

---

# Power station stack gas emissions

---

A review of control techniques:  
current and projected.

Presentation to the Sydney Branch of the Australian Institute of  
Energy, August 7<sup>th</sup>, 2006

**Richard J Hunwick**  
Phone: (02) 9410 9834

---

*Hunwick Consultants*

---

# The list of offenders

Increasingly strict limits are being imposed on emissions from power station stacks of:

- Particulates:  $PM_{10}$  and  $PM_{2.5}$
- Oxides of sulphur:  $SO_x$
- Oxides of nitrogen:  $NO_x$
- Volatile heavy metals esp. mercury
- CO and Volatile Organic Compounds (VOCs).
- Limits may in future be imposed on  $CO_2$

**Emphasis here will be on coal fired power stations**

---

# Whither these uninvited guests?

- **PM<sub>10</sub> particulates** mostly fly ash, from mineral matter in the fuel.
- **SO<sub>x</sub> (oxides of sulphur)** originate from “reduced” sulphur in coal; occur mostly as the dioxide SO<sub>2</sub>, but 1-2% is the trioxide SO<sub>3</sub>.
- **PM<sub>2.5</sub> particulates** are less familiar; as well as mineral matter in the fuel, reactions between SO<sub>3</sub> in stack gases and moisture in air form sulphuric acid aerosol. They are also from smoke, motor vehicle exhausts, and natural sources—forest haze.
- **NO<sub>x</sub> (oxides of nitrogen)** derive from nitrogen compounds in the fuel, but mostly from reaction at high temperatures between oxygen and nitrogen in the air. NO is first formed, much of this converts to the dioxide NO<sub>2</sub> (a brown gas) on contacting ambient air.
- **Mercury** occurs in trace quantities in the mineral matter in the fuel; it is of concern because it is volatile.

# Why are they a problem?

- **PM<sub>10</sub> particulates** are the most visible form of pollution: smoke, dust; their health and other impacts are obvious and well known.
- **PM<sub>2.5</sub> particulates** are of concern because they can penetrate more deeply into the lungs, and can be highly acid, perhaps carcinogenic. They are a prime cause of haze and photochemical smog.
- **SO<sub>x</sub> emissions** (mostly the dioxide SO<sub>2</sub>, but around 1.5% is the trioxide SO<sub>3</sub>) are major contributors to acid rain, and are particularly hard on structures and objects containing limestone. SO<sub>3</sub> is a major contributor to PM<sub>2.5</sub>-based haze.
- **NO<sub>x</sub> emissions** are also major contributors to acid rain, but through a complex series of reactions with VOCs (mostly from motor vehicle exhausts) promoted by sunlight are also the chief cause of ozone formation and photochemical smog.
- **Mercury** (as the element or other volatile form e.g. methyl mercury) is highly toxic even in extremely small quantities.

---

# How can they be controlled?

**Minimising emissions require *most* of the following:**

- ❑ Removal of pollution precursors from the fuel prior to combustion either by physical or chemical treatment.
- ❑ Combustion of fuel under conditions that minimise pollutant formation.
- ❑ Combustion of fuel in the presence of a substance that will immediately absorb or otherwise capture the pollutant.
- ❑ Stripping of the pollutant from stack gases (end-of-pipe solutions).

*Gaseous pollutants (incl. CO<sub>2</sub>) are acid precursors, so control generally involves neutralising them with alkaline substances.*

---

# How can they be controlled (cont.)?

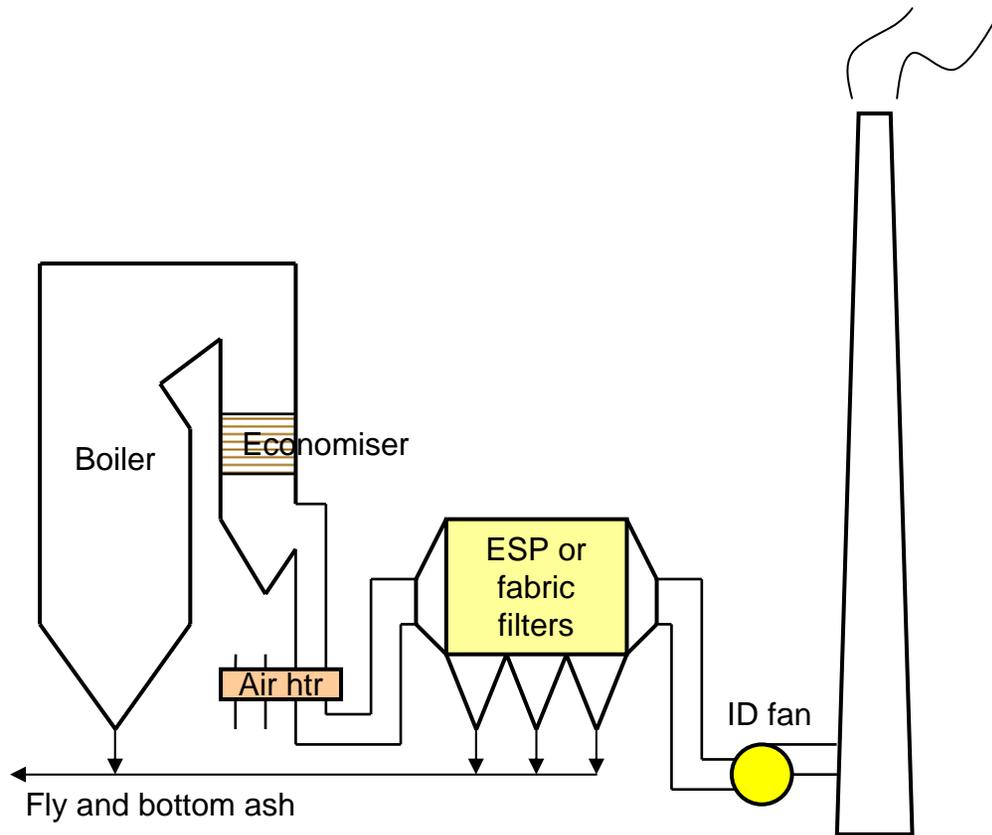
## Issues to be considered include:

