

FGD Chemistry: A Review

Chris Satterley

The logo for e-on, featuring the text "e-on" in a white, lowercase, sans-serif font with a dot over the "e", set against a solid red rectangular background.

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SO₂ and IED

- Current position under the LCPD:
 - Monthly ELVs at 400 mg/Nm³ or 94% removal efficiency (92% for FGD contracted before 2001)
- Position under IED:
 - ELV of 200 mg/Nm³ (existing plant) or 150 mg/Nm³ (new plant) monthly
 - Provision for equivalency achieving 96% removal on indigenous coal with detailed justification
 - BAT conclusions will supersede other requirements when finalised (likely to be finalised 2014/15 and implemented in 2019 at earliest). **First BREF revision draft still imminent (expected May 2013)**
 - Within the TNP period ELV that applies on 31 Dec 2015 must be maintained throughout TNP.

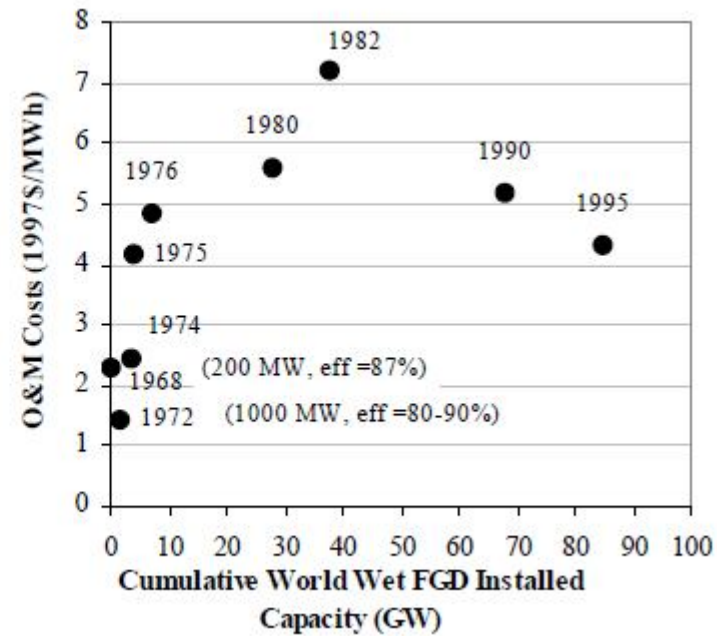
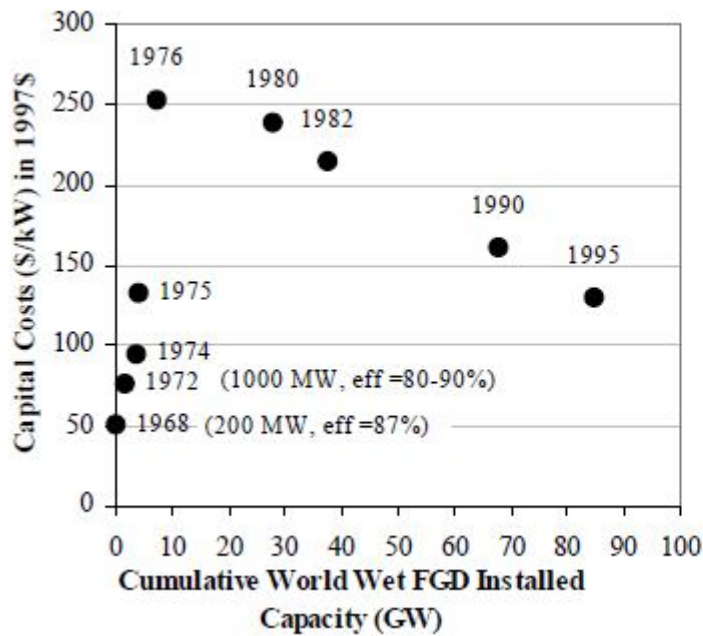
FGD on power plant in the UK



- First power plant FGD in the world were installed at Battersea, Bankside & Fulham Power Stations from 1933 onwards
 - Battersea & Bankside were alkali dosed sea water plant (once through)
 - Fulham was a recirculated lime slurry
- FGD technology was further developed & applied in Germany & Japan in the 1970's
- The next generation of FGD plant in the UK were constructed in the mid to late 90's (Drax, Ratcliffe, Uskmouth) in response to the 1988 LCPD
- The latest generation of FGD built in 2000's to meet 2001 LCPD (West Burton, Eggborough, Cottam, Aberthaw, Kilroot, Fiddlers Ferry, Ferrybridge, Longannet & Rugeley).

