# The Single Absorption – Scrubbing Sulfuric Acid Process

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## Introduction

The AE&C single absorption–scrubbing process has long been an alternate to double absorption for the production of sulfuric acid. In recent years regulatory pressure to reduce SO2 emissions from sulfuric acid plants to 1.0-1.25 pounds of SO2 per ton of acid produced (to about 120 PPM) or less coupled with the increased value of energy has enhanced the desirability of the single absorption–scrubbing process. The process offers lower capital cost, lower SO2 emissions, faster start-ups in compliance, increased steam production and reduced energy consumption (main blower horsepower) compared to double absorption.

This paper reviews the modern AE&C designed single absorption–scrubbing process, highlighting its advantages compared to double absorption, and reviews several recent projects where the process has been installed in sulfur burning and spent acid regeneration sulfuric acid plants.

## Background

Since 1971 when the U.S. Environmental Protection Agency (EPA) established new source performance standards (NSPS) for sulfur burning and spent acid regeneration sulfuric acid plants at 4 pounds of sulfur dioxide per ton of acid produced (equivalent to 99.7% conversion efficiency and about 400-450 PPM SO2), the double absorption process has been the chosen route for the production of sulfuric acid. Essentially all new sulfuric acid plants (sulfur burning or regeneration) constructed in the last 35 years are double absorption units.

Recently EPA has determined an emission level of 1.0 to 1.25 Lbs/Ton (99.9% conversion efficiency and about 100-120 PPM SO2) to be achievable, and has been using its enforcement division and permit process to convince acid producers to meet this lower emission level, although NSPS remains at 4 Lbs/Ton. Two possible process modifications in the double absorption plant are required to meet this reduced emission requirement: either de-rate the production capacity of the plant by about 15% by operating at reduced SO2 and higher O2 concentration to the converter; or add a fifth catalyst bed, increase catalyst loading to about 230-250 liters/ton (40% or more increase), and use a partial first bed and full fourth and fifth catalyst beds of expensive low ignition catalyst – in most cases requiring a new converter for existing plants and increased capital and operating costs for new plants.

Alkali scrubbing of sulfur dioxide has been used commercially since the early 1900's, re-born in the mid 1930's and early 1940's to treat weak metallurgical gases primarily from lead and zinc sulfide smelter operations using equilibrium data developed in the mid 1930's by Johnstone, et.al. (University of Illinois) for Cominco (lead-zinc producer) in Trail B.C. Canada, and again in the mid 1970's to treat tail gas from single absorption sulfuric acid plants to meet the new existing plant SO2 emission regulations. Many existing sulfuric acid plants added alkali scrubbing systems to reduce tail gas SO2 emissions to 4 Lbs/Ton or 10 Lbs/Ton as required by the various states. Alkali scrubbing has also been used to reduce emissions from Claus sulfur recovery units and coal fired power station gas. The alkali scrubbing process has demonstrated the capability of reducing SO2 emissions consistent with the new EPA level of 1.0-1.25 Lbs/Ton; even during acid plant cold start-ups with SO2 input levels as high as 40,000 PPM (4%) SO2.

**Single Absorption Process** - The single absorption sulfuric acid process typically has four catalyst beds with cooling between each bed to achieve a conversion efficiency of 98% to 98.5% with 8% SO2 gas, 1.6 O2/SO2 ratio to the converter, and a catalyst loading of about 180 liters of catalyst per STPD of acid produced. Cooling equipment between the catalyst beds include boilers, superheaters, and economizers producing high pressure superheated steam in sulfur burning plants, and gas heat exchangers to heat the cold incoming SO2 gas along with superheaters, economizers, and/or air preheaters in regeneration plants. The single absorption plant has one drying tower and one absorption tower system. Single absorption sulfuric acid plants are simple and easy to start-up and operate.

**Double Absorption Process** – A typical double absorption sulfuric acid plant has four catalyst beds with cooling between each bed for conversion (oxidation) of sulfur dioxide (SO2) with oxygen (1/2 O2) to sulfur trioxide (SO3). The double absorption process operates at 11.5%-11.75% SO2 to the converter with 165 liters/ton of catalyst. The process contacts the gas exit the third catalyst bed with 98.5% sulfuric acid in an absorption tower to remove sulfur trioxide (SO3), allowing the reaction in the following one or two catalyst beds to proceed further - to a conversion efficiency of 99.7%, the 4 Lbs/Ton NSPS emission level. To achieve a greater conversion efficiency (lower emission level) per the new EPA level, either the SO2 gas concentration to the converter must be reduced to about 9.5%-10%, reducing the acid production capacity of the plant, or a new plant can be built larger to maintain acid production to compensate for the increased gas flow from the lower SO2 gas concentration, or additional catalyst beds with increased catalyst loading (40%-50% more catalyst) and expensive, more active low ignition catalyst can be used in a five stage converter.