- ❑ Is it a new or an existing facility that requires control?
- ❑ What are the implications in terms of capital and operating costs, and sent-out cost of electricity?
- ❑ What utilities are required—water as well as electricity?
- ❑ What impacts (greenhouse and other) arise from sourcing inputs e.g. limestone, ammonia?
- ❑ Are there markets for byproducts?
- ❑ Are there secondary effects that need to be considered e.g. an increase in unburned carbon in ash, or even conversion of ash into a hazardous waste?

# Particulates: fly ash and other PM<sub>10</sub> (to meet 30 mg/m<sup>3</sup> limit—99.9% capture)

<i>Technique</i>	<i>Technical status</i>	<i>Limitations</i>	<i>Remarks</i>
Electrostatic precipitators	Mature, deployed in Aust.	Performance poor on some low S, refractory-ash coals	“Baseline” particulates control tech.
Fabric filters	Mature, deployed in Aust.	Cost of filter media, ID fan pressure drop	Preferable for “Gondwanan” coals
Wet scrubbers	Mature for non-utility apps. in Aust.	Produce wet slurry, consume much water	In Australia, widely used for sugar mill boilers

# Stack gas cleaning in local power stations currently



---

## Bayswater Power Station: world's largest fabric filter installation



# Controlling SO<sub>x</sub> emissions

- The first step is to *minimise pyrite content* in fuel, if only to minimise reagent consumption.
- *Fluidised bed combustion* involves burning fuel in the presence of limestone. SO<sub>x</sub> released are immediately absorbed as calcium sulphite and sulphate—90%+ capture is typical. Issues are the cost of limestone required, and the formation of a highly alkaline ash that can present disposal problems.
- *Coal gasification* allows highly efficient removal of sulphur, which is converted to the element, or sulphuric acid, both marketable.
- *Sorbent injection* systems (limestone added upstream of the economiser) can give 30%+ capture, are cheap to implement, but reagent costs are high, and byproducts present disposal problems.
- “*Dry*” scrubbers have appeal for low-S coals (and they work better with fabric filters than with ESPs), can give 80%+ capture, but use almost as much water as wet scrubbers, and complicate the disposal of fly ash.
- *Seawater scrubbers* are efficient and economical (they rely on the natural bicarbonates in seawater), but are almost certainly not an option for Australian coastal power stations.
- *Wet scrubbers (limestone slurry)* are now mature, efficient (95-98% capture) and widely accepted for existing as well as new power stations.

# SOx emissions control (PF boiler plant)

<i>Technique</i>	<i>Technical status</i>	<i>Strengths &amp; weaknesses</i>	<i>Remarks</i>
Sorbent (CaCO <sub>3</sub> ) injection into furnace before economiser	Mature	Performance poor, (c. 25% SO <sub>x</sub> capture), leaves alkaline ash. Requires no water.	Other sorbents promising, works better with fabric filters.
Dry scrubbing (with slaked lime slurry—Ca(OH) <sub>2</sub> )	Mature	75% SO <sub>x</sub> capture, inexpensive to install, requires slaked lime, leaves alkaline ash.	Still consumes substantial water, OK for low S coals.
Wet scrubbers	Mature	95+ SO <sub>x</sub> capture, produces wet slurry, consumes much water	“Benchmark” SO <sub>x</sub> control technology.

