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resources & energy

Carbon Capture Overview

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Abstract

Government research funding initially emphasizing *pre-combustion* (CO_2 capture from syngas) has led to the realization that less-glamorous *post-combustion* (flue gas scrubbing) most likely represents the best option for timely, cost-effective Carbon Capture and Storage (CCS) in the immediate future. A better understanding of capture costs resulting from the renewed interest in post-combustion has prompted the U.S. Government to increase the acceptable target for increased cost of energy required for flue gas scrubbing from 20% in 2006 to 35% today, highlighting the importance of advancing the current technology.

While acid gas removal from process streams using alkanolamines is a mature technology, flue gas scrubbing presents many new challenges still not adequately met on the scale necessary for GHG abatement. In addition to discussing those challenges, this paper reviews (1) flue-gas scrubbing facilities installed over the past 30+ years for commercial purposes such as EOR, urea manufacture, soda ash manufacture and food processing, and (2) current status of innovative technologies employing, for example, sterically hindered amines and aqueous ammonia.

While the GHG contribution of sulphur recovery activities is arguably insignificant, potential monetary CO_2 reduction incentives will likely improve the economics of reducing incineration fuel by simple, established means as discussed.

Introduction

Fossil fuel combustion supplies more than 85% of energy for industrial activities, and is thus the main source of greenhouse gases (GHG) in the form of CO_2. That Inconvenient Truth is expected to remain virtually unchanged over the next 25 years as world energy consumption doubles. Coal, which has the highest carbon footprint per unit of energy, accounts for roughly 25% of the world energy supply and 40% of the carbon emissions.

Most agree therefore that Carbon Capture and Storage (CCS), also known as sequestration, is necessary for meaningful GHG reduction in the immediate future. The generally accepted, and likely optimistic, goal is to limit the global temperature increase to 2°C above pre-industrial levels by 2100 **[1]**, which The

Intergovernmental Panel on Climate Change (IPCC) has estimated would require a 50-85% emission reduction from present levels by 2050, with emissions peaking no later than 2015. **[2]**

Potential pathways to sequestration are generally classified as follows:

- *Pre-combustion* – Fuel is gasified under pressure to form a mixture of H_2 and CO_2 known as synthesis gas ("syngas"), with CO_2 capture prior to combustion.

- *Post-combustion* – CO_2 is captured from flue gas produced by low-pressure combustion of a carbonaceous fuel with air.

- *Oxycombustion or Oxyfuel* – Fuel is combusted with essentially pure O_2, rather than air, yielding a nitrogen-free mixture of CO_2 and water that can easily be processed to produce pure CO_2.

In 2006, the US Department of Energy CCS goal was 90% CO_2 capture with 99% storage permanence at less than a 10% increase in the cost of energy for pre-combustion, and 20% for post-combustion. **[3]** More recently, in a disturbing – albeit realistic – trend, the allowable increase in the cost of energy for post-combustion capture has been revised upward from 20% to 35%. **[4]**

At this point there are no clear long-term winners, but post-combustion is currently the only proven technology compatible with the world's huge investment in the fossil fuel infrastructure. Herzog makes the point that, until very recently, it had been widely expected that IGCC (Integrated Gasification Combined Cycle) power plants with pre-combustion capture would offer the most cost-effective path forward for CCS. In early 2007, for example, there were more than a dozen IGCC project proposals in the US alone. Due in part to dramatic capital cost increases for all technologies, few IGCC proposals survive today, and most new power plants in the developing world continue to be coal-fired. This has stimulated a re-examination of post-combustion capture and belated expansion of R & D funding by the US Government. **[5]**

A generally perceived advantage of post-combustion capture systems is that they are installed downstream of the steam generation system, and thus separate from the power block where the electricity is generated. The implication is that (1) existing plants are easily retrofitted (contingent on plot space), and (2) if the capture system encounters difficulty the power plant can continue to operate while the CO_2 is vented to atmosphere. In contrast, for example, a pre-combustion system such as IGCC may have to be idled while capture equipment is down.

The flip side of that coin is that sophisticated heat integration with the power plant is crucial to the energy optimization necessary to temper worldwide economic impact. Retrofitting older plants of obsolete technology will require more than a simple bolt-on, and in many cases entirely new power plants may make economic sense. This is the consensus in the UK, for example, where many coal-fired power plants are 30-40 years old.

Historically, the motivation for CO_2 capture from flue gas was to satisfy commercial markets such as enhanced oil recovery (EOR), food processing, urea production and carbonation of carbonate brines to precipitate sodium bicarbonate for soda ash production. Herzog points out that the primary difference in CO_2 capture for commercial markets vs. sequestration is the role of energy. **[6]** In the former case,

energy is a commodity whereby the only concern is its price for the sake of comparing economic alternatives. In the latter case, however, the decision to capture CO_2 has been made with the recognition that energy usage will increase, and the conviction that the cost, however onerous, is warranted.

CO_2 capture for the sake of sequestration thus requires more emphasis on reducing energy inputs than the traditional commercial process. One such metric is the concept of the "energy penalty" or "parasitic power demand." Say, for example, a power plant consumes X BTU/hr to export 500 MW of electricity. If the same plant retrofitted for CO_2 capture continues to consume X BTU/hr but now has only 400 MW to export after satisfying the energy demand of the capture facility, the energy penalty is 20%.