The double absorption process has an interstage absorption system that requires gas heat exchangers and economizers to cool and reheat the gas leaving the converter to the interstage absorption tower and reheat the gas from the absorption tower to catalyst ignition temperature for the final conversion reactions. The interstage system includes the two or three gas heat exchangers, economizer, interstage absorption tower, pump tank, circulating pump, acid cooler, piping and instruments, etc. Double absorption plants are more complex than single absorption plants and more difficult to start-up in compliance within emission regulations, since it is difficult to heat the all of the catalyst beds to ignition temperature. The plants are more difficult to operate, requiring careful control to maintain efficient conversion in each catalyst bed to meet the emission requirements. In addition, the interstage absorption system must be operated to minimize acid carry-over and mist that will damage the interstage gas heat exchangers and catalyst.

**Alkali Scrubbing of Sulfuric Acid Plant Tail Gas** - Sulfuric acid plants incorporating AE&C's alkali scrubbing process to treat sulfuric acid plant tail gas have been in operation for over 30 years, consistently meeting the required emission levels. The process has also been installed to treat coal fired power station stack gas and Claus sulfur recovery plant tail gas. The process is low cost, simple and easy to operate and control. It is essentially an SO2 sponge at the end of the plant, reducing even very high levels of incoming SO2 gas to acceptable emission levels. Sulfur dioxide emissions are easily controlled at the required level by adjusting the feed rate of alkali and water, even during start-up and acid plant converter upsets.

The sodium based process uses soda ash (Na2CO3) or caustic (NaOH) as the alkali, removing the SO2 as a concentrated sodium bisulfite solution that can be sold for water treatment applications or to the paper industry. Regeneration type plants have a weak sulfuric acid purge stream from the gas cleaning section of the plant that is neutralized with soda ash or caustic. The scrubber sodium bisulfite solution is used to neutralize the weak acid stream, producing little or no additional effluent or using additional alkali. For plants that can not sell or react the scrubber sodium bisulfite solution with weak acid, the sodium bisulfite can be reacted with sulfuric acid to produce sodium sulfate solution for disposal, recycling the SO2 removed in the scrubber back to the acid plant for production of additional sulfuric acid.

The ammonia (NH3) based process produces an ammonium sulfate fertilizer product that is sold as a concentrated solution or in solid form as crystals. A number of plants feed the scrubbing system's ammonium sulfate solution to the ammoniated phosphate (MAP, DAP) system for grade control. A few regeneration plants feed the ammonium sulfate to the regeneration furnace where it is decomposed to nitrogen, water and sulfur dioxide, recovering the sulfur values as sulfuric acid.

## The AE&C Single Absorption-Scrubbing Process

**Single Absorption-Scrubbing Process** – The AE&C single absorption-scrubbing sulfuric acid process is an integrated sulfuric acid plant design incorporating an optimized single absorption process with the alkali scrubbing system to provide a low cost, efficient, and easy to operate and control sulfuric acid plant meeting even the most stringent SO2 emission requirements.

The optimized sulfuric acid process uses either three catalyst beds with 125 liters/ton of catalyst, or four catalyst beds with 165 liters/ton of catalyst. In either case, the inlet SO2 to the converter is about 11.5%-11.75% SO2 and 0.8/1 O2/SO2 ratio (the same as double absorption) with conversion efficiency in the converter catalyst system of 96%-96.5% for the three catalyst bed design, and 97%-97.5% for the four catalyst bed design. The gas from the absorption tower is treated in the alkali scrubber with a sulfite/bisulfite solution in a fiber reinforced plastic (FRP) scrubbing tower containing two packed beds of polypropylene packing. The scrubbing solution is circulated in FRP piping by two stainless steel horizontal centrifugal pumps. The cleaned gas exits the plant through an FRP stack mounted on top of the scrubbing tower.

