace and collected with the concentrated sulfuric acid mist in the absorption tower high efficiency mist eliminator. The brown nitrogen oxide gas is released when the high efficiency mist eliminator is opened and water or moisture in the air dilutes the nitrosylsulfuric acid, decomposing it to sulfuric acid and nitrogen oxides.

Contact Process

There are still a few chamber type plants in existence for the production of sulfuric acid, but essentially all of the sulfuric acid produced today is made by the contact process. The process was first patented in 1831, but there was no real incentive for its development until about fifty years later. Even then it was almost another twenty years before production on a commercial scale was achieved. In the light of today's technology, it is difficult to appreciate the misconceptions that delayed the development of the process.

The early contact plants, producing about twenty tons per day in a single train, bear little resemblance to today's plant. Early plants used platinum catalyst and required extensive gas cleaning systems to minimize poisoning of the catalyst. With the development of vanadium catalyst in the early 1900's (1899 through 1928) the contact process was on its way. A breakthrough about 1927 by Chemico with the development of the pressurized sulfur furnace combined with the use of vanadium catalyst produced a flow sheet very similar to today's design and opened the way to the plants of today. The more recent changes in materials and design have permitted the increase in single train plant capacities from a maximum of about 100 tons per day in the 1920' and 1930's to well over 4,000-5,000 tons per day.

Contact Process - Early History

For most of the early history of sulfuric acid processes we are indebted to a number of reference books: They are “The Manufacture of Sulphuric Acid and Alkali” by G. Lunge, 1913, Van Nostrand Co.; “Manufacture of Sulfuric Acid (Contact Process)” by F. D. Miles, published in Great Britain in 1925 by Gurney and Jackson; “Sulfuric Acid Manufacture” by Andrew M. Fairlie, published in 1936 By Reinhold Publishing Corporation; and “Manufacture of Sulfuric Acid” by W. W. Duecker and J. R. West, published in 1959 by Reinhold Publishing Corporation. Another interesting book describing the operation of the early plants is “American Sulfuric Acid Practice” by Philip DeWolf and E. L. Larison, of Anaconda Copper Mining Company, published in 1921 by McGraw-Hill Book Company, Inc.

The first observation of a “contact” or heterogeneous catalytic reaction seems to have been made by Edmund Davy in 1817. He noted that heated platinum wire introduced into a mixture of oxygen or air with hydrogen, carbon monoxide, or ethylene became hotter and finally glowed with rapid combustion of the mixture.

In 1831 Peregrine Phillips, a vinegar manufacturer in Bristol, England, patented a new process in British Patent No. 6096. The patent described the instantaneous union of sulfur dioxide with atmospheric oxygen when passing the mixture over platinum which had been heated to a strong yellow heat, with the sulfur trioxide formed rapidly absorbed when contacted with water to form sulfuric acid.

In spite of the obvious advantages of the contact process over chamber plants for the production of high strength sulfuric acid and oleum used for dyes and nitrocellulose (smokeless powder), the commercial development of the process was extremely slow. Chemical technology of the time, especially involving catalytic reactions, was limited.

Misconceptions

During the next forty years (1830 to 1870), there was some interest in duplicating Phillips’ work and in looking for other catalysts, but there were no meaningful developments. Other

catalytic effects had been observed and there was some thought that substances capable of this “contact” action owed their properties to their porosity. The gases were thought to be condensed in the pores and, with the resulting smaller volumes, the molecules were in closer “contact” so they could react more easily.

In 1852 Wohler and Mahle discovered that oxide of copper or chromium at a red heat caused formation of thick fumes of sulfur trioxide when the constituent gases were passed over it. They also demonstrated that oxide of iron or oxide of copper is capable of either reduction or oxidation under the conditions of the experiment, depending on whether dioxide or trioxide is present in excess. This should have generated recognition of equilibrium conditions with temperatures and partial pressures of reactants, but apparently it did not.

