



SPRINT Event



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**(Stakeholder, Policy, Research and Industry NeTwork)
GGS Indraprastha University (GGSIPU), New Delhi.**

UNDERSTANDING OF AEROSOL BASED AMINE EMISSIONS AND IT'S MITIGATION MEASURES

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INTRODUCTION

PARTICIPATE PARTENERS IN SCOPE

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- The SCOPE project, led by SINTEF (Norway) with research institutions and industry partners from Norway, Netherlands, UK, Germany, USA, Japan and India.
- 24 partners from industry, research and academia.
- The industrial partners support research also committed to directly invest and participate in the R&D and demonstration activities for accelerated decarbonisation of the industry.
- **Indian Consortia Members**
 - Prof N. C. Gupta, Guru Gobind Singh Indraprastha University (GGSIPU) Delhi India.
 - Dr. Aditya Kumar Patra, Indian Institute of Technology Kharagpur (IIT KGP) India.
 - Dr. Purvil Khakharia, Microfilt India Pvt. Ltd (MIPL) Umbergaon India.

POST COMBUSTION CARBON CAPTURE (PCCC)

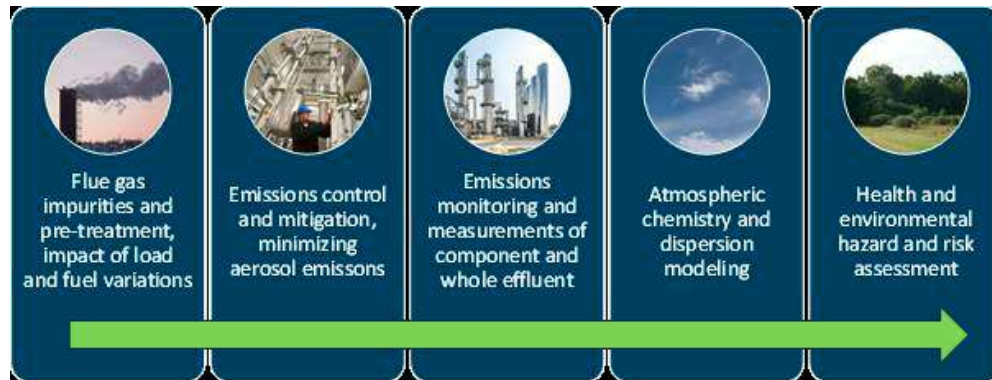
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- CO₂ Capture, Utilisation and Storage (CCUS) is an important pathway **for reduction of GHG emissions**.
- India's environmental emission norms and regulations are lacking due to knowledge gap and available data this will bridge this firstly, in terms of the current levels and subsequently, in the case of an installed CO₂ capture plant.
- New knowledge on emission control technologies and improved models and tools for prediction of aerosols and volatile based emissions, **thus lowering the risk of increased nitrogen** (ammonia, amines) emissions (and related nitrogen deposition issues).
- The collaboration with international participants will accelerate **knowledge exchange** about the technology.

SCOPE APPROACH

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- Development of effective **online monitoring systems and emission control guidelines**.
- Validation of predicted amine emissions from solvents against data generated in the project through test campaigns at **different pilot plants**.
- Effective utilization of knowledge about **environmental hazards** in **risk assessment** of amine-based CO₂ capture plants
- Identification of societal concerns, **policies and practices** that may affect the **credibility industrial decarbonisation using** amine-based CO₂ capture in different countries.



ABSORPTION DESORPTION BASED CO₂ CAPTURE PROCESS

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- Direct contact cooler DCC/SO₂ polisher for cooling the flue gas and reducing SO₂ levels in the flue
- Absorption column to capture the CO₂
- Stripper to thermally regenerate the solvent. The treated flue gas leaves the absorption column whereas a CO₂ rich stream is obtained from the stripper.

Operating condition of Co₂ capture mini plant.

Absorber Temp. 40 °C (±2°C).

Striper temp. (bottom): 120 °C (±0.5°C)

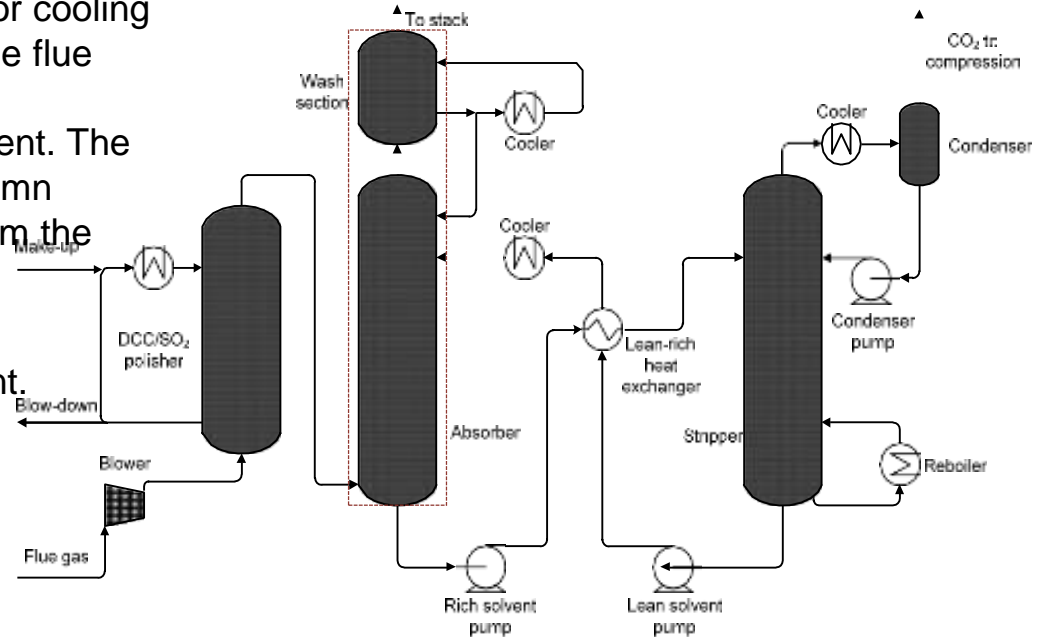
Lean pH: 9.8 (±0.2)

Rich pH: 8.9 (±0.2)

Stripper pressure (top) 1.8 bar (±0.05 bar)

Acid liquid flow rate 50 to 90 l/m.

MEA emission : ~45 mg/m³ STP



Typical configuration of an absorption-desorption based CO₂ capture process.

ACID GAS REMOVAL TECHNOLOGIES

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- **Chemical absorption process:** Chemical reaction
- Primary Amine: MEA, DGA
- Secondary Amine: DEA, DIPA, Sterically hindered.
- Tertiary Amines: MDEA, TEA.
- Potassium carbonate

- **Physical Absorption:** Henry Law
- Physical absorption is mostly effective at high pressures and low temperatures. Therefore, compared to amine process, usually physical absorption capital and operating costs is higher.
- **Hybrid Process:** In a hybrid process a physical and chemical solvent are applied simultaneously to benefit from the advantages of both processes
- **Membrane Separation Process:** Membrane separation systems are mainly used for bulk removal of CO₂.

Chem. Eng. Sci., 34, 443– 446, 1979.

Kohl, A.L., Nielsen, R., Gas Purification, Gulf Professional Publishing, Houston, 5th Edition, 1997.

