Cansolv Technologies Inc.

Cansolv® SO_2 Scrubbing System

Technology Review

July 2007

OVERVIEW

- Company History
- *Cansolv SO_2 Scrubbing System* Technology
- Design and Operation of Commercial Units
- Analysis of 10 Configuration Cases
- Cansolv-SRU System
- Theoretical Case of Cansolv-SRU
- Discussion

COMPANY HISTORY

- *Cansolv SO_2 Scrubbing System* invented in 1988 at Union Carbide
- Key employee buyout of technology in 1997
- Technology Optimization
- Startup of first three commercial units in 2002
- 1 startup in 2005
- 4 startups in 2006

CANSOLV® SO_2 SCRUBBING SYSTEM

- A regenerable SO_2 absorption process
- Similar to H_2S/CO_2 amine treaters
- Uses conventional equipment
- Aqueous diamine solvent is highly selective for SO_2

CANSOLV® SO_2 SCRUBBING SYSTEM

- Pure, water-saturated SO_2 byproduct
- A very robust, easy to operate process
- Almost zero emissions at low cost
- Patented technology

PROCESS CHEMISTRY

- Aqueous diamine solvent solution
- Buffering provides high capacity for SO_2 absorption
- Proprietary solvent has the proper absorption/desorption strength
- Solvent amine is non-volatile since it is always in salt form
- Regeneration provides pure, water saturated SO_2 as byproduct