In 1875 Clemens Winkler, professor in the School of Mining at Freiberg, Germany published a paper reporting his work. His experiments were obviously faulty and his conclusions contradicted the principles of mass action which had been enunciated eight years earlier by Guldberg and Waage. In spite of this, his paper was widely accepted and it influenced general opinion for many years. Based on Winkler’s experiments, he stated that *“the action of platinized asbestos and of all other contact substances is diminished in the same measure as the dilution of the sulfur dioxide by other indifferent gases is increased. Even sulfur dioxide and oxygen will naturally remain indifferent and act as diluents in so far as they are present in other than the stoichiometric ratio necessary for acid formation. That is, in so far as one gas or another is in excess.”* His paper did not report the ratio of oxygen to sulfur dioxide in his tests, but he reported 73.3% conversion when operating with pure sulfur dioxide and oxygen. If the oxygen was replaced by oxygen and air, the conversion dropped to 47.4%. When using a gas resulting from burning sulfur in air containing four to five percent sulfur dioxide, the conversion dropped to 11.5%.

This faulty information came at a most unfortunate time and undoubtedly delayed the commercial implementation of the contact process. At the time of Phillips’ patent, there was no particular need for a process which could produce fuming acid. The small quantities of oleum

that were required were produced by fortifying concentrated chamber acid with SO₃ made by decomposition of “copperas-slate”.

The Incentive

Shortly before the publication of Winkler’s misleading paper, the synthetic production of alizarine and other dye stuffs was developed. Most of these required the preparation of sulfonic acids in intermediate stages and the demand for fuming sulfuric acid (oleum) rose abruptly. The existing fortification plants in Bohemia were inadequate to meet the demand and various approaches to the new contact process were tried.

Early Plants

The first commercial plants were producing fuming acid, about 40% oleum, by 1880. Both Winkler in Germany and Quire and Messel in England developed commercial plants based on decomposing weaker sulfuric acid by heat to form SO₂, O₂, and water vapor. The water was condensed and the SO₂ and O₂, in essentially stoichiometric ratio, were passed over platinised pumice. The SO₃ produced was condensed as fuming acid. These plants produced several tons per week of trioxide.

The decomposition of acid to produce sulfur was short lived due to corrosion problems. It was still felt that rich SO₂ gas with a minimum of dilution was a necessity. Squire developed a process in which sulfur was burned in air and the resulting SO₂ was absorbed in water under a pressure of 4 atmospheres. The SO₂ was stripped by steam, mixed with the theoretical quantity of air, and passed over heated platinised asbestos. The trioxide formed was absorbed in concentrated acid to produce 40% oleum. The tail gas was recycled to obtain an overall yield of 90%. The daily production was 30 cwt of trioxide, which is equivalent to 2 tons of acid per day.

During this period and until the end of the 19th century, Winkler’s ideas of maintaining stoichiometric ratios of oxygen and sulfur dioxide with minimum dilution still affected the general approach to the contact process. In all cases, the catalytic apparatus was externally

heated and there was apparently no recognition of the fact that overall conversion efficiency could be improved at lower operating temperatures or that the heat of reaction could be used to preheat the feed gas stream.

The final blow to Winkler's ideas was Knietsch's lecture in 1901 before the German Chemical Society. In it, he described some of the work that had been carried out in the laboratory and the plant of the Badische Company. Knietsch and his collaborators had made extensive studies of operating conditions with platinum and other catalysts, had determined physical properties of fuming acid and sulfur trioxide and had found solutions to the technical problems that had plagued the use of pyrite burner gases. They found that contact vessels required cooling rather than heating, and they had generally made the contact process so successful that it could not only produce fuming acid cheaply, but it could compete with the established chamber process in the production of ordinary concentrated acid.

One of the problems was the contact mass gradually losing its activity even though the burner gases were passed through several stages of purification – cooled in long pipes, washed with acid, and filtered through coke and asbestos. They found that minute traces of certain elements, such as arsenic, that were carried through to the contact mass in the sulfuric acid mist were causing the loss of activity. This and other work made it obvious that gas purification is a most important section of a contact sulfuric acid plant.

Successful Plants

Successful contact plants were developed by several groups during the same period just before the end of the 19th century. There were differences in the form of the platinum catalyst, in the manner of heating and cooling gases, and in the type of gas purification, but the differences were no greater than those between different contractor's designs today.

