Waste Water Treatment for Fossil Fuelled Power Plant: Current Practice and Future Trends.

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Review of Discharge Consents and Permits

- Discharge Consents (pH, T, suspended solids, oil).
- North Sea Protocol (1980s).
- List I (Red List) - Limited the concentration of Cd, Hg and a range of organic species.
  - List II (Grey List) - As, B, Cr, Cu, Fe, Ni, Pb, V, Zn [Al, Ag, Co, Mn, Sn].
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  - Environmental Protection Act (1990).
- Integrated Pollution Prevention and Control (IPPC) – 2000.
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Sources of Contaminants in Aqueous Discharges: The Basic Power Plant

- Water Treatment Plant – acid and alkali regenerants.
- Cooling Water – chlorination and concentration factor.
- Boiler and Turbine Drains – oil; metal oxides; dissolved additives.
- Ash Lagoons – suspended solids; dissolved metals.
- Coal Stocks Drains – suspended solids; dissolved metals; acidity.
- Transformers and Transmission – oil.
- Air Heater Washing – acidic waste; particulates; metals.

Sources of Contaminants in Aqueous Discharges from Environmental Control Technologies

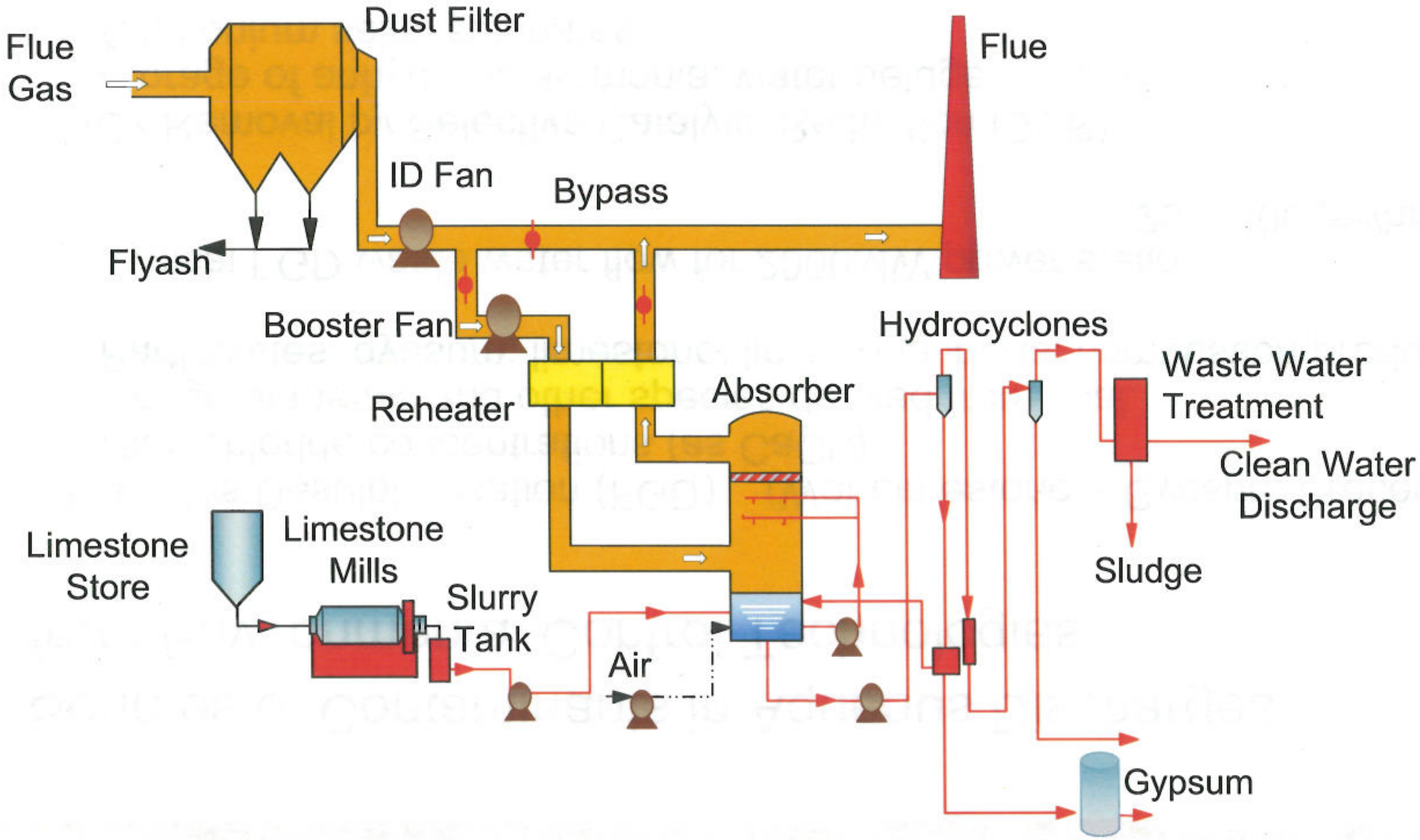
- Flue Gas Desulphurisation (FGD) (Wet Limestone – Gypsum Process)
  - High chloride concentrations (as $CaCl_2$).
  - Range of metals and other species derived from coal.
  - Particulates: gypsum; limestone; limestone inerts; combustion products.

