THE CANSOLV® SYSTEM PROCESS: A NEW PARADIGM FOR SO_2 RECOVERY AND RECYCLE

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ABSTRACT

Significant progress has been made in the last 25 years in the control of emissions resulting from the burning of sulfur bearing fuels and from other industrial processes. The dominant desulfurization technology today is limestone or lime-based scrubbing in various forms. While in general reliable and, in some forms, capable of high SO_2 removal efficiency, they produce large quantities of low value waste products, are relatively expensive to build and operate and are difficult to retrofit in constrained sites due to the large equipment size necessary for their implementation. With increasing concern over the cost and availability of landfill sites and public demand for resource recovery and recycling, recovery-type SO_2 removal processes are becoming increasingly more desirable.

The CANSOLV® System is an aqueous amine-based, regenerative gas desulfurization process capable of removing SO_2 down to a few ppm, if desired, from most stationary sources. The process can be applied to feed gases with <0.1 to 100% SO_2, it is flexible, robust, easy to operate and quickly responsive to changes in gas feed conditions. It represents an effective response to regulation-driven market needs, both domestically and internationally, and it does so in a manner which vastly improves upon existing desulfurization technologies in terms of physical dimensions, capital and operating costs, and environmental impact. In many cases, the CANSOLV® System can be integrated to an existing plant flowsheet to improve profitability of the process.

The CANSOLV®System can be applied to sulfuric, acid spent acid recovery plants, sulfide ore smelters, sulfur recovery units, SO_2 production and its safe storage and transportation, flue gas desulfurization units and pulp mills. This paper describes the CANSOLV® System process technology and its various applications, as well as pilot plant results from multiple industry applications.

INTRODUCTION

Environmental regulations are trending to stricter values of allowable emissions almost universally for all pollutants, from all sources and in all jurisdictions. Often, the utilization of Best Available Commercial Technology (BACT) is required by regulatory authorities and more recently Maximum Achievable Commercial Technology (MACT) which result in capital and operating cost increase for the industry. The CANSOLV® System Process as applied to receptive industries introduces a new paradigm for SO_2 recovery and recycle, by simultaneously reducing emissions and cost.

The dominant desulfurization technology today is limestone or lime-based scrubbing in various forms. While in general reliable and, in some forms, capable of high SO_2 removal efficiency, they produce large quantities of low value waste products, are relatively expensive to build and operate and are difficult to retrofit in constrained sites due to the large equipment size necessary for their implementation. With increasing concern over the cost and availability of landfill sites and public demand for resource recovery and recycling, recovery-type SO_2 removal processes are becoming increasingly more desirable.

Recovery processes have been used by some utilities and industrial companies to effect removal of SO_2 and to produce wallboard-grade gypsum or other useful products. For many utilities though, and for such industrial applications, such as oil refining, natural gas processing, smelting or pulp and paper, the preferred by-products are sulfur dioxide, elemental sulfur or sulfuric acid. Regenerable processes such as sodium sulfite and MgO processes have addressed this need, but have gained limited commercial acceptance, due to high costs.

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CANSOLV® SYSTEM TECHNOLOGY

PROCESS CHEMISTRY

Due to technical simplicity, economic advantage and lack of waste by-product, regenerable SO_2 absorption with homogeneous aqueous absorbents is generally preferred over once-through processes. In water solution, dissolved SO_2 undergoes reversible hydration and ionization according to the following equations:

$$SO_2 + H_2O \rightleftharpoons H^+ + HSO_3^- \qquad (1)$$

$$HSO_3^- \rightleftharpoons H^+ + SO_3^= \qquad (2)$$

Reactions (1) and (2) are half completed at pH values of 1.81 and 6.91, respectively, at 18°C [2]. The quantity of SO_2 dissolved can be increased by adding a buffer, such as an amine, to the water. The buffer drives the above equilibria to the right by reacting with the hydrogen ions to form ammonium salts:

$$R_1R_2R_3N + H^+ \rightleftharpoons R_1R_2R_3NH^+ \qquad (3)$$

In order for the process to be regenerable, the buffering agent should operate in a pH region sufficiently low so as to present a desirable value of SO_2 vapor pressure over the solution at the regeneration temperature. Steam stripping of the vapor phase SO_2 in a multiple stage column will then reverse reactions (1) - (3), regenerating the absorbent.

Sulfite anions, added to water as a salt such as sodium sulfite, can also be utilized as a buffer:

$$H^+ + SO_3^= \rightleftharpoons HSO_3^- \qquad (4)$$

This is the basis of the Wellman-Lord process. However, since the sulfite anion is a fairly strong base ($pK_a = 6.91$), it buffers at too alkaline a pH. This has the effect of making the regeneration of the solution more difficult, resulting in increased steam usage and/or incomplete stripping.

The CANSOLV® System process is based on a unique class of diamine absorbents that optimally balance the ability to absorb and regenerate sulfur dioxide. One of the amine functionalities of the absorbent is so strongly basic that it is not thermally regenerable under the CANSOLV® System process conditions. So, once reacted into a salt by SO_2 or any stronger acid, this strongly basic amine functionality will remain permanently as a salt while in process. This is illustrated in Eq. 5, for the case of virgin diamine reacting for the first time in process with an acid HX, where X^- is any anion of a relatively strong acid, such as Cl^-, NO_3^- etc. A strong dibasic acid such as sulfuric would protonate two amines and yield $SO_4^=$ as the anion X^-.

$$R_1R_2N\text{-}R_3\text{-}NR_4R_5 + HX \;\square\; R_1R_2NH^+\text{-}R_3\text{-}NR_4R_5 + X^- \tag{5}$$

The monoprotonated amine on the right hand side of Eq. 5 is the in-process lean amine which is used to scrub SO_2 . Because it is a salt, it is totally non-volatile and since it is non-heat regenerable, it will stay in salt form throughout the process.

The second amine functionality (the ‘sorbing nitrogen’) is less basic and it buffers in the desired range for regenerability of SO_2, which in practice is about pH 4 for the rich amine and pH 6 for the lean. This buffering range provides the proper balance of absorption and regenerability and is the essence of the CANSOLV□ System technology. This reaction is shown in Eq. 6.

$$R_1R_2NH^+\text{-}R_3\text{-}NR_4R_5 + SO_2 + H_2O \;\square\; R_1R_2NH^+\text{-}R_3\text{-}NH^+R_4R_5 + HSO_3^- \tag{6}$$

In Eq. 6, the anion X^- is not shown as it does not participate in the SO_2 reaction with the sorbing nitrogen. The nature of X^- can affect the functioning of the process: if it is sulfite, $SO_3^=$, it can contribute to SO_2 scrubbing according to Eq. 4. However, if X^- is the anion of a strong acid and is allowed to accumulate to more than 1 equivalent per mole of amine, it will neutralize the sorbing nitrogen and thereby decrease the SO_2 scrubbing capacity of the solvent. Thus, the level of these ‘heat stable salts’ (HSS), is kept below 1 equivalent per mole by a slipstream electrodialysis purification unit which replaces non-regenerable anions such as sulfate by sulfite or bisulfite.

The diamine absorbents are described in the basic process patent, U.S. Patent 5,019,361. Normally, a 25 - 30% solution of the amine in water is utilized in the process.

These absorbents provide significant advantages:

- since the amine absorbent is always present in the process as a salt, it is totally non-volatile and equilibrium vapor phase losses of solvent to the treated gas are zero
- up to about 1 equivalent of strong acid anions per mole of amine, i.e. heat stable amine salts (HSS) of the strong amine functionality, may be present in the absorbent without decreasing the normal scrubbing capacity by the sorbing nitrogen
- if the HSS level is kept below 1 equivalent/mole of amine, then extra scrubbing capacity or ability to scrub at higher temperature is gained through use of SO_2 absorption by sulfite, as in Equation (4), at the expense of higher steam consumption
- if the HSS are regenerated to bicarbonate salts as described in U.S. Patent 5,292,407 and then used in the "Superclean" flowsheet according to U.S. 5,262,139, the feed gas can be treated to an SO_2 level of a few ppm, limited only by mass transfer efficiency.

Compared to alkaline salt absorbents such as sodium sulfite or sodium phosphates, the amine absorbents of the CANSOLV® System technology have the very significant advantage of easy HSS removal by electrodialysis as described in U.S. Patent 5,292,407.

Other advantages of the CANSOLV® System absorbent are:

- inhibition of SO_2 oxidation by oxygen to sulfate
- high thermal and chemical stability
- high water solubility, giving a homogeneous liquid absorbent
- relatively low toxicity (no mortality at 20.0 g/kg, rats)
- low foaming tendency

The absorption of SO_2 by the absorbent is gas side mass transfer limited, since the reactions of SO_2 in solution are for all practical purposes instantaneous. This minimizes scrubber cost and makes possible the use of innovative mass transfer devices.

The absorbent is highly selective for sulfur dioxide over carbon dioxide - by a factor of about 50,000. Acids stronger than SO_2, such as sulfuric and hydrochloric acids, are also absorbed effectively. However, since they are not heat regenerable, they are removed from the solvent by electrodialysis in a slipstream solvent purification unit. The absorbed SO_2 is completely recovered as SO_2 product. There is negligible oxidation and loss to SO_3.

PROCESS DESCRIPTION

The generic CANSOLV® System scrubbing process was successfully piloted during a 9-month trial in 1991 at the Suncor Oil Sands plant in Fort McMurray, Alberta, in Flue Gas Desulfurization service(5). The process as shown in Figure 1 has four main components, excluding conventional equipment such as waste heat boilers, byproduct SO_2 conversion processes and wastewater treatment systems.