First Double Absorption Process - There was, however, one unique one – the forerunner of today's double absorption, or double catalysis process, developed to overcome the poisoning and loss of activity of platinum catalyst. This was the Mannheim process patented in 1898 and 1899. In this process, the first stage of conversion was carried out with a ferric oxide catalyst,

followed by absorption of the SO₃ produced, then by a second conversion stage using platinum catalyst, and a final absorption. This scheme had an obvious advantage in conversion efficiency and catalyst life, but its use was short lived. Heat recovery in those early days was inefficient, and the double absorption scheme required additional fuel firing as well as additional absorption equipment.

The acid plants built in the early part of the 20th century were unbelievably complex and large for their production capacity in comparison to the present day design. The first experimental contact plant in the U. S. was built in 1898 in New Jersey by Badische. By the time Miles' book was published in 1925, there were 53 contact plants in the United States.

Typical Early Contact Plant (1915-1930) - Miles provided an example of the type of plant built in the U. S. during that early period with a description of a plant built in 1918 for the U.S. Government at Nitro, West Virginia. It was a wartime rush job and did not include regenerative converters but it did include more combustion gas scrubbing apparatus than would normally be included to permit possible operation with pyrite instead of sulfur. Platinum (platinized asbestos) was the catalyst. The acid was required for the production of 300 tons per day of smokeless powder.

The plant consisted of seven units of four trains each, or a total of 28 individual trains. Each train had a capacity of 16 tons per day of sulfur trioxide, or about 20 tons of acid per day. The total building floor space required was about 300,000 sq. ft., or nearly seven acres, for a total acid production of about 550 tons per day. The trains were laid out in almost straight lines and one group of four trains required a plot area about 190 ft. wide by about 425 ft. long. The attached figure from Miles book shows a plan and section of two trains of this plant.

The following description applies to a single train producing nearly 20 tons per day of acid. Lump sulfur was delivered by wheel-barrow from a concrete storage bin to the feed hopper of a Glens Falls burner. This was a kiln 4 ft. diameter by 16 ft. long which rotated slowly to expose the sulfur-wetted walls to the combustion air stream. The air was induced through the burner by the blower downstream of the gas cleaning and drying system. The gas passed through a cast iron combustion chamber to complete the combustion and then through a bank

of vertical cast iron pipes where it was partially cooled by air. The gas then went to a hot gas scrubber, a water sprayed lead tube gas cooler, and a cool gas scrubber. Each of these scrubbers was 8 ft. square by 20 ft. high of lead construction with acid brick lining and quartz packing. The lead tube gas cooler consisted of 750 lineal feet of 6" lead pipe arranged in 16 runs 45 ft. long. The scrubbers acted as a gas cooler and pre-dryer. In the first scrubber, the hot gas was cooled by concentrating the acid returned from the second scrubber. Water was condensed from the gas in the water-cooled lead tube unit and more water was removed from the gas in the second scrubber by the cooled concentrated acid. The weak acid was then re-concentrated in the first scrubber.

The pre-dried gas passed to the coke filter, a lead box 30 ft. long by 12 ft. wide by 10 ft. high reinforced with timber. The filter was packed with coarse coke on the bottom and 3 to 4 ft. of fine coke on the top and the gas passed from the bottom at one end to the top at the other end. Next in order were the mineral wool filters, each train had five units in parallel. These were shallow cast iron vessels 6 ft. in diameter, each with two lead screen filter supports. On each screen was a 1" layer of cotton fiber and an 8" layer of mineral wool. The gas passed downward through the filter layers and then flowed to the bottom of the quartz packed drying tower where it contacted 98% acid. The dry gas passed through a quartz-packed steel tower to eliminate any carryover of spray from the drying tower before entering the blower.

The blower was motor driven with a capacity of 3,000 CFM. It provided sufficient suction to draw the air into the sulfur burner and through the entire gas cleaning section, and sufficient pressure to deliver the gas through the balance of the plant. Information was not available for this particular plant, but for this type plant, the blower suction was on the order of 1 to 5 inches water gauge and the discharge was 10 to 30 inches water gauge.

In this plant, there was no provision for recovery of the heat from the converted gas. The gas leaving the blower was indirectly heated by gas burners to 400°C in cast iron "U" pipes in two heating chambers. The gas then passed to four converters in parallel, each 5 ft. diameter by about 10 ft. high, with five layers of catalyst. The catalyst was 1/4" to 3/4" magnesium sulfate which had been platinised after sizing. The percentage of platinum varied from 0.15% to

0.30% with the richer mass in the first pass. The gas entering the converter normally contained about 5.5% SO₂.

