

# **CO<sub>2</sub>-Sequestration in Power Generation**

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# CO<sub>2</sub>-Sequestration in Power Generation

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## Abstract

To keep the effects of a climate change in acceptable limits the CO<sub>2</sub>-emissions from power production have to be reduced substantially. This task includes existing power plants as well as power plants which are under construction in the moment and new power plant concepts for the future power generation.

Each application of a carbon capture respectively CO<sub>2</sub>-capture has to be analysed with respect to its special boundary conditions. Capture technologies are presented, also with respect to an applicability for different power generation technologies. For existing plants and plants under construction just a post-combustion carbon capture can be applied. The plants are built "capture ready". Oxy-combustion carbon capture can be used for new plant and with some restrictions to existing plant. Post-combustion carbon capture is just suitable for new plants with coal gasification technologies (IGCC integrated gasification combined cycle). All capture technologies cause a dramatic reduction in net efficiency of the plant. The major effort in all R&D&D-work is to reduce this loss of efficiency. On the other hand, degradation of the absorption media is also a problem to be solved for an application in coal fired power plants.

The captured CO<sub>2</sub> has to be transported and stored in an appropriate way. For storage saline aquifers are of great interest onshore and are investigated in some projects worldwide. Under offshore condition enhanced oil and gas recovery is an additional possibility. The transport is realised under pressures between 120 and 200 bars. Therefore acid components and water have to be minimised to handle cavitation and corrosion problems. Also some overview is given in this field.

## Keywords

CCS Carbon Capture and Storage, CO<sub>2</sub>-Sequestration, Pre-Combustion Carbon Capture, Oxy-Combustion Carbon Capture, Post-Combustion Carbon Capture

## 1 Introduction

The announcement and publication of the IPCC-Report [1.1] in February 2007 led to a paradigm change concerning questions of climate change as a result of CO<sub>2</sub>-emissions caused by human activities. Up to that time doubts of a direct influence governed the discussion. Starting from that time, it is accepted that big efforts have to be undertaken to reduce the CO<sub>2</sub>-Emissions dramatically. The influence on the global temperature increase (global warming) has to be limited to 2 K to keep negative effects like weather and climate extremes (storms with very high windspeeds, hurricanes and tropical storms, wet and dry extremes by modified rainfall events and others) in a controllable range.

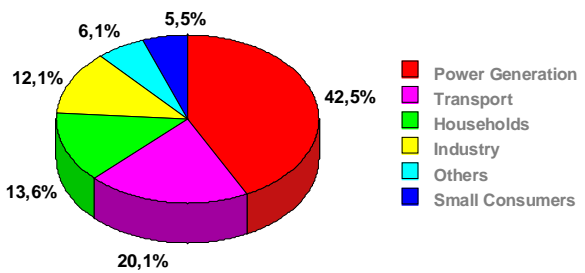
An idea of the global emissions is given in **fig. 1.1**. Roughly 30 Billion tonnes of CO<sub>2</sub> are emitted worldwide per year. The percentage caused by power production is about 40 % (**fig. 1.2**), which leads to 12 Billion tonnes from that sector.

**Fig. 1.1:** Global CO<sub>2</sub>-Emission worldwide in the year 2005

Region / Country	CO <sub>2</sub> -Emissions
Globe	29.166.000.000 t
USA	6.526.000.000 t
Asia und Oceania	10.757.000.000 t
China	5.327.000.000 t
Europe	4.632.000.000 t
Germany	880.000.000 t

From that point of view a dramatic reduction of the CO<sub>2</sub>-emissions in power generation is a big challenge for all countries. In Germany the aim is to reach 20 % or more of reduction up to the year 2020.

For the power industry big efforts are to be undertaken to realize this aim. From the economic point of view additional costs burden the power generation. This has to be seen in the context of CO<sub>2</sub>-certificates trade.