Learning curves

- Development is a good case study for other technologies at utility scale

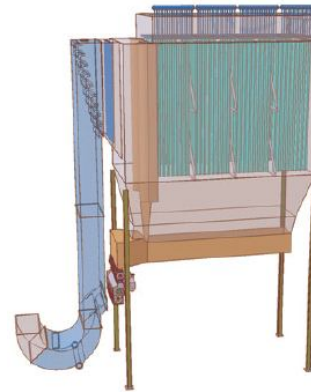


Rubin, *et al.* GHGT-8 proceedings, 2006



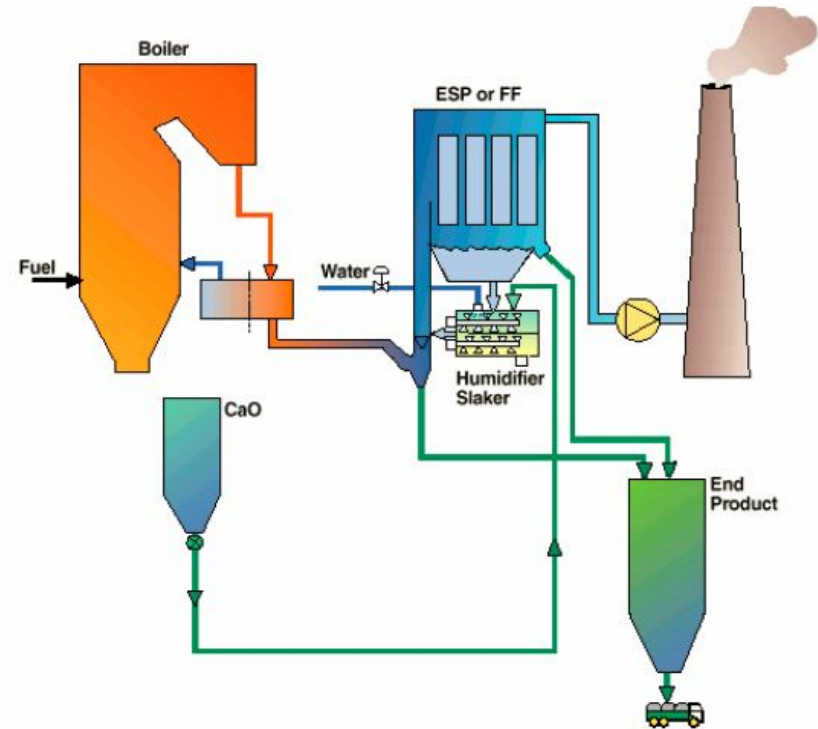
Technologies applied in the UK power sector

- Dry/Semi-dry NID process
 - Uskmouth
- Sea Water Process
 - Aberthaw
 - Kilroot
 - Longannet
- Limestone Forced Oxidation
 - Cottam
 - Drax
 - Eggborough
 - Ferrybridge
 - Fiddlers
 - Rugeley
 - Ratcliffe
 - West Burton