  - Typical FGD waste water flow for 2000MW power station : 20 – 100 m^3/hr.

- NOx Removal by Selective Catalytic Reduction (SCR).
  - Storage of anhydrous ammonia; water deluge for emergencies.
  - Ammonium salts; sulphates.

- Carbon Capture and Storage (CCS) (Post combustion processes).
  - Organic amines and associated products.
  - Ammonium salts.
  - Sulphate species.

Flue Gas Desulphurisation (limestone-gypsum process)



FGD Waste Water: Sources of Impurities

$$SO_2 + H_2O + CaCO_3 \rightarrow CaSO_3 + CO_2 + H_2O$$

$$CaSO_3 + [O] \rightarrow CaSO_4$$

[Absorber pH ~ 5.2 – 5.5]

Fine particulates:

- Gypsum.
- Unreacted limestone and inert materials from raw limestone.
- Flyash.
- Unburnt fuel.

Dissolved Species:

- Metal cations derived from fuel (fly ash and volatiles) and limestone;
  - eg Cd, Hg, Ag, Cr^{III}, Cu, Fe, Mn, Mo, Ni, Pb, Sn, V, Zn.
  - Metal oxy-anions – As, Sb, Se, B, Cr^{VI}, Mn(?), Mo (?), V(?).
- Anions – mainly from Cl and F in fuel.
  - Also sulphate (liquor saturated to gypsum) and trace of nitrate.

FGD Waste Water Treatment:
Typical Input Concentrations and Discharge Limits (mg/l)

Parameter	T °C	pH	TSS	Al	Ag	Cd	Cr	Cu	Fe	Hg	Mn	Mo
Input	40 - 50	4.5 – 5.5	5,000-10,000	100 - 500	0.01	0.2 - 0.3	0.02 - 0.5	0.02 - 1.0	0.5 - 100	0.001 -0.5	25 - 70	0.1 - 1.0
Outlet Limit	30 - 40	6 - 10	30	3.6	0.05	0.025	0.5	0.15	1.8	0.03	3.0	2.0

Parameter	Ni	Pb	Sn	V	Zn	As	B	Sb	Se	Cl	F	N (NH_3)
Input	1.0 - 5.0	0.02 - 1.0	0.01 - 0.5	0.05- 1.0	5.0 - 7.0	0.005 - 3.0	40 - 100	0.1 - 0.5	0.1- 0.25	5,000-30,000	20 - 100	?
Outlet Limit	0.2	0.2	0.5	0.1	0.5	0.1	175	0.08	0.15	30,000	20	10

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FGD Waste Water : Treatment Philosophy

- Raise pH with an alkali [NaOH or $Ca(OH)_2$] to precipitate metal hydroxides.
- Add a sulphide to precipitate metal sulphides.
  - Use either sodium sulphide solution or tri-mercapto triazine (TMT).
- Add a coagulant to capture precipitated hydroxides and sulphides, plus fine particulates.
  - Typically Ferric Chloride.
- Add a flocculation aid to promote settlement of sludge.
  - Generally a polyelectrolyte.
- Separate water and sludge in a clarifier and sludge thickener.
  - Dewater sludge and dispose to landfill or refire with fuel.
- Clarified water pH adjusted (HCl) and cooled prior to discharge.

FGD Waste Water – Future Developments

- There is pressure to improve the sulphur removal performance of existing FGD installations.

- This may be achieved by adding up to 1000mg/l of organic acids to the absorber liquor.
  - Typical acids are adipic acid, or a waste product di-basic acid (DBA).
  - These acids buffer the scrubber pH and enhance limestone dissolution.

- These organic acids will be present in the FGD waste water.
  - They will not be removed by currently installed technologies.
  - A form of oxidative or micro-biological digestion will be required.