# SOx scrubbing

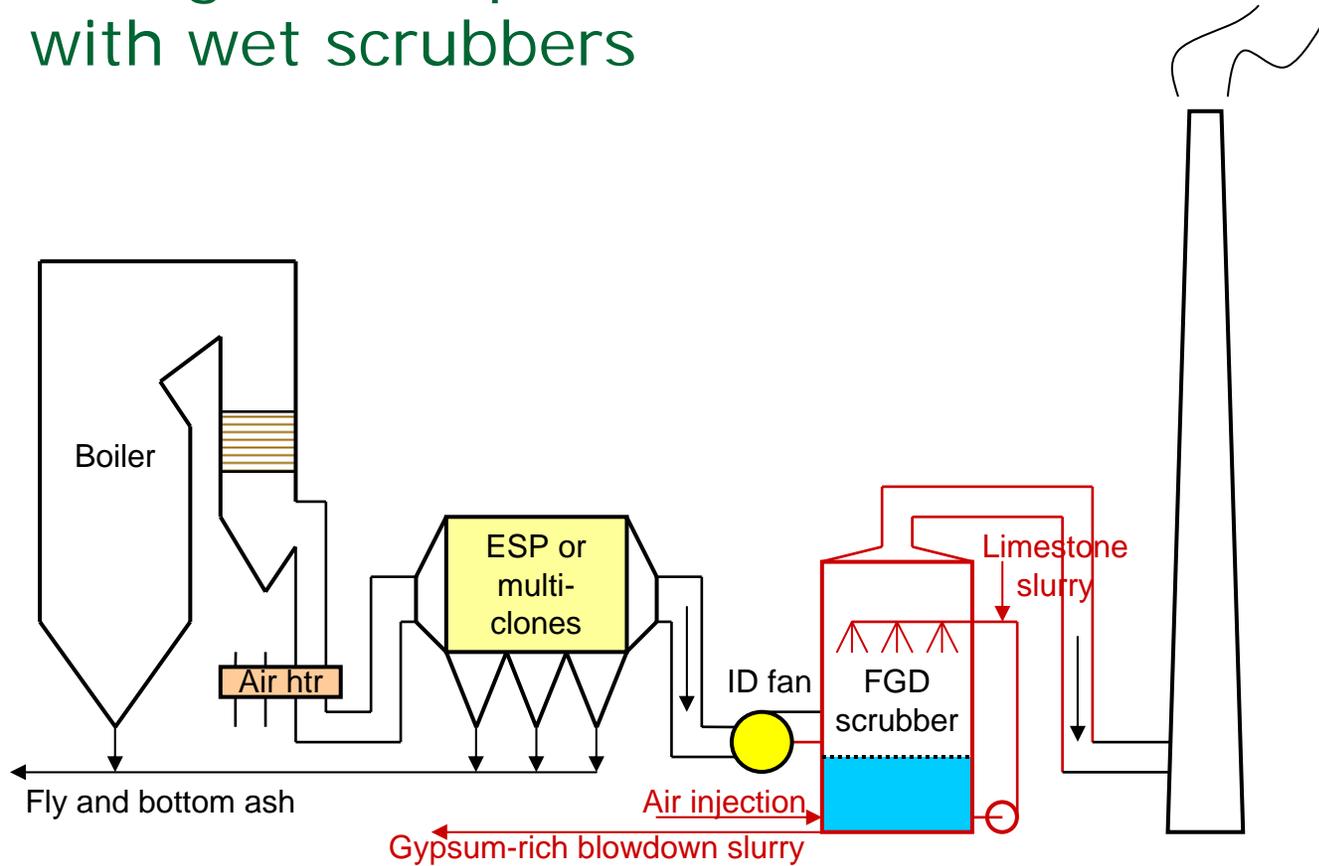
**Wet limestone scrubbing is now the “baseline” approach.**

- Limestone slurry is sprayed through stack gases (cleaned of particulates) in a large tower:  $\text{SO}_2 + \text{CaCO}_3 \rightarrow \text{CaSO}_3 + \text{CO}_2$ . ESPs or bag filters remove fly ash solids.
- The calcium sulphite-rich slurry presents disposal problems, so is converted to calcium sulphate by bubbling air through it:  $2\text{CaSO}_3 + \text{O}_2 \rightarrow 2\text{CaSO}_4$ .
- The calcium sulphate forms as gypsum crystals  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , which can be readily separated from the slurry using wet cyclones, dewatered by filtration a cake, and sold to wallboard manufacturers.
- Total system capital costs: around \$100/kW for new plant, \$140/kW for retrofit.
- Operating costs: for limestone, and parasitic power (around 2% of total power s.o.).

## **Issues:**

- The power industry went through a long and painful learning curve before it learned to specify the right materials to handle the corrosive solutions involved.
- Water consumption can be high, as the stack gases are saturated with water vapour in the scrubber. As well, vapour plumes can be prominent, and regulators now generally require abatement, achieved by re-heating the stack gases.
- Wet scrubbers are seen as being wanting for NO<sub>x</sub>, PM<sub>2.5</sub>, and Hg control.