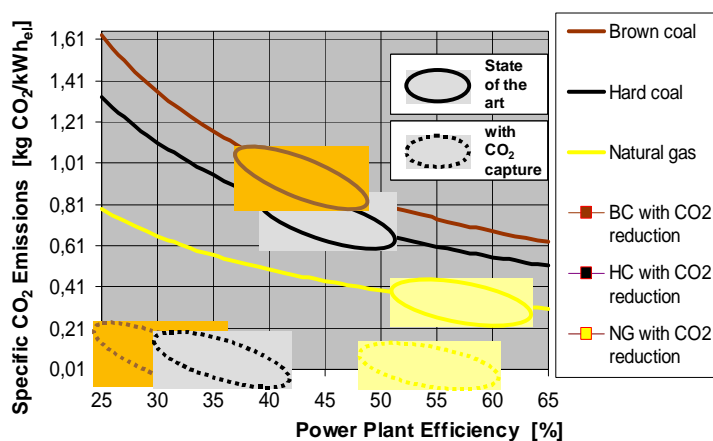
**Fig. 1.2:** CO<sub>2</sub>-sector emissions for Germany in the year 2005 [1.2]

## 2 Implementation in Power Plants

In general there are 3 possible strategies to reduce the CO<sub>2</sub>-emissions resulting from power generation in power plants:

- increase of efficiency,
- change of fuel and/or
- carbon capture and storage.

The increase of efficiency is a classical non regret strategy. It directly reduces the specific CO<sub>2</sub>-emissions per kWh<sub>el</sub> produced. In addition the fuel resources are saved, which is also a direct contribution to sustainability.



Reference:		Assumptions:	
Hard coal	0,333 kg CO <sub>2</sub> /kWh <sub>th</sub>	- Reference efficiency 45 %, hard coal	
Brown coal	0,407 kg CO <sub>2</sub> /kWh <sub>th</sub>	- 10 % efficiency points loss if CO <sub>2</sub> capture is included	
Natural gas	0,197 kg CO <sub>2</sub> /kWh <sub>th</sub>	- CO <sub>2</sub> capture rate of 90 %	
		- Energy demand per kg CO <sub>2</sub> is constant	

**Fig. 2.1:** Specific CO<sub>2</sub>-emissions as a function of fuel and power plant efficiencies. Solid areas indicate state of the art values without carbon capture. Broken lined areas stand for conditions with carbon capture

CO<sub>2</sub> is bond in the growing phase as is released in the usage phase by combustion or gasification. At present, the amount of regenerative energies are not able to replace the power production on the basis of fossil fuels. From that reason, carbon capture and storage CCS has to be applied for an intermediate phase of the next decades, at least.

Changing the fuel from brown or hard coal to natural gas also reduces the specific CO<sub>2</sub>-emissions per kWh<sub>el</sub> directly. Specific emissions as a function of the fossil fuel and the net efficiency of the power plant can be seen from **fig. 2.1**. The solid lines indicate the tendencies whereas the solid areas describe power plant efficiencies which are state of the art in the moment.

Carbon capture and storage is the final solution in reaching CO<sub>2</sub>-reduction degrees of 90 % or more related to the carbon in fossil fuels.

It is evident that the best CO<sub>2</sub>-avoidance strategy is to reduce energy consumption and/or use renewable energies like wind, sun or water. "Indirect" sun energy like biomass is, by definition, also neutral, because the same amount of

### 3 Capture Technologies

For power plant applications carbon capture methods can be classified into three main groups (fig. 3.1):

- pre-combustion,
- oxy-combustion and
- post-combustion.

They offer different alternatives of capturing the CO<sub>2</sub> from the flue gases ([3.1]) and will be discussed.

A very important point for all technologies is the loss of net efficiency for the power plant. Fig. 3.2 gives an impression of the net efficiencies of power plants on brown and hard coal basis as it is now and expected for the next two decades. Looking on the efficiency losses for the different capture methods in combination with the fuel conversion gives values between 6-14 %-Pts. These values bring us back to net efficiencies valid in the 70's in Germany. Also a much higher resource consumption (fuel) is a consequence. So the main task in all R&D&D-projects is to reduce these values.