The other cruel irony is that energy consumption required for CO_2 capture generates additional CO_2. It is thus important to maintain the distinction between CO_2 captured and CO_2 avoided, where the latter will invariably be less. Conversely, it follows that the cost/ton avoided is always greater than cost/ton captured. *(Figure 1)* The mitigation cost/ton CO_2 *avoided* is the key value with which the permit price for a cap-and-trade system should thus be compared.
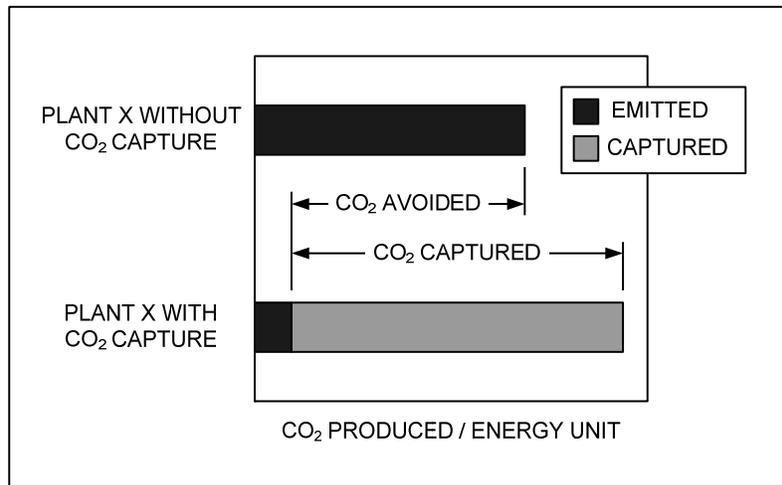

Fig. 1 - CO_2 captured vs. CO_2 avoided

Rochelle et al conclude that the total energy consumption for post-combustion capture can be 15-45% of the power plant fuel requirement, depending on the process configuration and energy integration. 15% is expensive but tolerable; 45% is prohibitive. With the addition of capital costs the total annualized cost of sequestering CO_2 is expected to be on the order of US$50/ton of CO_2 **[7]**, give or take 50%.

Challenges of Flue Gas Scrubbing

While technologies for gas sweetening and syngas purification using alkanolamines, for example, have been optimized over the past 80 years, the practical large-scale recovery of CO_2 from flue gas poses a whole new set of challenges. Candidate processes must be active at low CO_2 partial pressure and tolerate O_2 and NO_x. Flue gases from coal-fired boilers also contain SO_x, soot, fly ash and sometimes mercury which must be dealt with. Design issues relevant to CO_2 recovery processes in general and to amine processes in particular are discussed below. **[8]**

- *Low CO_2 Partial Pressure* – Flue gases from power plants have very low CO_2 partial pressures because they are typically available at or near atmospheric pressure with 3-15 vol-% CO_2. Many established acid gas treatment processes operate at elevated pressure and cannot remove CO_2 to less than ~ 0.1 bara (~ 1.5 psia) partial pressure. Commercial absorbents active enough for flue gas scrubbing have typically been primary amines such as MEA. Flue gas capture economics are usually favored by coal-firing due to better efficiencies inherent with the higher CO_2 content.

- *Regeneration Energy* – Absorption processes effective at low pressure are those with high reaction energies that require the most regeneration energy. The design challenges are to minimize regeneration energy by selecting a solvent with a relatively low reaction energy, and to use low-value heat sources to provide this energy.

- *Oxygen* – O_2 can cause corrosion and solvent degradation. While inhibitors have been reasonably effective in mitigating these effects, the need for continuous removal of unavoidable solution contaminants adds to the cost.

- *SO_x* – Flue gases can contain significant concentrations of SO_2 unless natural gas or low sulphur fuels are being fired. SO_2 reacts irreversibly with most amines to form undesirable contaminants. It is usually less expensive to pre-scrub flue gas to no more than 10 ppmv SO_2 than to accept the solvent losses or reclaiming costs. Coal-fired boilers produce the highest concentrations of SO_2 – often 300-5000 ppmv – but even oil firing can produce 100 ppmv SO_2. The limestone or wet lime FGD systems in large power boilers today can achieve reductions to ~ 35 ppmv SO_2, but further reduction to 10 ppmv typically requires secondary treatment with caustic soda solution in a spray scrubber. Below ~ 340°C (~ 640°F), SO_3 reacts with water to form sulphuric acid vapor (H_2SO_4) which will then condense to form aerosols as the flue gas is cooled. Less than one-third of the acid mist may be removed by the SO_2 scrubbing system unless a special mist eliminator is used. Any acid not captured will result in amine contamination with heat-stable salts.

- *NO_x* – NO_2 tends to form heat-stable amine salts similar to SO_2. However, NO_x is nominally 5-10% NO_2 and 90-95% NO, where the latter has no such adverse impact. It is often cheaper to remove the amine salt than the NO_2.

- *Fly Ash* – Fly ash in the absorption solvent may cause foaming in the absorber and stripper, equipment fouling, erosion, crevice corrosion, and increased solvent loss through chemical degradation and physical association with removed sludge. A coal-fired boiler flue gas has a typical loading of 2 grains of fly ash per dry standard cubic foot (gr/dscf), equating to ~ 2 tons of fly ash per 100 tons of CO_2. It is recommended that the loading be reduced to 0.0056 gr/dscf, requiring a removal efficiency of ~ 99.7%. Particulates should be removed upstream of the SO_2 scrubber.

- *Soot* – Soot from firing gas or very light fuel oils will typically pass through the amine absorber without adverse impact. However, soot from heavy fuel oil can stabilize amine aerosols in the absorber offgas not captured by the water wash, thus requiring special mist eliminators.