**Advantages** - Replacing the interstage system of the double absorption plant with the FRP scrubbing system has the following advantages:

- Control of SO2 emissions at any required level.
- Capable of very low emission levels at minimal additional cost.
- Reduces plant gas pressure drop by about 40”-60” H2O.
- Increases high pressure steam production by 7%-12%.
- Reduces main blower horsepower (high pressure steam usage) by 30%-40%.
- Reduces total plant capital cost by 15%-20%.
- Faster start-ups in compliance: Easier to heat all catalyst beds, or plant can be started on SO2 gas without all beds at ignition temperature.
- High reliability – Operating data over 30 years shows essentially no acid plant shut-downs caused by the scrubbing system.
- Easy to operate and control while meeting emission requirements.

**Concerns** – The only concern of the alkali scrubbing system and the reason all sulfuric acid plants are not single absorption-scrubbing designs is the production of a bisulfite or sulfate solution byproduct that must be used on site, sold, or routed to an effluent system.

**AE&C Alkali Scrubbing Process - Process Description**

The sulfur dioxide emissions from a single absorption sulfuric acid plant are reduced to acceptable levels by recovering the sulfur compounds in an alkali (sodium or ammonia) based tail gas SO2 scrubbing system. The system removes the inorganic sulfur compounds as chemically fixed sodium or ammonium salts. The resultant scrubber bisulfite salt solution is sold or decomposed by acidulation, with sulfuric acid to sulfur dioxide gas and a sodium or ammonium sulfate solution. The sodium or ammonium sulfate solution is air stripped of dissolved SO2 and sent to the plants existing liquid effluent system or sold. The scrubbing system is also designed to produce a saleable quality sodium bisulfite or ammonium sulfate solution. The stripping gas containing the SO2 removed in the scrubber is returned to the acid plant drying tower, increasing the plants sulfuric acid production.

The system is designed to remove sufficient sulfur dioxide from the sulfuric acid plant tail gas to meet sulfuric acid plant emission regulations. The system will reduce the sulfur dioxide in the tail gas to acceptable levels with a normal feed gas containing 2,000 to 4,000 PPMV of SO2, and a start-up or upset condition with scrubber inlet gas with up to 40,000 PPMV SO2. The unit is highly flexible and permits control of S02 emissions to meet environmental requirements, even during a cold start-up or upset.

**Gas Scrubbing**

Gas leaves the sulfuric acid plant absorption tower and enters the bottom of a two stage scrubbing tower where the sulfur dioxide is absorbed and converted to a sodium or ammonium sulfite/bisulfite/sulfate solution. The temperature is reduced to about 85 F by saturation of the gas with water contained in the scrubbing solution.

The scrubber consists of two packed beds of plastic packing, each independently irrigated with a sodium or ammonium sulfite/bisulfite solution. A scrubber circulating pump is provided for each circulating loop with one additional pump as a common installed spare. Alkali (caustic, soda ash or ammonia) required by the scrubbing system is pumped from storage to the upper and lower stage solution circulating loops and intimately mixed in the tower and pump. Alkali is added to the top stage at a rate sufficient to maintain the SO2 emissions at the required level. Water is added to the top stage circulating system as make up for the water evaporated from the solution by the gas, and to maintain the scrubber bottom stage solution dissolved solids at a value to maintain the salts in solution. Excess solution from the upper stage overflows a draw off tray (located between the two packed beds) to the top of the lower packed bed. The gas leaving the upper packed scrubbing stage passes through an entrainment separator before entering the exhaust stack. The gas is saturated with water vapor and may, under certain atmospheric conditions, have a white steam plume which will dissipate in a short distance.

**Chemistry (Sodium Case Using Soda Ash)**

Soda ash reacts with the sulfur dioxide in the tail gas by the following reactions:

$Na_2CO_3$ (sodium carbonate/soda ash) + 2 $S0_2$ + $H_2O$ = 2 $NaHSO_3$ (sodium bisulfite) + $CO_2$

$Na_2CO_3$ + $S0_2$ = $Na_2SO_3$ (sodium sulfite) + $CO_2$

$Na_2SO_3$ + $S0_2$ + $H_2O$ = 2 $NaHS0_3$

A review of the above reactions shows that sodium bisulfite consumes one mole of sodium for each mole of sulfur dioxide removed, while sodium sulfite consumes two moles of sodium for each mole of sulfur dioxide, therefore, the lowest soda ash usage would be obtained if all the sulfur dioxide were removed as sodium bisulfite. However, sulfur dioxide removal to low levels cannot be achieved with the bisulfite alone due to the high partial pressure of S02 over bisulfite solutions.