# Flue gas desulphurisation with wet scrubbers



---

Centralia Power Station (Washington State USA) wet scrubber retrofit



---

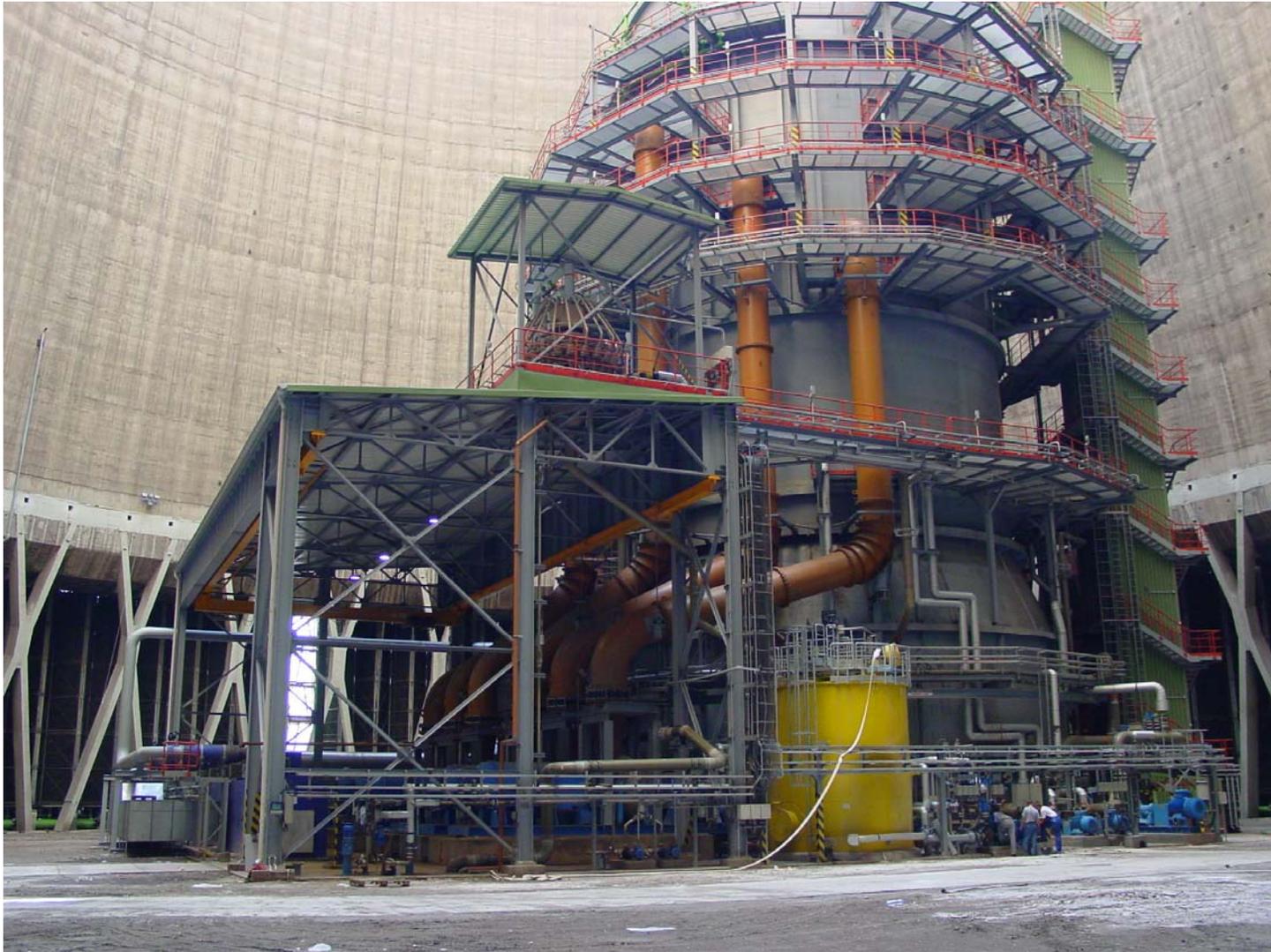
*Hunwick Consultants*

---

## Centralia Power Station (Washington State USA) wet scrubber components



# Wet scrubber installed within natural-draft dry cooling tower



## Filtration of gypsum byproduct from wet FGD scrubbers: Centralia



# Controlling NO<sub>x</sub> emissions

- ❑ The first step: minimise NO<sub>x</sub> formation by minimising peak combustion temperatures, and maintaining reducing conditions in the combustion zone: **Low-NO<sub>x</sub> burners**.
- ❑ Second: Complete combustion (under cooler conditions) with **overfire air** (this also converts reduced forms of nitrogen in the coal e.g. amines, ammonia, to nitrogen gas).
- ❑ Third: add a reducing agent to combustion gases upstream of the economiser: some fuel e.g. natural gas, or micronised coal (fuel reburning), or add ammonia or urea (**selective non-catalytic reduction—SNCR**).
- ❑ For the most complete control, pass stack gases plus the correct amount of ammonia or urea over a catalyst bed (**Selective Catalytic Reduction**); NO<sub>x</sub> are converted to nitrogen gas.
- ❑ **Fluidised bed combustion** avoids NO<sub>x</sub> formation in the first place by controlling combustion temperatures to below 900°C.

*SCR is required for gas turbines as well as coal-fired power stations where NO<sub>x</sub> emission limits are extremely tight: can achieve 2-3 mg/m<sup>3</sup> in GTs, and 50 mg/m<sup>3</sup> in coal-fired power station stack gases (90% reductions).*

# NOx emissions control (PF boiler plant)

<i>Technique</i>	<i>Technical status</i>	<i>Strengths &amp; weaknesses</i>	<i>Remarks</i>
Ultra-low-NOx burners.	Evolving	Requires very close control, hard to guarantee performance.	Increase in unburned carbon losses in ash.
Fuel reburning plus overfire air	Evolving	30% reduction, currently requires “clean” fuel, coal must be “micronised”.	Part of a package with low-NOx burners.
Selective catalytic reduction (SCR	Evolving	90% NOx reduction, reliable but expensive, requires ammonia dosing, risk of “slip”.	“Benchmark” NOx control technology.