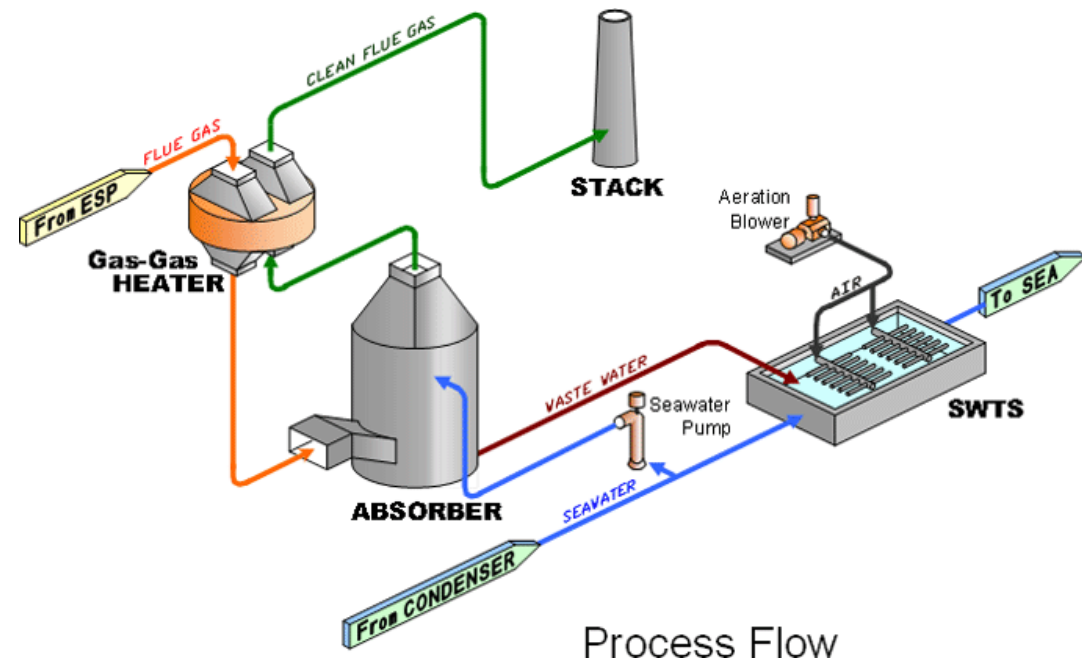


NID Dry/Semi-dry process

- Two step process:
 - $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$
 - $\text{SO}_2 + \text{Ca(OH)}_2 \rightarrow \text{CaSO}_3 \cdot 1/2\text{H}_2\text{O} + 1/2\text{H}_2\text{O}$
- Water addition provides some gas cooling (max. T of process ~ 200 °C), content in end product $\sim 5\%$
- Process efficiency sensitive to other acid gas species (e.g. HF, HCl, etc.)
- Generally lower CAPEX but higher OPEX than wet processes

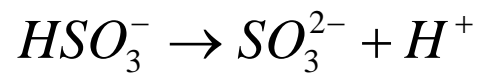
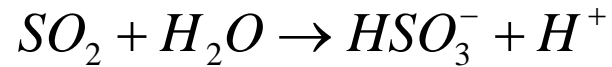


Sea Water Process

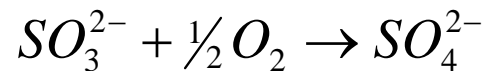
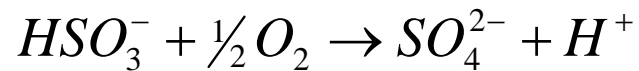


- Applicable for sea water/estuarine cooled power plant only
- A portion (typically 20%) of CW flow routed to absorber and contacted with flue gas over packed column
- Relies on natural alkalinity of seawater (carbonate & biocarbonate)
- Seawater pH typically 7.6 to 8.4 (site specific, with potential for seasonal variation)
- CW flow recombined and aerated to increase pH and reduce COD for discharge

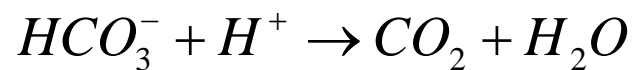
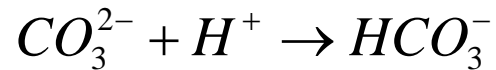
Sea Water Process Chemistry