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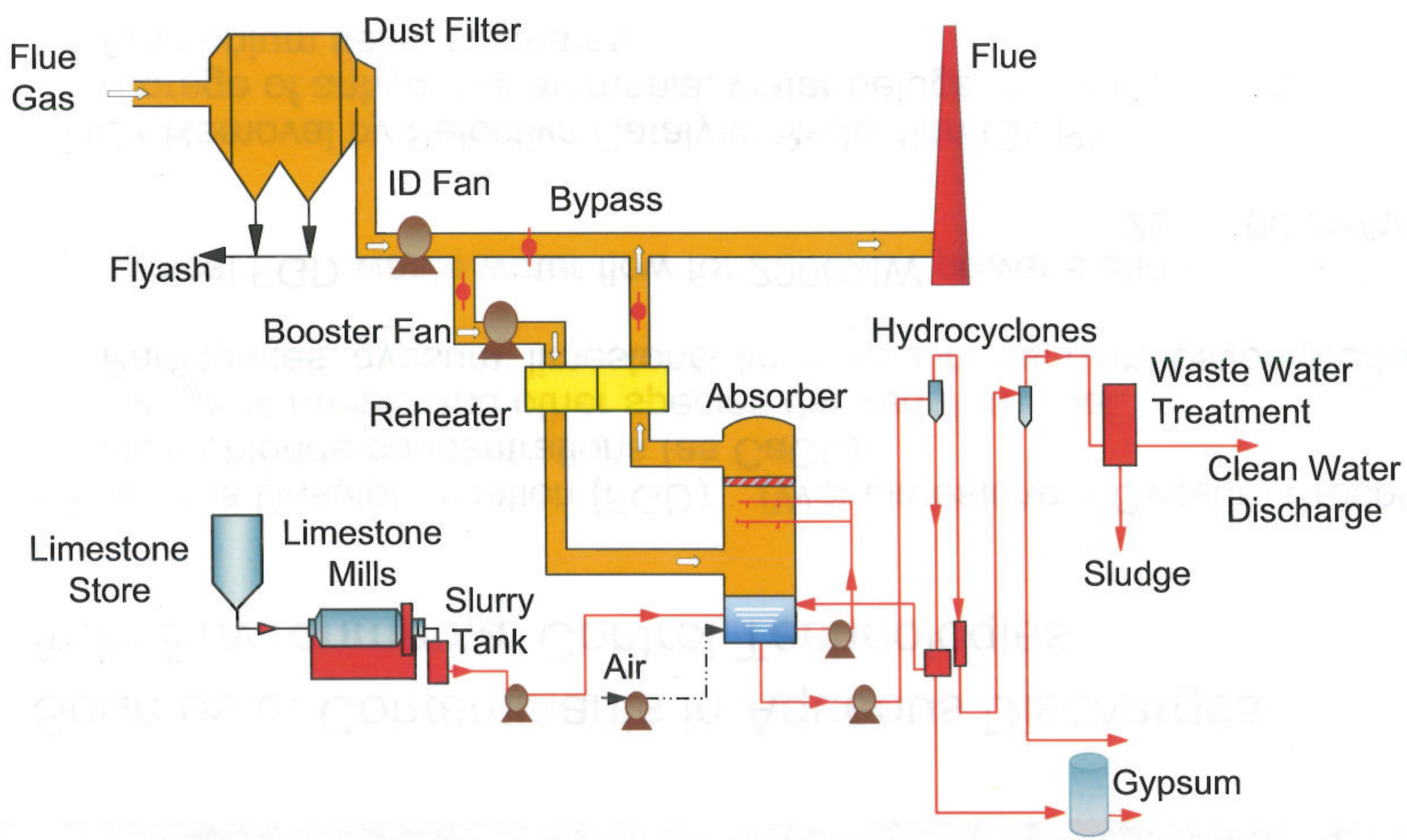