# More on SCR for NO<sub>x</sub> emission control

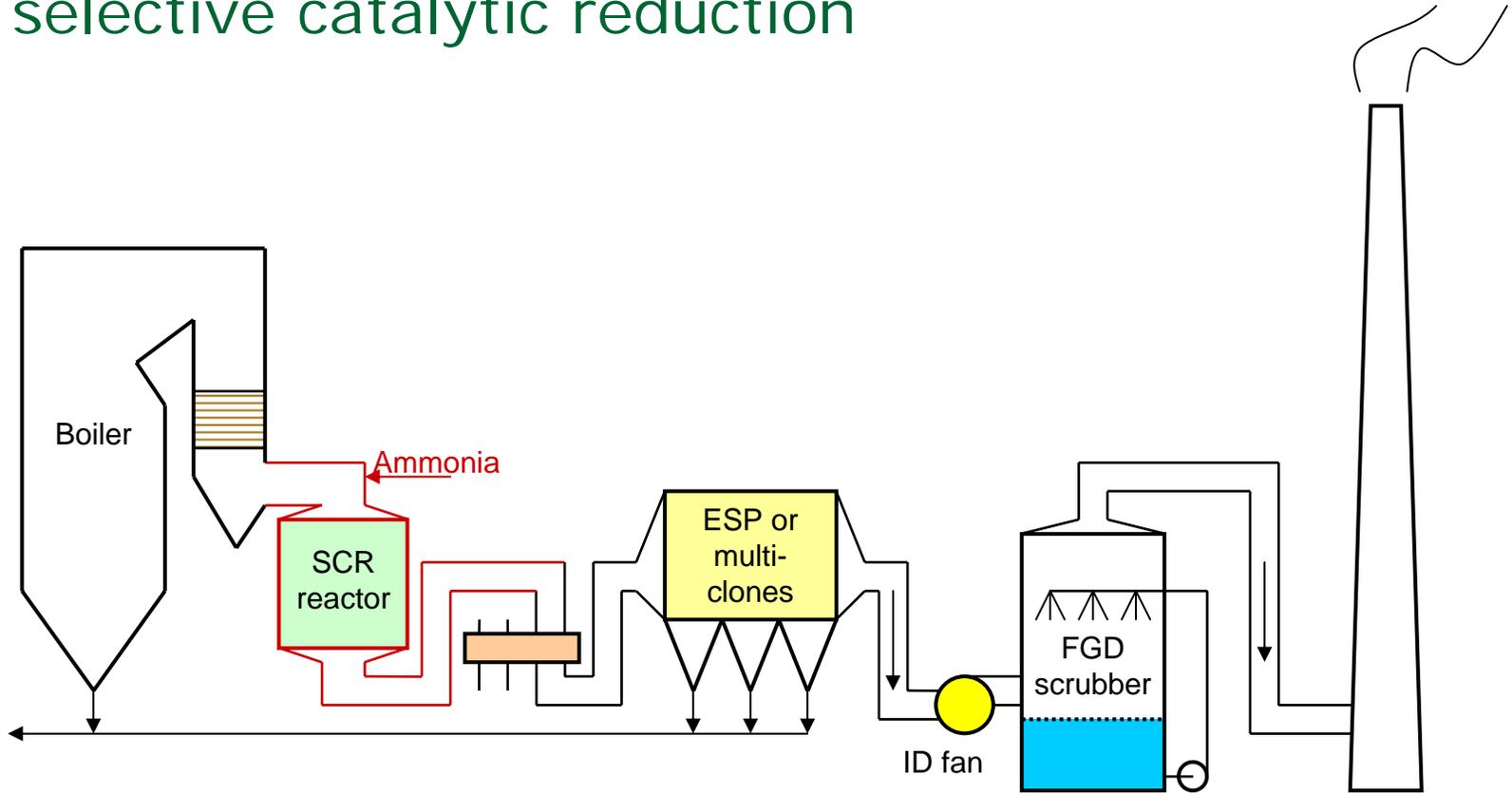
While effective, selective catalytic reduction (SCR) is not popular with utilities (c.f. the situation with wet scrubbers for SO<sub>x</sub> control):

- ❑ Retrofitting can be very expensive, since gases must be at economiser outlet temperatures, and catalyst contact times are relatively long—confined sites may require installation of thousands of tonnes of steelwork tens of metres above grade.
- ❑ Ammonia slip can create a bigger problem than NO<sub>x</sub>.
- ❑ Catalysts are expensive, and subject to poisoning.
- ❑ The catalysts create oxidising conditions, hence increase formation of the PM<sub>2.5</sub> precursor sulphur trioxide, requiring control measures for this.

There is much R&D being directed towards achieving NO<sub>x</sub> limits without recourse to SCR. Efforts are being directed to a combination of ever more efficient Low-NO<sub>x</sub> burners, fuel “reburning”, and overfire air, all precisely controlled. A concern is a rise in unburned carbon in fly ash.

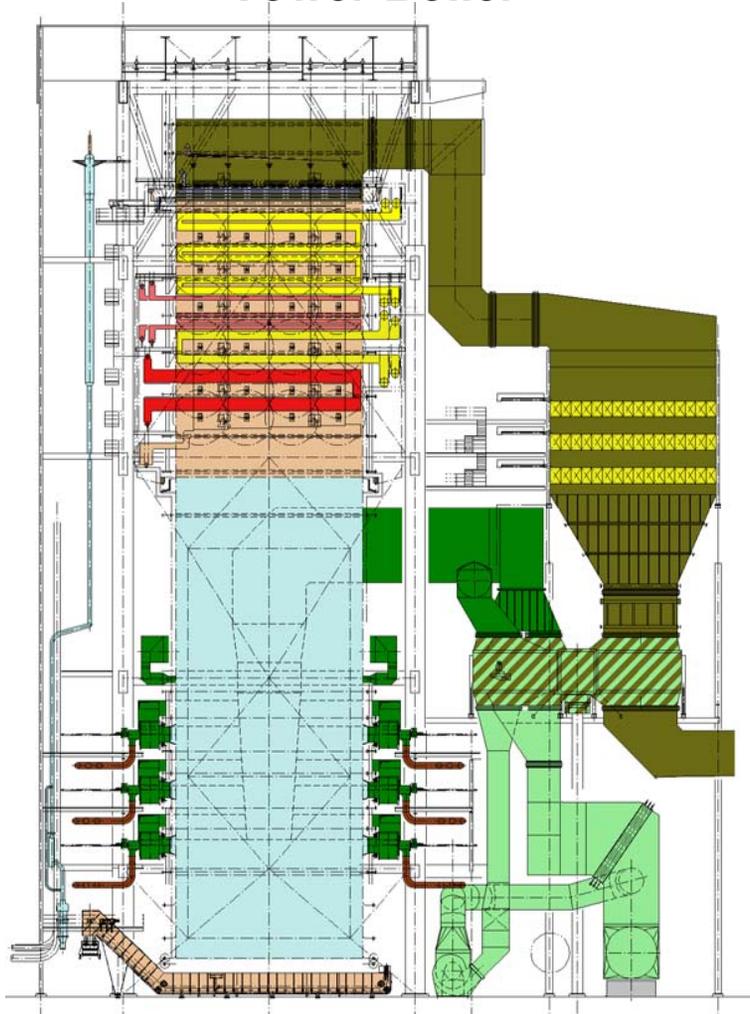
For **gas turbines**, new designs of combustors: Vortex, Reverse-flow, promise equivalent performance: 2-3 mg/m<sup>3</sup>, but are some years away.