PROCESS CHEMISTRY- SO_2 Amine Systems

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

$$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-} \quad (2)$$

$$R_1R_2NR_3NR_4R_5 + H^+ \rightleftharpoons R_1R_2NR_3N^+HR_4R_5 \quad (3)$$

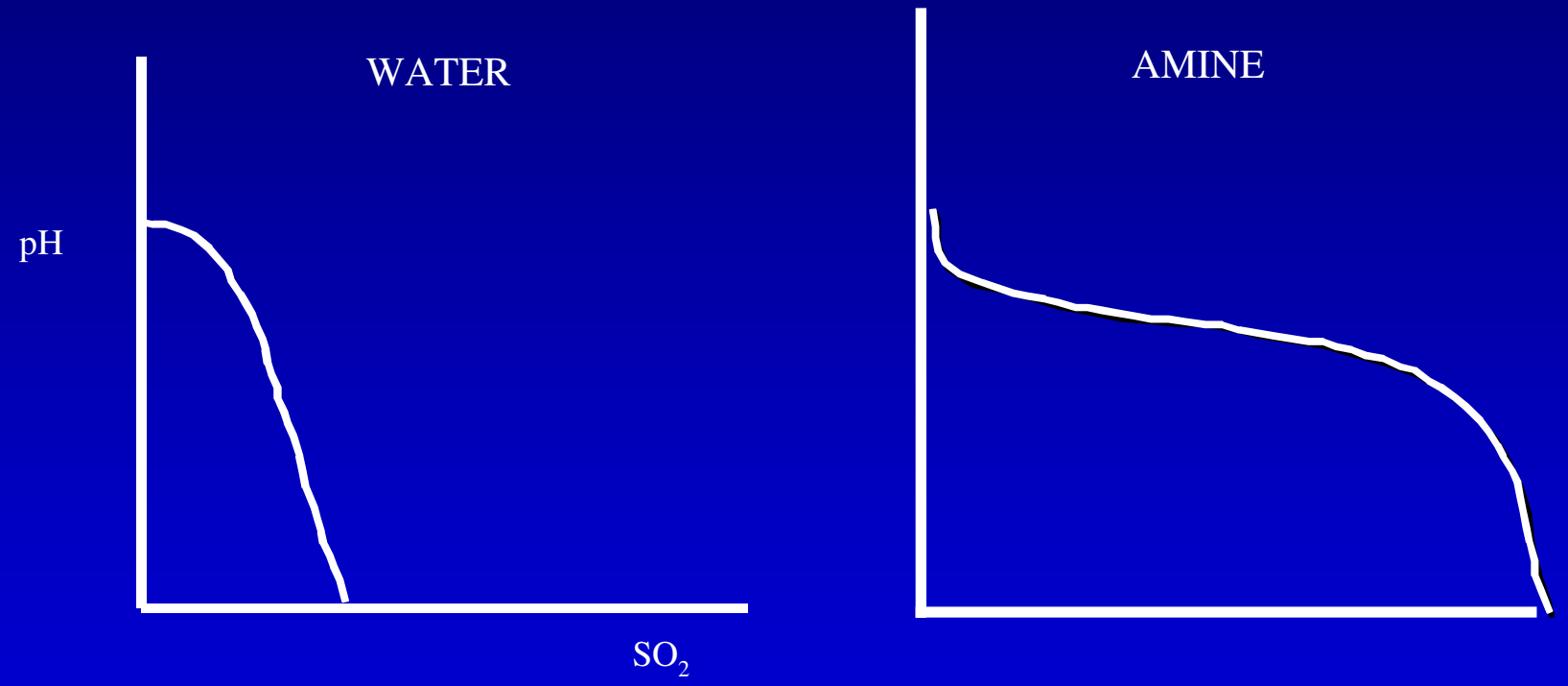
Eqns. 1 + 2

- Reversible hydration and ionization

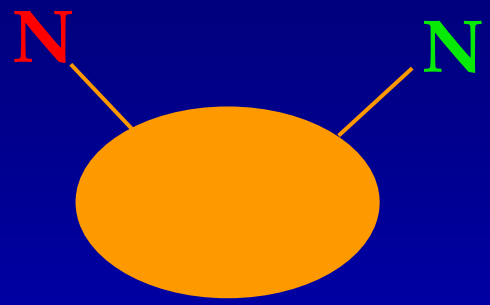
Eqn. 3

- The amine acts as a buffer
- Forms amine salts

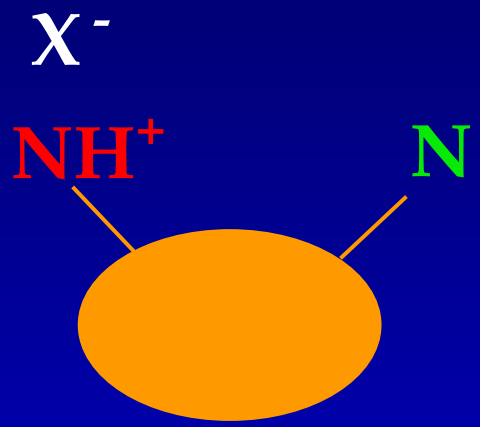
PROCESS CHEMISTRY



AMINE ABSORBENT



FREE DIAMINE



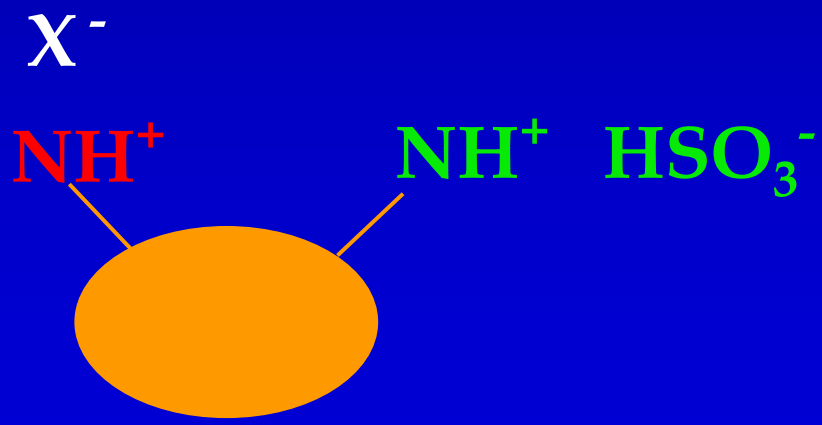
LEAN AMINE

N : Strongly basic amine functionality

N : "Sorbing nitrogen"