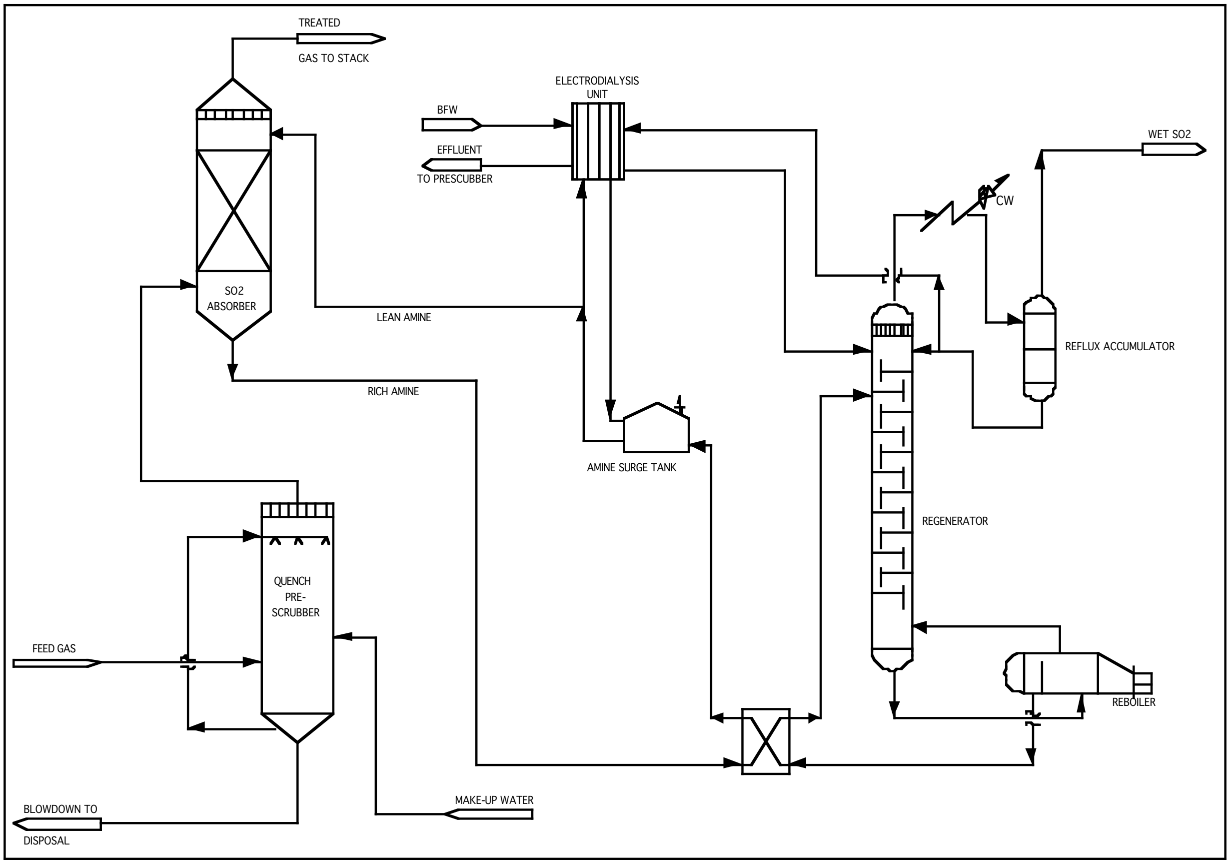


Figure 1. CANSOLV“ System PFD

Prescrubber

The prescrubber contacts the oxidized feed gas with recirculated water in a spray tower. This cools and saturates the feed gas and removes a large fraction of the particulates, depending on their size. Strong acids such as sulfuric and hydrochloric acid are also scrubbed, decreasing the duty on the HSS removal unit. In cases where the adiabatic saturation temperature of the feed gas is high (such as in a sulfur recovery unit tail gas cleanup unit application), the prescrubber is also used as a direct cooler by adding a heat exchanger to the water circulation loop (analogous to a Quench Column). The level of dissolved acids in the prescrubber water is controlled by blowdown, neutralization and discharge into a wastewater treatment system. Suspended solids are controlled by settling.

When treating strong acid and particulate free gas, such as sulfuric acid plant tail gas, the primary function of the prescrubber would be to saturate the feed gas prior to SO_2 absorption. Saturation of the feed gas will occur in the absorber in any case, making a separate prescrubber optional. In such a case, continuous water addition to the amine absorbent would be used to maintain the water balance of the amine solution.

Absorber

The absorber is a mass transfer device for contacting the absorbent with the feed gas. Since the CANSOLV® System absorbent reacts reversibly with SO_2, multi-stage countercurrent contacting must be used to achieve maximum loading of the acid gas in the rich absorbent. Any conventional absorber type may be used, such as a packed or trayed tower. The selection of absorber type is based on normal engineering and economic considerations.

Regenerator

The rich SO_2 laden absorbent from the absorber is pumped to the regenerator via a lean/rich heat exchanger. The regenerator is normally a trayed or packed tower with a steam heated reboiler. As the absorbent flows down the column, the SO_2 is stripped from the liquid and carried overhead into a reflux condenser, where most of the steam condenses and is returned to the top of the regenerator as reflux. The gaseous, water saturated sulfur dioxide leaves the regenerator via a blower or compressor. The lean amine leaves the reboiler and is pumped back to the absorber via the lean/rich heat exchanger, a trim amine cooler and a surge tank.

Amine Purification Unit

A slipstream of effectively about 0.1- 0.3% of lean amine flow is fed to the electrodialysis HSS removal unit. There, heat stable anions like sulfate are replaced by regenerable sulfite anions sourced from the stripper reflux. The heat stable anion containing waste stream is pumped into the prescrubber water loop.

EQUIPMENT MECHANICAL DESIGN

Since the CANSOLV® System SO_2 absorption process is very similar to the well known amine treating processes for removal of H_2S and CO_2 from refinery streams and natural gas, the same engineering methods, equipment selection and process control choices are generally applicable to both systems. Materials of construction are adjusted to handle the lower pH values resulting from the higher acidity of SO_2 compared to H_2S and CO_2.

Because SO_2 containing feed gas streams often contain stronger acids such as sulfuric acid, the rate of heat stable salt accumulation is higher than in conventional amine treaters. Disproportionation of sulfite may also contribute to HSS accumulation. Therefore, in contrast to conventional amine treaters, an HSS removal unit is included in the process equipment.

TECHNOLOGY DEVELOPMENT STATUS

Development of the CANSOLV® System SO_2 scrubbing process was begun by Union Carbide Canada Limited in 1988. Studies of possible novel absorbents led to the issue of U.S. Patent 5,019,361 in 1991 for the basic process. The required physical property and safety data were generated to support engineering of a large, versatile pilot plant, which was operated for 9 months at the Suncor Inc. Tar Sands Plant in Fort McMurray, Alberta. The unit operated from February 28 to November 28, 1991, scrubbing 3600 scfm of flue gas from the site's utility boilers. The fuel in the boilers was petroleum coke produced in the tar upgrading process and had a sulfur content of 7%. On many occasions in the course of performing the statistically designed experiments, SO_2 in the treated gas was <15 ppmv. Results of the test program exceeded expectations and demonstrated the CANSOLV® System process to be robust, effective and easy to operate. A statistical process model was developed based on the test data. Subsequently, a rigorous thermodynamic model was generated on the ASPEN Plus platform. The two models are in good agreement.

In 1992, Union Carbide received an award under the U.S. Department of Energy's Clean Coal Program to demonstrate the process at a 75 MW scale at Alcoa's Warrick Generating Station in Indiana, scrubbing flue gas from a coal fired boiler. Further engineering and laboratory studies were conducted to support this project and a Definition of Technology was compiled. At this point, Union Carbide cancelled the CANSOLV® System program due to a corporate strategic decision to concentrate on core competencies in the petrochemical area. Key technical personnel involved in the process development purchased the technology from Union Carbide in 1997 in order to commercialize the technology.

Heat stable salt removal from the process absorbent is effected by a metathesis electrodialysis (ED) process under U.S. Patent 5,292,407. Electrodialysis of this form, sometimes called double decomposition electrodialysis, is utilized commercially in other applications, while simple two-compartment ED heat stable salt removal from refinery amine treater solvents is practiced commercially (6). The Superclean CANSOLV® System process flowsheet modification has been patented (7). This modification permits removal of SO_2 in the treated gas to essentially zero.

A patent application has been filed for the SO_2SAFE® sulfur dioxide storage technology, an inherently safer method compared to liquid SO_2 storage. The sulfur dioxide is held in solution at atmospheric pressure and regenerated by steam stripping on demand. In the event of a leak or spill of the loaded solution, only a relatively small amount of SO_2 is released, greatly reducing the hazard. This process can be used as buffer storage of SO_2 in order to decouple process units, or to safely transport SO_2 and regenerate it on demand.

Another Cansolv Technologies Inc. process, “ CANSOLV® SRU”, is discussed elsewhere (8). This application of CANSOLV® System SO_2 scrubbing is covered by patents (9).

Cansolv Technologies Inc. along with their engineering company partners Black & Veatch and Simon-Carves Fenco Inc. are actively pursuing applications to various industries. During these efforts, these partners are critically challenging the process technology and current process designs to ensure successful commercial application. The companies are currently bidding for a first applications of the CANSOLV® System Technology.

MARKETS

The CANSOLV® System Technology can be applied to sulfuric acid manufacture, spent acid recovery plants, sulfide ore smelters, sulfur recovery units, SO_2 production and safe storage and transportation, flue gas desulfurization units and pulp mills. Details of these applications can be found in other Cansolv Technologies Inc. (CTI) publications as well as in CTI’s Web site (http://www.cansolv.com). The following paragraphs summarize the application of the CANSOLV® System Technology in the various industrial and utility markets.

SMELTER & ACID PLANT APPLICATIONS

The two largest sources of sulfuric acid are sulfur burning acid plants, which produce on-purpose or voluntary acid, and sulfide ore smelters where the acid is the byproduct of emission control. In both cases, conventional contact acid plants are used. Most acid plants built in the last 25 years are of the double absorption design illustrated in Figure 2, which emit a tail gas containing generally less than 500 ppm SO_2 into the atmosphere. The older single absorption plants produce a tailgas with up to 3000 ppm SO_2. Thus, while considerable improvement has occurred in air emissions, continuing environmental and cost reduction pressure is driving the search for more effective and efficient technologies.

In sulfide ore smelters, the adoption of oxygen based roasting has produced substantial decreases in total emission levels and improvements in the capture of fugitive emissions has improved plant industrial hygiene and pollution performance. However, considerable room for improvement remains, particularly in the areas of improving the economics of treating low strength SO_2 streams, both fugitive and primary, and in dealing with the often cyclical SO_2 load on the acid plant caused by the batch operation nature of current converter designs. Weak SO_2 streams introduce a high level of inerts into the acid plant, thereby requiring a larger unit to handle the gas flow, and in some cases even requiring the use of alternative technologies to control emissions. A varying SO_2 feed rate prevents optimal steady state operation of the unit, resulting in increased SO_2 emissions.

