# CHEMICAL ECONOMICES - REMOVING CARBON DIOXIDE FROM FLUE GAS

In a previous article I outlined the operation and issues for process plant designed to remove carbon dioxide from industrial gases. In essence the key method is the absorption of the gas at pressure against a descending stream of liquid absorbent which is subsequently regenerated by stripping out the absorbed gas. From this basic process there are many variants used to strip carbon dioxide out of a wide variety of industrial gases.

One of the principal concerns of greenhouse gas mitigation is the removal of carbon dioxide from flue gases which is the result of combustion of fossil fuels. These range in scale from industrial heaters and boiler stacks, to gas turbine exhaust for gas-fired power generation to large coal fired power stations. If successful the captured carbon dioxide would be geo-sequestrated in appropriate deep geological structures.

Most natural gas contains some carbon dioxide and process plant for this operation are widespread and relatively cheap. These processes often use alkanolamines as the absorbent which form a weak complex with carbon dioxide that is easily reversed in a regeneration process. Applying this technology to flue gas illustrates several problems with the current technology.

Suppose we start with a 100 parts of natural gas. If this is burned in a boiler the ideal equation approximates to:

$$CH_4 + air\ (2O_2 + 8N_2) = CO_2 + 2H_2O + 8N_2$$
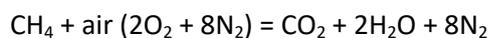
On a dry basis the percentage of carbon dioxide in the in the flue gas is 1/9 or 11.1% (vol.) . This is broadly similar to many natural gases where methane (and some higher hydrocarbons) substitute for the nitrogen. However, in practice the flue gas is far more complicated. Firstly it is common practice to conduct combustion with at least 10% excess air, this ensures minimum soot (particulate emissions) which means the flue gases contain significant volumes of oxygen. Secondly, the fuels used often contain sulphur leading to SOx gases. Furthermore, high temperature (generally more efficient combustion) and natural gas combustion, which has a high flame temperature, leads to nitrogen oxides (NOx) in the flue gases.

The figure below illustrates in volumetric terms a natural gas (containing 10% carbon dioxide) combustion and resulting flue gases to be treated. Striking is the volume increase of flue gas over the input gas. Furthermore, it should be noted that the input natural gas in an industrial operation is at high pressure (typically 20 bar or higher) so that process plant aimed at removing the carbon dioxide in the feed gas is quite compact. Not so for flue gas, where not only is there considerably more volume to process but also the flue gas pressure is near one atmosphere meaning process plant will be considerably larger. The alternative is to compress the flue gas which requires a considerable drain on electricity production.

Turning to process. The flue gases contain oxygen, NOx and SOx. In theory, NOx and SOx can be reduced prior to carbon dioxide removal but there is a practical limit. The main concern is the oxygen in the gas which leads to oxidation and degradation of preferred absorbents considerably increasing the cost of operation.

It is worth noting that for gas-turbines and coal boilers the flue gas composition is quite different as shown in the Table 1. The table shows a wide range of values but it is useful to note that modern gas turbine generators have a high level of air-bypass resulting in low carbon dioxide and high oxygen content of the flue gas whereas modern coal generators tend to have higher carbon dioxide and low oxygen content in the flue gas. In other words, *prima facie*, it would be easier to treat coal flue gas than that from a gas plant.

 Saxena and Flintoff (*Hydrocarbon Processing*, Dec. 2006, p. 57) have presented modelling data for treating flue gas using methylethanolamine (MEA, a commonly used absorbent) and another proprietary amine (SH amine). The data usefully gives estimates of typical flows through a flue gas treatment system (Table 2).