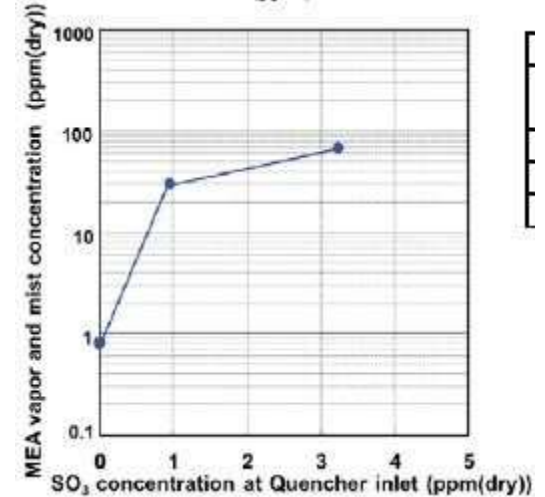
OBSERVATION OF AMINE MIST



REAL FUEL GAS

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- Presence of mist in flue gases under certain conditions (high S containing coal, aged SCR catalyst, etc.) is well known. Efforts were aimed to avoid the resulting plume, not necessarily reducing the SO_3 emissions completely¹.
- Its impact on the CO_2 capture process and specifically, amine emissions was not well known. First reference^{2,3} was only in 2013, which reported mist emissions being 2 orders of magnitude higher than vapor, and having a direct correlation with the amount of SO_3 in inlet flue gas.
- Emissions of amine mist have now been reported at several pilot plants; the NCCC, Alabama, TCM pilot plant, Bergen, RWE pilot plant, Niederaussem, and other locations.
- It is important to note that these emissions are site and condition specific. The range of observed excess amine emission (mostly MEA) was from 30- 500 ppm(v).



1 *J. Air Waste Manage. Assoc.*, vol. 54, no. 6, pp. 750–762, Aug. 2004.

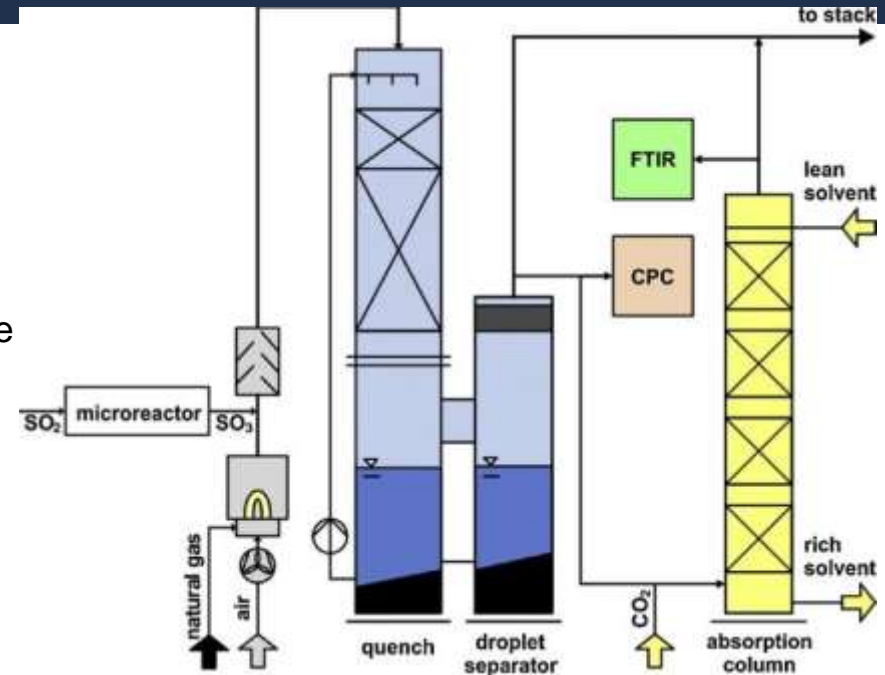
2 *Energy Procedia*, vol. 37, pp. 1793–1796, 2013.

3 *Energy Procedia*, vol. 37, pp. 778–783, 2013.

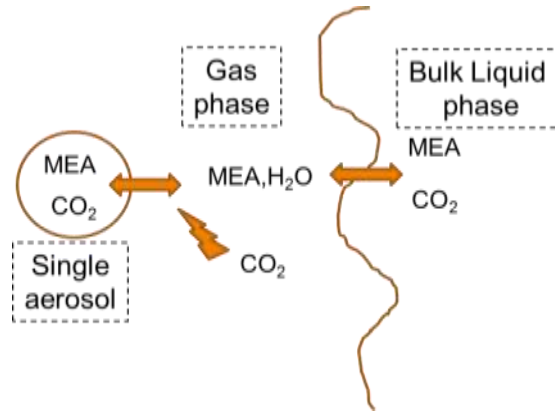
SIMULATED FLUE GAS

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- A common link that could be deduced from these observations was the presence of particulate matter in the feed stream in the form of dust, H_2SO_4 droplets, Na_2SO_4 particles, cracker catalyst fines, or their combination.
- Our group in collaboration with KIT, studied the influence of dust and H_2SO_4 droplets on amine emissions in a controlled laboratory environment⁴



MECHANISM AND INFLUENCING FACTORS



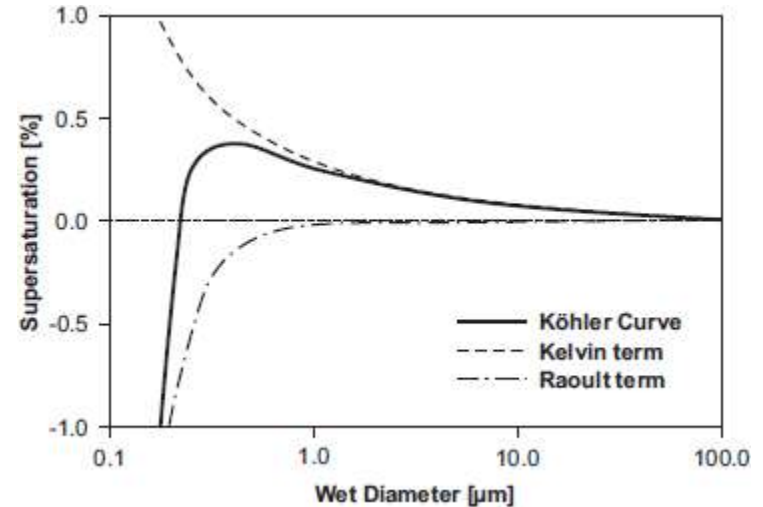
SATURATION RATIO (S)

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➤ Köhler-Theory,

$$S = \exp \left(\frac{4M_w \sigma_{sol}}{RT \rho_w d_p} - \frac{6M_w m_s}{\pi \rho_w M_s d_p^3} \right)$$

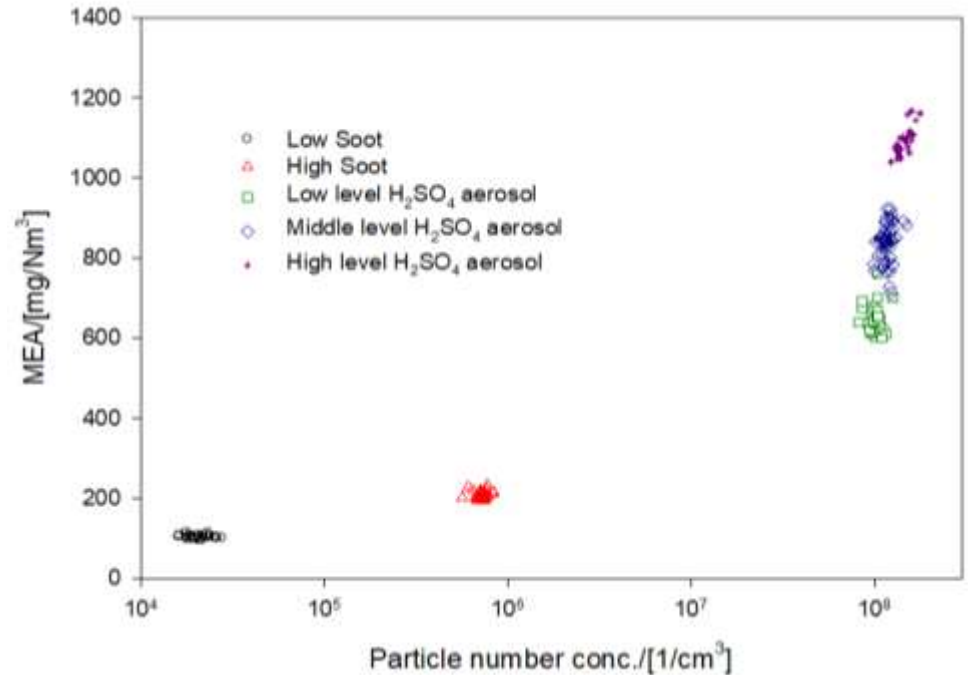
- Equilibrium saturation ratio, S , of a wet particle of diameter d_p is the result of two contrary acting effects⁷,
 - Kelvin term (contribution of the droplet curvature, which increases the necessary saturation for growth) and
 - Raoult term (contribution of the solute, which reduces the vapour pressure of the aerosol droplet and therefore also the necessary saturation for droplet formation and growth):



