

RECOVERY AND RECYCLING OF SO₂ IN A SULFITE PULP MILL

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ABSTRACT

Previous papers on CANSOLV[®] System technology described applications in smelters, acid plants, refineries and sulfur recovery units^{1,2,3}. This paper discusses integration of the process to sulfite pulp mills. 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 SO₂ from the cook is recovered by scrubbing the blowpit gases with aqueous ammonia. The sulfur and energy content 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 SO₂. Makeup SO₂ is provided by a sulfur burner and/or liquid SO₂.

Deficiencies of this mill flowsheet include significant SO₂ and/or ammonia emissions, chemical imbalance in the mill and the expense of SO₂ makeup, all of which complicate mill operation and raise operating and capital costs. SO₂ recovery and recycle with the CANSOLV[®] System SO₂ scrubbing process, rather than with ammonia, reduces emissions, makeup requirements and total cost. Recovery and recycle of the SO₂ 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 SO₂ recovery operations are decoupled. This decoupling removes severe operating constraints from the mill operation. Full application of CANSOLV[®] System SO₂ scrubbing has the potential to yield a major increase in mill operating margin, while improving environmental performance and safety.

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INTRODUCTION

Cellulose pulp of high purity and brightness is produced from wood by chemically dissolving the lignin content, thereby freeing the cellulose fibers from the matrix. The sulfite pulping processes is one of the oldest means of performing this operation and was the predominant commercial process until about 1937, when the sulfate or kraft process superseded it in importance.

The sulfite process, also called the acid sulfite process, uses bisulfite salt ("combined SO_2 ") plus physically dissolved SO_2 ("free SO_2 ") as the active chemicals in the pulping liquor. Various bases are used to form the bisulfite salt: ammonia, caustic, magnesium hydroxide and lime. Thus sulfite mills are classified according to the base used as ammonia, sodium, magnesium or calcium based mills. Recovery of cooking liquor chemicals is not practical for calcium based mills and is difficult for the sodium based process. Firing of Mg-based spent sulfite liquor (SSL) in a recovery boiler produces a flue gas containing both SO_2 and MgO. The magnesium oxide is recovered in cyclones, slaked to magnesium hydroxide and then used to scrub the SO_2 from the flue gas, forming magnesium sulfite. The MgSO_3 plus added SO_2 is then used to prepare cooking liquor again. In ammonia based mills, the ammonia is burned in the recovery boiler and fresh NH_3 is used for scrubbing the flue gas SO_2 .

Most pulp mills operate batch digesters to perform the delignification operation. The digesters are operated at elevated temperature and pressure to minimize batch times. At the end of the cook, the digester is partially depressurized ("top relief"). The top relief gas which contains SO_2 is directed to the digester acid accumulator tank. The batch is dumped into a blowpit for separation of the spend cooking liquor (SSL) from the pulp. The unreacted SO_2 flashes off in the blowpit, necessitating scrubbing of the blowpit gas to recover the SO_2 and prevent emissions. Being a batch process, the blowpit gas has a highly variable SO_2 content which may peak at 40-50% and bottom out at a few thousand ppm.

While NH_3 and Mg based processes each have their advantages, both suffer from two major drawbacks:

- The SO_2 recovery process yields only combined SO_2 (except for top relief gas which has free SO_2), necessitating makeup of pure SO_2 either from a sulfur burner or by costly purchased liquid SO_2 . Liquid SO_2 presents a significant potential hazard in case of a worst case release scenario⁴.
- More combined SO_2 tends to be produced by recovery operations than can be utilized in the preparation of fresh cooking liquor, creating a "chemical imbalance" in the mill which can only be resolved by reducing SSL feed to the recovery boiler or finding other uses for the combined SO_2 . Both options have negative impacts.

Ammonia scrubbing may also give rise to emissions of ammonia or ammonium bisulfite aerosol, further complicating environmental compliance.

The cost of cooking chemical recovery is one major reason for the decline of sulfite pulping, in spite of the excellent quality of pulp produced. A reduction of recovery and recycling costs would improve the competitiveness of this process.

CANSOLV[®] SYSTEM SO₂ PROCESS TECHNOLOGY

The CANSOLV[®] System process is a regenerable SO₂ scrubbing technology that utilizes a proprietary amine solution in a cyclic absorption-regeneration flowsheet shown in Figure 1. The captured SO₂ is regenerated from the solvent as a high purity water saturated SO₂ gas. The flowsheet is essentially identical to the well known amine treating process for removal of H₂S and CO₂ from natural gas and refinery streams, so conventional engineering methods and equipment are used in the CANSOLV[®] System process. The patented Cansolv Absorbent DS enables highly selective and efficient capture of SO₂ while rejecting other components of the feed gas such as CO₂ and organic materials. Other advantages of Cansolv Absorbent DS are:

- The amine is highly stable and totally non-volatile, so contamination of the product SO₂ and the treated gas is avoided and amine makeup is minimized.
- Oxygen does not degrade the solvent, so no inhibitors are needed.
- An optimal balance of absorption and desorption tendencies enables SO₂ removal to <100 ppm at low energy consumption.
- SO₂ removal to <10 ppm can be achieved at modest extra cost, if desired.
- Strong acid contaminants do not interfere with SO₂ removal. The level of strong acid amine salts is controlled by a patented electro dialysis process that requires no feed chemicals and produces minimum effluents.
- Good health, safety and environmental properties.