} Absorption & dissociation



} Oxidation

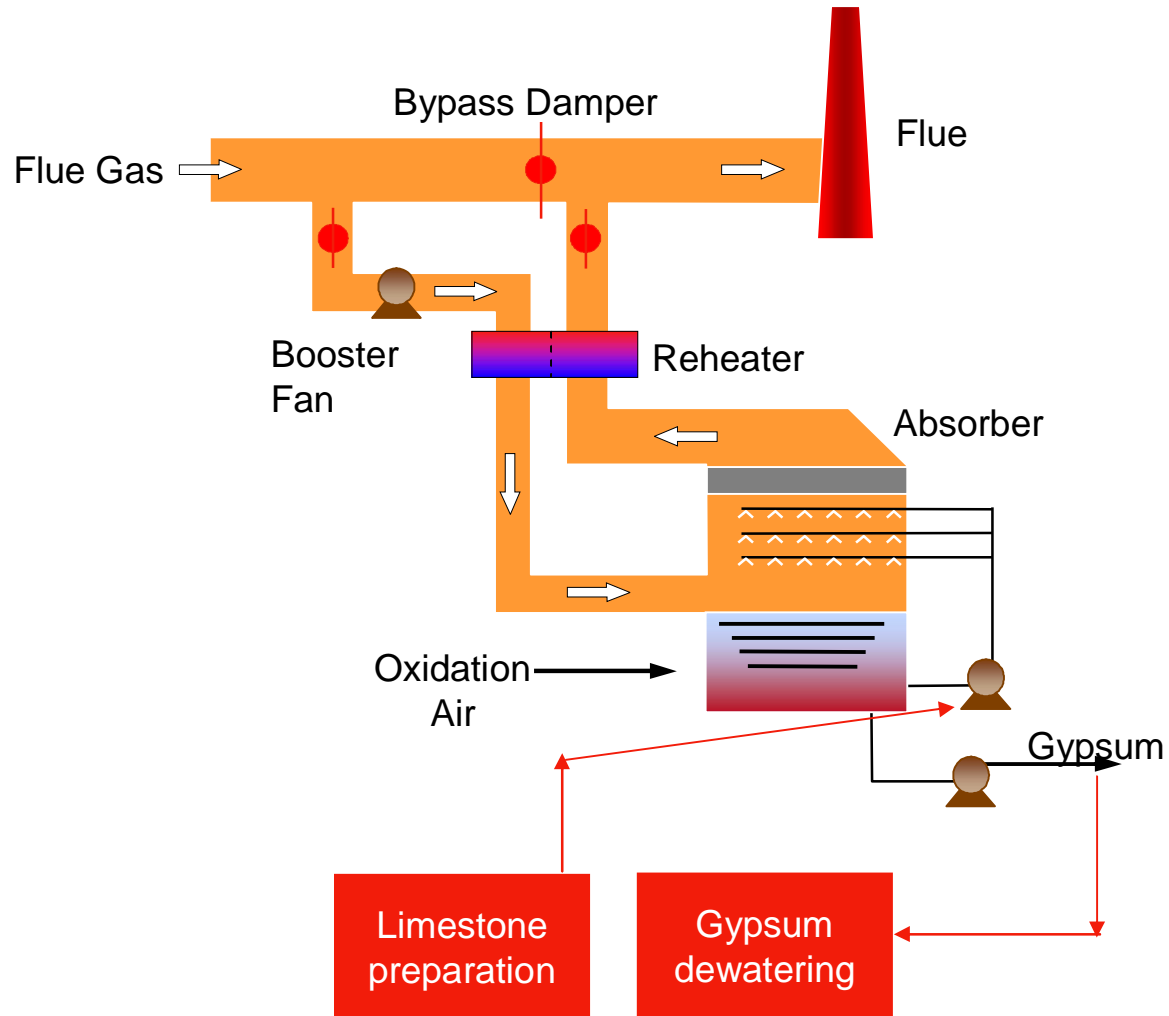


} Acid-Base Reaction

Sea Water Process Chemistry (2)

- Oxidation may be enhanced by addition of catalysts (e.g. Ferric Chloride/Sulphate), experience seems to be mixed on their efficacy
- Local sea water alkalinity is critical – should be considered in the early stages of technology selection
- Air sparging may cause issues with foaming depending on sea water quality
- Harsh, highly corrosive environment (low pH, high chloride) in absorber – materials selection is important

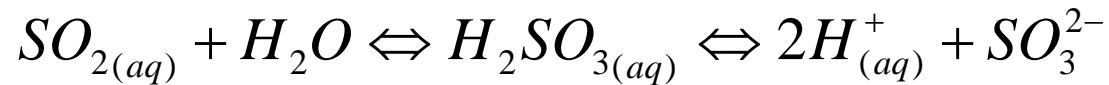
Limestone Forced Oxidation (LSFO)



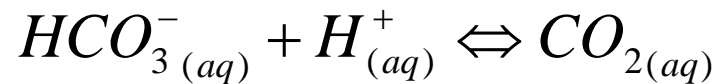
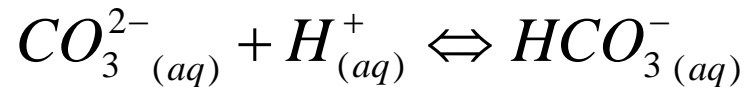
LSFO Chemistry