- *Temperature* – Flue gas temperatures must typically be cooled to 30-60°C (86-140°F) for acceptable absorption efficiency. This is accomplished in the SO_2 scrubber, if existing, or otherwise in a direct contact water cooler or "quench tower." The cooled flue gas is water-saturated, and relative gas temperatures in/out of the absorber will thus determine solvent water balance, whereby an inlet temperature lower than the outlet results in water loss, and an inlet temperature higher than the outlet results in water gain. Typically, the inlet gas temperature is equal to the lean solvent temperature, nominally resulting in water balance, or greater than the lean solvent temperature, resulting in water gain which is easily balanced by purging regenerator reflux and thus also avoiding potential accumulation of surfactants conducive to foaming.

Dissolved iron and copper are known to catalyze MEA degradation with the production of NH_3. Dissolved iron is of course a common corrosion product, and dissolved copper may be added to inhibit corrosion. EDTA is a mild inhibitor of iron catalysis and strong inhibitor of copper catalysis. However, EDTA is a chelating agent which may also increase corrosion by dissolving protective layers of ferric corrosion products. **[7]**

WorleyParsons Historical Practice

WorleyParsons amine or similar flue gas scrubbing system is shown in *Figure 2*. Clean flue gas is contacted with lean solvent in a packed contactor at 0-5 barg (~ 0-70 psig) and 30-60°C (86-140°F). Solvent vapor and mist is capture by a downstream water wash.
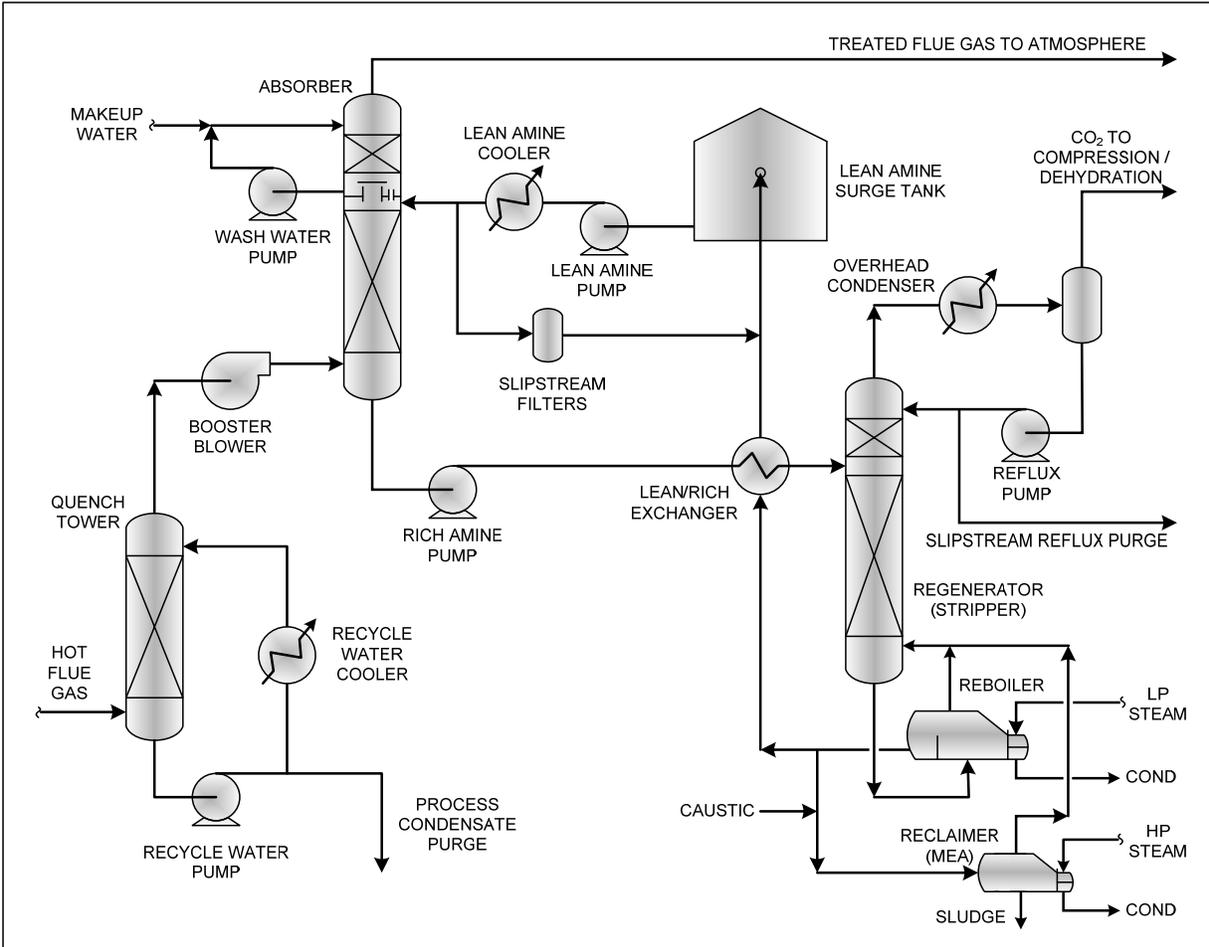
Fig. 2 - *WorleyParsons absorption / regeneration process*

Rich absorber bottoms is returned to the regenerator via lean/rich (cross) exchangers which preheat the regenerator feed while cooling the bottoms. In the regenerator reboiler, indirect heating with LP (40-60 psig, ~ 3-4 barg) steam, heat transfer fluid or fuel firing turns some of the water in the solvent to steam. As that steam passes up through the tower, some is condensed to further raise the solvent temperature (sensible heat) and satisfy endothermic heat of desorption (latent heat), and the balance serves as a carrier gas to promote stripping by reducing the CO_2 partial pressure.