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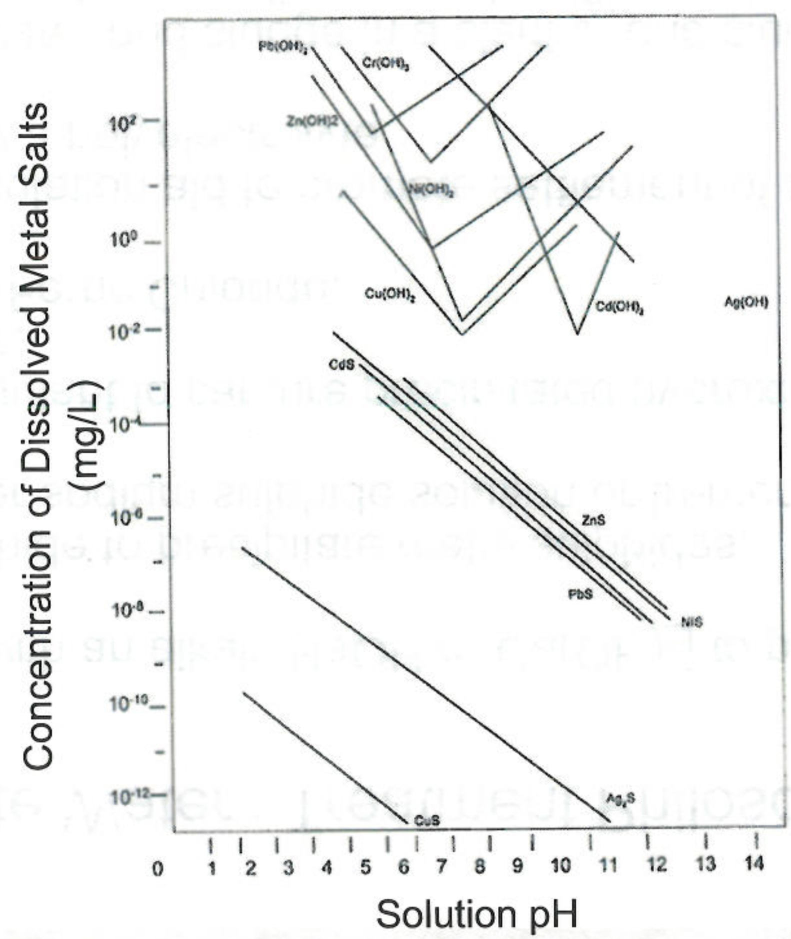
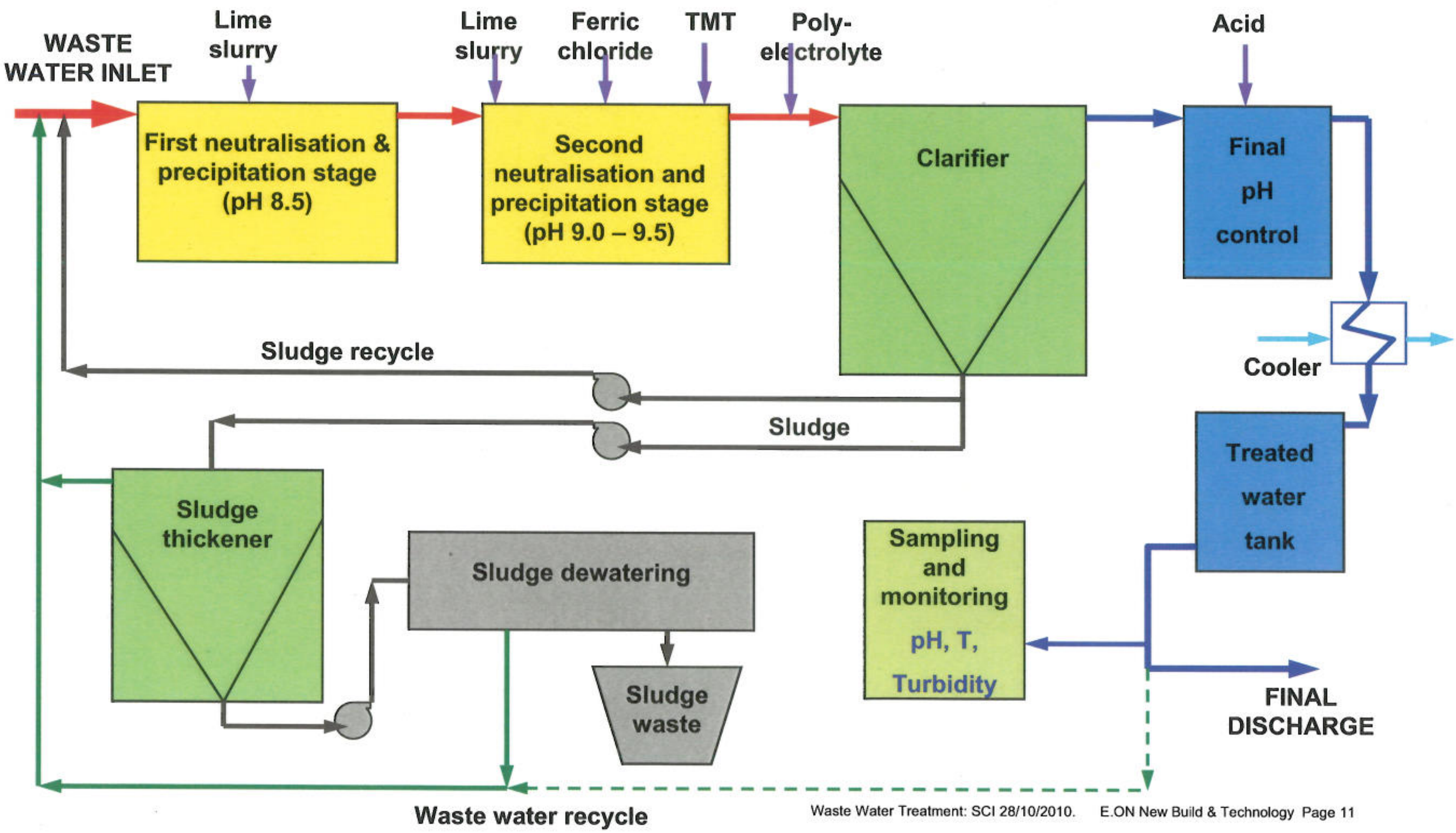
Solubility Data: Metal Hydroxides and Metal Sulphides



Schematic of FGD Waste Water Treatment



FGD Waste Water : The Fluoride Conundrum

- In theory Calcium Fluoride has a very low solubility that should always achieve fluoride discharge limits.
  - Solubility product data predicts 3 or 8 mg/l F for saturated CaF_2.
  - Background calcium concentration should reduce fluoride solubility due to the "common ion" effect.
- In practice, in some plants, it has been difficult to achieve the < 20 mg/l F limit.
- Fluoride precipitation is dependent on both pH and background calcium chloride concentration.
  - Fluoride concentration decreases as both pH and chloride (calcium) concentration increase.
- Optimal pH appears to be around pH 9.5 .