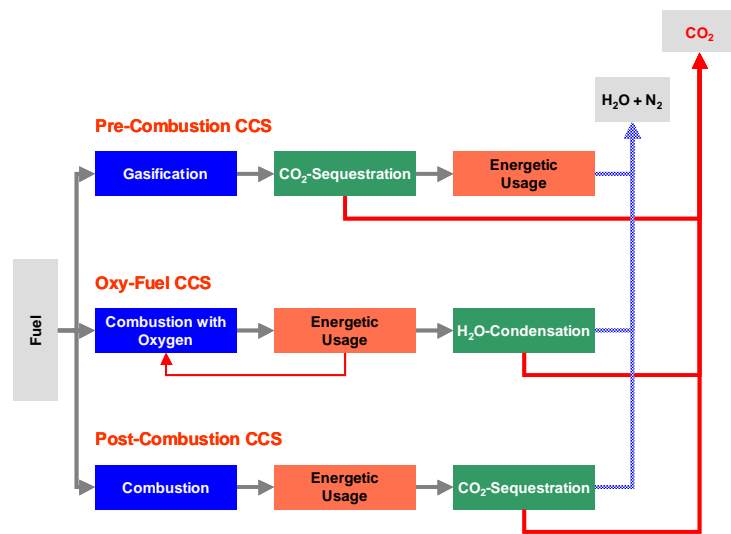


Fig. 3.1: Different carbon capture technologies

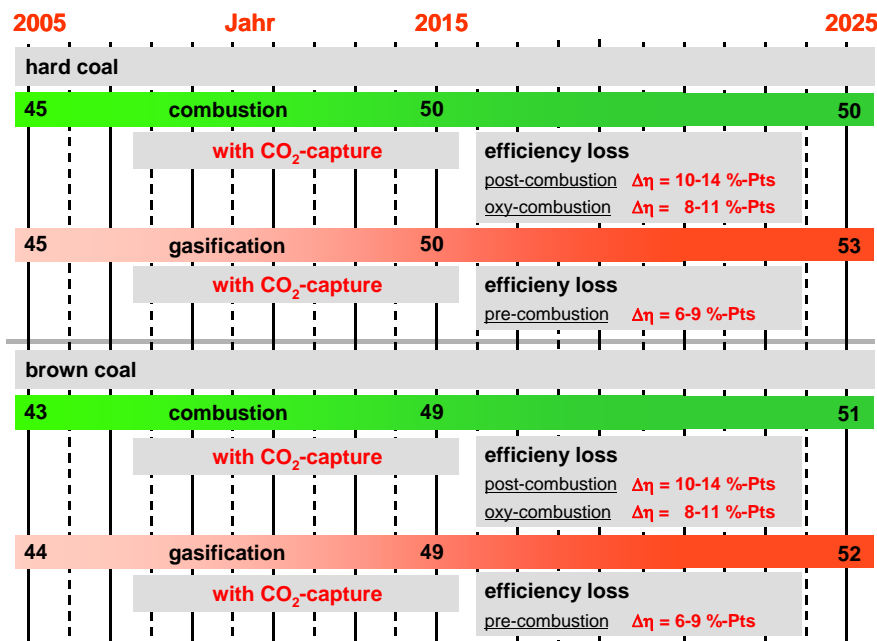
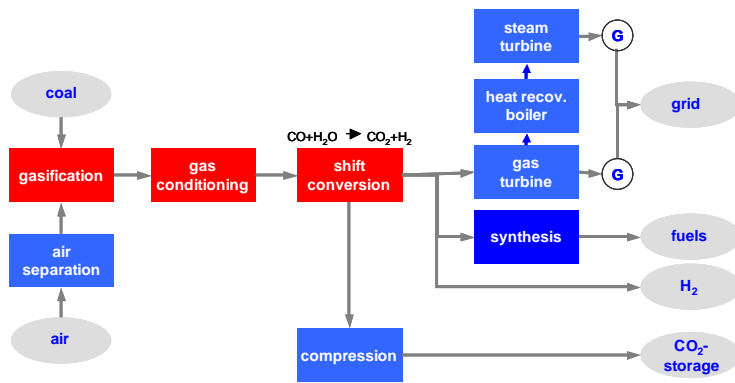


Fig. 3.2: Ranges for net efficiencies for brown and hard coal fired power plants and expected loss of efficiencies by applying carbon capture technologies.