X^- : Strong acid anion

HSO_3^- : Absorbed SO_2

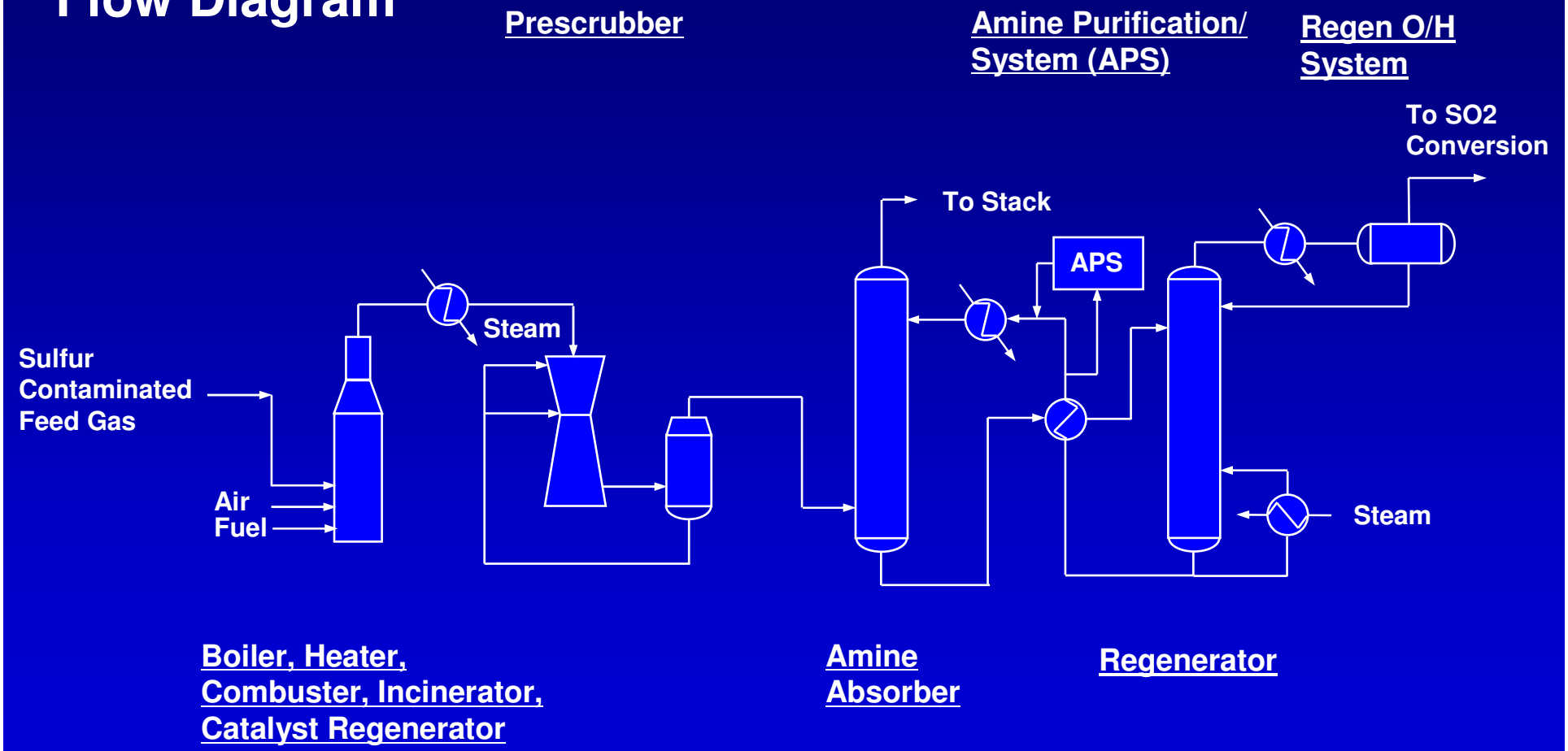


RICH AMINE

AMINE ABSORBENT

- The unique diamine absorbent is the key to the *CANSOLV® SO_2 Scrubbing System* technology
- The first amine group is always in salt form providing absorbent non-volatility
- The second amine has the optimum strength for balanced absorption and regeneration

CANSOLV SO2 Scrubbing System Flow Diagram



PROCESS DESCRIPTION

- **Prescrubber**
  - cools and water-saturates feed gas
  - subcooling of gas may be required
  - removes strong acids and particulates
  - available options include:
    - Venturi scrubber
    - Candle filters

PROCESS DESCRIPTION

- **Absorption Column**
  - countercurrent contact of feed gas with amine solution for SO_2 removal
  - treated gas to stack with SO_2 content <10ppmv, if desired
  - Low pressure drop: $\Delta P < 9$ in w.c. is typical
  - process is not tied to a specific tower design or supplier
  - design of tower takes into account specific needs of the site

PROCESS DESCRIPTION

- **Regeneration Column**
  - stripping tower with steam-heated reboiler
  - overhead condenser provides water reflux
  - water-saturated SO_2 product
  - typically utilize a structured packed column of conventional design