The system is normally operated at a balance point to provide maximum sulfur dioxide removal with minimum alkali consumption. The lower stage is designed to operate with a high bisulfite to sulfite ratio and a high dissolved solids concentration to minimize alkali consumption and bisulfite product solution volume. The upper stage is operated with a low bisulfite to sulfite ratio and a low dissolved solids concentration to maximize sulfur dioxide removal.

High $SO_2$ removal efficiency and minimum alkali usage are achieved by adjusting the alkali solution feed to the top and bottom stages to maintain the desired $SO_2$ emission and sulfite to bisulfite ratio, and water to the top stage to maintain the desired bottom stage solution dissolved solids concentration. Should a saleable sodium bisulfite or ammonium sulfate solution be required, the system variables are adjusted to obtain the required specification dissolved solids, pH and total reducing agents in the product solution.

**Acidulation Stripping**

The acidulation stripping system is designed to produce a sulfur dioxide gas stream and a sodium or ammonium sulfate liquor stream from a feed of sodium or ammonium sulfite/bisulfite solution and sulfuric acid. Sulfur dioxide dissolved in the sodium or ammonium sulfate solution is reduced to a minimum level by air stripping.

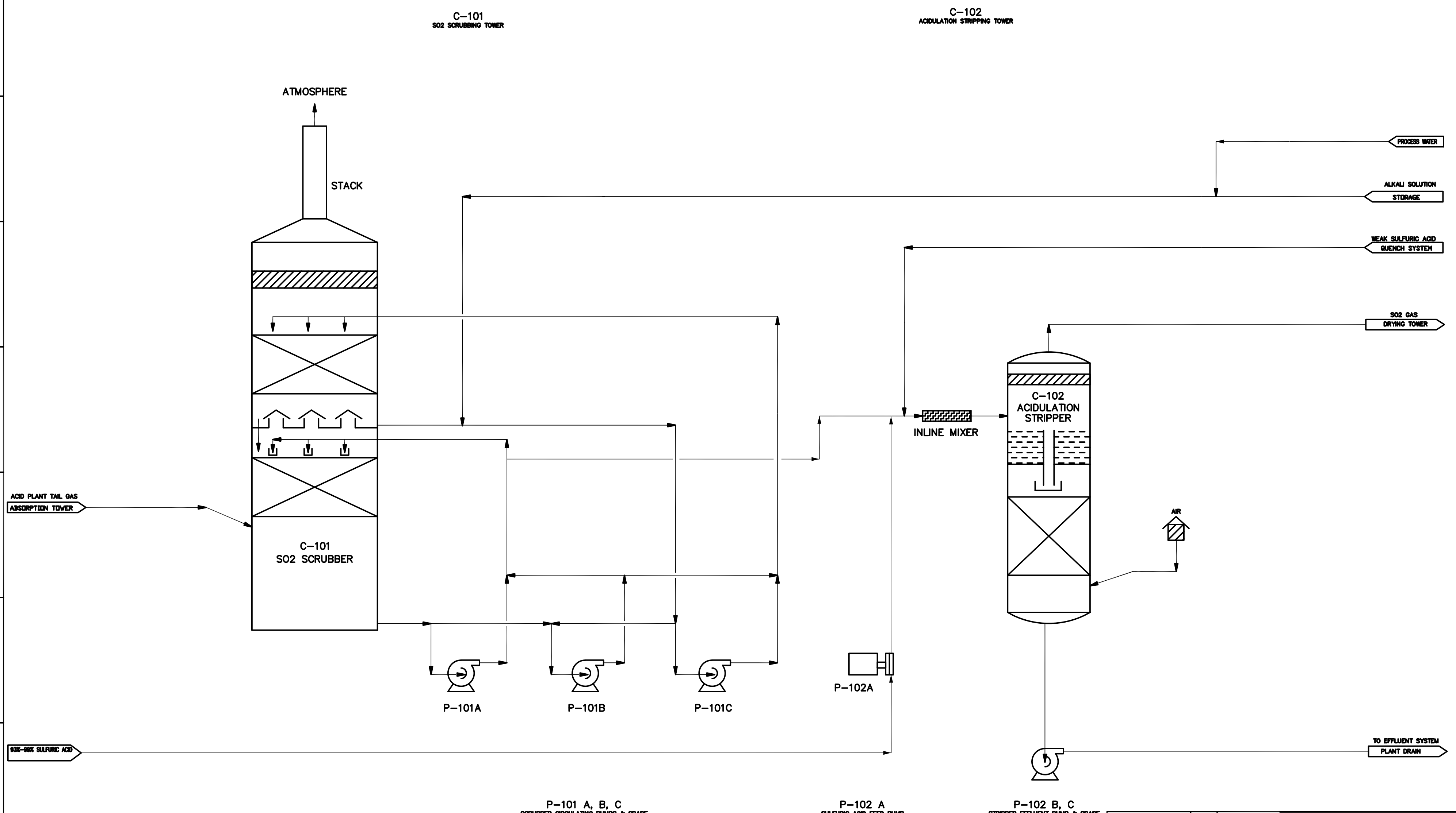
Sodium or ammonium sulfite/bisulfite/sulfate solution from the $SO_2$ scrubber is pumped from the bottom section of the scrubber to the acidulation stripper. Weak sulfuric acid (about 5%-20% $H_2SO_4$) purge from a regeneration sulfuric acid plant quench system is pumped to the acidulation stripper. For a sulfur burning plant or plant producing ammonium sulfate, the sulfuric acid required to react with the scrubber solution is pumped from the 93%/99% sulfuric acid product line/tank to the acidulation stripper. The 93%/99% sulfuric acid feed is controlled to maintain the desired pH in the acidulation stripper bottoms. The sulfuric acid converts the sulfite/bisulfite to sulfate and sulfur dioxide by the following reactions (sodium system):