# NO<sub>x</sub> control by selective catalytic reduction

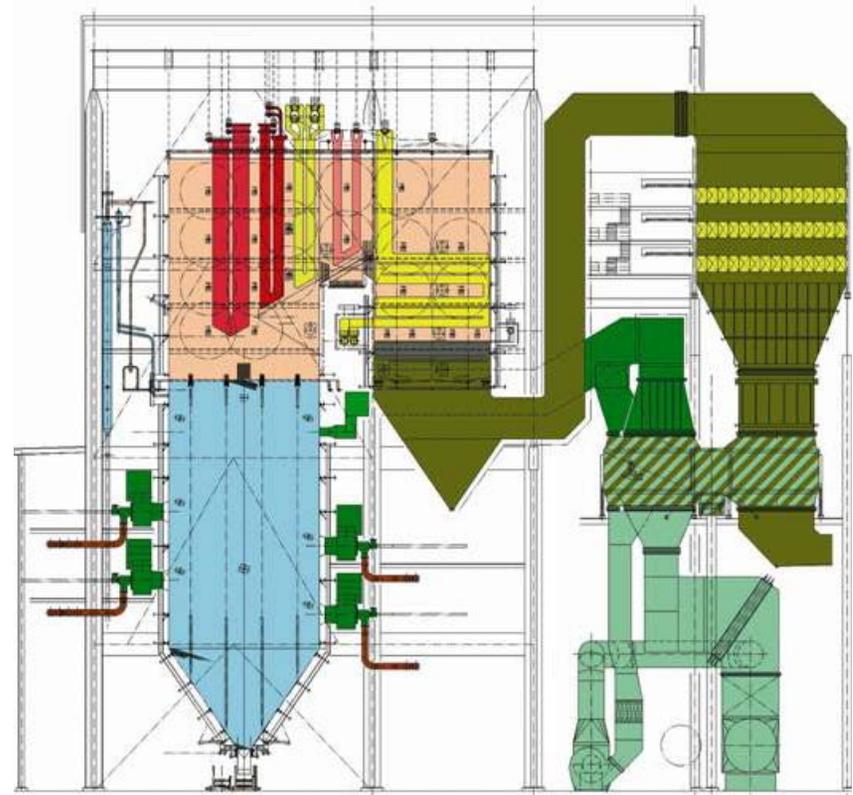


# Retrofitting SCR systems to 600 MW boilers (courtesy Siemens)

## Tower Boiler



## Two Pass Boiler



# Ultrafine Particulates: PM<sub>2.5</sub>

- Conventional stack gas particulates removal equipment is less effective than with PM<sub>10</sub>'s—fabric filters are probably better than ESPs.
- Hybrid ESP/fabric filters are a promising approach to better control of PM<sub>2.5</sub> particulates in stack gases: 99.99% capture may be possible.
- Power station operators overseas are being required to focus on removing SO<sub>3</sub> from stack gases, as this is a precursor to sulphuric acid. SO<sub>3</sub> formation is increased by selective catalytic reduction systems for control of NO<sub>x</sub>.
- Preferred control approach: add a solution of sodium bisulphite (SBS) to stack gases after the economiser. This absorbs SO<sub>3</sub>, to form sulphates, releases SO<sub>2</sub> back into stack gases. Make-up SBS is formed by scrubbing some stack gases with sodium carbonate solutions.
- An extra benefit: the acidity of stack gases is greatly reduced, so fabric filter and ESP lifetimes benefit, and it becomes possible to cool stack gases further to yield higher overall thermal efficiencies.