LINK WITH SOOT AND H₂SO₄ DROPLETS

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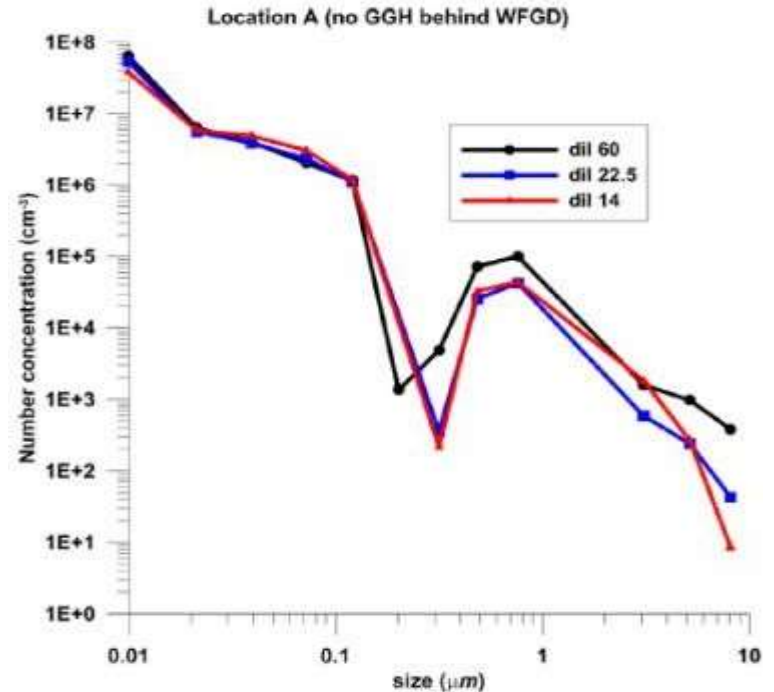
- › An important missing link was the detailed flue gas characterization in terms of particle number and size distribution
- › Field measurements showed flue gas contains particle number concentration in the range of 10⁶-10⁷ per cm³ with most below the size class of 100 nm⁹.
- › H₂SO₄ aerosol droplets are in the range of 10⁷ per cm³ and grown in size at higher H₂SO₄ conc.
- › High amine emissions are indeed possible with presence of H₂SO₄ droplets, but not with only soot in the flue gas.



LINK WITH SOOT AND H₂SO₄ DROPLETS

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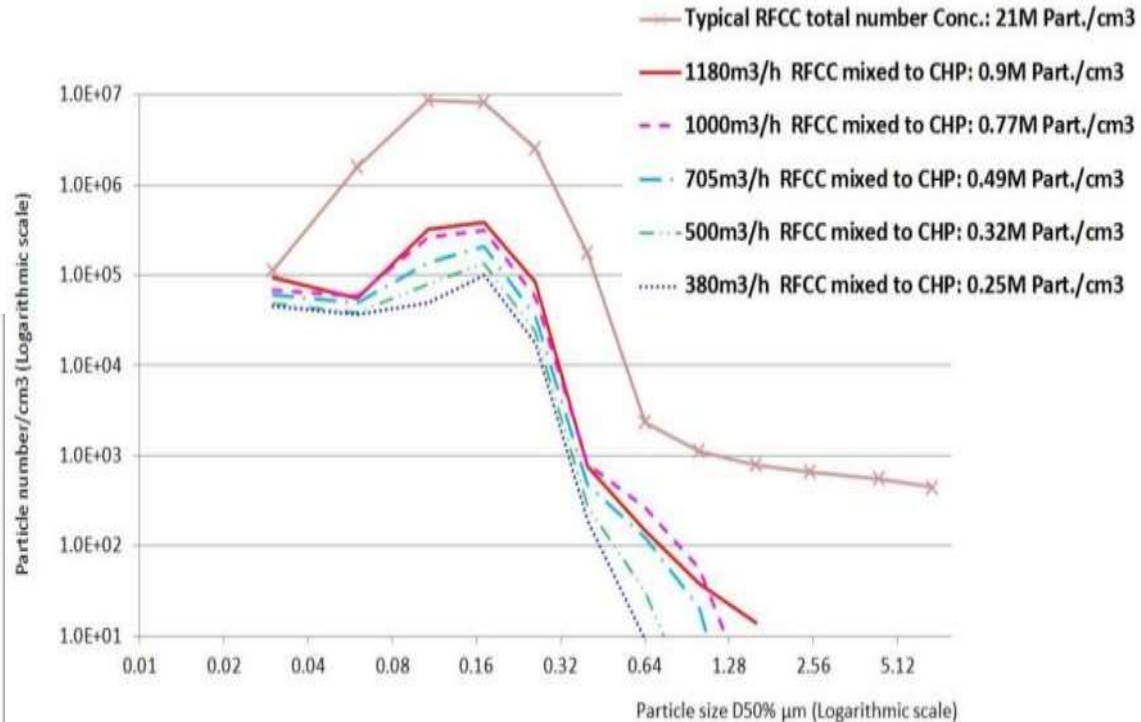
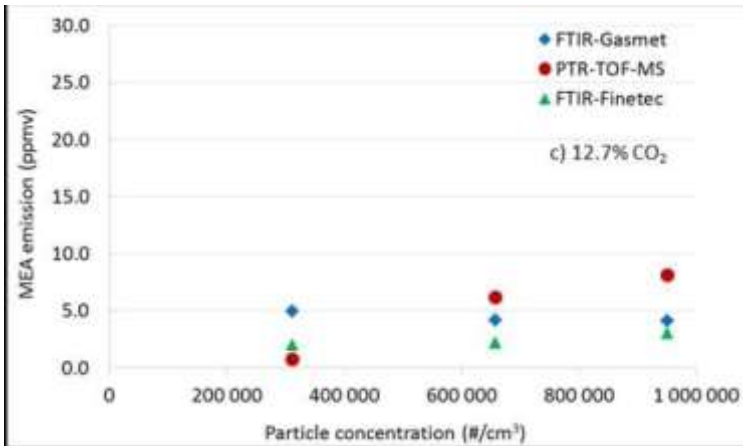
- › Flue gas particle size distribution for a flue gas from coal fired power plant as measured using ELPI+. ⁹
- › Corresponding H₂SO₄ conc. was 5-7 mg/Nm³ (dry, 6 % O₂)
- › Particle number exceeding 10⁷ per cm³ with most particles below 0.1 μm.
- › Confirms simulated flue gas generated at lab scale.