At normal amine concentrations, reboiler process temperatures correspond to the boiling point of water, as determined by the pressure. Higher tube skin temperatures directionally increase amine degradation. Consequently, regenerator overhead pressures are typically limited to ~ 1.5 barg (~ 20 psig) to nominally limit tube skin temperatures to 280°F (138°C). Since tube skin temperatures are seldom known, the corresponding rules-of-thumb are to limit the (1) bulk process temperature to 260°F (127°C), and (2) steam temperature to 285°F (141°C).

Regenerator overhead vapors are cooled to 50°C (122°F) to condense most of the stripping steam, most or all of which is refluxed to the tower. Often a reflux slipstream is purged to maintain water balance

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and/or limit the buildup of contaminants such as NH_3 and surfactants, both likely products of amine degradation. For the sake of a conservatively low target, NH_3 buildup is typically limited to 1 wt-%. Increased NH_3 levels proportionally increase CO_2 co-absorption, directionally increasing reflux corrosivity and required regeneration heat. Surfactants tend to promote foaming, often resulting in unstable tower operation due to flooding.

Reflux is normally returned to the tower via two to four rectification, or wash, trays above the rich amine feed point to knock down entrained amine, thus avoiding solvent loss in the reflux purge. Unlike hydrocarbon fractionation towers, for example, the reflux stream has minor impact on tower heat balance, and wide variations in reflux rates are thus possible without adverse impact on tower operating stability.

Lean amine from the lean/rich exchanger(s) is further cooled to optimum absorber temperatures of 30-50°C (86-122°F). A cool lean amine slipstream is typically filtered to remove microscopic particulates entrained in the flue gas and/or the products of corrosion. Particulate filtration is usually followed by a fixed bed of granular activated carbon to remove surface active amine degradation products conducive to foaming. In some cases, slipstream reclaiming is practiced whereby heat stable salts and other contaminants are removed by ion exchange, distillation or electrodialysis.

Pilot-scale tests and modeling efforts reportedly suggest that operating an amine stripper at a vacuum can achieve a 5-10% reduction in energy use per unit of CO_2 captured, including allowance for extra compression. **[3]**

Amines have been used for H_2S and CO_2 removal from gas streams in the chemical and oil industries for over 80 years, and the technology is consequently mature within that context. During 1978-2000, at least a dozen commercial CO_2 capture plants were commissioned worldwide, ranging in size from 90 to 1200 ton/day CO_2. **[9] In** comparison, a 500-MW coal-fired power plant will generate 5500 ton/day of CO_2. Virtually all utilized 20-30% MEA, inhibited or otherwise.

- The first noteworthy capture plant is currently the largest. In 1978, Kerr-McGee and ABB Lummus installed a 20% MEA system to capture 600 ton/day CO_2 from boilers firing a mix of coal and petroleum coke at Kerr-McGee's soda ash plant in Trona, California USA. Sub-surface brines from a mineral-rich dry lake bed, Searles Lake in the Mojave Desert, are carbonated to precipitate sodium bicarbonate. Prior to flue gas capture, CO_2 was generated by calcining limestone trucked in daily from a quarry 30 miles away. CO_2 capacity has since been increased to 800 ton/day. The plant is currently operated by IMC Global Inc.

- The largest plant to date recovered 1200 ton/day CO_2 from natural gas flue gas for EOR in Lubbuck, Texas USA. It only operated two years, 1982-84, before being shut down when low crude oil prices rendered EOR uneconomical.

- The Mitchell Energy Bridgeport, Texas USA plant similarly recovering ~ 500 ton/day CO_2 for EOR during 1991-99 was noteworthy in the lengths taken to protect the MEA from O_2 and NO_2. Residual O_2 in the combined refinery flue gas streams from fired heaters, internal combustion engines and gas turbines was consumed by sub-stoichiometric combustion of natural gas with waste heat steam recovery, followed by catalytic reduction of NO_x to N_2 and CO shift to CO_2. It
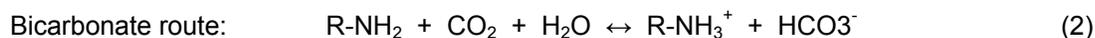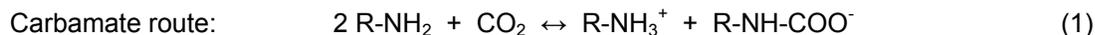
was considered a technical and commercial success, and again was only shut down when low crude prices rendered EOR uneconomical. **[10]**

Dow Chemical and Union Carbide developed corrosion-inhibited 30 wt-% MEA processes for recovery of CO_2 from flue gas in the 1970's and 1980's primarily for EOR. When crude oil prices collapsed in 1986, the EOR market disappeared and these licensors became less active. In 1989, Fluor Daniel purchased the Dow Chemical GAS/SPEC FT-1 technology, which it renamed Econamine FG. It was reportedly capable of 85-95% recovery of 99.95+% pure CO_2 product (dry basis). Fluor Daniels' second generation Econamine FG Plus technology, introduced in 2003, claims significant reduction in energy consumption, but at the expense of increased complexity and, hence, capital cost. **[11]**

Steric Hindrance

There two fundamental mechanisms for the reaction of primary / secondary amines (e.g.; MEA/DEA) with CO_2 as follows, where the indicated amine ($R\text{-}NH_2$) happens to be primary:

Carbamate route: $\quad\quad\quad 2\ R\text{-}NH_2\ +\ CO_2\ \leftrightarrow\ R\text{-}NH_3^+\ +\ R\text{-}NH\text{-}COO^-$ $\quad\quad\quad\quad$ (1)

Bicarbonate route: $\quad\quad\quad R\text{-}NH_2\ +\ CO_2\ +\ H_2O\ \leftrightarrow\ R\text{-}NH_3^+\ +\ HCO3^-$ $\quad\quad\quad\quad$ (2)

Because tertiary amines such as MDEA are limited to reaction 2, absorption rates at low CO_2 partial pressures are relatively slow as limited by CO_2 hydrolysis to carbonic acid.