The overall characteristics of the CANSOLV[®] System SO₂ scrubbing process are very attractive:

- Low cost sensitivity to SO₂ concentration in the feed gas, enabling economical treatment of high strength streams.
- Extremely high SO₂ removal capability, meeting the most stringent regulations.
- Minimum effluents.
- Low rate of SO₂ oxidation to sulfate.
- Very competitive economics.
- Small space requirements.

A related process, the SO₂SAFE[®] SO₂ storage technology, can be used for the safer storage and transport of SO₂ compared to liquid SO₂. The SO₂ is stored in solution with a low vapor pressure, so that in the event of a tank rupture or spill, the vapor plume is reduced by about 3 orders of magnitude compared to that from the release of an equivalent quantity of liquid SO₂.

APPLICATION TO SULFITE PULPING

CONVENTIONAL SULFITE PULPING

The principal chemical operations in ammonia based sulfite pulping are:

- Preparation of cooking acid by absorption of SO_2 into aqueous ammonia or ammonium sulfite to the required combined SO_2 level and fortification with gaseous SO_2 from a sulfur burner or liquid SO_2 source to obtain the desired level of free SO_2 .
- Cooking of wood chips at elevated pressure and temperature to effect delignification of the wood. The lignosulfonate produced dissolves in the cooking liquor.
- Release of the cook into the blowpit, where much of the unreacted SO_2 flashes off from the cooking liquor. The cellulose fibers are filtered off from the SSL. The blowpit flash gas is cooled and then scrubbed in a series of absorbers to produce ammonium sulfite/bisulfite. The blowpit gas may be scrubbed with caustic prior to release to atmosphere in order to control emission of SO_2 to the permitted level. Miscellaneous vent gases from storage tanks, evaporators, pulp washers etc. are also cleaned in the caustic scrubber.
- The SSL is burned, after concentration in evaporators, in the recovery boiler. The flue gas is scrubbed with aqueous ammonia to recover the SO_2 . Candle filters are required to control emission of ammonium bisulfite aerosol.
- The sulfur burner is used to generate the free SO_2 needed in the cooking liquor. The gas from the burner is cooled, compressed and absorbed into cool water under pressure and injected into the high pressure acid tank to complete the cooking liquor preparation. Elevated pressure is needed to obtain the desired concentration of dissolved SO_2 .

Most mills also use SO_2 in the pulp bleaching area, for generation of chlorine dioxide, and decomposing residual hydrogen peroxide bleach.

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 in the quantity of combined sulfur dioxide recovered versus 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, 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 SO₂ 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 SO₂ 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 SO₂ 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:

- The chemical imbalance between combined and free SO₂ is eliminated.
- The recovery and cooking liquor preparation operations are decoupled if provision is made for storage of recovered SO₂ in SO₂SAFE[®] solution form, or as liquid SO₂ 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 SO₂ 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 SO₂ scrubbing process maximizes sulfur recovery and minimizes emissions, both to air and water.

The Cansolv Absorbent DS actually inhibits oxidation of SO₂ to SO₃, reducing the amount of ammonia required for neutralizing sulfate. Also, since the absorbent is totally non-volatile, no amine bisulfite is emitted, avoiding the use of candle filters. Since the absorption of SO₂ 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 SO₂ 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 SO₂) is a desirable cost reduction and operating simplification step.

The application of CANSOLV[®] System technology to a sulfite mill is shown in Figure 2.

PILOT TESTING

PILOT UNIT DESCRIPTION

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 electro dialysis.

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 SO₂ respectively, were treated. The treated gas in both cases had less than 50 ppm SO₂ and the unit performed satisfactorily in all respects. It was then moved to the pulp mill for the trials.

Feed gas containing SO₂ 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 SO₂. The solvent is then regenerated in the regeneration tower and returned to the absorption tower in a cyclical mode to pick up additional SO₂. Instrumentation for monitoring process parameters consists of local indicators. Gas SO₂ concentration is monitored with a nondispersive infrared process analyzer.

The results obtained with this small scale pilot unit were consistent with data available from previous large scale (6,000 Nm³/h gas flow) testing and from a rigorous thermodynamic process model on the Aspen Plus[®] platform¹.

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 to 25+%	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 SO₂ 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 SO₂ 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 SO₂ 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 SO₂ removal, it is cooled and saturated in a direct cooler.