LINK WITH RFCC PARTICLES

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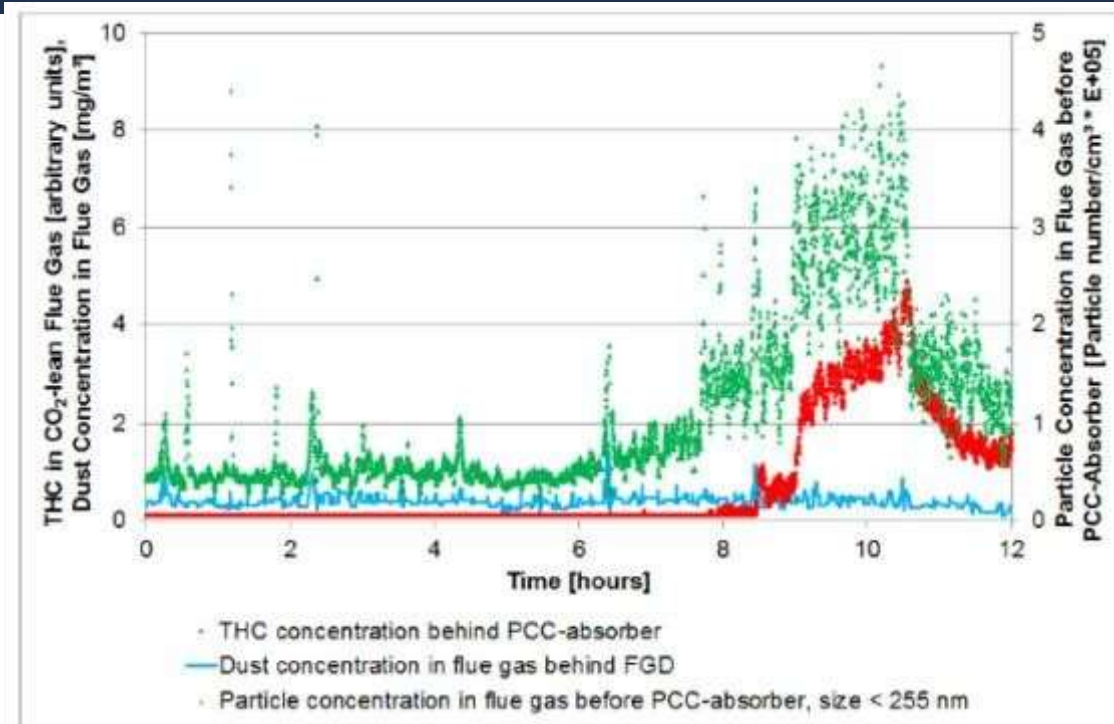
- RFCC catalyst fines¹⁰ are carried over in the flue gas resulting in particle number concentration of greater than 10^7 per cm^3 and sizes in the range of 0.04 to 0.65 μm .
- Results in high MEA emissions, relatively lesser than with H_2SO_4 droplets



LINK WITH Na_2SO_4 PARTICLES

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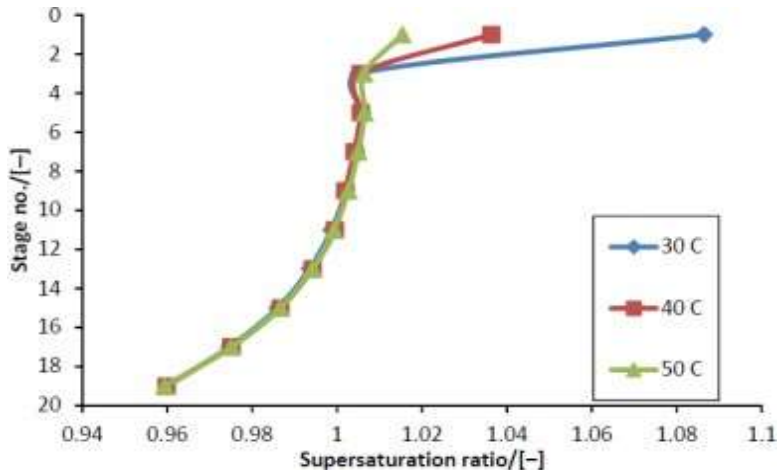
- For lignite fired power plant, SO_3 may be negligible but other inorganic solid particles like Na_2SO_4 could still act as nuclei ⁷
- Bimodal with two modes between 7 to 50 nm and 50 to 255 nm.
- Increase in THC emission by an order of magnitude as a function of particle concentration



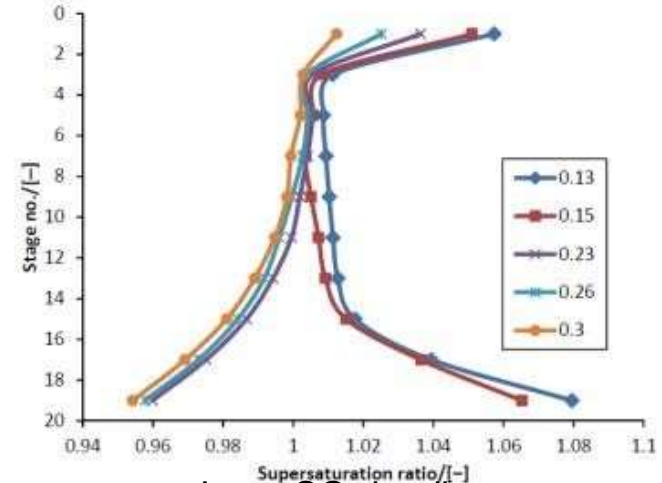
COLUMN OPERATING CONDITIONS

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- Lean solvent temperature and lean solvent loading, amongst the capture plant operating conditions, have the maximum impact on saturation ratio ¹¹
 - Lean temperature change results in variation in S at the top of the column. Increase in lean temperature decreases S.
 - Increasing the CO₂ loading decreases the S, both at the top and bottom of the column.



Lean temperature



Lean CO₂ loading

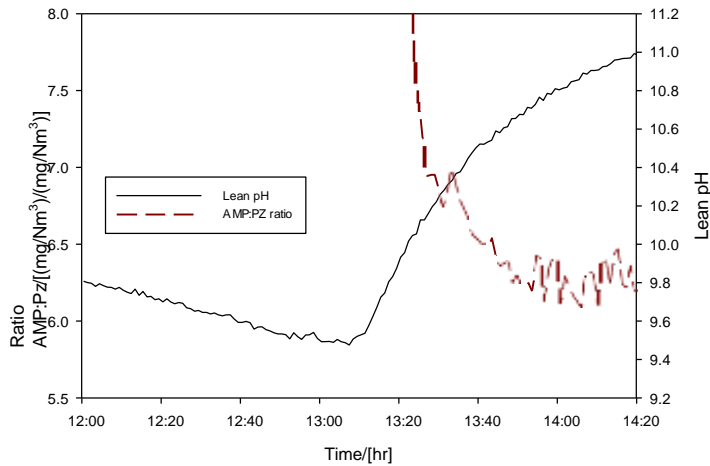
AMINES VOLATILITIES

- Volatilities of amines correlated with molecular groups and structural shapes. Amines have one or more polar groups.
e.g. Hydroxyl, and ether groups, tend to be less volatile due to favourable interactions with water.
- The presence of one or more methyl groups in a structure contributes to non-polarity or greater volatility, case of AMP. Second order effect, the presence of an N-CH₃ contribution in a straight chained amine, or a C-CH₃ contribution in a cyclic amine, correlates to lower volatility.
- Cyclic amines to be less volatile than straight chain amines.
- Amine volatility in water in the order: MDEA < DGA < PZ < 2-MPZ < MAPA < EDA < MEA < DAP < 1-MPZ < AMP.

AMINE REACTIVITY

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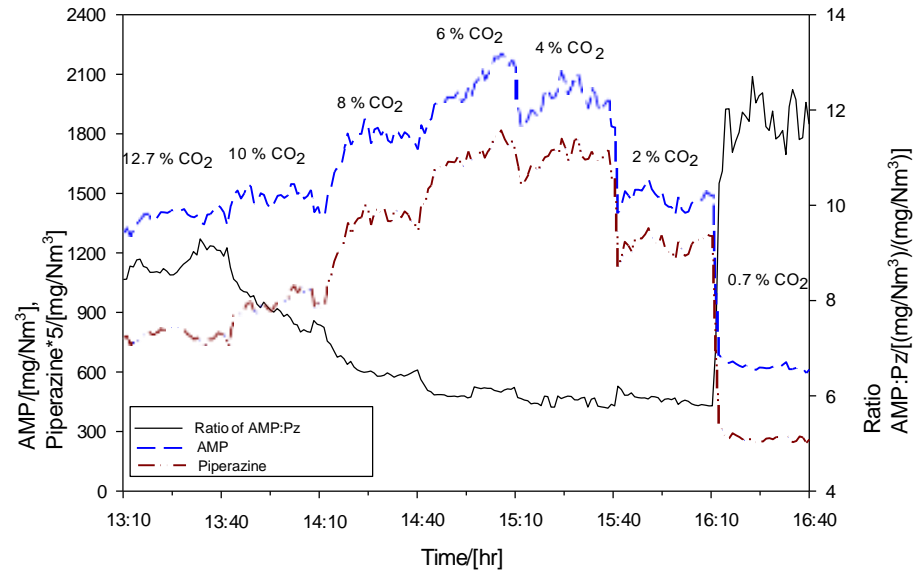
- At higher lean pH relatively more emissions of Pz are observed than of AMP .
- The ratio of AMP:Pz emissions decreases as the CO₂ content in the inlet flue gas is reduced. Ratio of volatile emissions of AMP:Pz is 26.