With common primary / secondary amines such as MEA/DEA, reaction 1 prevails to form a stable carbamate, requiring two moles of amine per mole of CO_2 and thus limiting solution capacity to nominally 0.5 mole/mole CO_2/amine. However, unstable carbamates will hydrolyze, advantageously, to the bicarbonate, requiring only one mole of amine per mole of CO_2 for a theoretical solution capacity of 1 mole/mole CO_2/amine.

Sterically hindered amines such as 2-amino-2-methyl-1-propanol (AMP) and piperazine (a cyclic diamine having the molecular formula $C_4H_{10}N_2$) belong to a special class of primary / secondary amines with bulky groups attached to the nitrogen atom of the amine molecule so as to partially shield the amine group from the reacting acid gas. Carbamate stability is thus reduced without significantly compromising reactivity, essentially combining the higher reaction rates of primary / secondary amines with the higher solvent capacity and lower regeneration heat of tertiary amines. Sterically hindered amines arguably appear poised to become the leading technology for CO_2 capture.

Addition of piperazine and its derivatives (e.g.; hydroxyethyl and hydroxypropyl piperazine) have been shown to significantly improve CO_2 reaction rates for amine and carbonate solutions in general, including MEA. They show particular promise as promoters for MDEA and potassium carbonate (K_2CO_3), which have low regeneration heats but otherwise insufficient reactivity for efficient CO_2 absorption at low partial pressures. Piperazine is more stable than MEA and is reclaimable by distillation under pressure, as in combination with MEA.

Since 1990, the Kansai Electric Power Co. (KEPCO) and Mitsubishi Heavy Industries, Ltd. (MHI) have jointly conducted research and development of new technology for CO_2 recovery from power plant boiler

flue gas and gas turbine exhaust using patented proprietary sterically hindered amines designated KS-1, KS-2 and KS-3. Compared with MEA, KS-I is claimed to require 20% less regeneration heat with less corrosion and amine degradation. **[6]** The first commercial MHI KM-CDR (Kansai Mitsubishi Carbon Dioxide Recovery) Process plant was commissioned in Malaysia in 1999 where flue gas containing 8 vol-% CO_2 is being treated with 90% recovery. Four commercial KM-CDR units for gas-fired plants have been built, with four more under construction. Pilot tests are currently being conducted on coal-fired flue gas. **[5]**

Suda has studied the savings from thermal integration of a CO_2 recovery processing the entire flue gas stream with a 600 MW, LNG-fired boiler. When the CO_2 recovery unit (1) uses steam extracted from the low pressure steam turbine to reboil the stripper, (2) preheats boiler feed water using the stripper overhead cooler, and (3) uses the KS-1 proprietary amine with a regeneration energy 12% lower than MEA, the steam demand of the CO_2 recovery unit reportedly drops from 20% to 7.3% of the total usable power plant steam enthalpy – a 65% energy savings. **[8]**

Cansolv Technologies Inc. was founded in 1997 as a Union Carbide spin-off to commercialize its regenerable SO_2 scrubbing system. The first Cansolv SO_2 plants were commissioned in 2002. As of September, 2008, there were ten in operation with ten scheduled to be commissioned by the end of 2010. Cansolv was subsequently acquired by Shell Global Solutions International BV, a member of the Royal Dutch Shell group, in November, 2008.

Since 2000, R & D focus has been on developing high performance solvents for NO_x, mercury and CO_2. Cansolv now offers a CO_2 capture process using proprietary tertiary amine formulations, likely promoted with piperazine and/or its derivatives. Absorption rates comparable to MEA are claimed, with a 40% reduction in regeneration energy. In addition to very low degradation rates compared with MEA, degradation products retain scrubbing capacity. Two demonstration plants have been built – one in Montreal, Canada, for capture from natural-gas-fired flue gas, and one in Virginia, USA, for capture from coal-fired flue gas. **[5]**

