While Australia seems to be focussed on carbon dioxide emissions from power stations, this gas is just one by-product of the combustion of fossil fuels. Blessed with abundant supplies of low-sulphur coals and with low population densities, pressures to reduce emissions other than particulates have been so far, fairly restrained.

But in the more densely populated regions of Europe, North America and Japan emissions of oxides of sulphur (SOx) of nitrogen (NOx) and increasingly, heavy metals in particular mercury, have been of major concern for decades, and power station owners and operators in those regions have been subject to increasingly stringent controls.

These control efforts are succeeding both technically and economically, to the point where models for their control are weakening grounds for resisting their deployment in Australia, while serving as pointers to possible initiatives to control carbon dioxide emissions.

Pressures for the reduction of emissions of the acid rain and photochemical smog precursors, the oxides of sulphur SOx and nitrogen NOx are increasing in Australia. What, then, is involved in their control, what is the state of the art, are there improved control system and equipment under development, and are there pointers in these systems for future likely requirements being imposed on combustion plant owners and operators (power stations in particular) for the control of carbon dioxide emissions?

This brief review focusses on coal-fired power stations, and on the technologies currently favoured for the control of the range of pollutants that are a byproduct:

- **Particulates**: $PM_{10}$. These are the familiar chimney smoke and dust, mostly particles of fly ash from mineral matter in the fuel. They are the most visible form of pollution; their health and other impacts are obvious and well known, and control efforts in Australia have tackled these aggressively, and generally successfully.

- **Oxides of sulphur**. These originate from “reduced” sulphur in coal, both organic, and also mineral, mostly pyrite (iron di-sulphide), which after combustion appear mostly as the dioxide $SO_2$, but around 1.5 per cent is produced as the sulphuric acid precursor sulphur trioxide $SO_3$. These gases are major contributors to acid
rain, and are particularly hard on structures and objects containing limestone. SO₃ as mentioned earlier is a major contributor to PM₂.₅-based haze.

- **Oxides of nitrogen**: NOₓ derive partly from nitrogen compounds in the fuel, but mostly from reaction at high temperatures between oxygen and nitrogen in the air. Nitric oxide NO is first formed, but much of this converts to the dioxide NO₂ (a brown gas) on contacting ambient air. These gases are also major contributors to acid rain, but as well, through a complex series of reactions with volatile organic compounds (VOCs) (mostly from motor vehicle exhausts) promoted by sunlight, are also the chief cause of ozone accumulation in the lower atmosphere and in turn, photochemical smog.

- **Particulates PM₂.₅**: These much finer particles are less familiar because being individually so small they tend to be invisible. They originate not only as mineral matter in the fuel, but reactions between sulphur trioxide (SO₃) in stack gases and moisture in air form sulphuric acid aerosol. They also derive from smoke, motor vehicle exhausts, and natural sources are significant—forest haze is an example. They 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 and contributor to haze and photochemical smog.

- **Volatile heavy metals** especially mercury, which occurs in trace quantities in the mineral matter in the fuel; it is of concern because as the element or other volatile form e.g. methyl mercury it is highly toxic even in extremely small quantities.

Pressures are also increasing around the world in favour of imposing limits on CO₂ emissions.

1. **A control strategy framework**

Minimising or otherwise controlling undesirable emissions require most of the following, and the task is best tackled by taking these measures more or less in the order listed:

- Removal to the extent possible, of pollution precursors from the fuel prior to its 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 (including carbon dioxide CO₂) are acid precursors, so control generally involves neutralising them with alkaline substances.

Issues to be considered when planning a control strategy include:

1. Is it a new or an existing facility that requires control?
2. What are the implications in terms of capital and operating costs, and sent-out cost of electricity?
3. What utilities are required—water as well as electricity?
4. What impacts (greenhouse and other) arise from sourcing inputs e.g. limestone, or ammonia, which some control techniques require?
5. Are there markets for any by-products of the processes employed?
6. 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?

The following paragraphs review the current state of the art regarding the control of the major categories of pollutant listed.

2. **Particulates: fly ash and other PM$_{10}$ (to meet 30 mg/m$^3$ limit—99.9% capture)**

The removal of particulates from stack gases to below these limits essentially represents the current extent of stack gas cleaning in Australia power stations.

The preferred approaches around the world are electrostatic precipitators (ESPs) and fabric filters; of note is that Australian power generators (particularly in New South Wales) have been leaders in the application of fabric filters, a consequence of a belief that the low-sulphur Gondwanan coals that make up our east-coast resources with their high-silica ash levels do not respond well to electrostatic filters.

Figure 1 shows the usual location of such equipment: downstream of the main boilers’ induced-draft fans, while Figure 2 shown Bayswater Power Station in the Hunter Valley of New South Wales, which still hosts the world’s largest fabric filter installation.