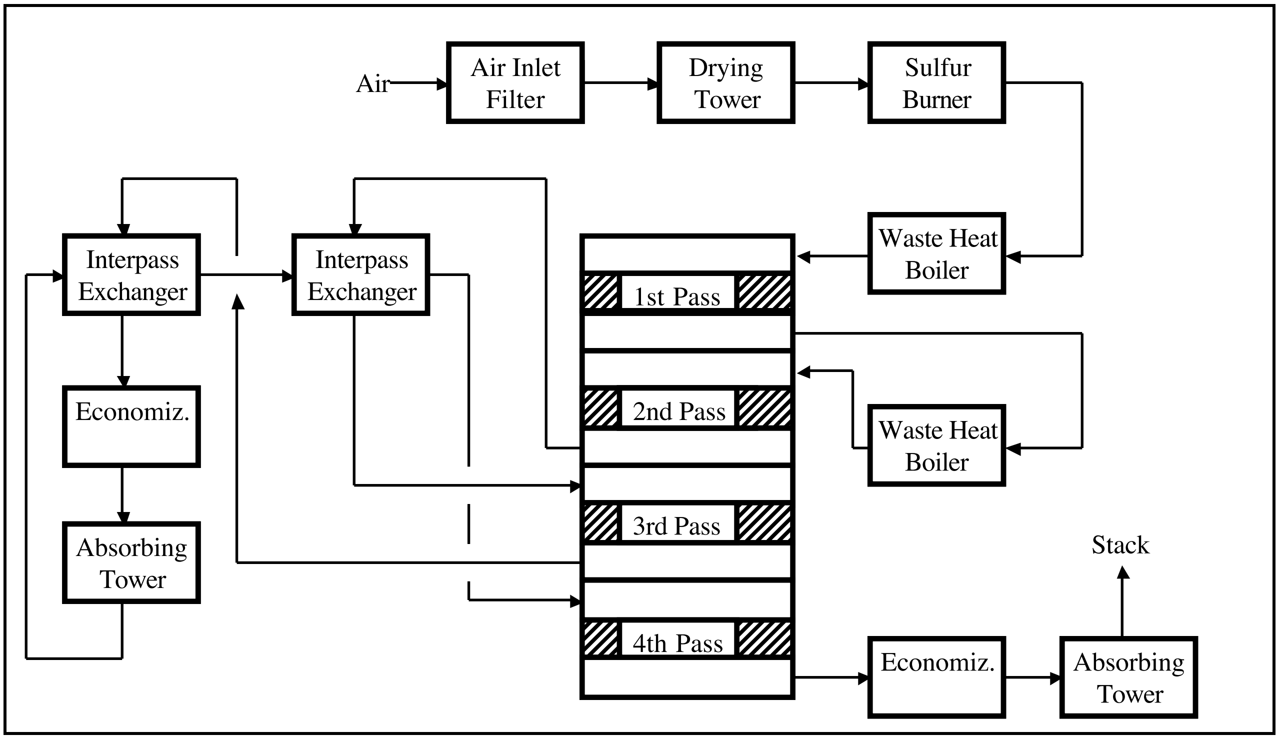


Figure 2. Double Absorption Acid Plant Gas Flow

CANSOLV® System SO_2 scrubbing technology can be used instead of a second absorption step to reduce sulfur emissions from sulfuric acid plants, as illustrated in Figure 3.

Since the capital and operating costs of the CANSOLV® System scrubbing unit are relatively insensitive to the concentration of SO_2 in the feed gas, in many cases three contact stages are the economic optimum, as shown in Figure 3. The advantages of the CANSOLV® System process over a conventional second absorption stage are:

- capital cost savings
- normal SO_2 concentration in tail gas is about 100 ppm or less
- SO_2 removal to essentially zero available at slight extra cost
- reduced emissions during start-up and upsets
- smaller process gas blower due to lower pressure drop
- small footprint and ability to locate regenerator remotely enable easy retrofits
- reduced stack height in some cases
- ability to produce pure SO_2 for other uses or for sale.

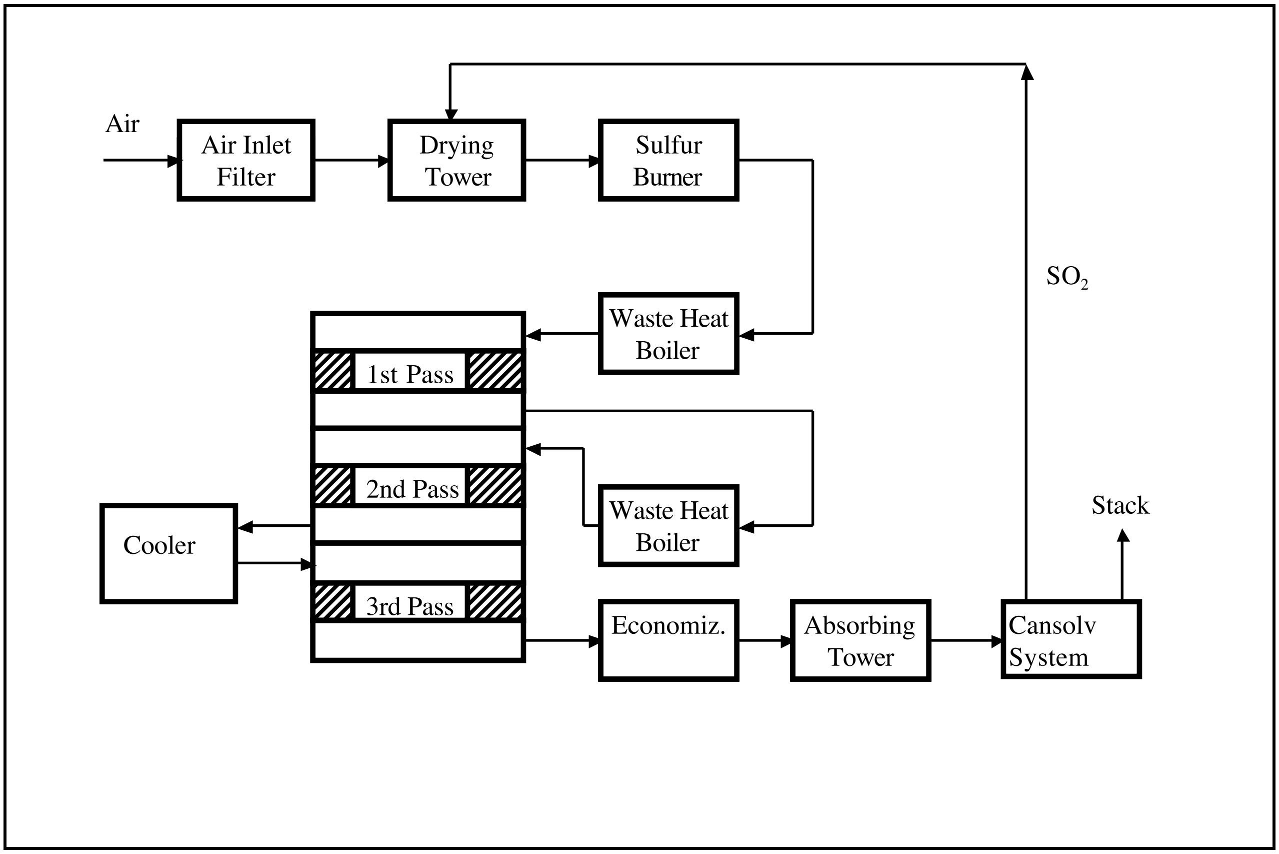


Figure 3. Single Absorption Acid Plant with CANSOLV® System Scrubber

SMELTERS

Sulfide ore smelters offer potential uses for CANSOLV® System SO_2 scrubbing in addition to the acid plant applications discussed above. Weak primary metallurgical gas and fugitive emission streams, from sources such as converters and driers, are costly to control by feeding them into the acid plant. Acid plant investment and operating costs are largely determined by gas flow. The large quantity of inerts in weak SO_2 streams necessitates a large additional capital investment for little increase in acid production, while increasing total SO_2 emissions to the atmosphere.

CANSOLV® System SO_2 scrubbing technology can address this deficiency by selectively capturing the SO_2 from weak streams and feeding it as a pure water saturated product to the acid plant drying tower. The inerts from these streams are rejected to stack. Very substantial savings in initial capital investment can be realized, while reducing total emissions. Alternatively, an existing sulfuric acid plant can be debottlenecked in the same manner, enabling an increased smelting rate with a very modest capital investment, since the acid plant often limits smelting rate.

Metallurgical acid plants often operate with a very cyclical inlet SO_2 concentration, due to the batch operating nature of current converter designs. This has the undesirable effect of preventing the acid plant from operating in a steady state optimum manner, which tends to increase emissions. Additionally, the mechanical stresses caused by thermal cycling tends to increase maintenance costs. The SO_2SAFE® Storage Technology can mitigate these effects by providing load-leveling capability. During peaks, SO_2 is scrubbed from the acid plant feed gas and the loaded solvent is held in a buffer storage tank. At times of low SO_2 concentration in the acid plant feed, rich solvent is regenerated and the SO_2 is added to the acid plant feed gas. The response time constant of the CANSOLV® System process is of the order of one minute or less, enabling accurate load following. The optimum degree of damping the cyclicality is site specific. In the limit, complete decoupling of the smelter and acid plant can be achieved by specifying a sufficiently high rate and storage capacity for the load leveling equipment.

Finally, the use of CANSOLV® System Flue Gas Desulfurization can enable the use of high sulfur, low cost fuels such as petroleum coke and heavy refinery residues in the site utility boilers or cogeneration unit. The SO_2 byproduct can be converted to H_2SO_4 in the existing acid plant. Payback periods of 2 years or less are projected for the additional plant investment over a gas fired cogeneration unit.

REFINERY & NATURAL GAS APPLICATIONS

In natural gas, growing demand and rising prices are making the production of sour gas economical, leading to a growth in sweetening and sulfur recovery capacity, while having to deal with the tightening of emission regulations.

The refining industry is facing three trends with serious cost increase implications. The global average crude oil is getting heavier and higher in sulfur, while regulations are requiring lower sulfur content in the products and lower emissions from the refineries. Exacerbating the situation is the shrinking market for residue fuels which in the past dealt with a substantial fraction of the crude slate sulfur content. In fact, disposition of the bottom of the barrel (very heavy residues and petroleum coke) is a growing problem for refiners. The impact of all these factors on refineries has been to require increased refinery complexity, increased hydrotreating, higher SRU capacity, cleaner refinery fuels and reduced emissions from the major sources such as the sulfur recovery unit (SRU), boilers and the fluidized catalytic cracking unit (FCCU) regenerator flue gas (CO boiler flue gas). The refining industry is thus facing major capital investments, while having to deal with a very competitive marketplace for products.

Reduction of sulfur emissions from SRU’s is being achieved by the application of various technologies:

- tail gas treatment with H_2S recycle processes (BSR/Amine, SCOT, etc.)
- selective catalytic oxidation (Selectox, Superclaus etc.)
- sub-dewpoint processes (Amoco CBA, MCRC, Sulfreen etc.)

The above processes reduce emissions adequately, but do increase costs significantly and some have operating constraints requiring careful control.

SRU capacity expansion, as an alternative to construction of a complete new train, is currently most often achieved by oxygen enrichment of the thermal stage combustion air. This reduces the inerts flow through the unit, making room for additional acid gas. At high levels of enrichment or with pure oxygen, extensive modifications to existing equipment must be made. The use of oxygen of course incurs a significant operating cost increase.