#### 3.1 Pre-Combustion Carbon Capture

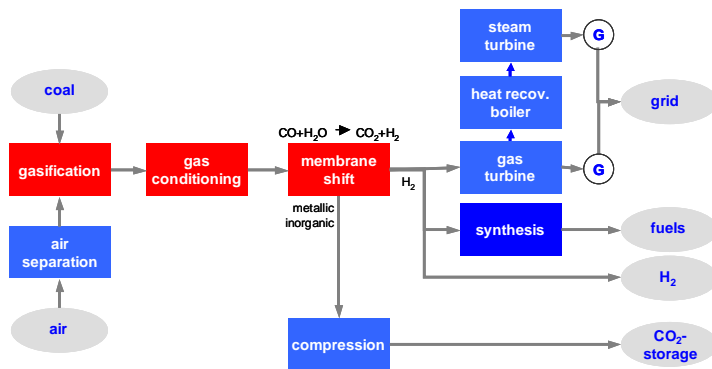
As the name suggests the CO<sub>2</sub> capture occurs before the combustion takes place. This offers some advantages. First of all the CO<sub>2</sub> has not yet been diluted by combustion air and second, the CO<sub>2</sub> containing stream is generally under elevated pressure [3.2]. This offers the possibility of using commercial capture processes that have proved themselves efficient, like the Rectisol or Selexol processes (fig. 3.3).

Pre-Combustion Capture can be applied in IGCC (Integrated Gasification Combined Cycle) power plants. Here the fuel will first be gasified in presence of an oxygen rich or air stream to produce a synthesis gas, that consists of carbon monoxide (CO) and hydrogen (H<sub>2</sub>). The gas will then react with



**Fig.3.3:** General scheme of pre-combustion carbon capture

[3.2]. The resulting flue gas is then sent to a heat recovery steam generator (HRSG) and more electricity will be produced with a steam turbine. Since the synthesis gas with high  $H_2$ -content is a valuable product. With a Fischer-Tropsch-synthesis it can be transformed to liquid fuels. Part of it can also be extracted before it reaches the turbine, in order to use the  $H_2$  for applications like fuel-cells for the transport sector or chemical processes. The captured  $CO_2$  will be compressed and will be then ready for its transport and storage.



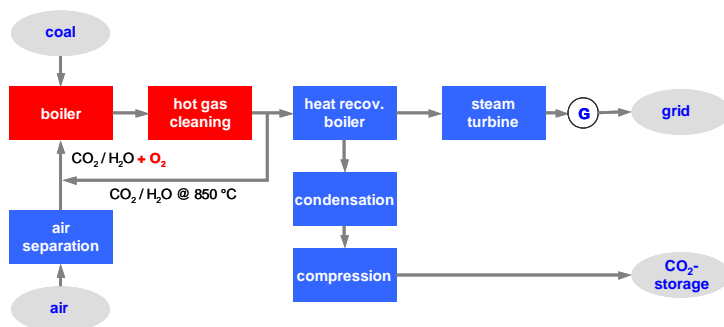
**Fig. 3.4:** General scheme of pre-combustion carbon capture with a membrane for the shift reaction and the gas separation (HotVeGas-project of FZ Jülich, [3.4])

attractive because of a lower energy loss as a consequence of a higher gas temperature to the gas turbine in relation to the “normal” IGCC-process.

water in a water-gas shift reaction to produce a stream rich in  $CO_2$  and  $H_2$ . According to [3.3] the concentration of  $CO_2$  in this stream is around 25-40 % and the total pressure varies between 2,5-5 MPa. Under these conditions the  $CO_2$  partial pressure is very high, compared to the one from a post-combustion process, where the flue gas is at atmospheric pressure; thus making it possible to use capture techniques like the ones mentioned above. Once the  $CO_2$  has been captured, the  $H_2$  will be sent to a gas turbine to generate electricity

A variation of the previously mentioned pre-combustion capture process was proposed by the Research Centre Jülich in Germany (fig. 3.4). The process is basically the same, with the exception that the water-gas shift reaction would take place thanks to gas separation membrane layers and not a reactor. This membrane has to be operated under higher temperatures and to be protected against corrosive attacks. For that reason a liquid slag removal and a chemical hot gas cleaning (gas conditioning) is placed before the metallic/inorganic membrane. This process is in the very beginning phase, but is very

### 3.2 Oxy-Combustion Carbon Capture



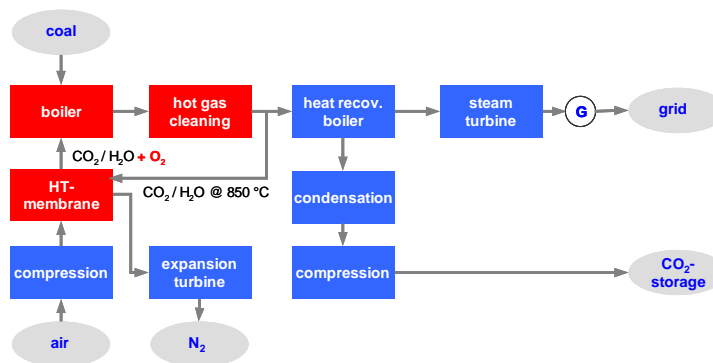
**Fig. 3.5:** General scheme of oxy-combustion carbon capture