(a)

Lean pH

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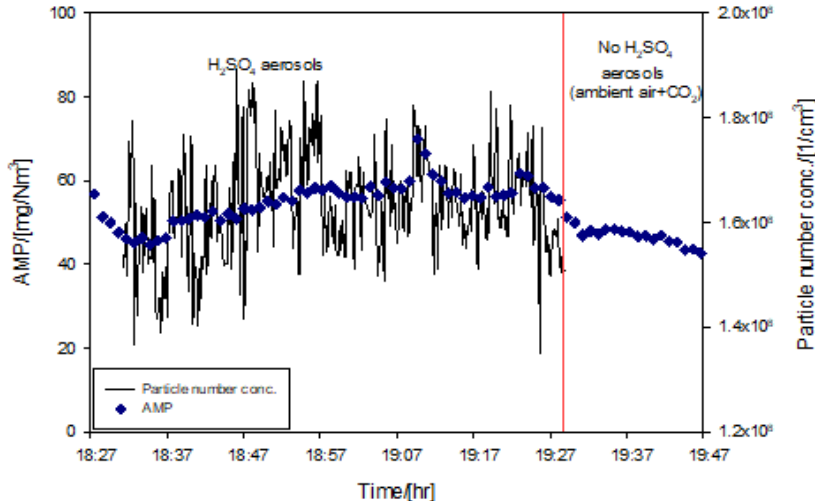


(b) CO₂ in flue gas

AMINE REACTIVITY

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- A mixture of AMP (2.2 M) and potassium taurate (1.5 M) was used. ¹⁶
- Surprisingly, high AMP emissions did not increase even in the presence of H₂SO₄ aerosol droplets
- A slow reacting (with CO₂) component cannot be present in aerosol droplet on its own.



COUNTER-MEASURES

WATER WASH & ACID WASH SCRUBBER.

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Water Wash:

- The water wash section minimizes solvent losses and condenses water vapour to maintain the water balance.
- This is achieved by means of cooling and recirculating water over the packed bed.
- The temperature and the circulation rate of the wash liquid are controlled to maintain the water balance in the system.
- A conventional water wash is a pump around system with cooling and a purge stream to avoid accumulation of absorbed components in the system.

Acid Wash Scrubber:

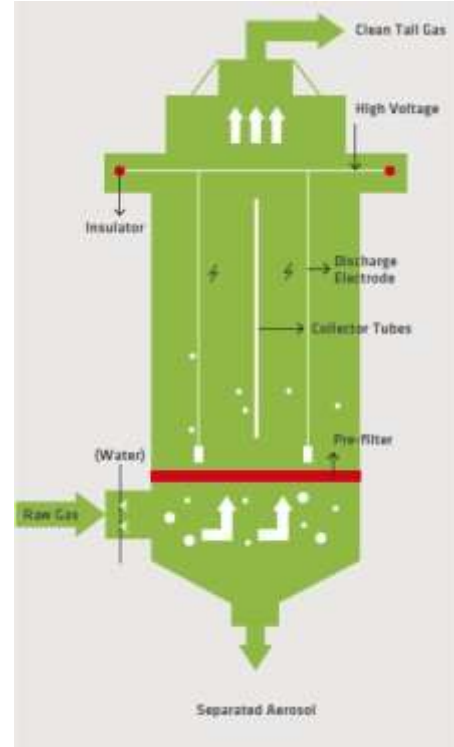
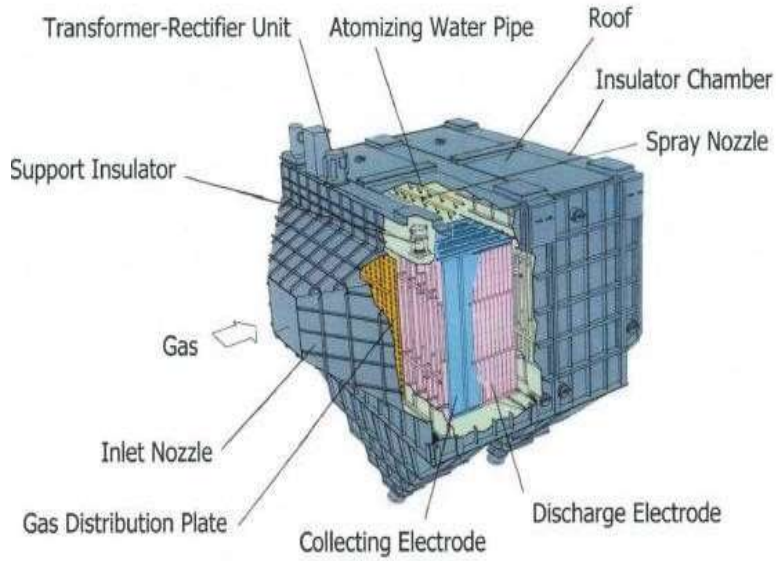
- Located downstream of the water wash as a separate column.
- The acid wash consists of an acid wash column and a buffer tank.
- Acid scrubbing occurs by means of counter-current contact of the flue gas with an acid. An aqueous solution of sulphuric acid (H_2SO_4) was used as the acid liquid. Sulphuric acid was used here because it is the most commonly used acid.



3D acid wash column. The total height of the column is 4.7 m from the base to the top

WET ELECTROSTATIC PRECIPITATOR (WESP)

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SCIENTIFIC DEBATE

A wet electrostatic precipitator (WESP) as countermeasure to mist formation in amine based carbon capture

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The wet electrostatic precipitator as a cause of mist formation—Results from the amine-based post-combustion capture pilot plant at Niederaussem

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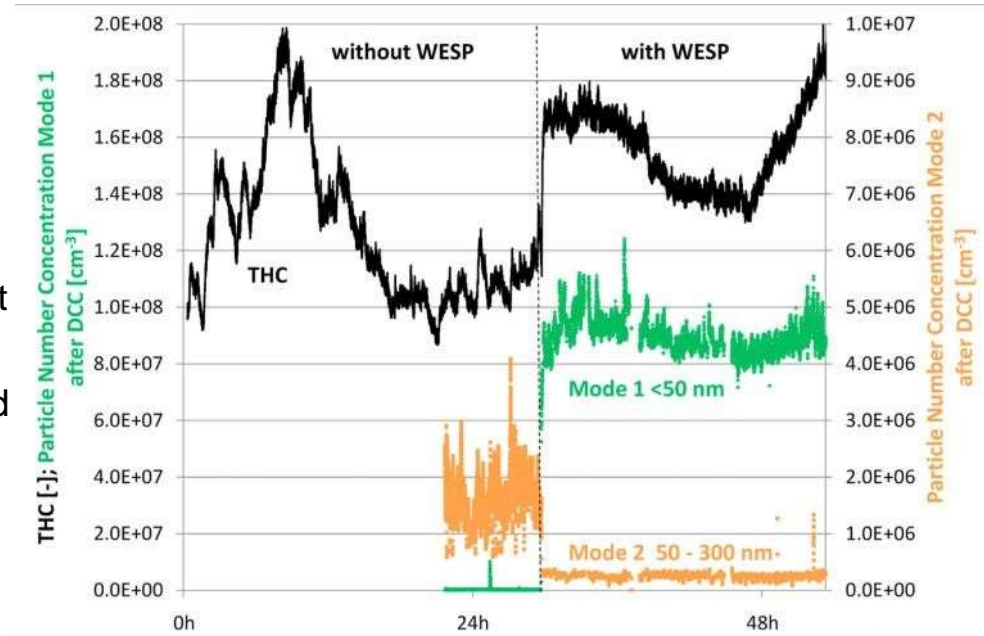
^c Linde-Engineering Dresden GmbH, Bodenbacher Str. 80, 01277 Dresden, Germany