The gas leaving the converter at 500 to 550°C was first cooled in cast iron pipe and then in water-sprayed steel pipe. The cooled gas passed through two absorbers in series and followed by a spray catcher before going to the stack. The first absorber was a steel shell 5 ft. diameter by 11 ft. high lined with acid proof brick and packed with quartz. Acid from the final absorber was advanced batch wise to the first absorber until the concentration reached 27% oleum. A second similar absorber was added later to produce 40% oleum. In that case, the first absorber produced 16% oleum. The final absorber was similar to the first but larger, 7 ft. diameter by 15 ft. high. The circulating acid was maintained at about 99% by feeding recovered spent acid from the nitration plant and weak acid from the gas cleaning section of the acid plant.

This plant installation, although larger than most, was generally typical of the type of equipment and size of the individual trains which made up the plant. It was, however, a wartime emergency installation and was dismantled some time prior to 1925.

A sulfuric acid plant installation list of about 1920 showed there were acid plants at 228 locations in the United States and that contact type plants were at 53 of these locations, the balance were chamber type.

Development of Vanadium Catalyst

In 1899 R. Meyers proposed vanadic acid deposited on the pores of various carriers as a sulfuric acid catalyst. DeHaen patented (1901 & 1902) vanadium catalyst prepared by depositing vanadic acid in the pores of asbestos, pumice stone, etc., and in the same time period, the Höchst works in Germany (patent 1901) investigated using vanadium oxide, prepared by impregnating asbestos with ammonium metavanadate followed by drying and ignition.

Modern Vanadium Based Catalyst - In 1913 & 1914 Franz Slama and Hans Wolf patented a vanadium catalyst composed of a salt of vanadic acid combined with alkali promoters on a

porous carrier. The patent was assigned to General Chemical Co. At the same time Badische patented essentially the same catalyst in Germany and England. In 1923 A. O. Jaeger and J. A. Bertsch were recruited from Germany to General Chemical (National Aniline and Chemical Co.) with claims they developed a new sulfuric acid contact mass. The mass was vanadium pentoxide zeolites. They formed an arrangement with Monsanto Company in 1926 to prepare their catalyst for use in a Monsanto plant. Numerous patents were obtained between 1925 and 1926. Disagreements between Jaeger and Monsanto resulted a separation and Jaeger joined Seldon Company in 1927. Through the late 1920's and 1930's there were many law suits between Jaeger and Monsanto, General Chemical and Seldon, Monsanto and Seldon, and Monsanto and General Chemical.

When the dust settled, the vanadium catalyst composed of vanadium pentoxide with alkali (potassium and/or sodium sulfate) promoters supported on a porous silica base (diatomaceous earth) was the standard sulfuric acid catalyst – and still is today. Many of the sulfuric acid manufacturers of the time made their own vanadium based catalyst. Monsanto, General Chemical and Consolidated (Stauffer) Chemical catalyst was extrudates (tooth paste) about 1/4" diameter by 1/2"-3/4" long. American Cyanamid produced tablets, and Catalyst and Chemicals (CCI) made spheres.

Process Design Breakthrough – 1927-1930's Plant

A major simplification of sulfur burning acid plants was introduced by Chemico in 1927. The novelty included pre-drying of the combustion air and pre-melting of the sulfur so that it could be spray burned in a furnace operating under pressure. These features eliminated the necessity for an extensive gas cleaning system and required only a hot gas filter to remove sulfur ash from the gas stream. With pre-dried air and pre-melted sulfur, there was practically no moisture in the gas stream and no acid mist to be removed. With the elimination of the need for wet scrubbing of combustion gas, the gas remained hot and did not require preheating before entering the converter. Actually, some cooling of the gas was required and a waste heat boiler was provided after the sulfur furnace. The steam production in this boiler was increased

by the use of the Selden converter where the inlet gas was preheated by the heat of reaction in a built-in heat exchanger in the converter.

The first units of this type were built for Standard Wholesale Phosphate and Acid Works in Baltimore, Maryland and for American Cyanamid Co. in Warners, New Jersey. The largest single train plant with Selden converters was normally 120 tons per day of H₂SO₄, and Fairlie provided a fairly detailed description of this size plant as built about 1928 to 1930. It is summarized in the following paragraphs.