FCCU sulfur emission control is now practiced by primarily two technologies - the use of sulfur transfer catalysts or caustic (or soda ash) scrubbing. Costs of both control options are quite sensitive to the concentration of SO_2 in the uncontrolled tail gas. Thus the trends to heavier, high sulfur crudes and to increased residue cracking are increasing emission control costs significantly. Units losing grandfathering and new FCCU's will have to bear the compliance cost.

While these and other advances in technology have helped operating companies to meet requirements, the pressures to improve environmental performance and reduce costs are unrelenting. CANSOLV® System technologies offer new tools to deal with these challenges. The processes, as described below, now provide a new options for SRU tail gas treatment, debottlenecking and for new sulfur recovery units of conventional design. The CANSOLV® System process also introduces a new paradigm for SRU design, due to its ability to economically, selectively and regenerably scrub SO_2 from gas streams. The ability to remove SO_2 from flue gas at lower cost, and to the most stringent standards, opens the door for FCCU emission control and the use of low value, high sulfur residuals and petroleum coke as refinery fuel or in cogeneration.

The following discussion is applicable to both natural gas and refinery SRU's. Refiners can take advantage of the considerable economies and operating advantages accruing from destruction of dirty feed streams containing ammonia, hydrocarbons etc. Natural gas processors with low H_2S to CO_2 ratios will benefit from the capital and operating cost advantages resulting from the almost complete equilibrium selectivity of the CANSOLV® System scrubbing process for SO_2 over CO_2. Conventional TGTU's can absorb large quantities of CO_2 along with H_2S , resulting in the recycle of inert material to the SRU.

CANSOLV® System TGTU

A CANSOLV® System unit can perform sulfur removal from natural gas plant and refinery Claus unit tail gas, simply replacing a conventional TGTU, as shown in Figure 4. The major difference is that the Claus tail gas is incinerated and then scrubbed, rather than reduced and scrubbed as in conventional technology.

The CANSOLV® System TGTU has very significant advantages over a conventional TGTU:

- competitive or lower capital and operating costs
- higher sulfur recovery - all sulfur species, including elemental sulfur and COS, are converted to SO_2 by incineration with excess air and removed to a few ppm, if required
- all combustible species in the Claus tail gas are destroyed, avoiding interference with the scrubbing process and emissions to air
- accurate control of H_2S / O_2 stoichiometry is not critical, since the Claus tail gas sulfur content is converted totally to SO_2 , regardless of whether it was H_2S or SO_2 rich
- need for reheater, reducing gas and catalytic reactor is eliminated
- recycle of inert CO_2 to the Claus unit along with the sulfur is eliminated, due to the very high equilibrium selectivity of the CANSOLV® System scrubbing process compared to MDEA treating
- problems due to SO_2 breakthroughs in conventional TGTU are eliminated
- low cost sensitivity to feed SO_2 content may enable elimination of third converter.

Debottlenecking

Even greater benefits can be obtained by actually integrating CANSOLV® System technology into the operation of the SRU, beyond just tail gas treatment, as is illustrated in Figure 5. In this configuration, a part of the acid gas bypasses the Claus unit and is incinerated with excess air, along with the Claus tail gas. The SO_2 recycled to the Claus thermal stage reduces the combustion air requirement, thereby also reducing the process gas flow by eliminating the nitrogen inerts. This effectively unloads the SRU, allowing for increased capacity at a low incremental cost over the CANSOLV® System TGTU alone. The high operating cost of oxygen enrichment is avoided, while realizing in addition to the above advantages the following additional benefits:

- capacity expansions of up to 170 - 200%+
- in refineries, streams containing troublesome species such as ammonia and hydrocarbons can be incinerated with excess oxygen, avoiding unit derating and operating problems
- acid gas replaces incinerator support fuel

Varying degrees of debottlenecking can be implemented by changing the amount of acid gas bypassed to the incinerator. Large capacity expansions will possibly require some modifications to the existing equipment, to deal with the higher sulfur production and heat release.

CANSOLV® System SRU

The end point for the paradigm shift driven by incorporation of CANSOLV® System technology into sulfur recovery units is the “CANSOLV® System SRU” illustrated in Figure 6. This new design paradigm is projected to have substantially lower capital cost than current designs. As can be seen by comparison to Figure 5, fewer pieces of major equipment are required, reducing cost and simplifying operation. Extremely high sulfur recoveries can be achieved in a simple, easier to operate process. Due to the rejection of inerts contained in the acid gas bypassed to the incinerator, the sulfur reactant concentrations in the feed to the catalytic stages are increased. This will push the application envelope of the CANSOLV® System SRU process to lower H_2S concentration acid gas than that treatable with conventional technology.

The operational advantages mentioned above are also obtained in the CANSOLV® System SRU process configuration. A further saving in this design is the lower air blower head required, because the combustion air is fed to the essentially atmospheric pressure incinerator, rather than the thermal stage of a conventional unit which operates at a pressure of 6 - 12 psig.