FGD Waste Water – Future Developments

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- This may be achieved by adding up to 1000mg/l of organic acids to the absorber liquor.
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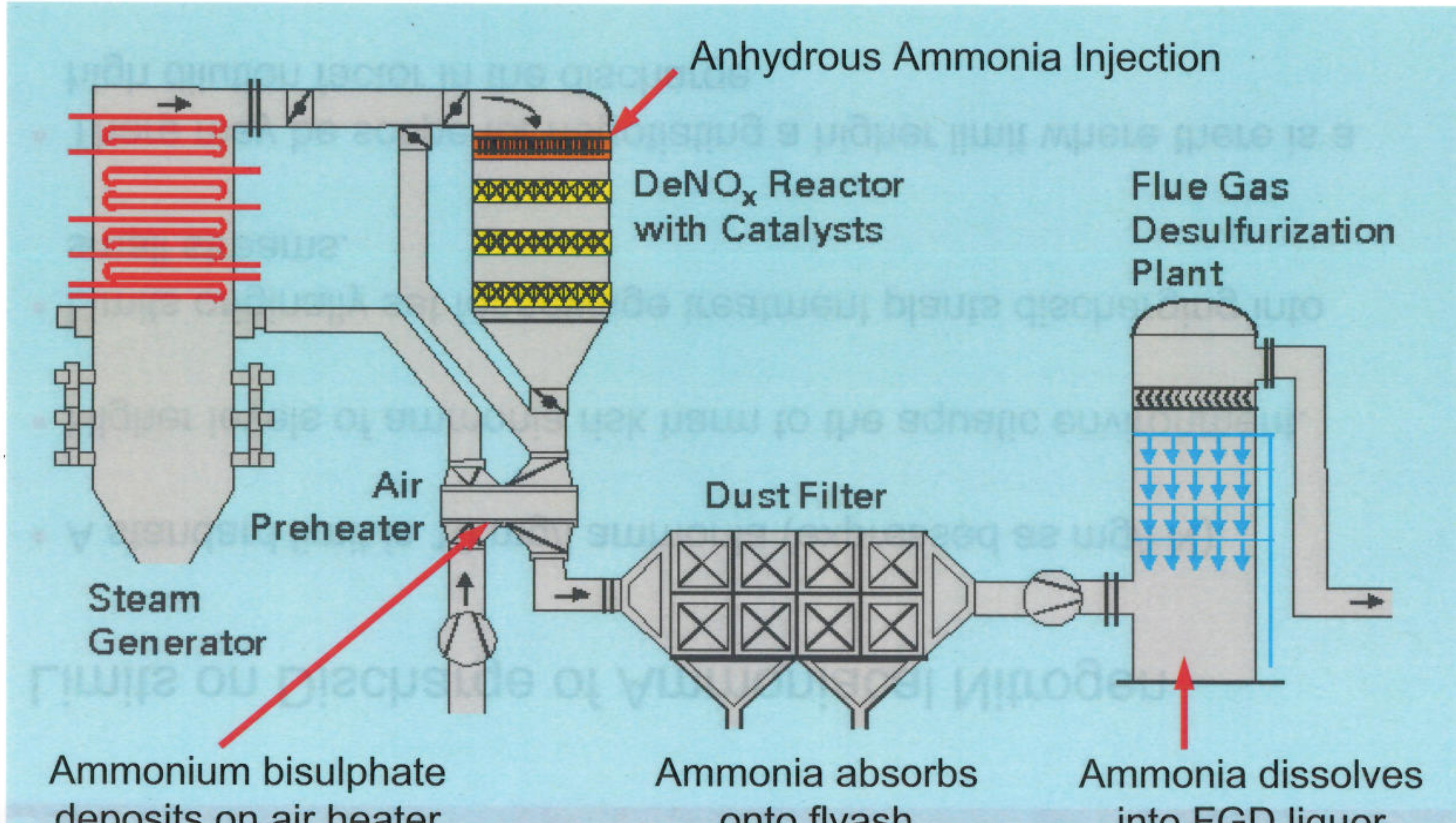
Schematic of NOx Removal by SCR

$$8\,NH_3 + 6NO_2 = 7\,N_2 + 12\,H_2O$$



Limits on Discharge of Ammoniacal Nitrogen

- A standard limit is 10 mg/l ammonia (expressed as mg/l N).
- Higher levels of ammonia risk harm to the aquatic environment.
- Limits originally set for sewage treatment plants discharging into small streams.
- There may be scope for negotiating a higher limit where there is a high dilution factor in the discharge.