Chemico Design - The entire acid plant, with the exception of the acid towers, was normally installed in a building 60 ft. wide by 100 ft. long by 40 ft. high to the roof trusses with an overhead crane for repair work.

The brick lined below grade concrete sulfur melting pit was generally located next to the sulfur furnace. For the 120 ton per day plant, the sulfur pit was approximately 30 ft. long by 8 ft. 8 in. wide by 3 ft. 6 in. deep with five transverse steam coils. Steam was supplied to the coils at 75 psig and solid sulfur was charged to the pit by buggy at regular intervals. A vertical submerged turbine-driven sulfur pump installed in a partitioned section with an underflow opening at one end of the pit delivered the molten sulfur at 275°F through a steam jacketed sulfur line to a specially designed jacketed spray burner installed in the sulfur furnace.

The two air drying towers were located in a line with the three absorption towers outside of the building at the opposite end from the sulfur melter and furnace. All five of the towers were 11 ft. diameter by 28 ft. high steel shells lined with 4 in. of acid brick. The first drying tower, was downdraft, and packed with 14 ft. of 3" spiral rings, stacked and staggered, plus 3 ft. of dumped 3" rings over which 93% acid was circulated. The second drying tower was updraft and packed with 17 ft. of dumped 3" spiral rings. It operated dry and served only to remove entrained acid droplets from the dried air. The air went to a 220 hp turbo-blower which discharged it at 45" W.G. pressure to the sulfur furnace.

The sulfur furnace was a horizontal steel vessel 11 ft. diameter by 30 ft. long with 9 in. of fire brick and 4-1/2 in. of insulating fire brick lining. There were two fire brick baffles spaced

several feet apart with over and under gas openings. The normal furnace operating temperature was 700°C with a 7% SO₂ gas being produced. The hot furnace gas flowed down through a “rock filter” where fly ash from the sulfur was removed. The hot gas filter was a vertical steel shell 10 ft. diameter by 18 ft. high lined with 4 1/2 in. of insulating fire brick and packed with about 7 ft. of 3” and 4” quartz lumps. This was followed by a waste heat boiler operating at 150 psig cooling the gas to about 300°C.

The gas next flowed to the Selden converter. In the 120 ton per day plant, there were three 40 ton per day converters in parallel. These were cast iron vessels 10 ft. 6 in. diameter by 16 ft. high with two stages of conversion and two sets of built-in heat exchangers. The gas entered at the side of the bottom section and passed upward through a tube sheet and tubes. The tubes were fitted with cast iron caps of larger diameter that extended almost back to the tube sheet so that the gas reversed direction. In the space between the capped tubes, there was a 3” layer of quartz pebbles on the tube sheet and above that about 3 ft. of 3/16” pill-shaped vanadium catalyst pellets. The heat of reaction in the catalyst bed preheated the incoming gas as it passed through the many parallel tubes and caps imbedded in the catalyst bed. The built-in exchanger also cooled the upper portion of the first catalyst bed so that the conversion reaction could proceed further than it could if the bed were not cooled. The second catalyst bed was supported on a screen on a perforated plate. It was cooled by a similar set of double tubes extending down from the top of the vessel with air blowing through the tubes. The upper bank of tubes was eliminated in later plants, and additional cooling was provided by extending the lower set of tubes above the catalyst in the first bed.

With the two-stage converter and cooling carried out within each of the two layers, conversions of more than 97% were reported for operation with a 7% SO₂ gas from sulfur burning and with a catalyst loading of about 190 liters per daily short ton of acid produced. When cooling of the upper bed was eliminated, the conversion efficiency was reported to have dropped by about 0.5%.

The gas leaving the converters was cooled to about 105°C before going to the absorbers. The cooling was accomplished in an air-cooled carbon steel shell and tube exchanger with the SO₃

gas flowing down through the tubes. In some cases, this low temperature resulted in acid mist in the stack gas and the cooling had to be limited to 140 or 150°C.