PROCESS DESCRIPTION

- **Amine Purification System**
  - HSS must be removed from a small slipstream
  - ED is a proven unit operation
  - Metathesis ED in Cansolv unit does not require addition of reagents
  - The high HSS concentration and differential removal ED maximizes efficiency and economics
  - Amine in ED waste stream is low

Technology Comparison

- Leading Technology
- Environment Respect
- Comprehensive Economic Sense

Gas Absorption Solutions

Leading Technology

- **High efficiency**
  - > 99% (up to 50mg/Nm^3)
  - Also can remove 62%-95% SO_3
- **Insensitive to SO_2 from the feed gas**
  - From 800 ppm to 12.5%
  - Cost has little increase with the increased SO_2 concentration
  - Low requirement on Coal (high sulfur coal)
- **Energy consumption**
  - Very low steam pressure needs(3.5kg),low electricity consumption
  - Use steam exhaust in Power plant
  - Electricity + Steam as energy source
- **Simple process, no corrosion**
  - no gypsum producing device (liquid/gas phase, PH 5-6)
  - Low pressure circulation, no abrasion, no corrosion

Gas Absorption Solutions

- **Superior reliability**
  - Scientific, concise, well established process
  - Five years no shutdown guarantee achievable

- **Easy to operate & to maintain**
  - ***Low maintenance cost***
  - Easy to learn and to operate
  - Less commissioning time

- **Upgrade**
  - Efficiency
  - (CO_2 Capture)
  - Increase the deSOx efficiency by increasing steam supply accordingly
  - Can upgrade to Multipollutant control – CO_2 Capture

Environment Respect

- No secondary pollution
  - No impure Gypsum produced
    - Landfill needs
    - Produce in great quantity
  - No < PM2.5 particulate produced
  - Do not produce CO_2
- Regenerable Amine
  - Amine solvent can be reused for 50,000 cycles, about 7~10 years
  - The initial fill is only 5-10% of total invested cost
  - 5-10% make-up annually (1% Sulfur Coal)
- Valuable byproducts
  - Reduce operational cost
    - Acid (98%)
    - Sulfur
    - Liquid SO_2 (99.9% dry basis)

Comprehensive Economic Sense

- **Transportation Demands minimized**
  - No need for warehouse (Limestone, Gypsum)
  - Transportation demands minimized
    - For 300 MW, 17 containers by train/week, 126 by truck/week
- **Less Water Needs**
  - Liquor/Gas Ratio: 0.25 – 0.35 L/m^3
  - Mainly cooling water, 90% can be recycled if needed
- **Less Energy Consumption**
  - 2-3 % internal plant energy consumption
  - 1.5-1.8% from waste heat (low pressure)
- **Less Plot Space Required**
  - Minimized land space needed for Cansolv FGD Unit
  - Flexible – Remote Regeneration tower
  - Ideal for the retrofit power plant which has no enough space
    - For 100MW, Land space needs 240M^2, or 75M^2 +else; 1500M^2.for lime-gypsum

It’s possible to combine Economic and Social progress with Environment respect

We do it all the time

COMPARISON OF AMINES

- **CANSOLV PROCESS**
  - Diamine salt absorbent
  - Absorbent non-volatile
  - 100% slip of CO_2
  - Stainless steel metallurgy
  - Corrosion allowance minimal
  - No Fe S formation
  - Only source of solids is feed gas
  - Filter rich amine stream
- **CONVENTIONAL AMINE**
  - MEA, DEA, MDEA
  - Amine volatile
  - Difficulty in slipping CO_2
  - Carbon steel metallurgy
  - Corrosion allowance important
  - Fe S formation
  - Fe S precipitation and scaling source of solids
  - Filter lean amine stream

COMPARISON OF AMINES

- **CANSOLV PROCESS**
  - Rate of formation of HSS high due to oxidized gas feed
  - Continuous reclaimer (ED)
  - Amine stable to O_2
  - Amine degradation lower by factor of 2 to 3
  - Operation and control similar
  - Can achieve low (<10 ppmv) SO_2. Not used for H2S..
  - Foaming not an issue
- **CONVENTIONAL AMINE**
  - Low rate of HSS formation
  - Reclaiming not essential
  - Amine not stable when exposed to O_2
  - Amine degradation important
  - Operation and control similar
  - Can achieve low ppmv H_2S but CO_2 can be a problem
  - Foaming often a problem

APPLICATIONS

- **Refineries**
  - SRU tail gas cleanup and capacity expansion
  - Power boiler FGD
  - FCCU tail gas
  - Fluid Coker CO boiler flue gas
  - Co-generation
  - Total sulfur management