![Figure 1. The current extent of stack gas cleaning in local power stations](image-url)
3. **Controlling SOx emissions**

Whether one is considering a new or an existing power station the first step is to minimise pyrite content in fuel, if only to minimise reagent consumption. Many designs of coal-pulverising mills manage to strip out some lumps of pyrite and other heavy minerals such as siderite (iron carbonate) into so-called pyrite traps by virtue of their high density. More powerful, effective, but also more expensive approaches being developed rely upon the weakly magnetic (paramagnetic) properties of pyrite.

With a new project there should be more freedom to choose the primary combustion technology. *Fluidised bed combustion* involves burning fuel in the presence of limestone at temperatures around 850°C. SOx released are immediately absorbed chemically by the limestone to create 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. This plus the higher parasitic energy cost of fluidised-bed combustion have tended to relegate this technology to niches—usually where the fuel is waste, or otherwise of extremely low quality.

*Coal gasification* involves reacting the fuel with steam and a small amount of oxygen—either pure (from a cryogenic air-separation plant) or as air, to yield a pressurised mixture of hydrogen, carbon monoxide and dioxide, which after cleaning, can be fired efficiently in more or less conventional gas-turbine combined-cycle power plant equipment. The volumes of gas to be treated are very much smaller (less than 0.5 per cent) than the volumes of stack gases from a conventional power station, allowing sophisticated and
highly efficient processes to be used for the removal of sulphur. This may be converted to the element, or sulphuric acid, both of which are readily marketable.

When options are limited because of the need to retrofit an existing power station, or if the decision has already been made to adopt pulverised-fuel technology (and this is still being specified for the overwhelming proportion of new coal-fired power stations), there are still a number of options that may be adopted:

- **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-sulphur coals (and they work better with fabric filters than with electrostatic precipitators), 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 because of fears over the consequences of acidification of seawater.
- **Wet scrubbers** (limestone slurry) are now mature, efficient (95-98% capture) and widely accepted for existing as well as new power stations. The learning curve was painful for the industry, mainly because of problems with selecting the best materials for construction. One benefit is that the byproduct, gypsum, generally finds a ready market from wall-board manufacturers.

The following table provides a summary of the status of these alternatives—none of these are currently employed in Australia.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Technical status</th>
<th>Strengths &amp; weaknesses</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorbent (CaCO3) injection into furnace before economiser</td>
<td>Mature</td>
<td>Performance poor, (c. 25% SOx capture), leaves alkaline ash. Requires no water.</td>
<td>Other sorbents promising, works better with fabric filters.</td>
</tr>
<tr>
<td>Dry scrubbing (with slaked lime slurry—Ca(OH)2)</td>
<td>Mature</td>
<td>75% SOx capture, inexpensive to install, requires slaked lime, leaves alkaline ash.</td>
<td>Still consumes substantial water, OK for low S coals.</td>
</tr>
<tr>
<td>Wet scrubbers</td>
<td>Mature</td>
<td>95+ SOx capture, produces wet slurry, consumes much water</td>
<td>“Benchmark” SOx control technology.</td>
</tr>
</tbody>
</table>

Table 1.

**Options available for controlling SOx emissions from pulverised-fuel boiler plant**

Figure 3 shows where the currently preferred technology, wet scrubbers, fit into the power station: downstream of the particulates control equipment, while Figure 4 shows a photograph of a wet scrubber installed within a dry (non-evaporative) cooling tower, at Matra Power Station in Hungary.
Wet limestone scrubbing is now the “baseline” approach. In the process, limestone slurry is sprayed through stack gases (cleaned of fly ash solids and any other articulates by electrostatic precipitators or fabric filters) in a large tower: $\text{SO}_2 + \text{CaCO}_3 \rightarrow \text{CaSO}_3 + \text{CO}_2$. 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 are around A$100/kW for new plant, A$140/kW for retrofit.

Operating costs: for limestone, and parasitic power are around two per cent of total power sent out.

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. As well, 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. Also, wet scrubbers are seen as being wanting for NOx, PM$_{2.5}$, and Hg control, meaning that additional equipment and systems must be installed to control these.
A wet scrubber installation for cleaning stack gases that are a byproduct of 400 MW of power. Note the large pipes used to circulate the limestone slurry scrubbing medium.

Dewatering the gypsum byproduct of a wet scrubber on a horizontal belt filter

Plume abatement

A problem associated with wet scrubbers is that in quenching the still warm (at least 135°C) stack gases consumes considerable quantities of water by evaporation, saturating
these gases, leading not only to substantial losses of water, but also to the formation of substantial, highly visible vapour plumes, particularly in cold weather. Figure 6 shows such a plume at the Centralia Power Station in Washington State, USA, in December. The two units of this 1970s vintage 1,500 MWe coal-fired power station were successfully retrofitted with wet scrubbers in 2003, leading to a 98 per cent reduction in emissions of SOx (the photograph shown as Figure 5 was also taken at Centralia).