The solvent can also reversibly absorb SO_2 and NO_2, the recovery of which can be integrated with CO_2 capture. *(Figure 3)* In December, 2009, Shell announced that Cansolv will design and provide an integrated SO_2-CO_2 demonstration plant to recover 50 tonne/day of CO_2 from flue gas at RWE power's Aberthaw coal-fired power station in Wales. The plant is expected to be commissioned in early 2011 and operate for two years.
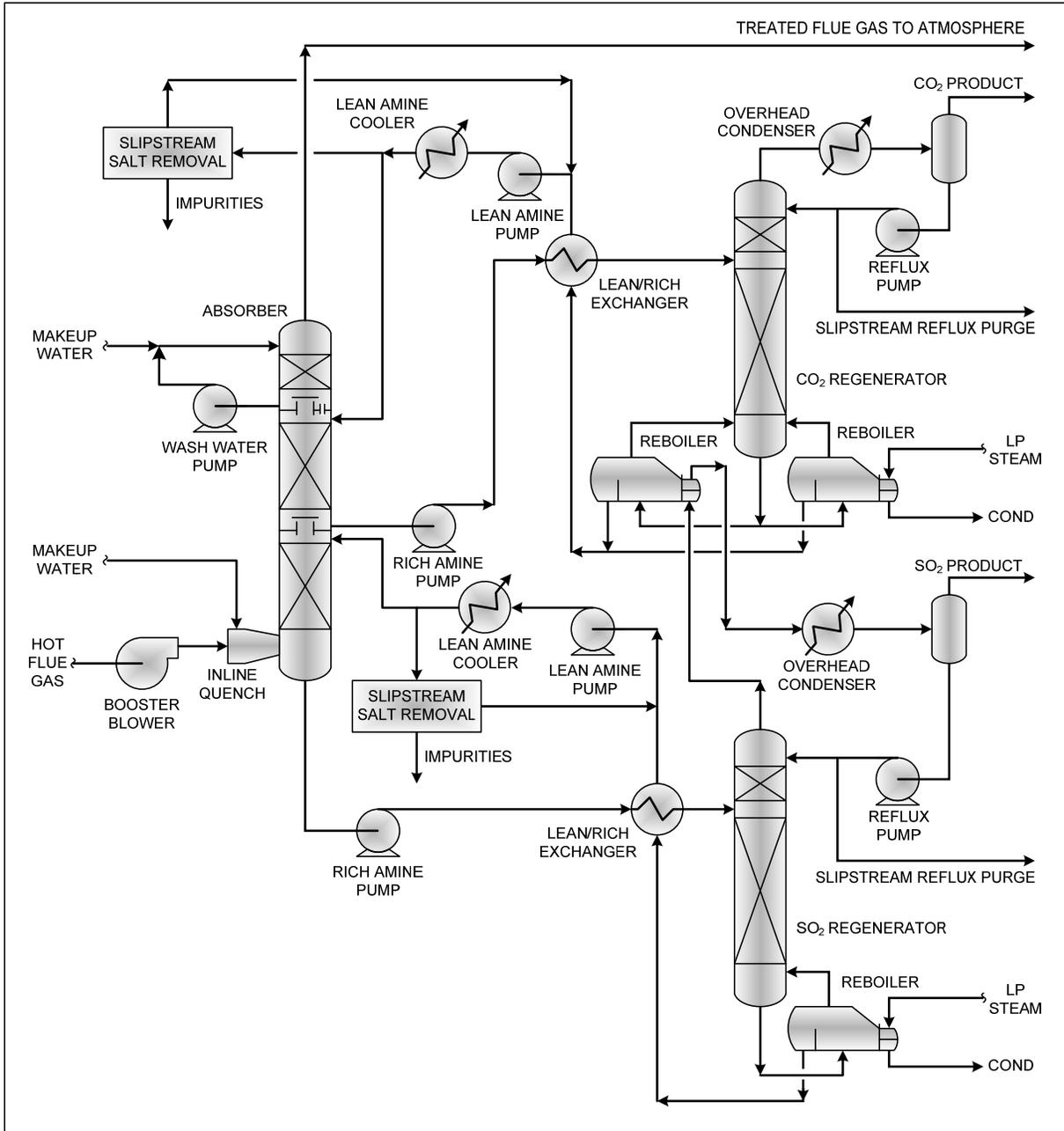
Fig. 3 - Cansolv Integrated SO_2-CO_2 Capture

In order to optimize the balance between capital cost and operating cost for a given facility, Cansolv now offers two variants of its second generation CO_2 capture solvent – DC-103 and DC-103B. DC-103 is kinetically slower, thus requiring a larger absorber, but requires less regeneration heat. DC-103 thus favors operating cost, while DC-103B favors capital cost.

PSR solvents developed at the University of Regina, Saskatchewan, Canada, use proprietary mixtures of simple and hindered amines designed specifically for CO_2 capture from flue gas. Compared with MEA,

both higher amine concentrations and rich mole/mole loadings are possible. Key features claimed are lower regeneration temperature, lower solvent circulation rate and reduced degradation and corrosion. **[12]**

Lower solvent circulation rates not only reduce equipment size, but lower the energy for regeneration. PSR solvents require lower circulation rates due to their ability to maximize rich solvent loading, while achieving a leaner amine through better regeneration. Thus, overall working capacity (mole of CO_2 removed / mole of solvent circulated) is higher than that of MEA by 70-130%. *(Table 1)*

Table 1. PSR Working Capacity vs. MEA

Solvent	Mole CO_2 / Mole Amine		
	Lean Loading	Rich Loading	Δ (Working Capacity)
MEA	0.22	0.45	0.23
PSR-1	0.06	0.60	0.54
PSR-2	0.16	0.61	0.45
PSR-3	0.19	0.59	0.40

Relative energy requirements are reportedly 55-85% of conventional amines. The ability to regenerate PSR solvents at temperatures 5-10°C (9-18°F) lower than with MEA not only reduces amine degradation, but potentially facilitates process integration by permitting the use of lower pressure steam. **[13]**

The PSR process is being tested on a 4-tonne/day CO_2 capture facility at the SaskPower 875 MC lignite-fired Boundary Dam Power Station under the auspices of the International Test Centre for CO_2 Capture (ITC), a consortium of 13 industry and governmental organizations including two Canadian Universities. HTC Purenergy is the technology commercialization partner with ITC.