REFINERY SULFUR MANAGEMENT

Boiler Systems	→	SO_2	Emissions Controlled by Feed Sulfur Content or Scrubbing
FCC Regen Gas	→	SO_2	Emissions Controlled by Feed H/T, Transfer catalyst or Scrubbing
Claus Tail Gas	→	SO_2	**Emissions Controlled by Claus Catalyst, Multiple Staging or Tail Gas Unit**
Spent Acid Regen	→	SO_2	Emissions Controlled by Plant design, or Tail Gas Unit

COMMERCIAL UNITS

- CTI has demonstrated the successful startup of the 7 initial *CANSOLV® SO_2 Scrubbing System* commercial applications
- Commercial units exceeded expectations
  - Cost
  - Removal Efficiency
  - Energy Consumption
  - Amine solvent stability
- Range of commercial applications demonstrates the versatility of *CANSOLV® SO_2 Scrubbing System*

Gas Absorption Solutions

Application	Location	Appl.	Size (Nm3/hr)	Size $MW_{equiv.}$	SO_2 Content	Emissions	Phase
Sulfur tail gas	Belgium	SO_2	18,000	n/a	1 %	<30 ppm	Oper. since 2002
Zinc smelt. gas	Canada	SO_2	5,600	n/a	8%	30 ppm	Oper. since 2002
Acid Tail Gas	US	SO_2	45,000	n/a	3000 ppm	15 ppm	Oper. since 2002
FCCU Flue Gas	US	SO_2	640,000	175	800 ppm	25 ppm	Oper. since 2006
Coker Flue gas	US	SO_2	375,000	100	2000 ppm	25 ppm	Oper. since 2006
Lead Smelt.Gas	India	SO_2	20,000	n/a	1 to 11 %	150 ppm	Oper. since 2005
Sulfur tail gas	US	SO_2	32,000	n/a	4%	200 ppm	Oper. since 2006
Catalyst Roaster	Canada	SO_2	48,000	n/a	9600 ppm	150 ppm	Forecast start 2007
Copper Smelter	China	SO_2	42,000	n/a	19000 ppm/ 900 ppm	150 ppm	Forecast start 2007

COMMERCIAL ZINC SMELTER

- Startup May 2002 at a zinc smelter in Quebec
- SO_2SAFE™ process
- Reduce hazard of SO_2 storage and transportation
- Dissolve SO_2 in high capacity amine solvent
- Limit release of gaseous SO_2 in event of leak or spill
- Regenerate SO_2 in an automated unit

ZINC SMELTER

- Daily startup and shutdown
- SO_2 emissions < 100 ppmv
- Treat acid plant feed gas
  - 6-9% SO_2 content

Acid Plant Tail Gas Options

- **Cansolv SO_2 instead of a second absorption uncouples emissions from acid plant operation**
  - Catalyst efficiency drop (lower conversion and/or screening intervals can be maximized) doesn't affect emissions
  - Acid plant operation can be maximized by maximizing gas flow without concern for emissions (ex. Conoco Phillips, Wilmington Ca)
  - All the captured SO_2 gets recycled to the acid plant maximizing SO_2 concentration and acid production

Gas Absorption Solutions

Conoco Phillips – Case Study

- Oil Refinery Spent Acid recovery plant application in Los Angeles, California
- CANSOLV replaced ammonium sulfate scrubber on single absorption acid plant
- Ammonium sulfate scrubber frequently did not meet emissions due to poor reliability
- Refinery could not sell byproduct ammonium sulfate easily during some seasons