Plume abatement is generally required in most parts of the world. The usual approach is to discharge the scrubbed, saturated stack gases into a natural-draft cooling tower; this is particularly effective when this is a dry-cooling installation as shown in Figure 4—no plume is normally visible from afar above the cooling towers of this power station: Matra, in Hungary. But water losses are still significant: they increase total water losses from a power station employing evaporative cooling by 15 per cent.

An approach winning favour in Japan in particular, is to cool the stack gases before they enter the scrubber, by exchanging sensible heat in some form of heat exchanger, perhaps similar to the rotary air heaters used in boilers. In this way, water consumption is halved, while the stack gases are heated several tens of degrees Celsius above their saturation temperature, thereby essentially eliminating plume formation.

4. **Controlling NOx emissions**

As with SOx emissions control, the best approach to minimising NOx emissions starts with seeking to prevent their formation in the first place. *Fluidised bed combustion*, mentioned earlier, avoids NOx formation by controlling combustion temperatures to
below 900°C, i.e. below levels that allow some nitrogen and oxygen in the atmosphere to react in this way.

With other, in particular existing plant, there is a step-wise process to go through:

- The first step in controlling these emissions is to minimise peak combustion temperatures, and to maintain reducing conditions in the combustion zone: low-NOx burners are becoming increasingly sophisticated in their design, as are their burner management and control systems, to the extent where current designs can achieve a 50-80 per cent reduction over levels achievable a quarter of a century ago.

- The second step, also directed at minimising combustion temperatures, should be to complete combustion in a staged manner, by resorting to overfire air, which also converts reduced forms of nitrogen in the coal e.g. amines, ammonia, to nitrogen gas.

- The third step: 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. These are forms of 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--SCR); wherein oxides of nitrogen NOx are converted (reduced) to nitrogen gas.

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**Figure 7**

Retrofitting SCR systems to 600 MWe boilers (courtesy Siemens)

Limitations to NOx control systems and technologies

While effective, selective catalytic reduction (SCR) is not popular with utilities (this contrasts with the situation with wet scrubbers for SOx 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 (the escape in stack gases of ammonia surplus to the requirements of the NOx reduction reactions) can create a bigger problem than NOx.

Catalysts are expensive, and subject to poisoning, which limits their lifetime.

The catalysts create oxidising conditions, hence increase formation of the PM$_{2.5}$ precursor sulphur trioxide, requiring more powerful control measures for this.

SCR is required for gas turbines as well as coal-fired power stations where NOx emission limits are extremely tight: the technology can achieve 2-3 mg/m$^3$ in GTs, and 50 mg/m$^3$ in coal-fired power station stack gases (90% reductions).

Because of these problems there is much R&D effort underway overseas directed towards achieving NOx limits without recourse to SCR. Efforts are concentrating on a combination of ever more efficient low-NOx burners, fuel “reburning”, and overfire air, all precisely controlled. But a concern is that these will lead to a rise in unburned carbon in fly ash.

For gas turbines, new designs of combustors: Vortex, Reverse-flow, promise 2-3 mg/m$^3$ performance, but these are still some years away from being commercially available.

Table 2 shows the current state of the art regarding NOx emissions control, while Figure 5 shows where NOx emissions control equipment is located within the power station.

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

Table 2
NOx emissions control options for pulverised fuel boiler plant
5. **Ultrafine Particulates PM$_{2.5}$**

On such fine particles, conventional stack gas particulates removal equipment is less effective than with PM$_{10}$’s—although fabric filters are probably better than electrostatic precipitators, but hybrid ESP/fabric filters are a promising approach to even better control of PM$_{2.5}$ particulates in stack gases: 99.99% capture may be possible.

Power station operators overseas are being required to focus on removing SO$_3$ from stack gases, as this is a precursor to sulphuric acid. SO$_3$ formation is increased by selective catalytic reduction systems for control of NOx. What is emerging as the preferred control approach is to add a solution of sodium bisulphite (SBS) to stack gases after the economiser. This chemical absorbs SO$_3$, to form sodium sulphates, in the process releasing SO$_2$ back into stack gases (this is then removed by the wet flue-gas desulphurisation scrubbers downstream). Make-up SBS solution is formed simply by scrubbing a small side-stream of stack gases with sodium carbonate solutions.

An extra benefit deriving from this process is that the acidity of stack gases is greatly reduced, so fabric filter and ESP lifetimes benefit, and it becomes feasible to cool stack gases further than in current practice to yield higher overall thermal efficiencies.