# Mercury

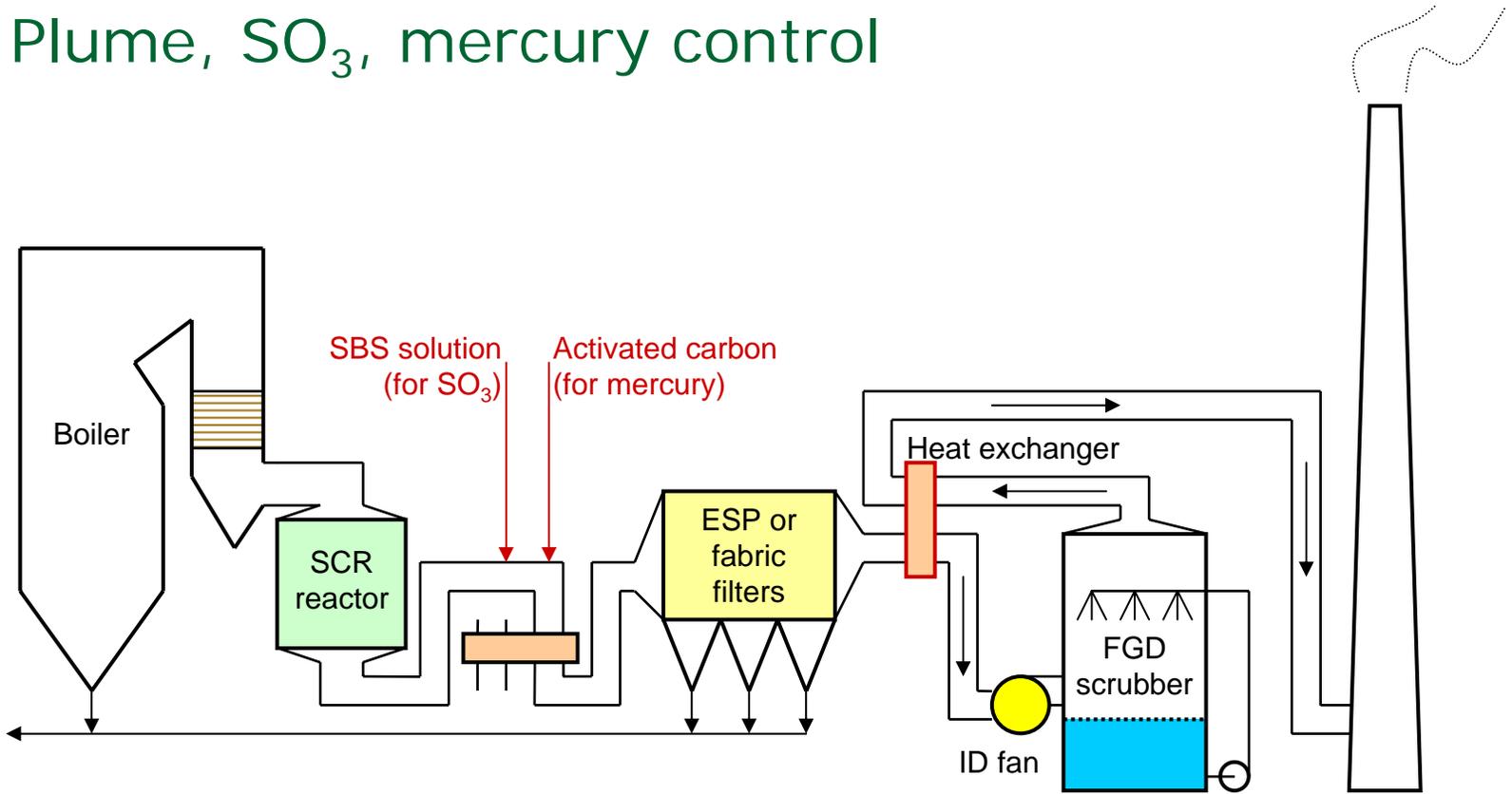
There are no current solutions generally accepted by utilities.

- The problem is with elemental mercury (Hg), as this is (in relative terms) volatile. The oxide (HgO) is not volatile.
- The only solution currently available is to dose stack gases with powdered activated carbon: expensive, and fouls ash.
- New processes under development seek either:
  - To convert the mercury to the oxide, allowing its removal in conventional stack gas cleaning equipment, or
  - To cool stack gases to such an extent that mercury vapour pressures are low enough to ensure emission limits are met.