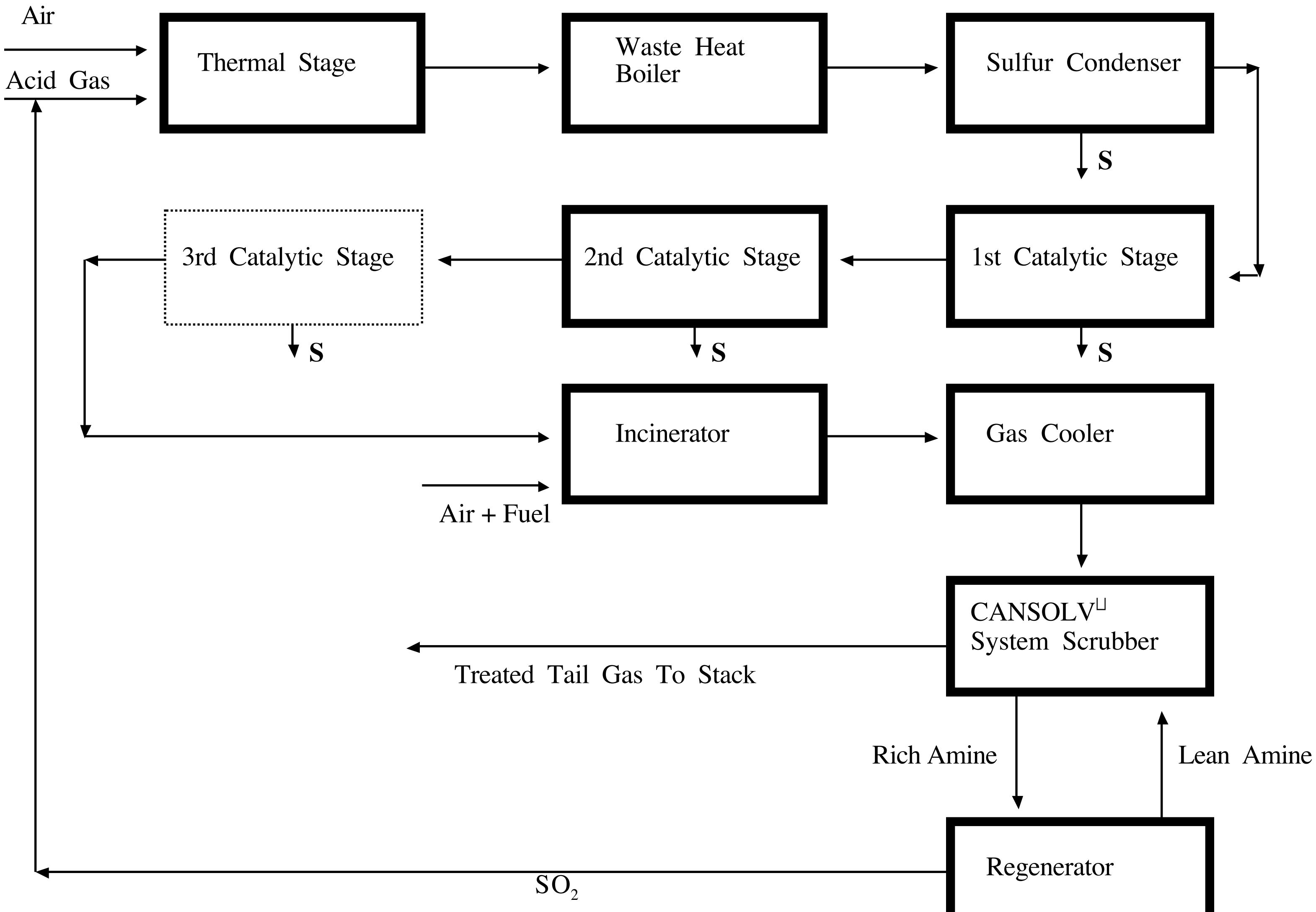


Figure 4. Claus Unit with CANSOLV® System TGTU

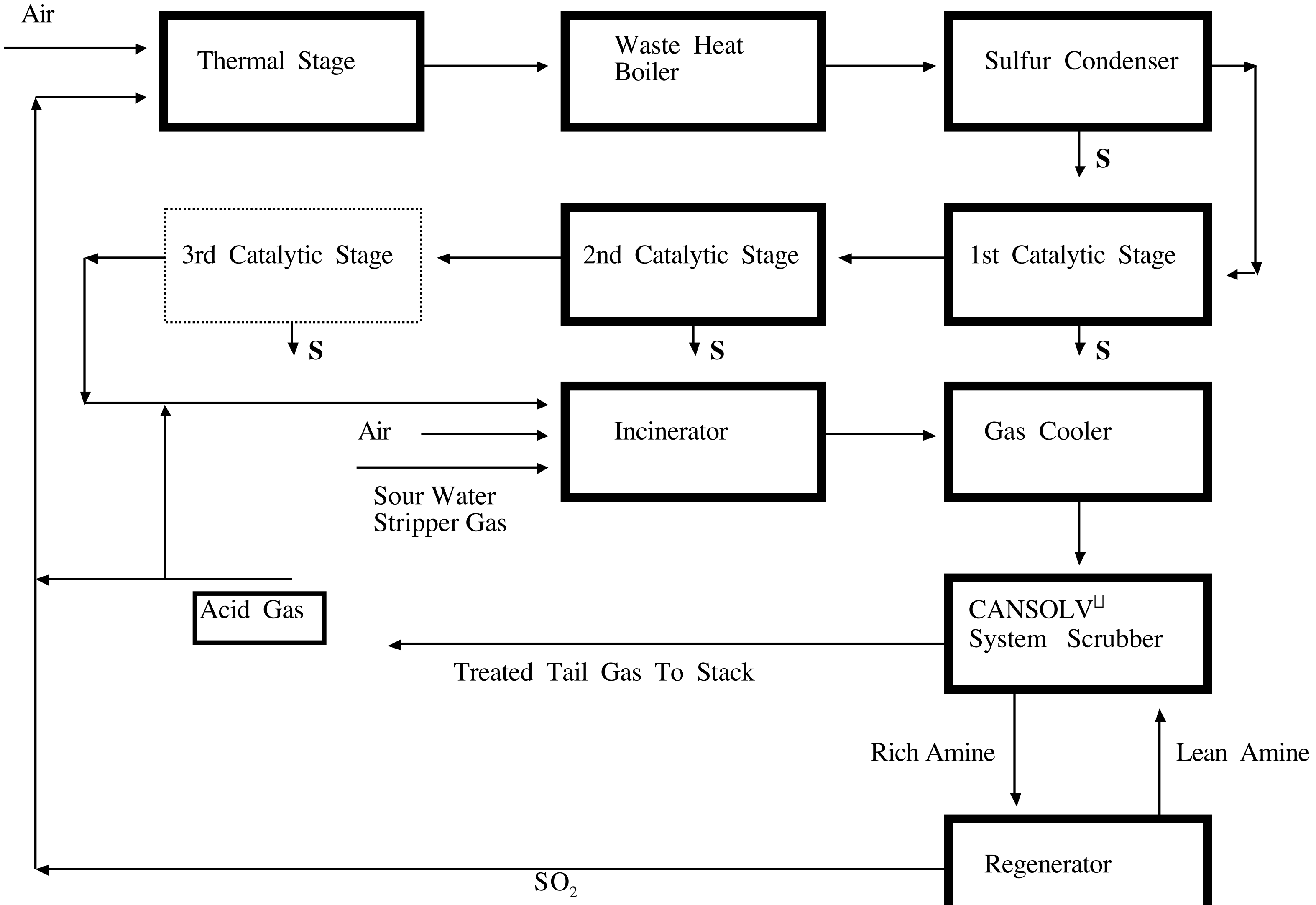


Figure 5. Claus Unit Debottlenecking with CANSOLV□ System Unit

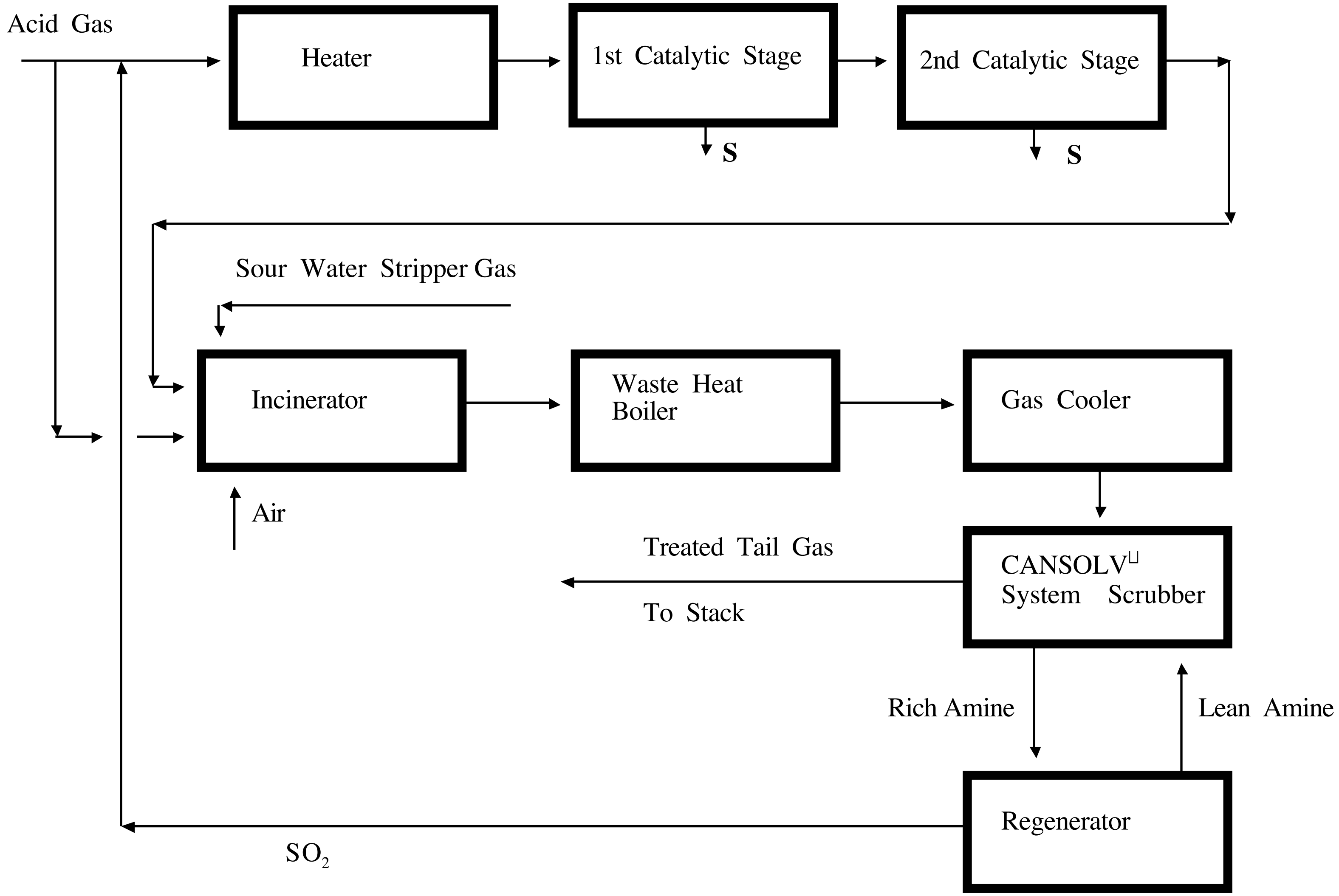


Figure 6. CANSOLV□ System SRU

FGD APPLICATIONS

One of the principal attributes of FBC is its ability to combust most solid fuels, including low reactivity materials. Its use can be most attractive when using low cost fuels such as high sulfur coal or petroleum coke.

Combustion of such high sulfur fuels requires that an efficient desulfurization method be utilized in order to meet the increasingly stringent regulatory emission limits. Traditional methods using limestone involve the introduction and later collection and disposal of large quantities of solids.

Disposal of these solid by-products can be problematic. In certain jurisdictions the solids may be considered hazardous waste, increasing disposal costs and reducing disposal options. In those areas where waste disposal is difficult, expensive or impossible but where an economic incentive to burn low cost high sulfur fuels exits, a regenerable SO_2 scrubbing technique would be advantageous, especially when this technique is cost competitive with conventional limestone scrubbing.

The CANSOLV® System FGD process is a regenerable SO_2 scrubbing process that utilizes a solvent specific for the capture of SO_2, and produces a pure SO_2 by-product. The solvent is not consumed in the process and does not contribute to the by-product stream. The cost of the scrubbing process is largely insensitive to SO_2 concentration in the flue gas or the sulfur content in the fuel. Thus the highest sulfur, lowest cost fuel can be consumed, maximizing the economic benefits.

With limestone desulfurization, FBC only converts an air emission problem into a waste solids disposal problem. As much as a half-ton of waste may be generated per ton of fuel burned or ten tons per hour for the equivalent of a 50 MW boiler.

The problem is becoming more severe as the higher sulfur removal efficiencies being mandated by current legislation are forcing boiler operators to increase the ratio of limestone to fuel in their feed. This leads to greater costs and difficulty in disposing of the solid by-products, as well as a decrease in boiler efficiency.

CANSOLV® SYSTEM FGD WITH FBC

The use of limestone with FBC's is a proven technology for controlling SO_2 emissions. Limestone is introduced in the furnace where it is calcined to lime. The lime reacts with the SO_2 released by the combustion of the fuel to form calcium sulfite and calcium sulfate. Excess limestone is added in order to increase overall SO_2 capture.

The calcium sulfite/sulfate by-product is collected with the unreacted quicklime, carbon and ash as a solid waste requiring disposal. The calcium sulfite/sulfate and residual lime can represent more than 80% of the overall solid waste collected depending on sulfur and ash content in the fuel and SO_2 removal efficiency in the FBC.

The CANSOLV$^{\circledR}$ System FGD process is an alternative to limestone FGD. Similar to conventional amine treating for H_2S and CO_2 scrubbing, it is a regenerable process which utilizes a water soluble amine that is highly selective to SO_2. The amine, once regenerated, is reused. The SO_2 recovered can be used as is, or converted to sulfur or sulfuric acid. CANSOLV□ System FGD is a robust and easy to operate process. It consumes no chemicals and, other than the ash collected, generates virtually no additional wastes. Total emissions, to air, water and landfill are minimized.

The CANSOLV$^{\circledR}$ System process is located after the air preheater of the FBC (figure 7). Baghouse filter capital and operating costs would be lowered due to the reduced by-product solids load. A prescrubber serves to quench the gas to scrubbing temperatures of between 120°F and 140°F, remove particulate matter and saturate the gas stream. The gas is then passed into the absorption section where it is contacted with the absorbent. SO_2 outlet concentrations are typically between 100 and 150 ppm, but the units can be designed for outlet concentrations as low as 10 ppm.

The gas is then reheated and sent to a traditional stack or, without reheat to a wet stack.

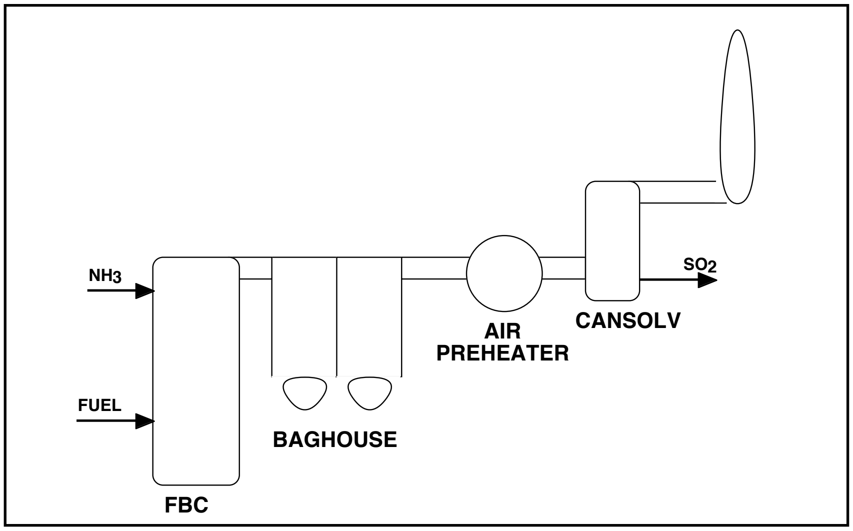


Figure 7, CANSOLV$^{\circledR}$ System FGD with FBC

The aqueous amine absorbent is regenerated by conventional steam stripping and recycled to the absorber. CANSOLV□ System FGD units can be operated at high turndown ratios. Start-up is simple and rapid. Absorbent circulation rates can be quickly changed to match changes in SO_2 inlet concentrations.