WESP AS A SOURCE OF FINE PARTICLES

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- › At sufficiently high voltages, WESP generates ultrafine aerosol nuclei causing further aerosol based mist emissions
- › In a high voltage electrical field,
 - › Electrostatic repulsion → increase in size
 - › Surface energy → reduce surface area
- › Maximum charge capacity is given by Rayleigh limit
 - › Fission of droplet at charge above limit
 - › Practical limit is 55-80% of theoretically defined limit
- › Although limit for droplets 50nm to 10 μm is less than that expected in WESP, in-homogeneity and space charge effect can lead to localised effects¹⁴



WESP DESIGN

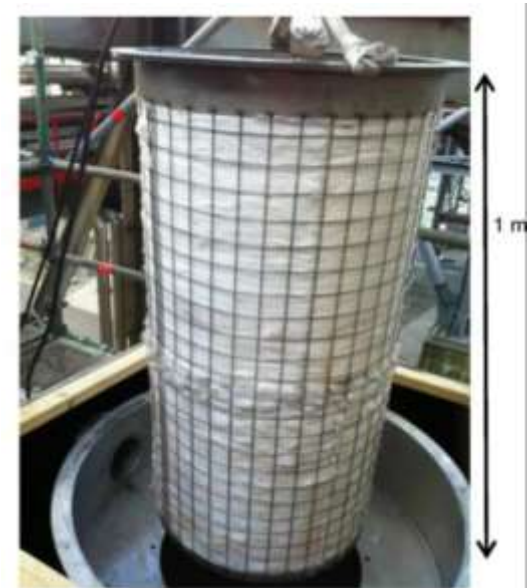
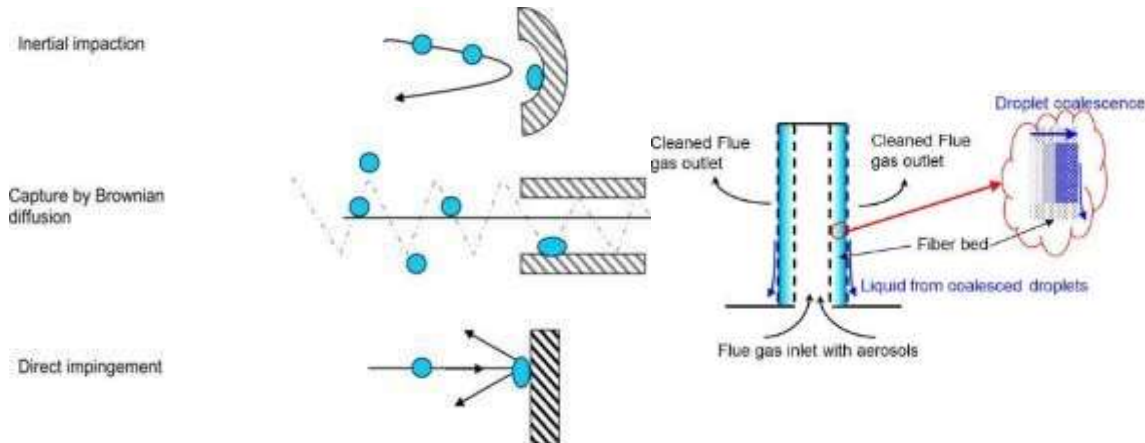
The parameters that are important for the design of WESP are;

- › Power input/ applied voltage: Typically, increasing the power input leads to increased collection efficiency. However, the power supply system should be design to avoid arcing or sparking. Moreover, at very high voltages generation of ultrafine aerosols can occur.
- › Flue gas velocity/Gas residence time: Sufficient residence time must be provided in order to achieve optimal charging and collection efficiency. Typical gas velocity is in the range of 1-2.5 m/s.
- › Particle size distribution: WESP is efficient for particles below 1 μm . Thus, larger particles must be eliminated prior to WESP by a pre-filter.
- › Particle composition: The chemical composition of the particle influences the particle resistivity. A too high resistivity of the particles impairs the charge exchange.
- › Gas temperature: The gas temperature influences the resistivity of the particle. Operating temperature

BROWNIAN DEMISTER

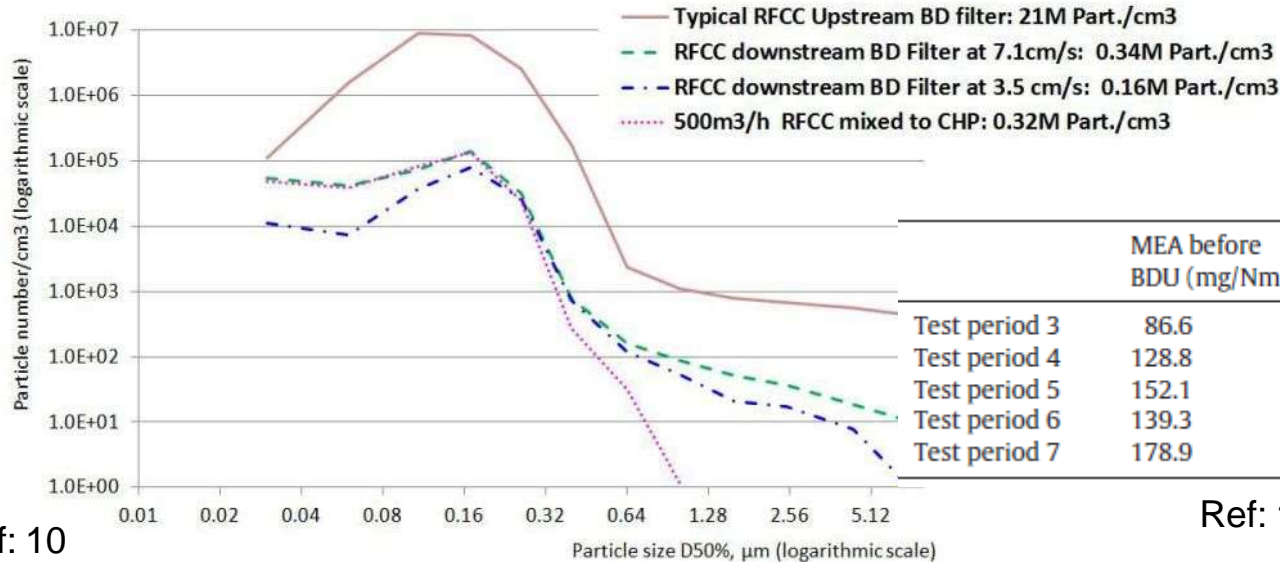
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- › Low approach velocities (~ 0.1 m/s) are necessary in order to attain the diffusion velocities associated with Brownian movement.
- › Removal of very fine mist droplets of less than $1\ \mu\text{m}$.
- › Candle filter element made up of polypropylene



BROWNIAN DEMISTER

- ▶ Particle removal and MEA emission reduction efficiency greater than 98 % (note both the measurements were at different location.)
- ▶ However, it comes at a cost of additional pressure drop, in the range of 10-25 mbar. Increase in operating cost is about 0.2 €cent/tonne CO₂ captured for 20 mbar pressure drop across the BD filter.