Gas Absorption Solutions

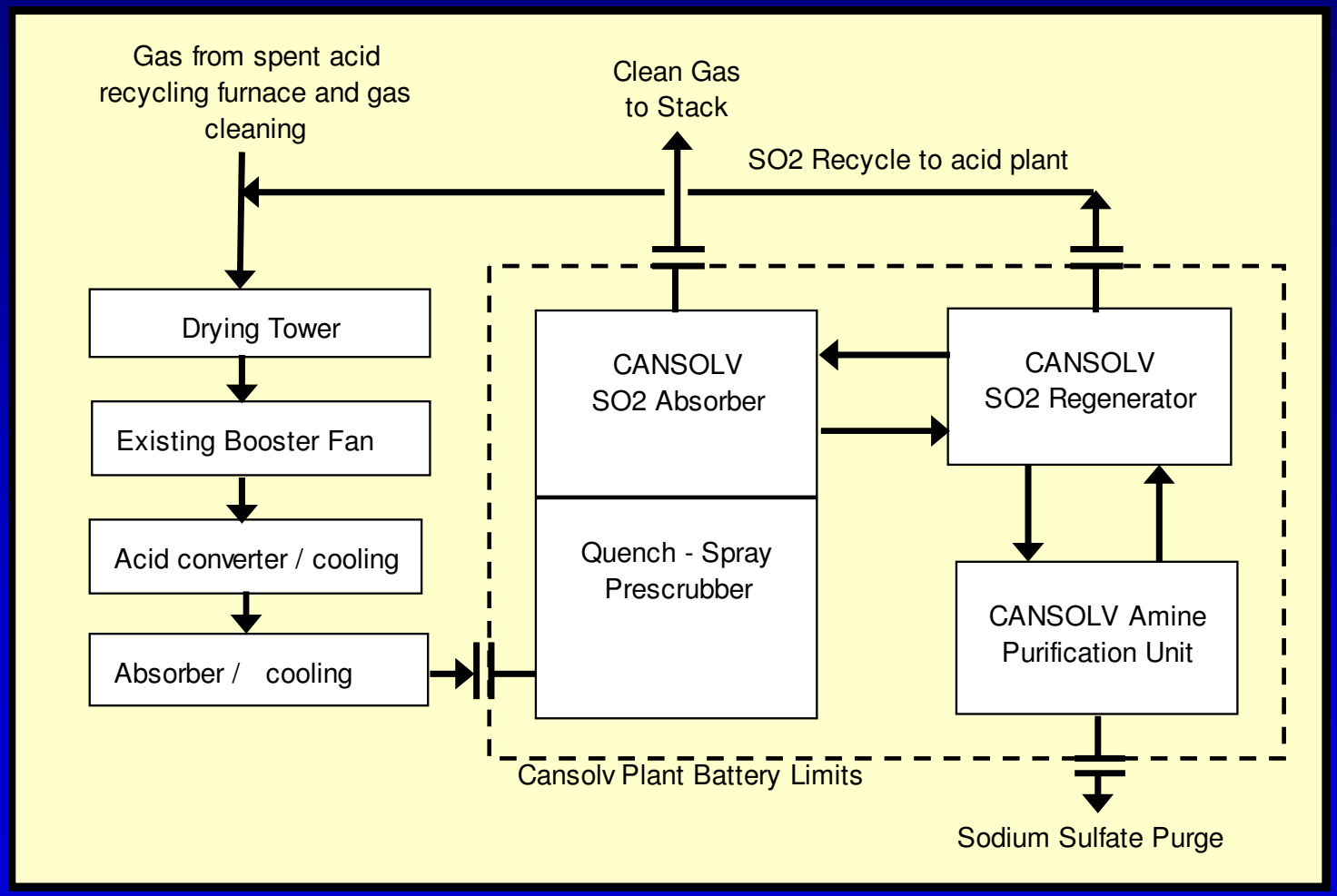
Conoco-Phillips Case Study

- Cansolv SO_2 scrubber commissioned in 2002
- Allowed owner to extend period between catalyst screening / replacement despite catalyst performance drop
- Designed for 50 ppmv emissions, operates betweeen 15 and 25 ppmv
- Designed for 3000 ppmv inlet, 10 tons/day SO_2 capture, exceeded emissions performance with up to 5000 ppmv inlet, 16 tons/day SO_2
- Increased acid production by 25 tons / day and eliminated unwanted ammonium sulfate byproduct

Cansolv	Gas Flow (Nm^3/hr)	Inlet Content (ppmv)	Emission (ppmv)	SO_2 production (tons/day)
Designed	10,000	3000	50	10
Actual	16,000	5000	15-25	16

Gas Absorption Solutions

Conoco-Phillips Bloc Diagram



Cansolv

Gas Absorption Solutions

Conoco-Phillips

Skid Mounted CANSOLV Regeneration Unit

30 t/DAY CLAUS TAIL GAS UNIT

- Startup May 2002 at a chemical plant in Belgium
- CANSOLV® SO_2 Scrubbing System
  - 30 tonne/day SRU with CANSOLV Tail Gas Unit
  - Treat flue gas from an incinerator receiving feed from SRU unit tail gas and waste (high S tar source)
  - 11,000 Nm^3/hr at 14,300 ppmv (1.4%) SO_2 inlet
  - SO_2 concentration cycles between 6,000 ppm and 11,000 ppm
- Process cost less than conventional tail gas treating
- Operation of plant has been stable and better than design