## Centralia Power Station—a need for plume abatement



# Further modifications: Plume, SO<sub>3</sub>, mercury control



## Costs and consequences of emissions control retrofit to one typical 700 MWe coal-fired unit.

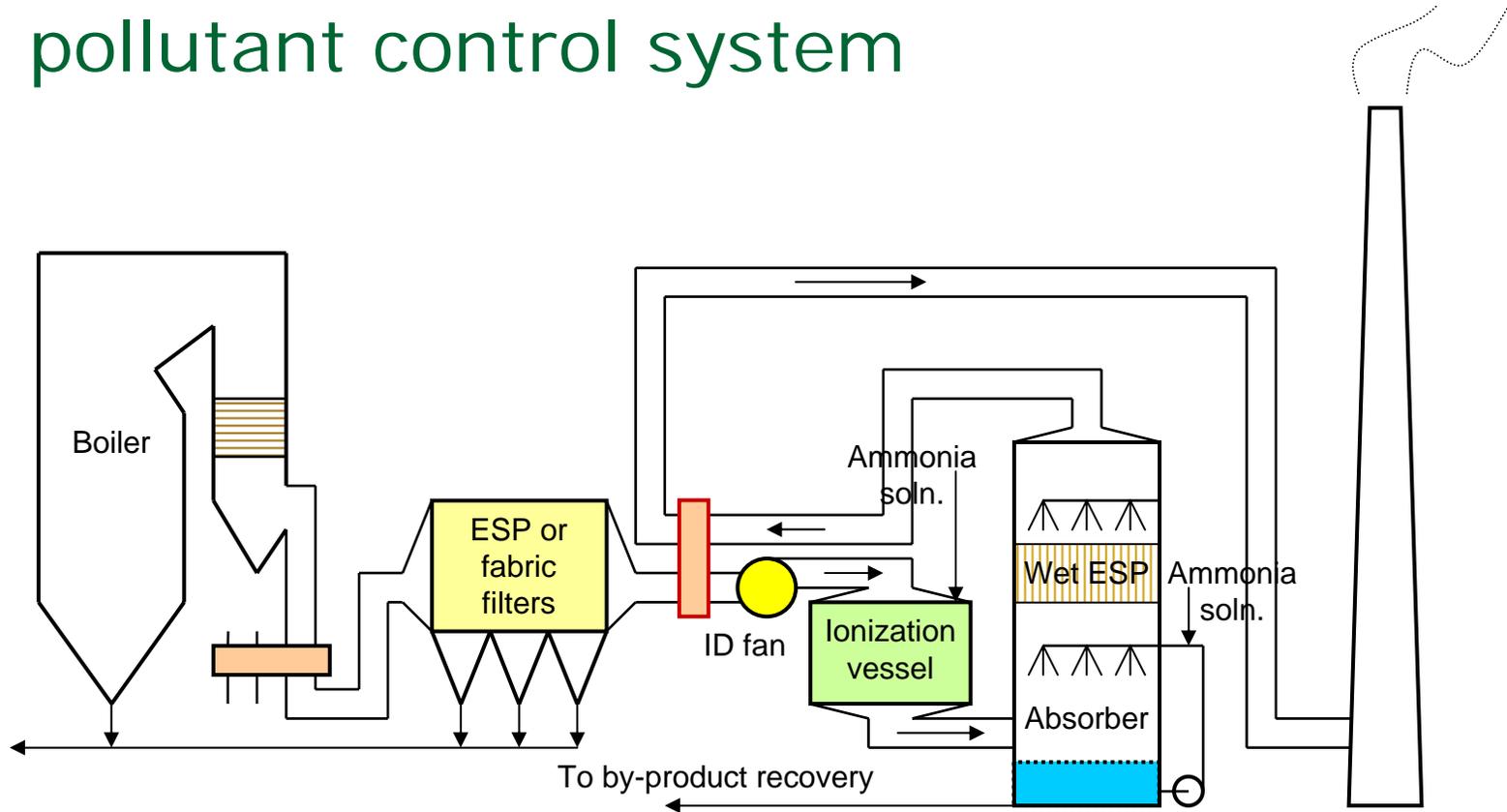
	Extra water reqd, Megalitres p.a.	Extra power reqd, MWe	Capital cost for retrofit, A\$mill.
NO <sub>x</sub> to 350 mg/m <sup>3</sup> (Ultra low-NO <sub>x</sub> burners, over-fire air)	-	2	30
NO <sub>x</sub> to 50 mg/m <sup>3</sup> (above modifications plus SCR)	-	4	150+
SO <sub>x</sub> down 33% (from 1,200 mg/m <sup>3</sup> ) by limestone injection	-	2	20
SO <sub>x</sub> down 80% to 250 mg/m <sup>3</sup> , by “dry” scrubbing	900	5	60
SO <sub>x</sub> down 96% to 50 mg/m <sup>3</sup> , by wet limestone scrubbing	1,100 (halved with heat exch.)	12	100

# Trends and future directions

- The “stack gas gauntlet” grows ever longer, the limits on emissions ever tighter. Some argue that this will kill pulverised-fuel (PF) based power stations, that the future belongs to gasification. Are these fears justified?
- Despite misgivings every time a new limit has been imposed, PF seems set to endure—it has coped with all challenges so far--but at a cost.
- Multi-pollutant control systems using appropriate sorbents as scrubbing media are gaining support and credibility. Two such approaches of particular interest are to:
  - Irradiate cooled stack gases to create a strongly oxidising environment, then add ammonia: form ammonium sulphate and nitrate that can be sold as a fertilizer (demonstration plants in Poland, Japan, USA).
  - Inject sodium bicarbonate (baking soda) into stack gases upstream of wet scrubber, to form sodium sulphate and nitrate. Regenerate sodium bicarbonate using ammonia to yield ammonium sulphate and nitrate as by-products that can be sold as a fertilizer (Canmet Canada is developer).

***Fears for the imminent demise of PF firing are greatly exaggerated.***

# An ionization-based multi-pollutant control system



---

# What about carbon dioxide?

- ❑ The designers of PF plant systems appear set to achieve carbon capture (in a form suitable for sequestration) at acceptable cost. **Feasible CO<sub>2</sub> capture should stem from an extension of the various multi-pollutant control systems under development.**
- ❑ Amine solution scrubbing effectively removes CO<sub>2</sub> (and all other acid gases) from stack gases—at issue is the energy penalty to regenerate the amine solution (perhaps 30% of gross output of the power station), and yield CO<sub>2</sub> in a form suitable for sequestration (i.e. under pressure).
- ❑ Ammonia promises to overcome these problems: scrub stack gases with an ammonia solution to form ammonium carbonate, heat the solution under pressure to drive off the CO<sub>2</sub> and re-cycle the ammonia. The ammonia solution needs to be chilled to keep ammonia gas out of stack gases—the Chilled Ammonia process. Energy penalty is c. 10%, cost by 2020 perhaps A\$10-15/t CO<sub>2</sub>.

---

## In conclusion:

### **For coal:**

Foreshadowed emission limits do not yet justify a shift away from pulverised-fuel firing.

---

Thank you