Looking to the oxy-combustion process (oxy-fuel-process, fig. 3.5), it will often be referred to in the literature as an integrated process of  $CO_2$ -Capture, since the combustion takes place in an oxygen rich environment, making it theoretically possible to produce a stream pure in  $CO_2$  in absence of  $N_2$  from the air. However this is not the case in reality. In the common oxy-combustion process the oxygen required for the combustion will be provided

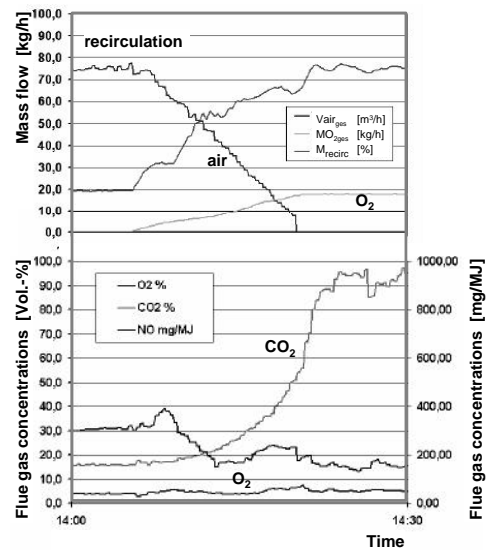
by an air separation unit (ASU). The coal will burn in presence of this oxygen to produce a stream with a high CO<sub>2</sub> concentration (> 80 vol.-%, see **fig. 3.6**), which can be easily increased with simple gas cleaning technologies [3.3]. Once the stream has been submitted to a hot gas cleaning, a part of it will be recycled and added to the gas (O<sub>2</sub>) coming from the ASU, in order to limit the maximum combustion chamber temperature and to increase the concentration of CO<sub>2</sub> in the flue gas. The switch-over from normal air combustion to oxygen combustion with flue gas recirculation can be seen from **fig. 3.6**. Strictly speaking, the CO<sub>2</sub> capture in the oxy-combustion process occurs after the combustion, which is the reason why the authors prefer to call this method oxy-combustion. Once the flue gas has been cleaned, it will be conducted to a heat recovery boiler, which directly feeds a steam turbine, for the purpose of electricity generation. The CO<sub>2</sub> rich flue gas then leaves the heat recovery boiler and can be compressed for its transport and storage.

Though this process sounds simple, it is far from being perfect. There are still some issues that require special attention. For example, the separation technologies that could be used here (like cryogenics) still need to be tested and optimized for an application like a power plant, with its large industrial utility boilers. According to [3.2], the ASU could consume up to 15 % of a power plant's electric output, which represents a huge efficiency loss.

The OxyCoal-AC-Process (**fig. 3.7**) represents a variation of the previous process. This technology is developed by RWTH Aachen in Germany. In this case, the oxygen will be provided by a membrane, instead of an ASU. For this purpose, air will be compressed before it enters to the membrane, since this improves its separation performance.



**Fig. 3.7:** Oxy-combustion process with O<sub>2</sub>-enrichment by a membrane process (OxyCoal AC-Process; AC stands for Aachen)