The absorbers were the same design as the first drying tower described previously. There were three towers in series, with the gas flowing upward in all three. The first two were absorbers with 98% acid recirculated over them and the third was a dry spray catcher the same as the second drying tower. The acid was circulated over the first absorber at 80°C and over the second at about 45°C. The acid flowed by gravity from the towers through cascade type cast iron pipe coolers to the pump tanks. These were horizontal cylindrical steel tanks with acid brick lining and vertical submerged pumps. In the smaller plants, the acid reservoir was in the base of the tower and horizontal suction lift pumps were mounted on a platform above the acid coolers.

Monsanto Design - At about the same time that Chemico was building the above plants, Leonard Construction (Monsanto) was building a somewhat similar plant for Merrimac Chemical at Everett, Massachusetts. This was a plant to produce 75 tons per day of acid using molten sulfur and pre-dried air. The solid sulfur was melted with steam coils in a similar below grade pit. The sulfur was elevated to the top of the vertical sulfur furnace by a submerged deep well type of plunger pump driven through a variable speed reducer.

The air drying tower was a rectangular lead tower 8 ft. 6 in. square by 22 ft. high supported by a steel frame. The tower was brick lined and packed with glass plates on edge supported on brick courses. The dried air went to a high pressure blower with a capacity of 5,000 CFM. At full plant rating, the required blower discharge pressure was 40" W.G.

The sulfur furnace was a vertical steel cylinder 13 ft. diameter by 25 ft. high divided into two compartments by a fire brick arch. Molten sulfur, admitted at the top, fell on a splash plate on top of a checker work brick pyramid built on the brick arch. Air was delivered under pressure at two points, one near the sulfur feed and the other at the level of the arch. The sulfur burned as it flowed down through the pyramid. The combustion gas and any unburned sulfur passed down through the arch where the sulfur was exposed on additional brick checker work for more complete combustion. This plant is reported to have operated with a 9% SO₂ gas and a

vanadium catalyst loading of only 113 liters per ton, with a conversion efficiency of about 95%. The plant did not have a waste heat boiler, but cooling of the SO₂ gas leaving the furnace and the SO₃ gas going to the absorber was accomplished by preheating air for the boilers of the power house next door.

A gas filter was installed ahead of the converter. It was 11 ft. diameter with a 14” layer of catalyst pellets, without the vanadium, as the filter material. Two converters, operated in series, were cast iron shells 11 ft. diameter. There were two beds of catalyst in the first converter, each about 7-1/2 in. deep, supported on woven wire shelves. The gas was heated in the first converter from about 405°C to 580°C and was cooled to about 405°C before entering the second converter. The second converter had three catalyst beds, each about 12-1/2 in. deep, and the gas exited at about 460°F. The above catalyst depths indicate a catalyst loading of about 160 liters per ton based on 75 tons per day operation, as compared to the 113 liters per ton indicated above.

Shell and tube gas to gas exchangers were used to cool the gas leaving each of the converters and to preheat the SO₂ going to the first converter. The exchanger cooled the SO₃ gas to 275°C and further cooled in an air-cooled unit. The SO₃ was absorbed in a conventional acid brick lined steel tower packed with ceramic rings and quartz pebbles.

This plant had an unusual feature for its time that anticipated the EPA. It had a device that automatically stopped the blower and the sulfur pump in case of an interruption of the flow of acid to the absorption tower.

Eighty Years Later

The flow diagram of a sulfur burning sulfuric acid plant today bears a close resemblance to that of eighty years ago. Molten sulfur is spray burned in pre-dried air. The gas is cooled in a boiler before going to the converter, and the converted SO₃ gas is absorbed in a packed tower. The flow scheme remains the same but there have been changes in nearly every aspect of the plant. One change that was not adopted is shown in the flow scheme for the Dixon plant where a whimsical engineer was apparently promoting a “make work” project.

Capacity - The maximum capacity of a single train plant has increased about fifty fold. With today's technology, plants of 4,000 and 5,000 ton per day are the world class size. The increase is partly the result of larger equipment. It is also the result of experience which has proved that residence times could safely be reduced and gas strengths and velocities increased.

Sulfur - Originally, lump Frasch sulfur was shipped and stored in the open. After it was melted some of the contaminants settled in the melting pit, some were skimmed off, and the rest were stopped either in the hot gas filter or in the catalyst. Sulfur filters replaced hot gas filters in the 1960's for plants receiving solid sulfur. In North America, filtered molten sulfur shipments became available from strategically located terminals, and plants in North America have no sulfur melting facilities or sulfur filters. Around the world most plants receive dust free solid sulfur as prills, etc. The sulfur is melted, lime is added to neutralize acid components, and the sulfur is filtered to remove solid contaminants.