30 t/DAY CLAUS TAIL GAS UNIT

- Partial List of Performance Guarantees and Results

Performance Guarantees		Actual Performance
SO_2 in Treated Gas	≤ 122 ppmv dry	84 ppmv average; 55 ppmv optimized
Steam Consumption	≤ 20 lb/lb SO_2	11 lb/lb SO_2 average to date; 7 lb/lb SO_2 optimized

- High average steam due to deliberate over-circulation of the solvent
- Current steam consumption 20% less than design
- Degradation of the amine solvent is less than expected
- SO_2 emissions less than 60 ppmv, as low as 10 ppmv

INDIA - LEAD SMELTER OFFGAS

- Startup - December 2005
- Smelter batch operation
- Load leveling:
  - vary amine circulation to absorber
  - constant regeneration rate
  - delivers constant SO_2 flowrate to acid plant
- Gas Flowrate 16,000 SCFM
- Inlet SO_2 concentration vary from 1,000 ppmv to 12%

India - View of Absorber and Regenerator

External steel structure provides support for thin wall SS towers for wind and seismic loads.

INDIA - LEAN AND RICH CANSOLV DS TANKS

Large lean and rich tanks provide load leveling feature for SO_2 conversion process.

DELAWARE - FCU CO BOILER FLUE GAS

- Startup - September, 2006
- Refinery application: Fluid Coker CO Boiler
- Gas Flowrate: 280,000 SCFM
  - Absorber diameter: 26 ft
- Inlet SO_2 concentration: 2,000 ppmv
- Advantages of Cansolv:
  - Minimal liquid effluent & no solids handling
  - Very low SO_2 emissions (25 ppmv)
  - SO_2 product routed to SRU

DELAWARE - FCCU CO BOILER FLUE GAS

- Startup - December 2006
- Refinery application: Cat Cracker CO Boiler
- Gas Flowrate: 435,000 SCFM
  - Absorber diameter: 32 ft
- Inlet SO_2 concentration: 800 ppmv
- Designed for 5 years run-time
- Advantages of Cansolv:
  - Minimal liquid effluent & no solids handling
  - Very low SO_2 emissions (25 ppmv)
  - SO_2 product routed to SRU

WASHINGTON - SRU TAIL GAS

- Startup - July 2006
- Refinery application:
  - Common system for 2 SRU tail gas trains (2 x 100 LTPD)
- Gas Flowrate: 12,500 SCFM (6,250 SCFM per SRU)
- Inlet SO_2 concentration: 4% on acid gas bypass

WASHINGTON - SRU TAIL GAS

- Implement Cansolv-SRU design
  - Bypass 10% acid gas to oxidizer
  - Recycle SO_2 product to SRU
- Advantages of Cansolv-SRU design:
  - Increase total SRU capacity by 12.5% (25 t/day)
  - Eliminate O_2 enrichment & 3rd Claus stage
  - SO_2 emissions < 140 ppmv

CHINA GRASS ROOTS COPPER ANODE SMELTER

- Under Construction. Startup year-end 2007
- Designed to treat Copper Anode Furnace Effluent
  - Feed flow varies +/- 14% of Design
  - SO_2 Concentration varies from 900 ppm to 19,200 ppm
- Advantages of Cansolv design:
  - Recycles SO_2 back to acid plant instead of generating massive amounts of waste

CHINA GRASS ROOTS COPPER ANODE SMELTER

Skid Mounted Supply

Cansolv® SO2 Scrubbing System can also be provided modulated into pre-fabricated, skid mounted sections for easy transport and installation. Pump and exchanger skids can be made small enough to satisfy the transport limitations and towers and pressure vessels can be made to a maximum of 5 meters in diameter to respect load limitations.

Four Skid Components (example case):

- Absorber Skid
  - Absorber Diameter: 2.4 meters
- APU Skid
  - 5 kg/h HHS removal capacity & filtration to 1 micron
  - Skid size: 5200mmL × 2000mmW × 3500mmH
- Equipment Skid
- Regeneration Skid
  - Stripper Diameter: 0.5 meter
  - Skid size: 4000mmL × 4000mmW × 16000mmH