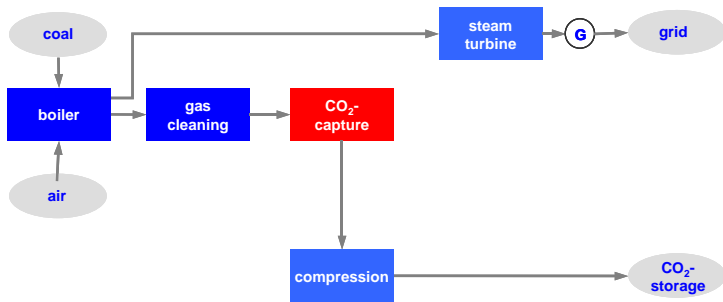


**Fig. 3.6:** Switch-over from air combustion to oxygen combustion [3.5]

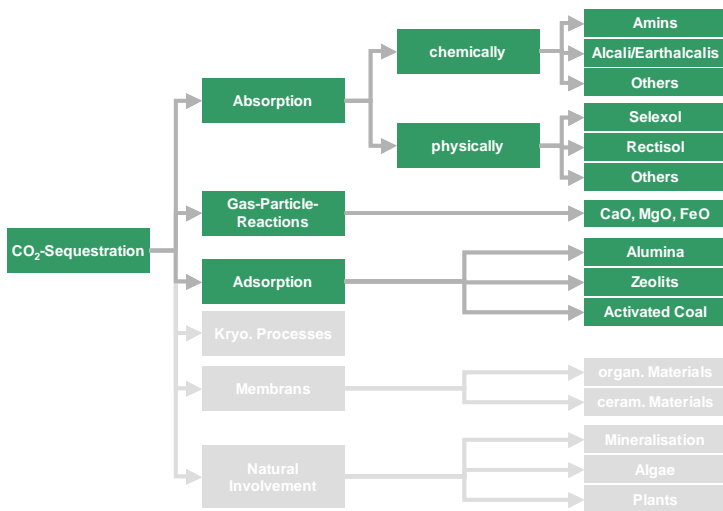
The coal will burn in the combustion chamber under the presence of a rich oxygen stream and the cycle remains the same as the common Oxy-combustion process, with one exception: the nitrogen obtained during the air separation with the membrane, will be used in an expansion turbine. This gives the possibility of generating more electricity as in the common oxy-combustion process. Thus resulting in a higher process efficiency.

### 3.3 Post-Combustion Carbon Capture

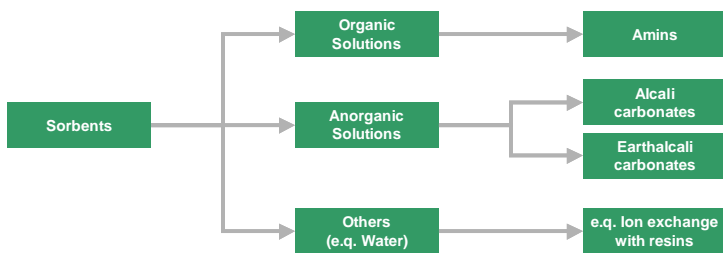
This capture method can be applied to conventional fossil fuel power plants. The flue gas to be treated comes from the combustion of coal (or gas) with excess air (**fig. 3.8**). For modern power plants the concentration of CO<sub>2</sub> in this gas is 12-15 vol.-% for coal and 2-3% vol.-% for natural gas. Post-combustion capture offers the possibility to operate a power plant as usual, without changes to key parts of the power cycle like the boiler house or the turbines. This would not apply to other power generation technologies like IGCC or oxy-combustion, which are still relatively new. Unlike these two technologies, post-combustion capture also offers the possibility of retrofitting a power plant years after it was built, as long as some measures are taken that would ensure this option, like leaving enough space for the capture plant to be built when needed. This is called a "capture ready plant".



**Fig. 3.8:** General scheme of post-combustion carbon capture



**Fig. 3.9 :** Process families for post-combustion carbon capture technologies



**Fig. 3.10:** Sorbents for chemical absorption (chemical scrubbing)

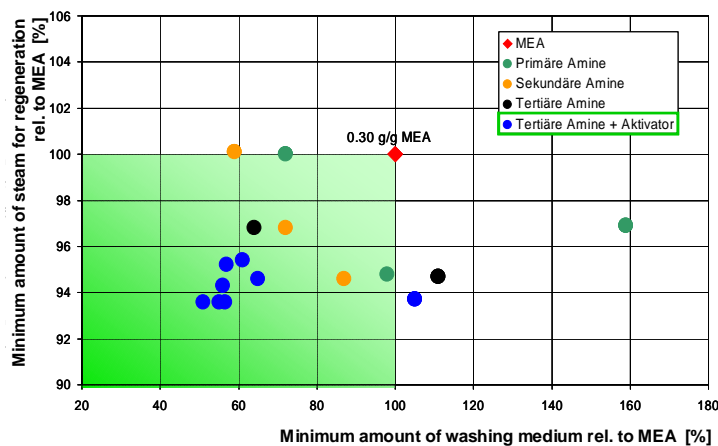
For post-combustion capture there are different options to be considered like physical and chemical absorption, membranes, cryogenics, adsorption (see **fig. 3.9**).