In interpreting this data, it is useful to note the quantum of carbon dioxide in flue gas. This is shown for typical systems in Table 3. Using typical realised thermal efficiencies, gas generation for a 500M station producing 400MW with load factor of 80% emits 1.35 $MtCO_2$/y with the most efficient gas turbine/combined cycle plant and 1.85$MtCO_2$/y for gas-turbine alone (this is the most common in Australia). For large coal generators generating approximately 1GW of power (nominal capacity 1300MW with 80% load factor) the emission is about 7.6 $MtCO_2$/y for a black coal generator and over 10$MtCO_2$/y using lignite. It is interesting to note that a gas turbine generator (not very efficient) producing 1GW or electricity would emit 4.62MtCO2/y at the generator plus large amounts of CO2 emitted during gas production and transmission to the generator site, not much different from an efficient coal generator.

Using these values as guide and applying them to the figures of Table 2, it is quite clear that the capture of carbon dioxide from the flue gas of electricity generators is very costly in terms of power required and consumption of absorbent. Estimates for power demand lie in the range 25to 40% of the total power generated.

Over the past decade there have been many attempts to devise an efficient method of removing carbon dioxide from flue gas. There is still extensive research into finding an efficient absorbent which is robust to oxygen, NOx and SOx. One of the main problems is that demonstration is very expensive (well over $100million and up $500million for a commercial operation on an existing generator). To-date none have been successful in demonstrating a process for extracting carbon dioxide from flue gas which is economically viable.

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Table 1: Typical flue gas compositions of gas turbines and coal fired boilers

Flue gas composition	Gas-turbine exhaust	Coal boiler exhaust
CO2	2.75%	9 to 15%
H2O	9 to 10%	6 to 16%
N2	72-73%	70%
O2	4.4 to 18%	21.5 to 3%

Table 2. Typical utility usage for a standard absorbent (MEA) and an amine developed for flue gas treatment (SH amine)

	MEA	SH Amine
Steam for solvent boiling, t/tCO_2	1.95 to 3.0	1.2
Regeneration heat, GJ/tCO_2	4.2 to 6.5	2.6
Solvent flow, m^3/tCO_2	17 to 25	11
Power for pumps, KWh/t CO_2	150 to 300	19.8
Cooling water, m^3/tCO_2	75 to 165	150
Solvent consumption, kg/t CO_2	0.45 to 2.0	0.35
SO_2 tolerance, ppm	10 to 100	<10

Table 3. Typical annual CO2 emissions from generating plant

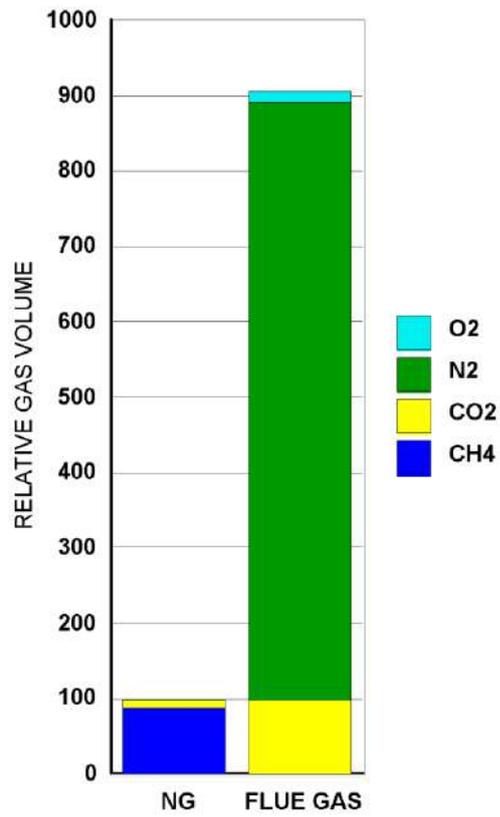|	Thermal. Efficiency (%)	Capacity (MW)	Load factor (%)	MtCO2/y
Gas turbine/combined cycle	48	500	80	1.348
Gas turbine	35	500	80	1.849
Black coal	39	1300	80	7.569
Lignite	30	1300	80	10.384
Gas reciprocating engine (often used in banks of >100)	42	4	98	0.015

Figure 1. Schematic showing relative volumes of natural gas and resulting flue gas (10% excess air)