$$2\ NaHS0_3 + H_2S0_4 = Na_2SO_4 + 2\ SO_2 + 2\ H_2O$$

$$Na_2SO_3 + H_2S0_4 = Na_2SO_4 + S0_2 + H_2O$$

The acidulation reactions occur in the inline mixer and upper section of the stripper.

Sulfur dioxide is air stripped from the acidic sodium or ammonium sulfate solution in the packed section of the tower. The stripped liquor is pumped to storage for ammonium sulfate product or for a regeneration plant, to the existing plant liquid effluent system. A small stream of atmospheric air is used to strip $SO_2$ from the sodium or ammonium sulfate solution. The air reduces the sulfur dioxide content of the sulfate liquor to a minimum level. The gas stream containing the sulfur dioxide is returned to the sulfuric acid plant at the inlet to the drying tower, increasing the plants sulfuric acid production.

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**ACID ENGINEERING & CONSULTING, INC.**

BOCA RATON FLORIDA

**TYPICAL**
**ALKALI SO2 SCRUBBING SYSTEM**
**FLOW DIAGRAM**

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**Examples of AE&C Single Absorption-Scrubbing Projects**

Acid Engineering & Consulting, Inc. (AE&C) has provided the design for over forty (40) alkali scrubbing systems in the last thirty (30) years. Recent scrubbing projects include Claus sulfur recovery plants, single absorption sulfuric acid plants and regeneration type sulfuric acid plants. Each of the designs easily met required emission requirements, with some required emission levels as low as 20 PPM SO2.

**1 - Sulfur Burner – Single Absorption-Ammonia Scrubbing Plant** – A new sulfur burning sulfuric acid plant was designed by AE&C using the single absorption-scrubbing process. The plant site produces crystalline ammonium sulfate for the areas cotton and other crops by reacting ammonia with 93%-98% sulfuric acid. The new sulfuric acid plant provides the acid required by the ammonium sulfate plant, with the scrubber's ammonium sulfate solution as additional feed to the crystallizer. About one-half of the sulfuric acid produced is sold. The plant incorporates a three bed converter system operating at 11% SO2 concentration to the converter with 96%-96.5% conversion efficiency. To obtain a permit to construct in a reasonable time, state regulators and EPA required an SO2 emission limit of 1.25 Lbs/Ton, that was easily met, even during cold start-up. Steam produced in the plant is used to drive plant equipment (main blower, cooling water pump, boiler feed water pump), with the remainder currently letdown to low pressure and condensed in an air cooled condenser. Future plans include the addition of a steam-electric turbogenerator using a portion of the plant high pressure steam to eliminate the site electric bill. With little economic incentive for increased energy recovery, main blower discharge pressure is 130" H2O clean, higher than normal for a single absorption-scrubbing plant, and the economizer gas exit temperature is designed at 400 F. Plant capital cost was estimated to be 20% less than a double absorption plant of the same capacity and emissions.