EMISSIONS

The CANSOLV$^{\circledR}$ System FGD process in conjunction with an FBC produces little waste (Figure 8). The only solid wastes would the ash recovered from the boiler. This ash having no calcium would be relatively neutral in pH. In addition, the quantity of ash generated would not be a function of the sulfur content of the fuel. Unlike with conventional limestone scrubbing, there would be no disincentive to burning the highest sulfur, lowest cost fuels possible. The economic advantages of burning high sulfur fuels could now be fully realized.

Because the process can reduce SO_2 flue gas concentrations to 10 ppmv or lower, the process will never be out of compliance with even the most stringent regulations that may be imposed in the future. Existing CANSOLV® System FGD units could easily and inexpensively be retrofitted to meet the most stringent requirements.

The capital cost of the CANSOLV® System FGD process is competitive with conventional wet limestone scrubbing, while the operating costs are significantly lower, especially for higher sulfur fuels.

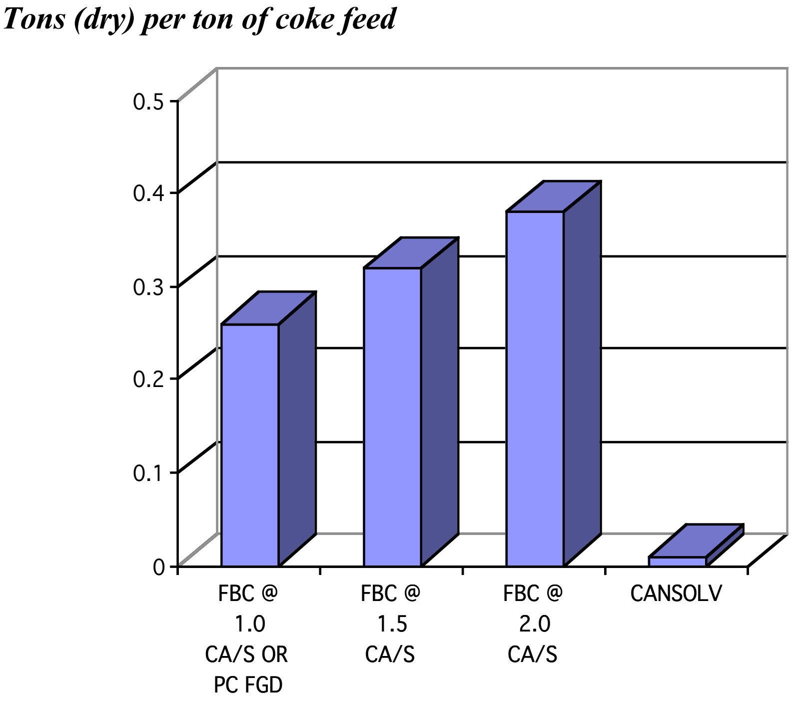


Figure 8. **Solid By-product from High Sulfur Petroleum Coke (7%S, 0.5% ash. 95% sulfur removal)**

NO_x emissions levels from FBC are in general lower than from pulverized coal boilers, so uncontrolled NO_x emission levels from FBC may meet the applicable requirements. If lower levels of NO_x are required, SNCR can be utilized. This is a relatively low cost control method giving NO_x reductions of 60% to 70%.

The degree of NO_x emission reductions with SNCR is typically limited by ammonia slip, which manifests itself as a plume. The first unit operation of the CANSOLV® System FGD process, the prescrubber water spray which serves to quench the gas, remove particulates and strong acid such as sulfuric, nitric and hydrochloric. The acidic nature of the prescrubber spray ensures that any residual ammonia (slip) is collected. Ammonia slip thus being controlled, the SNCR ammonia additions can be increased to achieve a higher level of NO_x reduction.

BY-PRODUCTS

The process produces a pure, water saturated SO_2 stream (97%+ SO_2, balance water), that may be utilized on site as such, converted to sulfuric acid or sulfur, or shipped offsite using the SO_2SAFE™ technology. There are numerous industrial uses for SO_2, currently supplied as liquid SO_2 or produced on site by burning sulfur.

SO_2SAFE™ SO_2 Storage Technology consists of shipping the SO_2 dissolved in the absorbent and regenerating the absorbent at the user's site on demand. In this manner, the costs of handling and storage and the hazards associated with liquid SO_2 are avoided. Transportation within a radius of up to 300 miles would be economical.

The water saturated pure SO_2 by-product is utilized extensively in the pulp and paper and corn wet milling industries. It can also be used to produce certain chemicals such as sodium sulfite, bisulfite and hydrosulfite. Liquid SO_2 which is utilized in these applications is priced at $275/ton CAD, fob Copper Cliff, Ontario. If desired, the sulfur dioxide can be converted to sulfur or sulfuric acid by conventional technology.

In the continental U.S. there are about 100 sulfuric acid plants. Sulfuric acid is utilized in a large number of industrial processes. The largest consumer is the phosphate fertilizer industry which is concentrated in Florida. Areas such as these where the value and demand for sulfuric acid is highest, would provide attractive returns on the byproduct.

Every petroleum refinery has a Claus sulfur unit on site. It is relatively simple to feed the SO_2 directly into the Claus unit for conversion to elemental sulfur. The addition of pure SO_2 to the Claus unit feed would result in an increase in the sulfur production capacity of the unit. Refineries also are the source of petroleum coke. Ideally a refinery supplying petroleum coke to a nearby FBC operator would accept the by-product SO_2 and convert it to elemental sulfur.

SULFITE PULP MILL APPLICATIONS

Ammonia based sulfite pulp mills utilize ammonium bisulfite plus dissolved sulfur dioxide as the chemical reagent to delignify wood in order to produce a cellulose pulp. Unreacted SO_2 from the cook is recovered by scrubbing the blowpit gases with aqueous ammonia. The sulfur and energy contents of the lignosulfonate present in the spent sulfite liquor (SSL) are recovered by burning the SSL in a recovery boiler. The flue gas is also scrubbed with aqueous ammonia to recover the SO_2. Makeup SO_2 is provided by a sulfur burner and/or liquid SO_2.

Deficiencies of this mill flowsheet include significant SO_2 and/or ammonia emissions, chemical imbalance in the mill and the expense of SO_2 makeup, all of which complicate mill operation and raise operating and capital costs. SO_2 recovery and recycle with the CANSOLV® System SO_2 scrubbing process, rather than with ammonia, reduces emissions, makeup requirements and total cost. Recovery and recycle of the SO_2 as a pure gas, rather than as ammonium bisulfite, is a further major advantage of using the CANSOLV® System process: the chemical imbalance is eliminated and the cooking liquor preparation and SO_2 recovery operations are decoupled. This decoupling removes severe operating constraints from the mill operation. Full application of CANSOLV® System SO_2 scrubbing has the potential to yield a major increase in mill operating margin, while improving environmental performance and safety.

DEFICIENCIES OF CONVENTIONAL FLOWSHEET

Ammonia based sulfite pulping as currently practiced has a number of deficiencies which detract from the economics, environmental impact and operability of the process. Reduction in the impact of these factors could enhance the competitiveness of sulfite pulping, which otherwise is a very desirable process. The deficiencies of the conventional process are discussed below.

Chemical Imbalance

The most serious drawback to the conventional sulfite mill flowsheet is the fact that while the cooking liquor consumes both combined and free SO_2 , the recovery operations yield mainly combined SO_2 . This inevitably leads to chemical imbalance: the quantity of combined sulfur dioxide recovered is greater that required in cooking liquor preparation. By mass balance, the excess must be either emitted to air or water, or transferred off site. This loss must then be balanced by fresh SO_2 makeup from the sulfur burner or purchased SO_2 . The operating, maintenance and raw material cost of a sulfur burner is a considerable cost penalty resulting from this deficiency. In addition, many mills supplement their SO_2 requirements with purchased liquid SO_2 to adjust free SO_2 to levels not attainable with the sulfur burner. The difficulties of coping with the chemical imbalance constraint are exacerbated by the fact that operation of the recovery boiler is coupled to that of the acid plant (cooking liquor preparation area). Unscheduled recovery boiler outages, the production of pulp grades requiring high free SO_2 , changes from a high total SO_2 grade to one requiring less combined SO_2 all cause changes in the inventory of SSL and weak acid (ammonium bisulfite) and create scheduling and inventory management difficulties, adding to plant operating complexity.

Feed Chemical Usage

The recovery of sulfur fed to the digesters is typically about 80%. About 2% of the sulfur leaves with the washed pulp and essentially all of the rest is due to the inefficiency of the recovery system. While some of the losses will be difficult to control, being in the form of dilute equipment wash waters for example, a significant reduction in losses is possible by application of better technology.

The ammonia is not recycled at all, since it is burned in the recovery boiler. However, excess ammonia consumption can be caused by air oxidation of sulfite to sulfate in the recovery process. Since ammonium sulfate is not active in the pulping process, the contained ammonia is wasted.

If caustic is used for the final cleanup of gas streams prior to venting to atmosphere, it is lost to waste water on a once through basis, as is the captured SO_2.

Energy Consumption

The use of multiple stages of absorption in the SO_2 scrubbing system leads to an unnecessarily high gas side pressure drop, requiring powerful fans. If candle filters are used on the recovery boiler to control ammonium bisulfite aerosol emissions, these add to the pressure drop in the flue gas cleaning system. Also, in cases where the cooling water temperature is high, chillers may be required to cool the gas stream in order to get acceptable SO_2 removal.

Capital Cost

The complexity of the SO_2 recovery system, with multiple absorbers, storage tanks, pumps, candle filters, chillers etc. leads to a high capital and maintenance costs and large space requirements for the SO_2 recovery system.

Environmental Compliance

Meeting stringent emission levels with ammonia scrubbing requires operating the recovery system at the limit of its capabilities. With ammonia scrubbing, a delicate compromise has to be struck between high SO_2 removal and low ammonia or ammonium bisulfite emissions: it is very difficult to obtain both simultaneously. This is the justification for final polishing of some streams with caustic prior to venting to atmosphere. Disposal of the sodium sulfite produced is usually to the waste water treatment system, adding chemical oxygen demand that must be treated. If candle filters are used, the water washes required to remove the captured ammonium bisulfite can contribute to ammonia discharged to receiving streams.