Energy Recovery - Most modern sulfur burning plants recover the heat of combustion and reaction as steam at a high pressure and superheat. Boilers in the early plants usually operated in the 150 to 250 psi range producing saturated steam, compared to today's 450 to 600 or 900 psig superheated steam. Today's higher pressure and superheat provides more potential energy per unit heat recovered than the early low pressure plants.

Recovery of the heat in the acid cooling system started in the early 1980's with acid heat producing hot water for in plant process use or for town heating in Europe. Monsanto patented the use of austenitic stainless steel in 99% to 99.9% sulfuric acid at high temperature based on 25 years experience of General (Allied) Chemical operating absorption towers at 450 F with 99%-99.5% sulfuric acid using austenitic stainless steel. This "discovery" formed the basis of the Monsanto HRS (acid heat recovery system), where acid heat at 350 F – 450 F is recovered as low pressure steam from 99%+ sulfuric acid. Outotec (Lurgi) has its own version of the acid heat recovery system, and Chemetics has a paper design.

Catalyst-Conversion – The same basic vanadium pentoxide catalyst used in the late 1920's and 1930's is used today, with 5%-7% vanadium for upper bed catalyst and 7%-9% vanadium used in lower bed catalyst. The major change is the catalyst shape. In the 1980's Topsoe,

followed closely by BASF, developed and marketed a ring shaped catalyst (similar to a Raschig ring) with reduced gas pressure drop compared to the standard tooth paste extrudates. At about the same time, Monsanto marketed their 516 catalyst (5/16" vs. 1/4" diameter extrudates), claiming reduced pressure drop. Tests and operating experience showed little advantage for the 516 catalyst shape and it disappeared from the market. Further advances led to the ribbed ring (Topsoe "Daisy", BASF "Star" rings) for increased dust holding capacity and lower pressure drop. Currently all three major catalyst manufacturers market a ribbed ring catalyst.

A variation of the potassium/sodium sulfate promoted vanadium catalyst, developed in the late 1940's and early 1950's, substituted some cesium sulfate for a portion of the potassium sulfate in the vanadium catalyst. The resulting mixed salts melted at a lower temperature reducing the ignition temperature of the vanadium catalyst by about 100 F. There was little use of the low ignition catalyst (also called "cesium" catalyst) until the 1970's when a South African company offered low ignition catalyst, marketed in North America by Canada Colors. There were a few installations, mostly as a topping layer for the first bed in metallurgical and regeneration type plants. In the late 1980's, Topsoe introduced its low ignition catalyst, and its use has increased over the last 25 years for topping layers in first catalyst beds with very low or high SO₂ gas concentrations, and for entire 4th and 5th catalyst beds for increased conversion to meet more stringent SO₂ emission regulations. Both Topsoe and Monsanto currently market low ignition ring catalyst.

Converter design has been improved with more stages and better temperature control. Conversion efficiency has improved from 90%-95% to 98% for single absorption plants, and to more than 99.7% by the reintroduction of the double absorption process, (that first appeared in 1899). Stack gas SO₂ emissions are also reduced by tail gas scrubbing of SO₂ with sodium of ammonium salts, and recycle of the recovered SO₂ to the acid plant.

Numerous converter types have been used over the years, including: horizontal cylindrical vessels with one or two beds of catalyst per vessel; vertical cylindrical vessels with multiple catalyst beds with and without internal heat exchangers (Seldon converters with SO₂ gas preheater coils, internal air preheaters, internal steam superheaters), and external heat

exchangers mounted as a part of the exterior converter shell. Today, two types of converters are used; vertical cylindrical multi-bed vessels with carbon steel shells (first pass insulating brick lined) with cast iron posts and grids; and stainless steel converters with stainless steel bed support beams and screens. Some designs install a gas heat exchanger inside a central tube in the converter, but most have kept the heat exchangers separate from the converter. Carbon steel-cast iron converters have a demonstrated life in excess of 30 years, while stainless steel converters (the status symbol of the late 1990's and early 2000's) have experienced scaling problems and significant cost increases in recent years (about 30%+ more expensive than a carbon steel-cast iron converter). Many are re-thinking the choice of a stainless steel converter.