Technologies for Removal of Ammoniacal Nitrogen

Technology	For / Against
Chemical Oxidation NaOCl; ClO_2; H_2O_2 / UV; O_3.	Oxidation of variable effectiveness Risk of tri-halo methane production Risk of scaling and S-N compounds
Adsorption / Precipitation Zeolite adsorption Struvite precipitation	Reaction rates slow Effect of high $CaCl_2$ background Scaling
Microbiological Digestion (i) Aerobic : $NH_3 \rightarrow NO_2^-$ (ii) Aerobic : $NO_2^- \rightarrow NO_3^-$ (iii) Anaerobic : $NO_3^- \rightarrow N_2$	Well established for sewage treatment Prefers stable flow, concentration, temp. Conditioning to high Cl^- background Potential for process kill
Reed bed wetlands	Large open area Low temperature – low activity Management of reed beds

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Optimal Management of Ammonia Discharges from SCR

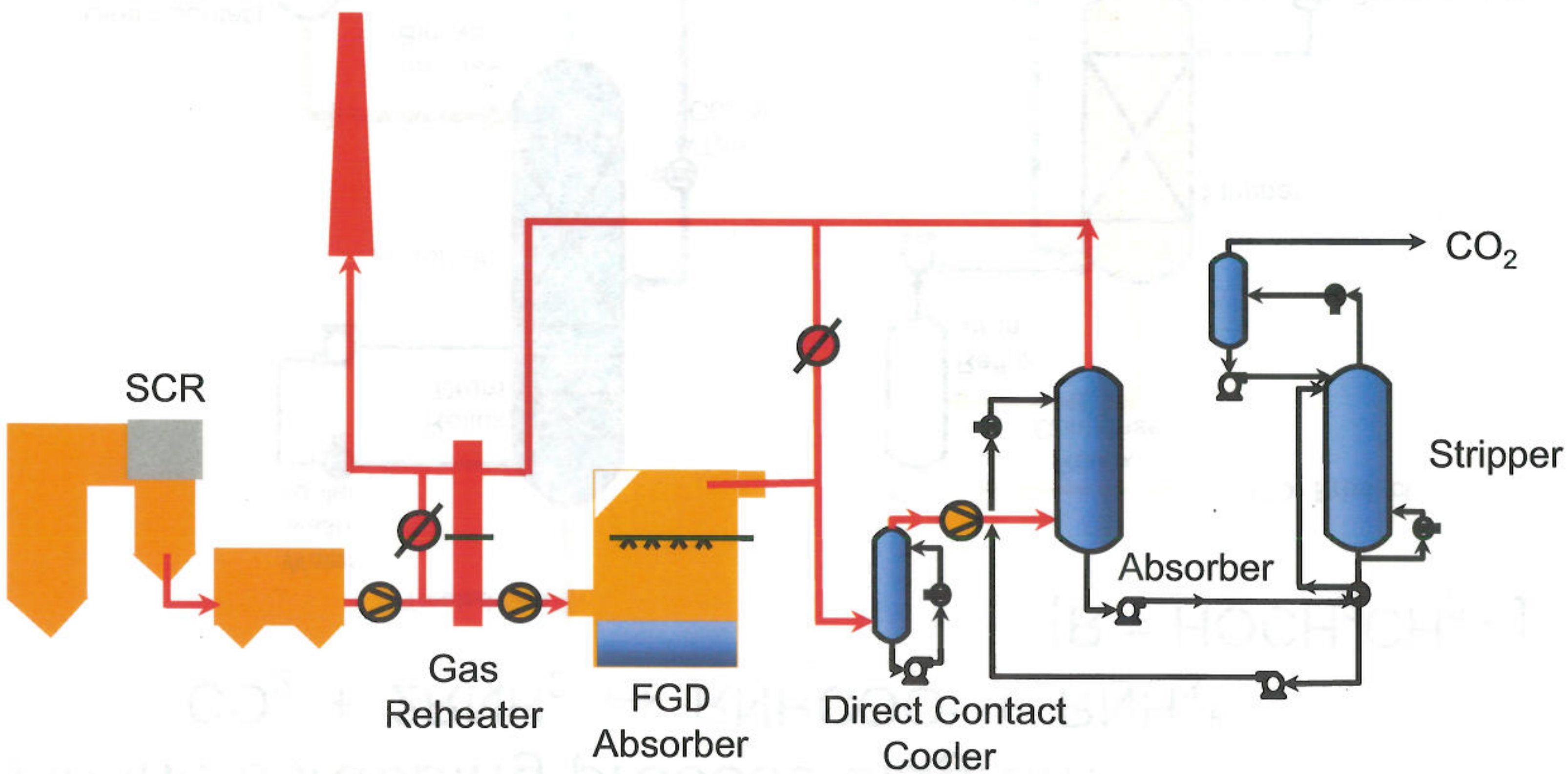
- Manage catalyst grids to minimise ammonia leakage.
  - Minimise air heater deposition and washing.
  - Minimise ammonia uptake in FGD absorber liquor.
  - Sulphate from air heater washing an equal problem to ammonia.