If all the lignosulfonate cannot be burned in the recovery boiler due to chemical imbalance, disposal of the material can be problematic. While there are established uses for lignosulfonate as a cement additive for example, the market is not very large. Use of lignosulfonate as a road dust suppressant is possible, but it has raised questions of environmental impact.

Fugitive emissions from various sources such as pulp washers, sulfur burner etc. can also impact on the emissions and particularly the level of ambient SO_2 within the plant itself.

CANSOLV SYSTEM TECHNOLOGY IN SULFITE PULPING

All of the deficiencies of current sulfite pulping technology can be reduced or eliminated by the use of CANSOLV System SO_2 recovery and recycle instead of ammonia or magnesium hydroxide scrubbing. The most important benefits result from the recovery of the sulfur as pure sulfur dioxide:

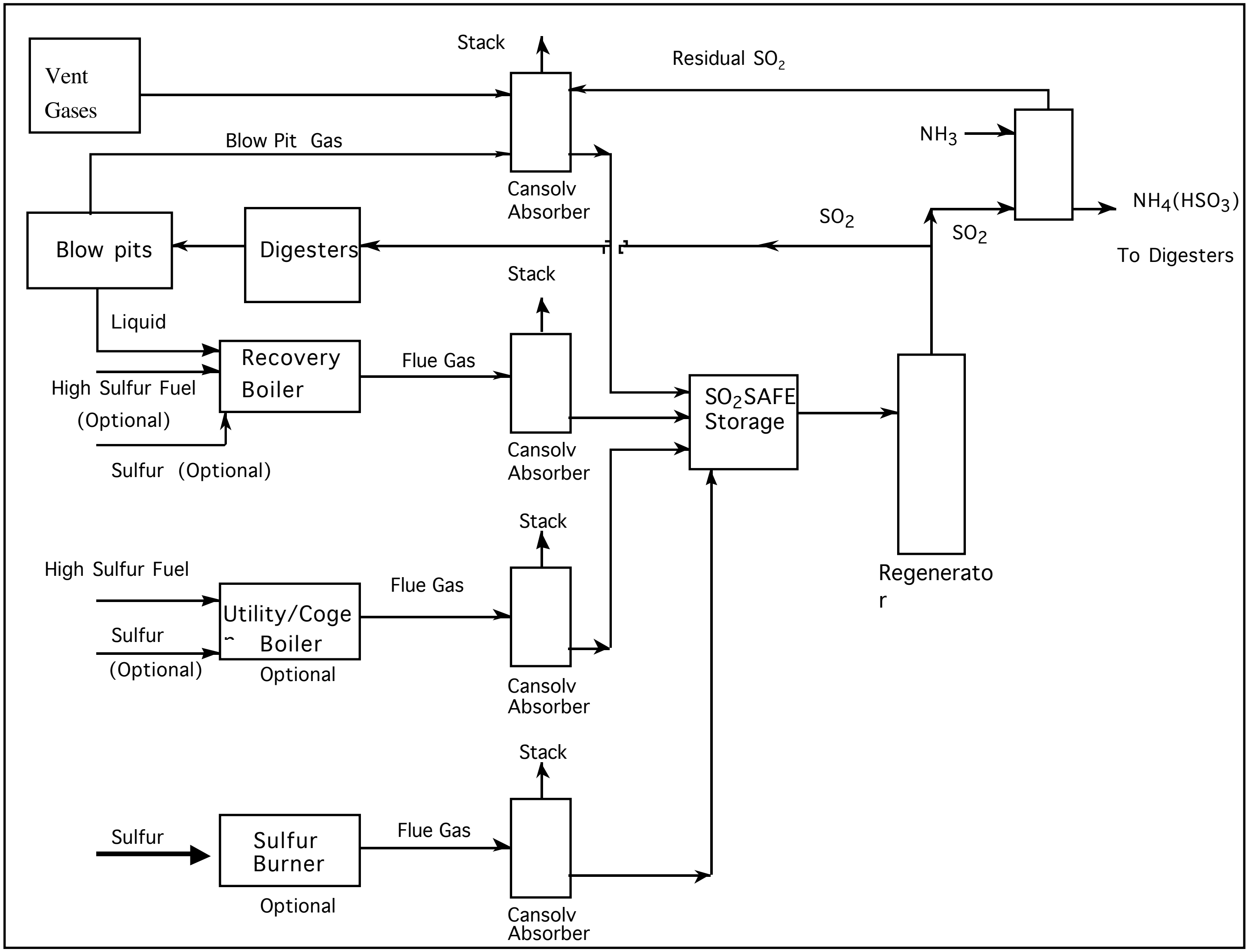
1. The chemical imbalance between combined and free SO_2 is eliminated.
2. The recovery and cooking liquor preparation operations are decoupled if provision is made for storage of recovered SO_2 in SO_2SAFE solution form, or as liquid SO_2 under pressure, if the safety issues are properly addressed.

Removal of these two constraints simplifies plant operation, reduces equipment complexity, allows maximum use of free SO_2 where this improves quality or reduces cooking time and allows total burning of SSL in the recovery boiler. The very high recovery efficiency of the CANSOLV System SO_2 scrubbing process maximizes sulfur recovery and minimizes emissions, both to air and water.

The Cansolv Absorbent DS actually inhibits oxidation of SO_2 to SO_3, the amount of sulfur dioxide is increased due to reduced losses to sulfate. Also, since the absorbent is totally non-volatile, no amine bisulfite is emitted, avoiding the use of candle filters. Since the absorption of SO_2 can be performed in a single vessel, equipment complexity, fan power, space and maintenance can all be reduced compared to current technology.

Beyond the obvious application of CANSOLV System technology to simply replace the conventional SO_2 absorption system with a more efficient and less costly technology, new possibilities for further simplification and cost reduction become possible. Firstly, if the mill operates a fossil fuel fired boiler, replacement of low sulfur emission compliant fuel by a cheaper high sulfur product such as petroleum coke, liquid fuel or coal becomes an option. The payback for the investment in CANSOLV System flue gas desulfurization is usually less than 2 years, particularly if a common regenerator is used for the absorbers on all the different gas streams. The sulfur dioxide recovered from the high sulfur fuel can be used to reduce the sulfur burner duty, reducing sulfur purchase requirements. In effect, the sulfur content in high sulfur fuel has a negative cost. Considering the reduced sulfur makeup requirement resulting from the higher recovery efficiency of CANSOLV System scrubbing, the extra sulfur input from the high sulfur fuel may be sufficient to shut down the sulfur burner. If required, elemental sulfur added to the boiler or the recovery boiler could make up any shortfall. Elimination of the sulfur burner (or purchased SO_2) is a desirable cost reduction and operating simplification step. The application of CANSOLV® System technology to a sulfite mill is shown in Figure 9.

FIGURE 9. CANSOLV SYSTEM APPLICATIONS



THE SO_2SAFE□ TECHNOLOGY FOR STORAGE AND TRANSPORT OF SO_2

Sulfur dioxide, SO_2, is a widely used chemical in industries such as wood pulping and bleaching, corn wet milling, water treatment and the production of sulfuric acid(1). It is a colorless, non-inflammable toxic gas, with a boiling point of -10.0° C at atmospheric pressure of 1013 mbar. Currently, the normal method of storing and transporting bulk quantities of SO_2 is as a liquefied gas in suitable pressure vessels. This presents a serious risk due to the possibility of a catastrophic release of SO_2 in the case of storage vessel or fitting failure. In such a case, while the probability of occurrence is low, the effects are extremely serious. Gaseous SO_2 is very toxic, showing adverse health effects at concentrations as low as 3 parts per million. Since SO_2 gas is heavier than air, any release will tend to stay at ground level, maximizing human exposure.

The majority of SO_2 for captive use or for merchant sale is produced either by sulfur burning or by capture from metallurgical gas streams. Both processes are rather expensive and the latter usually requires transportation over long distances to the consuming site. Since transportation routes often pass through metropolitan centers, large segments of the population are exposed to risk in case of a spill. On the other hand, SO_2 produced by burning sulfur containing fuel is either emitted as a pollutant or turned into low-value gypsum by limestone scrubbing. The CANSOLV□ System SO_2 scrubbing technology, when combined with the SO_2SAFE□ SO_2 Storage and Transportation process, addresses both issues by enabling economical, safe and efficient pollution control and SO_2 recovery and recycle.

CANSOLV□ SYSTEM TECHNOLOGY

The patented CANSOLV□ System SO_2 scrubbing process has been described in detail elsewhere[2,3,4,5]. It utilizes an aqueous amine absorbent that is highly selective for removal of SO_2 from various gas streams such as flue gas. The process flowsheet is very similar to the well known alkanolamine process for removal of H_2S and CO_2 from natural gas and refinery gas streams. The essence of the process is absorption of SO_2 into the solvent in an absorber and recovery by stream stripping in a regenerator. The byproduct SO_2 is recovered as a pure, water saturated stream and the regenerated solvent is recycled to the absorber. Removal of SO_2 from the feed gas to <10 ppmv is economically viable.

A patent application has been filed for the SO_2SAFE□ SO_2 storage technology, which is an extension of the CANSOLV□ System scrubbing process. It consists of storing and shipping the SO_2 dissolved in the absorbent and regenerating the absorbent at the user's site on demand. The same or a different absorbent may be used for scrubbing and storage, depending on the specific requirements of a particular application. A 25 - 30% solution of the amine in water is utilized in the process. These absorbents provide significant advantages:

- since the amine absorbent is always present in the process as a salt, it is totally non-volatile and equilibrium vapor phase losses of solvent to the treated gas are zero
- the product SO_2 is pure with no amine contamination

- a high usable loading of SO_2 in the rich solvent
- up to about 1 equivalent of strong acid anions per mole of amine, i.e. heat stable amine salts (HSAS), may be present in the absorbent without decreasing the normal scrubbing capacity by the sorbing nitrogen
- HSAS are removed easily and efficiently by a patented electrodialysis process
- inhibition of SO_2 oxidation to sulfate by oxygen
- high thermal and chemical stability

For economy in transportation cost, the rich amine produced by scrubbing a feed such as flue gas may be further loaded with SO_2 by saturating it to an SO_2 vapor pressure of close to one atmosphere with the pure SO_2 produced by regenerating a part of the rich amine from the scrubber. In this manner, transport of SO_2 in SO_2SAFE Solvent within a radius of some 500 km is economically competitive. A simplified process flow diagram for the production of rich SO_2SAFE Solvent is shown in Figure 10.