TEST RESULTS

Very high removal of SO₂ was obtained from both gases. The treated recovery boiler flue gas had SO₂ concentrations consistently below 30 ppmv at steady state operation. Due to the cyclicity of SO₂ concentration in the blow pit gas, the absorbent flow rate

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

was increased for the duration of the SO₂ peak during a digester blow. This minimized the average absorbent flow rate. Treated blowpit gas contained less than 45 ppm SO₂, proving the load following capability of the CANSOLV[®] System process.

The water saturated SO₂ 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 SO₂ 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 SO₂.

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 field testing of the CANSOLV[®] System SO₂ scrubbing process demonstrated the ability to recover and recycle SO₂ in a sulfite pulp mill as free SO₂. Extremely low levels of SO₂ emissions are achievable, while reducing plant complexity and costs. The decoupling of recovery and pulping operations will reduce operating complexity and constraints.

The application of CANSOLV[®] System SO₂ scrubbing to sulfite pulping is expected to provide a major improvement to the economics and environmental impact of this type of mill.

The excellent results obtained on the 4 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 early 1999.

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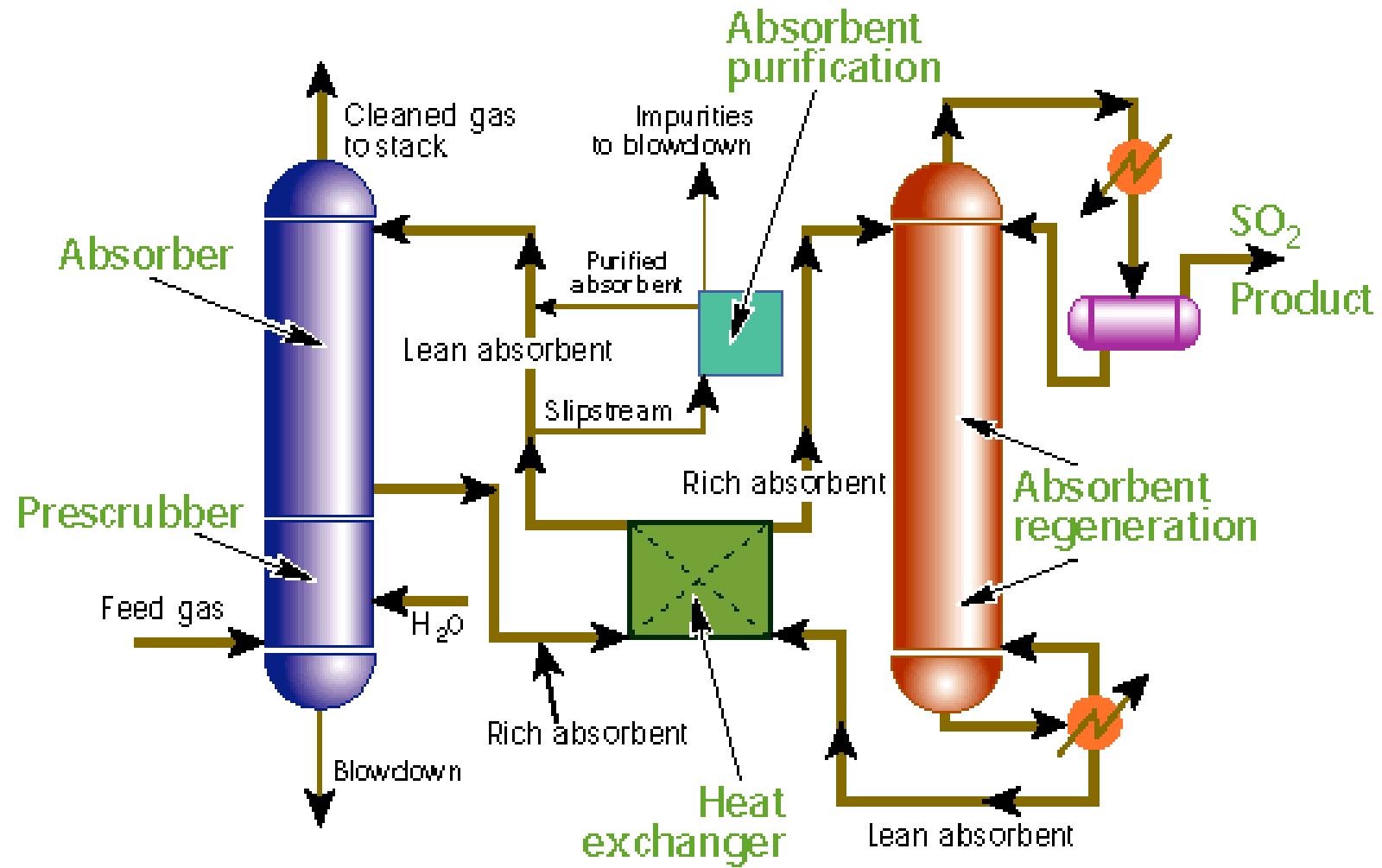
FIGURE 1. CANSOLV[®] SYSTEM PROCESS

FIGURE 2. CANSOLV[®] SYSTEM APPLICATIONS