Aqueous Ammonia

So-called aqueous NH_3 is in reality ammonium carbonate solution with which CO_2 reacts to form the bicarbonate ostensibly as follows:

$$(NH_4)_2CO_3 \ + \ CO_2 \ + \ H_2O \ \leftrightarrow \ 2 \ NH_4HCO_3$$
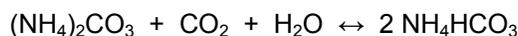
According to research by the DOE National Energy Technology Laboratory (NETL) and others, aqueous NH_3 has the following advantages compared, for example, to generic MEA:

- Up to twice the CO_2 absorption capacity
- 49-64% less regeneration heat
- 80+% reduction in solvent makeup cost
- Negligible oxidative or thermal degradation, even at much higher regenerator pressures
- Potential integration with SO_2, NO_x, mercury and fly ash removal

However, these conclusions are not universally held. Rochelle **[14]** believes that:

- Such estimates of reduced regeneration heat are optimistic, and that stripping steam requirements might actually be comparable to MEA.

- CO_2 absorption rates with NH_3 are actually much slower than for MEA, potentially requiring triple the absorber height.
- The high volatility of NH_3 is a major obstacle, requiring post-absorber scrubbing of sufficient cost and complexity as to negate many of the advantages of NH_3.

Process simulations in conjunction with laboratory data by CSIRO concluded that CO_2 capture from coal-fired power plant flue gas will require limiting the NH_3 concentration to 5 wt-% and absorber temperature to 10°C (50°F) or less to contain NH_3 vapor losses and avoid precipitation of ammonium bicarbonate. Under this scenario, aqueous NH_3 has overall energy requirements comparable to conventional 30 wt-% MEA. **[15]**

In any case, a particularly unique feature is ability to operate the stripper at pressures as high as 20-35 barg (~ 300-500 psig) without thermal degradation, dramatically reducing CO_2 compressor costs. Also as a result, NH_3 and water evaporation is very small, further reducing energy consumption for heating and cooling.

As mentioned, a fundamental problem with aqueous NH_3 is its high volatility, raising concerns about toxic emissions. The Alstrom Power Chilled Ammonia Process (CAP) operates the absorber at 0-10°C (32-50°F) to facilitate recovery of NH_3 vapor in the exhaust flue gas, while also increasing CO_2 solubility and reportedly enhancing mass transfer, both of which result in smaller equipment. Alstrom is testing a 35 ton/day chilled-ammonia process at the We Energies Pleasant Prairie Power Plant. **[5]**

In 2009, American Electric Power commissioned a 270 ton/day chilled-NH_3 demonstration CCS facility at its Mountaineer coal-fired power plant near New Haven, West Virginia USA. Captured CO_2 is compressed to 140 bar (~ 2000 psi) for injection into porous rock formations 8000 feet (~ 2400 m) deep. **[16]** Whether it uses Alstrom Power technology is unclear.

PowerSpan Corporation's aqueous NH_3 process, known as ECO_2, absorbs CO_2 at "ambient" temperatures of 25-40°C (77-104°F). Under a 3-year cooperative R & D agreement with NETL beginning in 2004, PowerSpan conducted lab, and later pilot, testing to integrate CO_2 capture with its established ECO process for SO_2, NO_x, mercury and fly ash removal. PowerSpan is currently operating a 20 ton/day CO_2 pilot facility at FirstEnergy's R. E. Burger plant, and plans to commission a larger demonstration facility in 2011.

Storage

While CO_2 compression levels as low as 70 bar (~ 1000 psi) are referenced in the literature, upstream pipeline pressures are probably more commonly 140 bar (~ 2000 psi). The critical point is at 31°C (88°F) and 74 bara (1073 psia). By maintaining the temperature at 100°F (38°C) or less, pipeline pressure can drop to, say, 100 bar (~ 1500 psi) before recompression, and the stream retains flow properties approximating a liquid. Typical pipeline specifications are -40° dew point, N_2 < 300 ppmv, O_2 < 40 ppmv, and Ar < 10 ppmv. **[17]**

The CO_2 is injected into geological formations such as sedimentary rock, depleted oil/gas fields, saline aquifers, unmineable coal seams, etc. at depths greater than 800 m (~ 2600 ft). Proper storage sites will

retain CO_2 without appreciable seepage for tens of thousands of years. Monitoring will be required for decades into the future, undoubtedly combined with techniques to remediate deficiencies.

Sulphur Recovery Carbon Footprint

In terms of global warming, the impact of sulphur recovery on CO_2 emissions is negligible. In most cases, net CO_2 reduction to any significant extent can only be achieved by reduced tail gas incineration temperatures in the absence of waste heat recovery. Since such reduction is already justified by energy savings, the general lack of emphasis on doing so is puzzling. In the likely event of future mandated CO_2 reduction and/or carbon tax, greater incentive to conserve fuel will of course result.

In general, thermal oxidation efficiency is a time/temperature function. Based on 1-second residence, nominal thermal oxidation temperatures for various components are summarized in *Table 2.*

Table 2 - Nominal TGU Thermal Oxidation Temperatures

Combustible	°F	°C
CO, H_2	1300 – 1500	~ 700 – 800
H_2S, COS, CS2, CH_3SH	900 – 1000	~ 480 – 540

It is thus evident that CO limits, if imposed, may well be the governing factor.   Many locales still do not impose such limits. For those that do, the limits very often range from 100 to 500 ppmv (typically corrected to 0-3% O_2 in the stack). For a WorleyParsons BSR-Amine Tail Gas Unit (TGU) with fresh cobalt/moly-on-alumina catalyst and an inlet temperature of 550-600°F (288-316°C), residual non-H_2S sulphur compounds in the absorber offgas should be as indicated in *Table 3.*

Table 3 - Optimum TGU Absorber Emissions

Contaminant	PPMV
Carbon monoxide – CO	< 200
Carbonyl sulphide – COS	< 20
Carbon disulphide – CS_2	0
Methyl mercaptan – CH_3SH	0

Within reason, normal catalyst activity loss due to hydrothermal aging can be compensated for by increased reactor inlet temperatures. WorleyParsons designs the reactor train for inlet temperatures as high as 700°F (371°C).