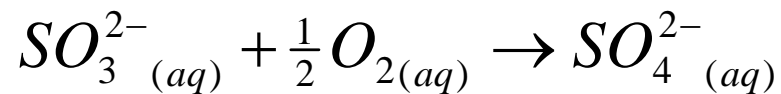
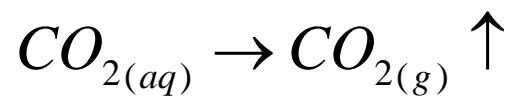
- Absorption & acidification



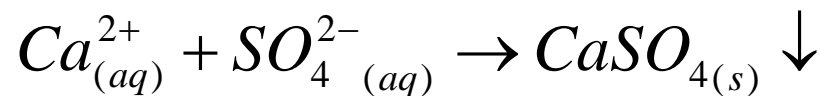
- Dissolution



- Acid-base reaction



- Oxidation



- Crystallisation

Oxidation

- Oxidation is critical to LSFO FGD performance
- Proceeds via free radical mechanism

Chain initiation	$M^{3+} + HSO_3^-$	$\rightarrow \bullet SO_3^- + M^{2+} + H^+$	Ri
Propagation	$\bullet SO_3^- + O_2$	$\rightarrow \bullet SO_5^-$	Rii
	$\bullet SO_5^- + HSO_3^-$	$\rightarrow \bullet SO_3^- + HSO_5^-$	Riii
	$HSO_5^- + 2M^{2+} + H^+$	$\rightarrow SO_4^{2-} + 2M^{3+} + H_2O$	Riv
	$2M^{3+} + 2HSO_3^-$	$\rightarrow 2\bullet SO_3^- + 2M^{2+} + 2H^+$	Rv
	Termination	$\bullet SO_3^- + \bullet SO_3^-$	$\rightarrow S_2O_6^{2-}$ (dithionate)
$\bullet SO_3^- + \bullet SO_5^-$		$\rightarrow S_2O_8^{2-}$ (peroxodisulphate)	Rvii
Where M = e.g. Co, Fe, Mn, Ni			



Non-ideality in LSFO chemistry

- **Absorption** – series of equilibria linked to oxidation of sulphite to sulphate. Inhibited oxidation can affect SO₂ removal
- **H₂SO₃ dissociation** – reduced by presence of stronger acids (e.g. HCl, H₂SO₄)
- **Limestone dissolution** – High levels of CaCl₂ can inhibit, also Al & F can cause blinding
- **Limestone overdosing** - high residual limestone levels in slurry possibly leading to demister fouling and gypsum quality issues
- **Gypsum crystallisation** – low solids concentrations can inhibit nucleation within the slurry – this can lead to poor crystal growth (difficult dewatering) & scaling

Oxidation inhibition

- Radical 'killers' can enter the FGD from upstream

Inhibitors (X^n)	$\bullet\text{SO}_3^- + X^n$	$\rightarrow \text{SO}_3^{2-} + X^{n+1}$	Ra
	$\bullet\text{SO}_5^- + 3X^n + 2\text{H}^+$	$\rightarrow \text{SO}_4^{2-} + 3X^{n+1} + \text{H}_2\text{O}$	Rb
	$\text{M}^{3+} + X^n$	$\rightarrow \text{M}^{2+} + X^{n+1}$	Rc

- Iodide can act as a strong inhibitor and is reduced to iodine.
- SN compounds (formed by reaction of NO_x with sulphite) can also act as inhibitors (e.g. HADS = HON(SO₃H)₂)
- **Indicators** – Reduced performance, low redox potential (<300 meV), presence of significant levels of sulphite or iodide, halogen odour, presence of SN compounds



Conclusions

- FGD is a technology with a well-established history in the UK
- A range of FGD techniques are currently applied by the UK power sector with varying degrees of complexity of chemistry
- Understanding process chemistry is key to optimising performance and diagnosing operational issues
- IED compliance is likely require better control of chemistry as well as potential engineering modifications

Thanks for listening

Contact me:

Dr Chris Satterley

T +44 24 76-18 23 12

chris.satterley@eon.com

www.eon.com/technology

E.ON New Build & Technology Limited
Technology Centre
Ratcliffe-on-Soar,
Nottingham,
NG11 0EE, UK