- Maintain a regular routine for air heater washing.
  - Store wash liquor and trickle feed into FGD absorber.

- Manage FGD waste water purge flow to maintain low residual concentration of ammonia.

- Monitor ammonia in FGD absorber liquor / waste water continuously.

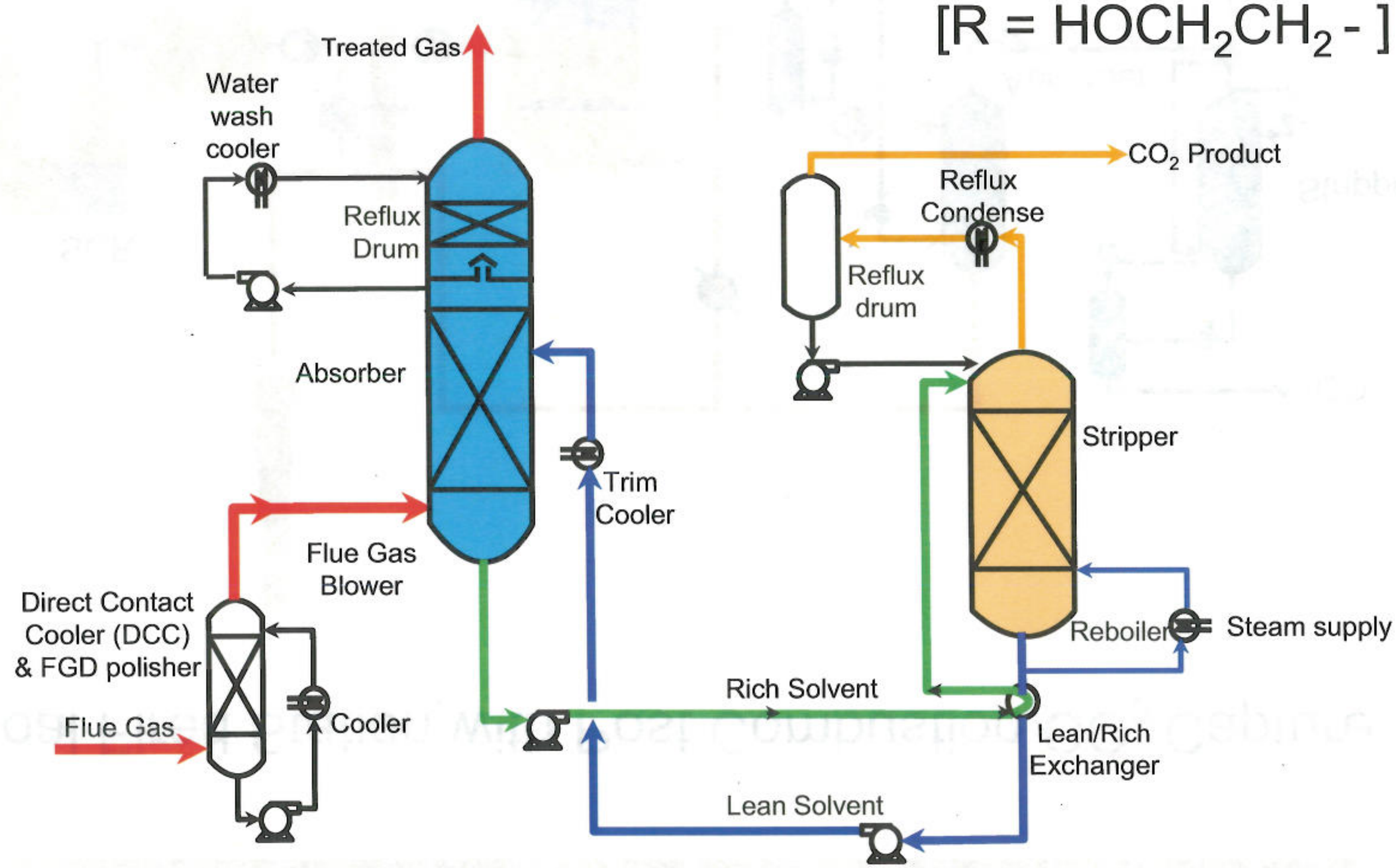
Coal Fired Station with Post Combustion CO_2 Capture