There is a general trend toward the use of so-called low-temperature TGU catalysts which permit the use of indirect HP steam reheat in lieu of inline firing of, for example, natural gas or propane, thus limiting reactor inlet temperatures to around 450°F (232°C). The advantages are reduced capital cost, operating simplicity and no risk of catalyst damage from improper air/fuel ratios. However, the hydrolysis reactions responsible for conversion of CO, COS and CS_2 require higher initiation temperatures than do the hydrogenation of SO_2 and S_x to H_2S. Consequently, CO conversion efficiency often suffers, particularly

as the catalyst ages. If residual CO exceeds emission limits as a result, higher incinerator temperatures are thus required.

With the possible exception of relatively small units, a properly designed TGU will recover waste heat from the reactor effluent to generate LP steam. In the absence of a waste heat boiler on the incinerator, CO conversion in the reactor is thus best maximized if it obviates oxidation of CO in the incinerator. However, equilibrium CO levels in the reactor effluent invariably exceed 100 ppmv, and residual CO will likely be even higher in the event of excessive hydrocarbons in the SRU feed gas, or excessive hydrogen in the tail gas as due to hydrocarbons or O_2 enrichment, since hydrogen is a reaction product of CO hydrolysis.

When thermal oxidation of CO is not required, the mandated incinerator temperature – in the US at least – is probably most commonly 1200°F (649°C). This would appear to be a holdover from pre-TGU days. For TGU tail gas, 900-1000°F (482-538°C) is generally adequate to thermally oxidize the < 200 ppm H_2S present. However, higher temperatures can require proportionally less fuel once oxidation of tail gas H_2 kicks in.

Catalytic incineration, requiring substantially lower H_2S thermal oxidation temperatures, has long been popular in Europe, if not the US. WorleyParsons offers Selectox catalyst, an extremely rugged vanadium-oxide-based catalyst with an initiation temperature of 400-500°F (204-260°C) and negligible SO_3 generation.

For thermal oxidation of Claus tail gas, WorleyParsons now also offers the 2-stage Rameshni Catalytic Thermal Incineration (RCTI)[TM] process (patent pending), whereby low-temperature hydrogenation catalyst converts virtually all sulphur to H_2S while capitalizing on the resultant exotherm to initiate thermal oxidation in the subsequent Selectox stage. *(Figure 4)*
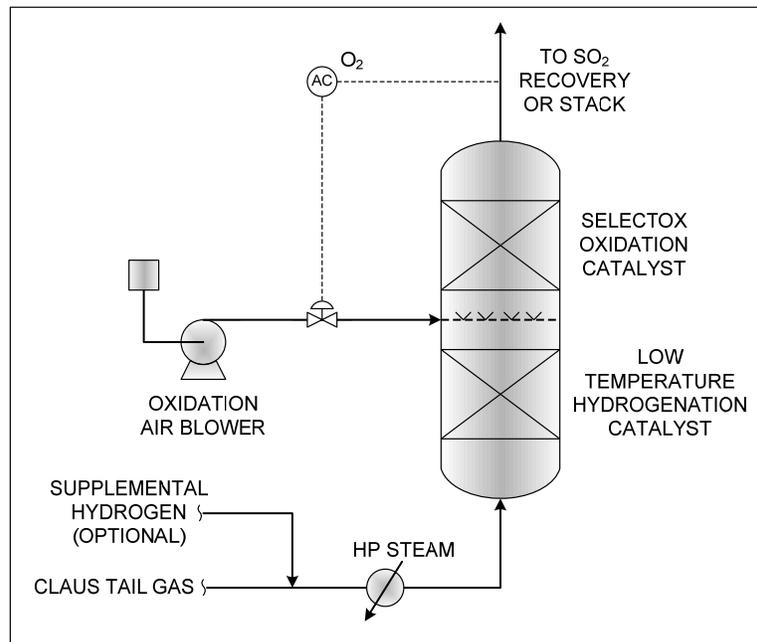

Fig. 4 - Rameshni Catalytic Thermal Incineration (RCTI)[TM]

When thermal oxidation of CO is not required, incineration can be completely eliminated by the use of a protonated, or "acid aided," TGU amine such as Dow UCARSOL HS-103 (probably the first such commercial solvent in the 1980s), Ineos GAS/SPEC TG-10, Huntsman MS-300 and ExxonMobil Flexsorb SE+. In simple terms, controlled establishment of heat-stable amine salts lowers the solvent pH to facilitate stripping to lower residual H_2S to achieve < 10 ppmv H_2S in the absorber offgas, which also improving H_2S selectivity over CO_2. **[18]** Again, it is puzzling that the use of protonated amines is not more common in view of the substantial savings in incinerator fuel.

Compared with generic MDEA, for example, treating to < 10 ppmv H_2S with protonated amines makes cooling the lean solvent to 90-105°F (32-41°C) more important, and regenerator steam demand may be 10-20% higher.

In venting the cold absorber offgas to atmosphere, TGU reactor temperatures and catalyst activity must be sufficiently high to not only shift CO to legal concentrations, but also avoid formation of methyl mercaptan by hydrogenation of CS_2. Based on one such incident, less than 40 ppm can result in extremely objectionable downwind nuisance odors. A standby incinerator should be provided to accept off-spec absorber offgas resulting from upsets.

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