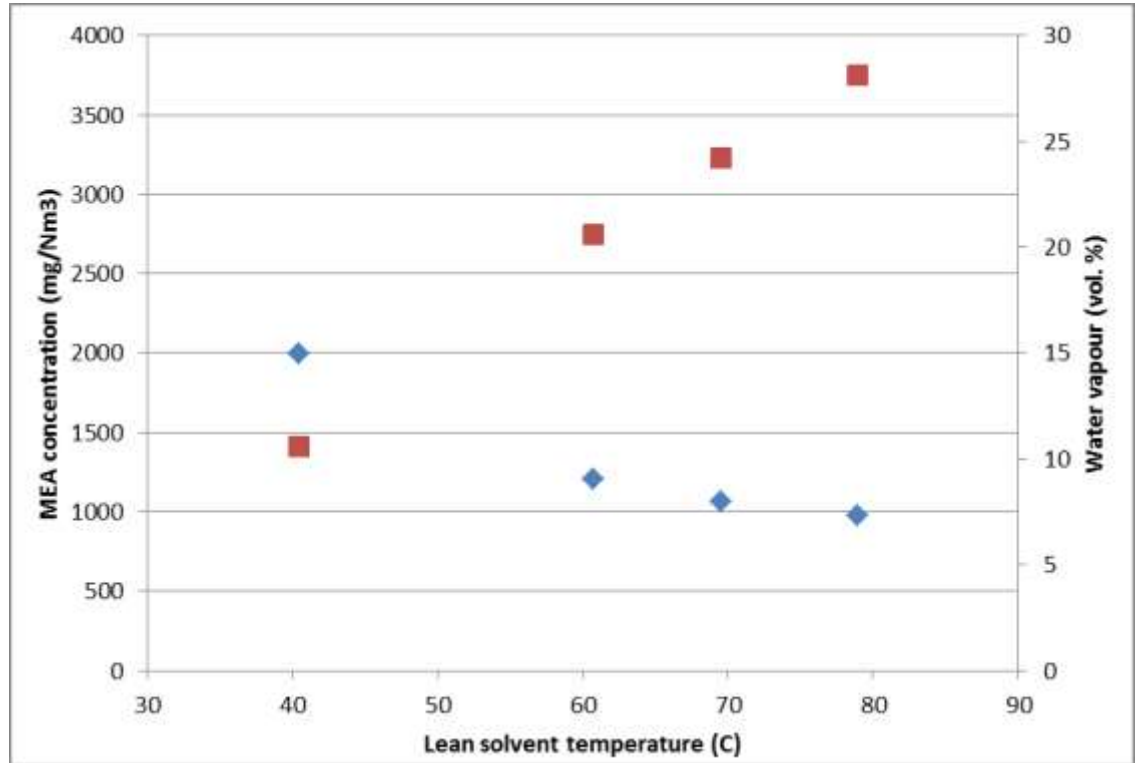
	MEA before BDU (mg/Nm ³)	MEA after BDU (mg/Nm ³)	BDU removal efficiency (%)
Test period 3	86.6	1.2	98.6
Test period 4	128.8	1	99.2
Test period 5	152.1	1.3	99.2
Test period 6	139.3	1.9	98.6
Test period 7	178.9	4	97.8

ABSORBER OPERATION-CHANGE IN LEAN SOLVENT TEMPERATURE

TEMPERATURE

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- › Lower emissions at higher lean solvent temperature
- › Cause linked to lower supersaturation i.e. driving force



PROPRIETARY COUNTER-MEASURES

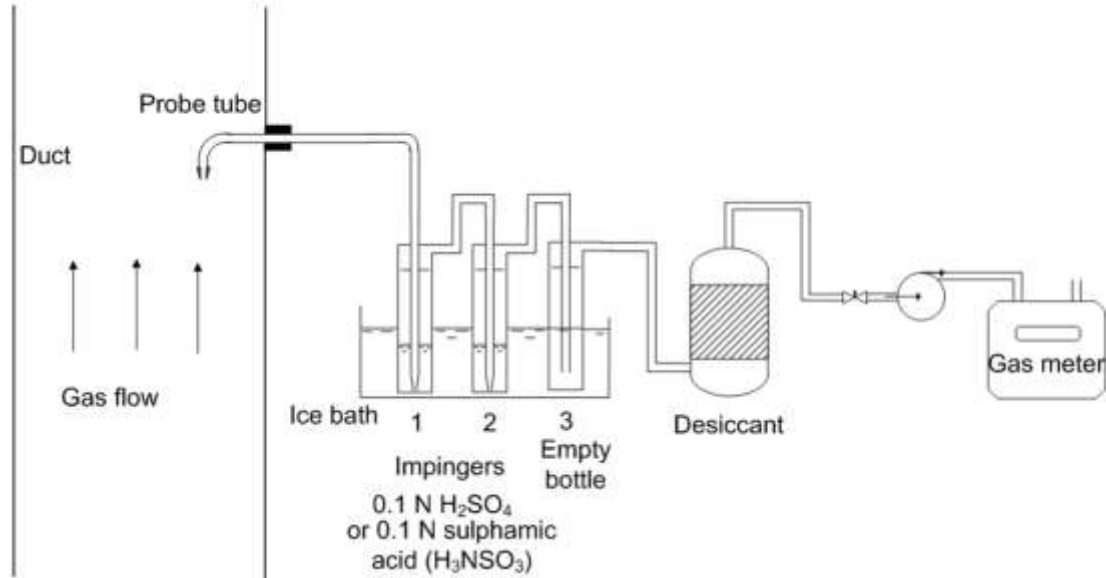
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- › BASF's "Dry Bed" and "Pre-treatment" counter-measure
 - › A pre-treatment method based on increasing the size of the nuclei entering the absorber (by cooling or steam injection) so that they can be removed by inertial separation was tested in combination with a WESP.
 - › Packed bed downstream the CO₂ lean flue gas, with a small stream of wash liquid to recover the organics in the vapour phase. This prevents further amine condensing on the aerosol droplets in the water wash section. However the water based aerosol droplets which are not removed by conventional demister will still persist.
- › Aker solution's Anti-Mist system
 - › Aker solution's Anti-Mist design consists of a novel absorber design to prevent amine mist formation and a pH-controlled wash stage to capture the volatile alkaline compounds
- › MHI's amine reduction system and a special demister
 - › MHI concluded that a proprietary wash system combined with water repellent demisters could drastically reduce emission (Nagayasu et al., 2013)

GAS SAMPLING TECHNIQUE

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- Analysing MEA and Nitrosamines in the gas phase.
- The gas is sucked by means of a vacuum pump through a probe tube from the duct of the gas flow.
- Two impingers containing liquid (sulfamic acid or sulphuric acid) captures the gaseous components and a third impinger is kept empty to trap any carryover liquid.



Schematic representation of the gas sampling technique.

KEY TAKEAWAYS

- › Aerosol mist emissions is a serious point of concern in PCCC when considering the **entire life time** of both the power and capture plant
- › Suitable counter-measures must be included in the **design stage** of the PCCC plant
- › **Main governing factors** for mist emissions are particle number concentration, size distribution, H₂SO₄ droplet concentration, and activity of the amine. However, only a qualitative relationship between these factors is known, due to the **complex interplay** of various effects, plant design and operation.
- › Underlying fundamental mechanism of supersaturation based prediction of aerosols is incomplete.
- › WESP and BD filter are 2 known and readily available counter-measures;
 - › WESP is a **proven and efficient** counter-measure for aerosol nuclei removal and for avoiding corresponding amine mist emissions. However, it can also lead to **generation of ultrafine mist** resulting in amine mist emissions.
 - › Brownian demister has also been proven to reduce ultrafine nuclei and avoids amine mist emissions
- › Site specific appropriate design of each counter-measure is essential for achieving required efficiency and cost-effective operation

- In process of getting permissions for site visit i.e. in National Thermal Power Corporation (NTPC), Vindhyachal India.
- Initiated procurement of instruments.
- Expect to perform site measurements at (NTPC), Vindhyachal in 1-2 months from now.
- Expect to carry out site measurements in 6 months from now, at Alkali Chemical and Fertilizers Limited Tuticorin India.

ACKNOWLEDGEMENT



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QUESTIONS



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Thank you for your attention

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IDEAL SOLVENT AND DIRECT IMPACT ON A PCCC

Table 1. Criteria for an ideal solvent and its direct impact on a PCCC process.