Amine scrubbing process diagram

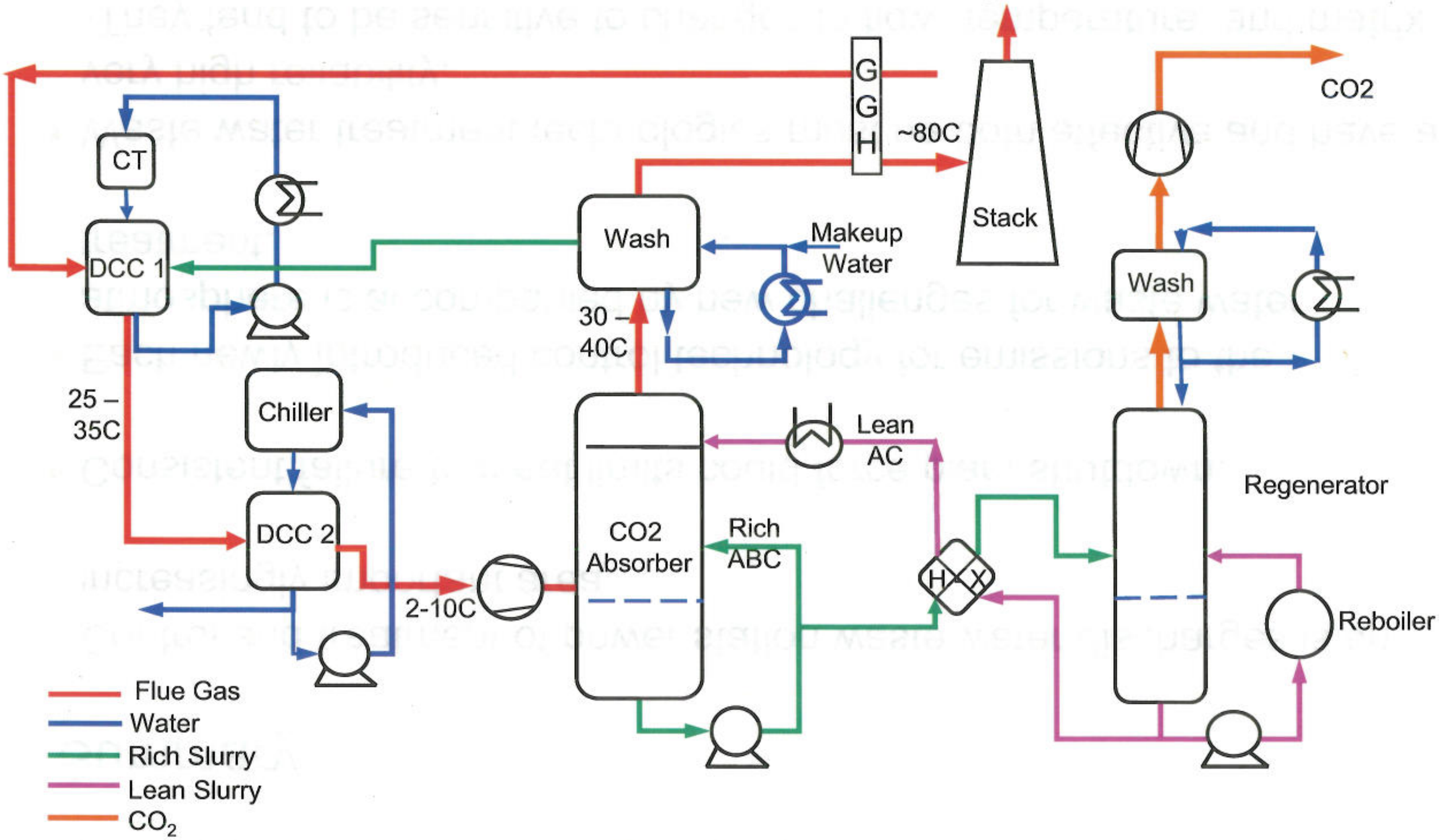
$$CO_2 + 2RNH_2 \leftrightarrow RNHCOO^- + RNH_3^+$$

$$[R = HOCH_2CH_2-]$$



Chilled Ammonia Process Diagram

$(NH_4)_2CO_{3\,(aq)} + H_2O_{\,(l)} + CO_{2\,(g)} \leftrightarrow 2\,NH_4HCO_{3\,\mathbf{(s)}}$



Summary

- Control and treatment of power station waste water discharges is an increasingly important area.
- Consistent failure to meet limits could force plant shutdown.
- Each newly introduced control technology for emissions to the atmosphere is accompanied by new challenges for waste water treatment.
- Waste water treatment technologies must be both effective and have a very high reliability.
  - They tend to be sensitive to changes in flow, temperature, and matrix.
- Future legislation may pose increasing challenges for waste water treatment.