Acid Towers - A change in the type of packing from 3" stacked and staggered and dumped triple spiral rings or 1" and 3/4" Berl saddles to first 2" then 3" ceramic saddles permitted a tripling of the gas velocity in the tower with a reduction in pressure drop. For over 80 years General Chemical has operated cast iron acid towers, constructed of flanged 12' diameter by 12' high sections, packed with stacked and staggered triple spiral rings topped with Berl saddles, with some cast iron towers still in use today. Improvements have been made in lining materials and acid-proof mortars, as well as in the techniques for their installation. Early towers were constructed of a carbon steel shell with lead lining for dry towers, and mastic and asbestos paper for absorption towers, covered by acid brick. The towers had a flat bottom and a side acid outlet. Modern towers have a carbon steel shell, lined with mastic, Teflon sheet and acid brick, and have a dished bottom. Carbon steel-brick lined towers have a demonstrated life of over 30 years. An alternate design using unlined stainless tower construction has been in use for about 20 years. Cost for the stainless towers (4%-5% silica stainless) is currently about 30% higher than the carbon steel-brick lined tower, with corrosion problems in non-fully wetted areas of the tower due to dilute acid in dry towers and SO₃/oleum corrosion in absorption towers.

Mist and entrainment separators have been developed to take the place of the early dry spray catcher towers or the later use of a layer of dry packing or quartz near the top of the tower. Current entrainment separators use woven Teflon or alloy mesh pads, or impaction type

compressed fiberglass candles in dry towers, and impaction or Brownian diffusion type compressed fiberglass candles in absorption towers.

Acid Coolers - There has been a considerable change from the early cascade type cooler using banks of 6" cast iron pipe of the 1930's. Acid coolers changed almost entirely in the 1940's to stacks of cast iron AX sections. These were more efficient and permitted a reduction in the size of the acid cooler pit. In the 1970's, several new types of coolers appeared on the market. These include stainless steel shell and tube units with and without anodic passivation, tanks with Teflon tube bundles for cooling water, air-cooled stainless steel or cast iron units and plate type coolers. These have met with varying degrees of acceptance as well as of success. General Chemical still uses stainless steel shell and tube acid coolers based on maintaining the acid concentration above 99% with success. All of the newer units have eliminated the traditional acid cooler pit with its steam plume in cold weather but most of them require cooling water and therefore probably a water cooling tower. Plate type acid coolers constructed of Alloy C-276 or the newer D-205 are used for acid cooling in small acid plants and for product coolers in many plants. Air coolers (due to their high cost) are limited to locations where cooling water is not available or expensive. The standard of the industry is the anodic protected shell and tube stainless steel acid cooler. It has demonstrated over 35 years life in acid plants around the world. A number of plants in recent years have installed non-anodically protected shell and tube acid coolers using silicon stainless steel with success.

Pressure Plants - Plant operation at high pressure has attracted attention at various times over the years and one commercial plant was built in the late 1970's in Europe by UGINE Kuhlmann. The reduction in equipment size and the improved conversion efficiency of pressure operation were overcome by the extensive corrosion and energy inefficiency of the process. No other designs have been suggested.

Summary

The old adage "those that ignore history are doomed to repeat it" does not appear to apply to the sulfuric acid process. The double absorption process was patented in 1898, and re-

invented, re-discovered, and re-patented again in the late 1960's. Low ignition catalyst was first introduced in the 1940's, and later in the 1970's and 1990's. Converters with internal heat exchangers were the norm in the 1930's through the 1960's, and reappeared as a novel design in the 1990's. Horizontal cylindrical acid pump tanks were the standard through the 1950's, replaced by vertical cylindrical tanks in the 1960's to 1990's, and used again in recent years.

In many cases the knowledge of the past has provided alternate designs with advantages compared to the then current standard, sometimes due to changing economics, materials or instruments and controls. In some cases, the problems with the early designs are rediscovered, and knowledge of history would have saved much heartache. It is hoped this work will provoke an interest in the history of the contact sulfuric acid process, encourage others to use history as a basis of future innovation and process improvement.