6. **Mercury**

There are no current control solutions generally accepted around the world by utilities (although pressures to control emissions of this element have so far been concentrated in the USA). The problem is with elemental mercury (Hg), and compounds formed between the metal and organic compounds such as methyl mercury, as both are (in relative terms) volatile. In the USA, dosing stack gases with powdered activated carbon is being promoted, but this is expensive, and fouls ash, limiting options for its possible sale, or ultimate disposal.

In contrast, the oxide (HgO) is not volatile, and can be removed readily in scrubbers or other particulates control equipment. Hence, control 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.

![Diagram of power station stack gas emissions](image)

**Figure 9**  
Adding plume abatement, SO$_3$, and mercury control systems to the power station.

Table 3 summarises the costs involved in NOx and SOx control

<table>
<thead>
<tr>
<th>Description</th>
<th>Extra water reqd, Meqlitres p.a.</th>
<th>Extra power reqd, MWe</th>
<th>Capital cost for retrofit, A$mill.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOx to 350 mg/m$^3$ (Ultra low-NOx burners, over-fire air)</td>
<td>-</td>
<td>2</td>
<td>30</td>
</tr>
<tr>
<td>NOx to 50 mg/m$^3$ (above modifications plus SCR)</td>
<td>-</td>
<td>4</td>
<td>150+</td>
</tr>
<tr>
<td>SOx down 33% (from 1,200 mg/m$^3$) by limestone injection</td>
<td>-</td>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>SOx down 80% to 250 mg/m$^3$, by &quot;dry&quot; scrubbing</td>
<td>900</td>
<td>5</td>
<td>60</td>
</tr>
<tr>
<td>SOx down 96% to 50 mg/m$^3$, by wet limestone scrubbing</td>
<td>1,100 (halved with heat exch.)</td>
<td>12</td>
<td>100</td>
</tr>
</tbody>
</table>

**Table 3**  
Costs and consequences of emissions control retrofit to one typical 700 MWe coal-fired unit.

7. **Trends and future directions**

Apparent from the above is that the “stack gas gauntlet” grows ever longer, the limits on emissions ever tighter. Some argue that this will ultimately kill pulverised-fuel (PF)
based power stations, and that the future belongs to gasification. Are these fears justified?

Despite misgivings every time a new limit on an existing or “new” pollutant 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, their intuitive appeal being that they avoid the increasingly lengthy train of clean-up systems. Two such approaches of considerable potential are to:

- Irradiate cooled stack gases to create a strongly oxidising environment within them, then add ammonia to form ammonium sulphate and nitrate, compounds that can be sold as a fertilizer (demonstration plants are in operation in Poland, Japan, China and the USA).
- Inject sodium bicarbonate (baking soda) into stack gases upstream of a wet scrubber, to form sodium sulphate and nitrate. Then, regenerate the sodium bicarbonate using ammonia to yield ammonium sulphate and nitrate as by-products that can be sold as a fertilizer (Canmet Canada is the developer).

Figure 10 shows where one of these approaches, an ionization-based multi-pollutant control system, might fit into an overall power station flowscheme.

All this suggests that fears for the imminent demise of PF firing are greatly exaggerated.

8. What about carbon dioxide?

The designers of PF plant systems appear likely to be capable of achieving carbon capture (in a form suitable for sequestration) at acceptable cost within a decade. Feasible CO\textsubscript{2} capture systems should stem from an extension of the various multi-pollutant control systems under development such as that shown in Figure 10.
Amine solution-based scrubbing systems are widely deployed in the oil and natural gas industries for purifying gas streams. They effectively remove CO$_2$ and all other acid gases from gas streams including power station boiler stack gases, and yield CO$_2$ in a form suitable for sequestration i.e. highly concentrated, and under pressure. But in a power station stack-gas cleaning context the costs of these systems are high in terms of the energy penalty to regenerate the amine solution: perhaps 30% of the power station’s gross output.

Ammonia promises to overcome these problems. In a promising process under development: the *Chilled Ammonia Process*, the stack gases would be scrubbed with an ammonia-rich solution to form ammonium carbonate. This solution would be heated under pressure to drive off the CO$_2$ and re-cycle the ammonia. The title reflects that the ammonia solutions will need to be chilled to keep ammonia gas out of stack gases. This process’ energy penalty is around 10%, while by 2020 its cost is estimated (by the Electric Power Research Institute) to be of the order of A$10-15/t CO$_2$. Even after the costs of sequestering this carbon dioxide permanently have been absorbed, near-emissions-free coal-fired power generation is likely to be able to sustain its competitive advantage as a clean source of electricity in comparison with nuclear power and natural gas for decades to come.

This is to say, foreshadowed emission limits do not yet justify a shift away either from coal, or from pulverised-fuel firing.

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