**2 – Sulfur Burner - Conversion of Double Absorption Plant to Single Absorption-Scrubbing –** An existing sulfur burning double absorption sulfuric acid plant is converted to a single absorption-scrubbing system with a 50% capacity increase and production of sodium bisulfite for internal use and/or sales. The plant obtained a construction permit in less than two months by maintaining SO2 and acid mist emissions at a non-significant level above existing emissions using the alkali scrubbing system. The interstage absorption system is removed, and replaced by a steam superheater. The four bed converter system is rearranged as a three bed system, and the existing interstage and final economizer and absorption tower systems are operated in parallel as a final absorption tower. Other modifications include the furnace and converter boilers augmented with steam superheaters. Main blower discharge pressure at the increased capacity is 145" H2O compared to original blower discharge pressure at the reduced acid production rate of 260"-280" H2O. High pressure steam production is increased, and energy usage by the main blower at the increased plant rate is 20% less than at the lower production rate.

**3 – Regeneration – Single Absorption-Scrubbing –** A number of spent acid regeneration sulfuric acid plants were designed and constructed as single absorption-scrubbing systems. The regeneration plants process an ammonium bisulfate-sulfuric acid-hydrocarbon effluent stream from a methyl-methacrylate (MMA) production operation. The scrubbing systems were initially designed to produce ammonium sulfate solution that was decomposed along with the plants primary sulfate feed stream in the regeneration furnace to sulfur dioxide, water, nitrogen and carbon dioxide. Regeneration type sulfuric acid plants produce a weak acid purge stream in the gas cleaning section of the plant that is neutralized. The acid plants scrubbers were later converted to use caustic or soda ash as the alkali with the sodium sulfite/bisulfite solution used to neutralize the weak acid purge from the gas cleaning section of the plant. The change increased acid plant capacity by eliminating the scrubber feed to the furnace, and eliminated the ammonia requirement of the scrubbing system with no increase in caustic usage.

There are many regeneration sulfuric acid plants that are single absorption-scrubbing using either ammonia or sodium based systems. Some produce ammonium sulfate that is sold to a fertilizer operation or burned in the furnace, most of the plants are using sodium based scrubbing to produce sodium bisulfite for sales or to neutralize weak acid from the plants gas cleaning system.

**4 – Single Absorption-Scrubbing – Sodium Bisulfite Sales –** A number of spent acid regeneration and sulfur burning plants use the AE&C alkali scrubbing system to control SO2 emissions to required levels while producing sodium bisulfite for sales. The AE&C scrubbing process operating conditions are easily adjusted to produce a commercial quality concentrated sodium bisulfite solution that is sold for water treatment and/or to the paper industry.

**5 – Claus Sulfur Recovery Plant Tail Gas Alkali Scrubbing -** A number of Claus sulfur recovery plants process acid gas (normally >80% H2S with CO2) from oil refinery sulfur removal systems. The tail gas containing as much as 2%-3% H2S and SO2 is incinerated to sulfur dioxide, cooled in boilers to produce steam, and further cooled to about 100 F – 120 F for feed to an alkali scrubbing system. AE&C designed alkali scrubbing systems were installed at a number of refinery and refinery service companies to reduce sulfur emissions to non-significant levels (SO2 as low as 20 PPMV), while producing a sodium bisulfite solution for sales.

## Conclusion

The AE&C single absorption-alkali scrubbing system is a proven, reliable, process that is easy to operate and control. Over 40 units are in operation around the world for over 30 years, all easily meet or exceed even the most stringent SO2 emission requirements. The process has many advantages over the double absorption process, including; lower SO2 emissions, increased steam production, reduced main blower horsepower (energy usage), lower capital cost, faster start-ups in compliance, and easier operation and control.

The single absorption-scrubbing process is the optimum route for regeneration type plants neutralizing weak acid purge streams, and for sites where a saleable sodium bisulfite or ammonium sulfate product is desired.