Sr.No	Criteria	Direct Impact
1	High CO ₂ capacity	Lower amount of required solvent
2	Fast reaction kinetics	Shorter absorption column
3	Resistance to degradation	Reduced solvent make-up
4	Resistance to corrosion	Increased lifetime of the plant
5	Health, Safety and Environmental	Easy to handle and dispose
6	Cost and procurement	Lower operating costs and easy availability

Mini Column MIPL

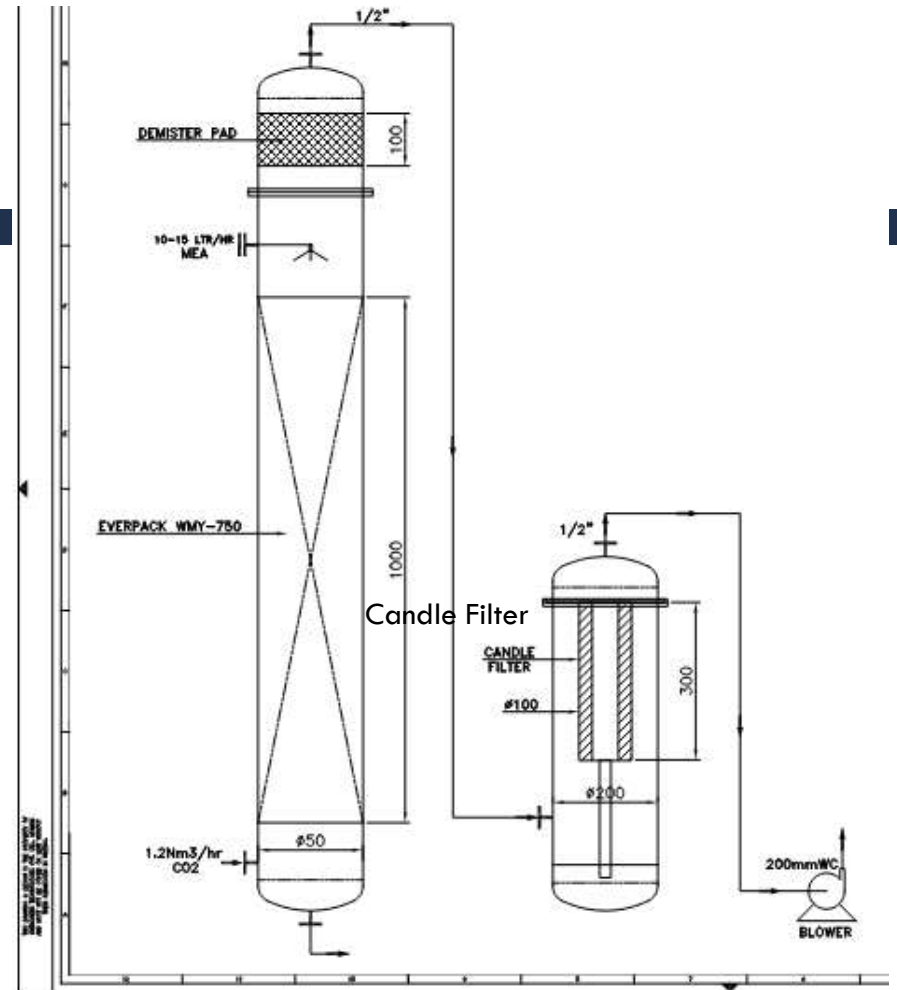
Demister Pad

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10/15LTR/HR MEA

- Liquid circulation pump of about 50 lit/hr.
- Gas sampling ports up and downstream of absorber.
- The column be in +ve pressure
- Gas Flow rate: $\sim 1\text{-}5\text{ m}^3/\text{h}$ is the minimum for stack monitoring kit
- Heat the liquid to 40 deg.c

1.2 Nm³/hr CO₂



Sites measurement: MIPL, IIT KGP GGS IPU

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- ❖ The consortium has chosen the only two sites available with a Post Combustion CO₂ capture plant.
- ❖ **Case1 - Single emission: Tuticorin Alkali Chemical and Fertilizers Limited.** India produces all grades of soda ash and co-produces Ammonium Chloride Fertilizer. It is located at Thoothukudi (formerly Tuticorin), a industrial port city in Thoothukudi district in the Indian state of Tamil Nadu.(www.tacfert.in). The major raw materials are Ammonia (imported), CO₂ gas (separated from boiler flue gas) and the locally produced salt. In 2016, TFL partnered with Carbon Clean to create the world's first fully commercial carbon capture, storage and utilisation plant. It has been achieving over 90% carbon capture rates since it began operation. Installed on a coal-fired boiler, the plant is designed to capture 60,000 tonnes of CO₂ per year. The plant is also able to convert the CO₂ into soda ash.

- **Case 2- Single emission: National Thermal Power Corporation, Vindhyachal.**
- It is located in Singrauli district in the Indian state of Madhya Pradesh. One of the coal-fired power stations of NTPC, it is the largest power station in India, and the 9th largest coal-fired power station in the world, with an installed capacity of 4,760 MW (Units operational: 6×210 MW, 7×500 MW). The coal for the power plant is sourced from Nigahi mines. The CO₂ capture plant at NTPC, Vindhyachal is expected to be in operation by May 2022 and based on proprietary technology (absorption-desorption based) using CDRmax, a proprietary solvent of Carbon Clean Ltd.
- Historic pollutant emission data and meteorological information will be collected for the two sites and a range of emission scenarios to assess the impact of CO₂ capture plant on the pollution levels and further on the nearby environment.

- ❑ **Emission measurements at CO₂ capture- plant test sites in India.**
- **Feed flue gas:**
- ❑ Stack monitoring kit from GGS IPU: To be used for sampling flue gas for all measurements below.
- ❑ Multi-gas analyser from GGS IPU: VOC as C_xH_y, NH₃, SO_x, NO_x, CO₂, O₂.
- ❑ CPC from IIT KGP: Total particle number concentration
- ❑ Cascade impactor from IIT KGP: Particle mass distribution
- ❑ Impingers: GGS IPU: SO₃

- **Flue gas from mini-CO₂ capture plant:**
 - Mini-CO₂ capture absorber from MIPL: Total gas Flowrate ~ 1-5 m³/h
 - Multi-gas analyser from GGS IPU: VOC as C_xH_y, NH₃, SO_x, NO_x, CO₂, O₂.
 - CPC from IIT KGP: Total particle number concentration
 - Cascade impactor from IIT KGP: Particle mass distribution
 - Impingers from GGS IPU: SO₃, Monoethanolamine, Piperazine, 2-Aminomethyl propanol (AMP), 2-Aminoethyl piperazine (AEP)., Nitrosamines.

- **Flue gas from pilot-CO₂ capture plant:**
 - Mini-CO₂ capture absorber from MIPL: Total gas Flowrate ~ 1-5 m³/h
 - Multi-gas analyser (Add make & model no.) from GGS IPU: VOC as C_xH_y, NH₃, SO_x, NO_x, CO₂, O₂.
 - CPC from IIT KGP: Total particle number concentration
 - Cascade impactor from IIT KGP: Particle mass distribution
 - Impingers from GGS IPU: SO₃, Monoethanolamine, Piperazine, 2-Aminomethyl propanol (AMP), 2-Aminoethyl piperazine (AEP), Nitrosamines.

Ultrafine particle counter



P-TRAK Ultrafine particle counter, Model no. 8525 from TSI; Concentration range: 0 to 5×10^5 particles/cm³, Particle size range: 0.02 to 1.0 μm ; Flow Rate: 100 cm³/min; Weight: 1.7 kg. P-Trak gives direct, real-time measurement of workplace ultrafine particulate levels (Picture below).



Cascade impactor

Particle mass distribution (Mini-MOUDI Impactor)

(non-rotating) Model: 135-8B, 8 Stage (cut point diameters: 0.18, 0.32, 0.56, 1.0, 1.8, 3.2, 5.6 and 10 μm), Inlet Cone; Impactor is made of anodized aluminum for light weight (0.325 kg; D x H: 66 x 77 mm), durability and nozzle dimensional stability; Low pressure drop (10 kPa); Flow rate: 2Lpm vacuum pump: 4.8V, 2.15 A-h NiMH battery; Operating conditions: 10–50°C (50–122°F); 0%-90% RH (non-condensing). (Picture below)



Impinger