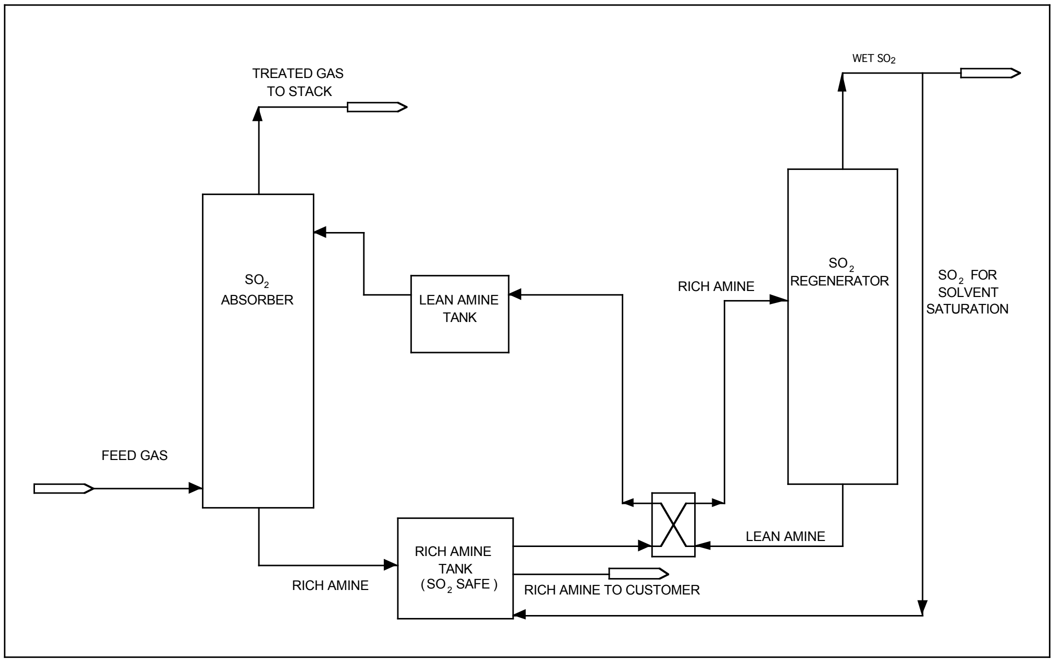


Figure 10. SO_2SAFE SO_2 Storage Technology Flow Sheet

LOSS OF CONTAINMENT COMPARISON

The vapor pressure of liquid SO_2 at temperatures that may occur in normal storage and transport operations can be up to 8 bar. Thus, in case of a leak in or rupture of the pressure vessel used to store or transport liquid SO_2, particularly if the damage occurs towards the bottom of the vessel, large quantities of SO_2 can be released from the tank very rapidly. Since the SO_2 at ambient temperature is above its boiling point, any liquid SO_2 released to atmosphere will vaporize rapidly, creating a vapor cloud of toxic gas that tends to stay at ground level, being heavier than air. Prevailing winds can then disperse the vapors, creating conditions hazardous to health or even lethal conditions over a large area. Concentrations of 5–10 ppmv of SO_2 in air will lead to irritation of the respiratory tract and concentrations above 400-500 ppmv, even for a few minutes, are dangerous to life. Areas adjacent to industrial SO_2 storage sites and railroads or roads used for the transport of SO_2 are thus at risk in the event of such a release.

The release of SO_2 from solution in the SO_2SAFE™ SO_2 solvent is much less and slower. While the initial partial pressure of SO_2 over the solvent is up to 1 atmosphere, evolution of the gas from solution is inhibited by a) formation of a liquid side SO_2 depleted boundary layer which decreases the mass transfer rate, and b) cooling of the liquid by the heat of vaporization of the SO_2 which i) decreases the equilibrium vapor pressure and ii) increases liquid viscosity, making the boundary layer thicker.

The impacts from the loss of containment of a storage tanks containing SO_2 rich solvent and liquid SO_2 are compared in Table 1. An average SO_2 partial pressure of 0.0188 bar absolute over the rich SO_2SAFE™ SO_2 Storage Technology solvent was assumed for dispersion modeling. The impacts from the loss of containment of storage tanks containing SO_2 rich solvent and liquid SO_2 are compared in Table 1.

Table 1. Loss of Containment Comparison

	Liquefied Gas SO_2	SO_2SAFE™ SO_2 Rich Solvent
Inventory, kg	60,000 kg	323,000 kg
Available SO_2, kg	60,000	60,000
Temperature, °C	35	35
Vapor pressure, bar(a)	7.48	0.0188
Dike area, m^2	100	100
Hole size, mm	25.4	N.A. Storage tank dike area covered with SO_2 Rich Solvent
Wind condition and Stability, m/s	5D	5D
Emission rate, kg/s	12.9	0.02
Distance to 15 ppm, m*	2,700	60
Distance to 3 ppm, m*	7,300	140

*Dispersion calculations done with Phast Version 5.01 software

The distances to similar toxic concentrations of SO_2 are much shorter for a loss of containment of SO_2 rich solvent than for liquefied gas SO_2 : 60 m vs. 2,700 m for 15 ppm and 140 m vs. 7,300 m for 3 ppm, respectively. The loss of containment consequences for the SO_2 rich solvent are thus almost three orders of magnitude less than for liquid SO_2. In an urban SO_2 storage facility, liquid SO_2 storage has the potential to affect a large population, while the SO_2 Rich Solvent impacts only the immediate vicinity of the site. The SO_2SAFE® SO_2 rich Solvent is by its nature intrinsically safer.

PILOT TESTING

FLUE GAS

The generic CANSOLV® System scrubbing process was successfully piloted during a 9-month trial in 1991 at the Suncor Oil Sands plant in Fort McMurray, Alberta, in Flue Gas Desulfurization service. Removal rates in excess of 99% were consistently demonstrated. The absorbent was found to be very stable and capable of effecting high removal rates at low liquid to gas ratios. The unit operated from February 28 to November 28, 1991, scrubbing 3600 scfm of flue gas from the site's utility boilers. The fuel in the boilers was petroleum coke produced in the tar upgrading process and had a sulfur content of 7%. On many occasions in the course of performing the statistically designed experiments, SO_2 in the treated gas was <15 ppmv. Results of the test program exceeded expectations and demonstrated the CANSOLV® System process to be robust, effective and easy to operate.

METALLURGICAL GAS AND PULP & PAPER

CTI designed and constructed a highly versatile mobile pilot unit, for the purpose of demonstrating the CANSOLV® System Process technology, and obtaining fundamental site specific scale up data. The pilot plant unit is mounted on a 16-foot trailer. It consists of a 13 foot, 4" ID insulated absorption tower with structured packing mass transfer elements and an 18 foot, 4" ID insulated regeneration tower, also containing structured packing. The regenerator has a steam heated reboiler, and an overhead condenser and condensate accumulator. The associated peripheral equipment consist of three process pumps, a plate and frame heat exchanger, a vacuum pump, a feed gas blower, two absorbent particulate filters and an activated carbon filter. The CANSOLV® System mobile pilot plant also includes an absorbent heat stable salt removal unit based on the principle of electrodialysis.

Feed gas containing SO_2 enters the absorption tower, where the Cansolv Absorbent DS solvent picks up the sulfur dioxide, thus cleaning the effluent gas down to a few ppm SO_2 . The solvent is then regenerated in the regeneration tower and returned to the absorption tower in a cyclical mode to pick up additional SO_2. Instrumentation for monitoring process parameters consists of local indicators. Gas SO_2 concentration is monitored with a non-dispersive infrared process analyzer.

The unit was commissioned and run in at a metallurgical acid plant. Both acid plant feed and tail gases, at 7.5% and 1500 – 2000 ppm SO_2 respectively, were treated. The treated gas in both cases had less than 50 ppm SO_2 and the unit performed satisfactorily in all respects. It was then moved to the pulp mill for the trials.

The results obtained with this small scale pilot unit were consistent with data available from previous large scale (6,000 Nm^3/h gas flow) testing and from a rigorous thermodynamic process model on the Aspen Plus® platform[1].

GAS STREAM CONDITIONS

Field tests were run at an ammonia based sulfite mill on both blowpit gas and recovery boiler flue gas. The two streams are quite different, as can be seen from Table 1.

TABLE 1

DESCRIPTION OF GAS STREAMS

Parameter	Blowpit Gas	Recovery Boiler Flue Gas
SO_2	1 to25+%	3200 ppmv
Pressure	± 1 bar	± 1 bar
Temperature	40°C	35°C
Water content	Saturated	Saturated
Organics	Present *	Absent

* The organic content was not quantified. Compounds identified by GC/MS included methanol, acetone, furfural and p-cymene .

The blowpit gas presented the greater challenge due to the highly cyclical SO_2 concentration resulting from the batch nature of the digester operation. When a cook was blown into the blowpit, a large fraction of the unreacted free SO_2 flashed off with the steam generated from the superheated cooking liquor. This gas stream also contained organics originating from the wood resin and from the reaction products of the cooking process. Prior to being treated for SO_2 removal, the blowpit gas is cooled in direct and indirect coolers. Between blows, a vacuum relief valve admits air into the blowpit.

The recovery boiler flue gas results from the excess air combustion of SSL concentrated to a solids level of about 55-60% and therefore has a high water content. Prior to SO_2 removal, it is cooled and saturated in a direct cooler.

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[1] Aspen Plus is a registered trademark of Aspen Technology, Inc.

TEST RESULTS

Very high removal of SO_2 was obtained from both gases. The treated recovery boiler flue gas had SO_2 concentrations consistently below 30 ppmv at steady state operation. Due to the cyclicality of SO_2 concentration in the blow pit gas, the absorbent flow rate was increased for the duration of the SO_2 peak during a digester blow. This minimized the average absorbent flow rate. Treated blowpit gas contained less than 45 ppm SO_2, proving the load following capability of the CANSOLV® System process.

The water saturated SO_2 byproduct from blowpit gas contained only very minor quantities of organics, demonstrating the capability of the process to reject these and prevent their accumulation in the overall mill process. The SO_2 produced was greater than about 95% purity, with the balance being essentially water. In particular, no Cansolv Absorbent DS could be detected in the byproduct SO_2.

The total on-stream time of the test was about 160 hours. No adverse effects on the absorbent or treating performance were noted.

CONCLUSIONS

The CANSOLV® System Process has introduced a new paradigm for SO_2 recovery and recycle, by simultaneously reducing toxic emissions and cost.

The field testing of the CANSOLV® System SO_2 scrubbing process demonstrated the ability to recover and recycle SO_2 from metallurgical gas and in a sulfite pulp mill, as free SO_2. Extremely low levels of SO_2 emissions are achievable, while reducing plant complexity and costs. The decoupling of recovery and pulping operations will reduce operating complexity and constraints.

The excellent results obtained on the four different gas streams tested with the unit support the general applicability of the technology to other uses such as in smelters, acid plants, flue gas desulfurization, refineries and sulfur recovery units. A larger test unit is under construction for demonstrations of the process, starting with a smelter application in mid 1999.