However, the last three options are at very early research stages, or better, their performance in the power generation sector still needs to be improved, before they can be implemented. Physical absorption would only work efficiently under a high pressure like in the case of the IGCC power plant, but not at atmospheric conditions. That leaves the chemical absorption as an option for the CO<sub>2</sub> capture. There is a lot of experience in this sector, since this method has been used for over 60 years now [3.3], but not in power plant applications.

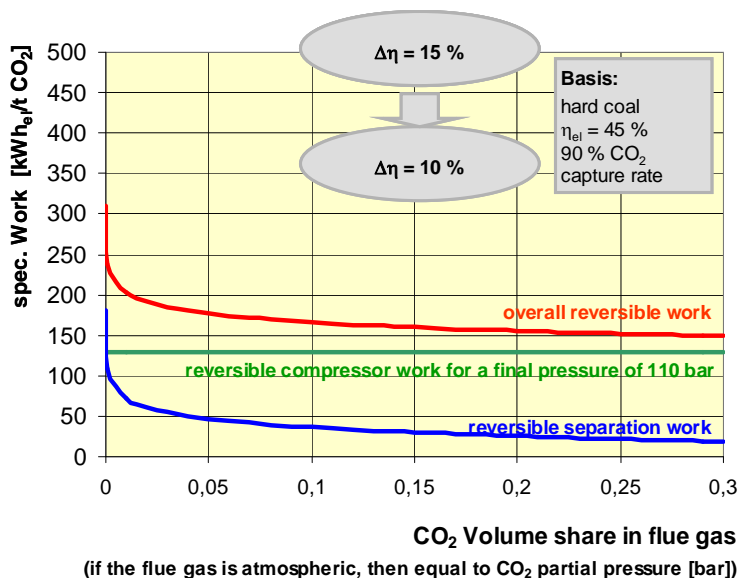
In a chemical absorption (**fig.3.10**) the flue gas has previously been treated in the FGD and DENOX-plants. The flue gas then enters an absorber column at the bottom and comes in contact with a solvent in counter current. The clean gas leaves at the top of the column. The rich solvent accumulates at the bottom of the column and leaves for the stripper, but before it has to go through a heat exchanger, in order to raise its temperature and be able to reverse the absorption reaction. In the stripper the solvent is regenerated under a temperature of around 100-120 °C. The CO<sub>2</sub> leaves at the top of the column, while the lean solvent leaves at the bottom with a temperature of almost 120 °C. This stream will also be sent to the previously mentioned heat exchanger to be cooled down to a temperature between 40-65 °C before it enters the absorber column again.

A common solvent to use is Monoethanolamine (MEA, **fig. 3.11**) which is a primary amine. A frequent problem with MEA is its degradation rate, when it comes in contact with impurities in the flue gas, such as Sulphur compounds, NO<sub>x</sub>, etc. MEA reacts with those components to heat stable salts, which will have to be removed sooner or later. If the impurities are not kept at a certain level, then they can also react with the inhibitors in the solvent, that prevent corrosion in oxygen containing streams like flue gas [3.6]. The Fluor Daniel ECONAMINE FG CO<sub>2</sub> recovery process sets for instance a maximum of 10 ppmv SO<sub>2</sub> as the feed specification and in the case of ABB-Lummus, there is a range of 1-100 ppmv. However the ABB-Lummus technology includes a desulphurisation step, in order to also maintain the SO<sub>2</sub>-levels at a maximum of 10 ppmv [3.7].





**Fig. 3.11:** Demand of absorption medium and regeneration energy [3.10]



**Fig. 3.12:** Energy demand for carbon capture and compression of CO<sub>2</sub> as a function of CO<sub>2</sub>-volume share in the flue gas

**Fig. 3.12** shows some theoretical calculations concerning the energy demand as a function of CO<sub>2</sub>-volume share in the flue gas. For 15 % of CO<sub>2</sub> flue gas concentration a minimum demand of 200 kWh/t CO<sub>2</sub> is required. In the moment values of 500 kWh/t CO<sub>2</sub> are discussed. 350 kWh/t CO<sub>2</sub> seems to be realisable.

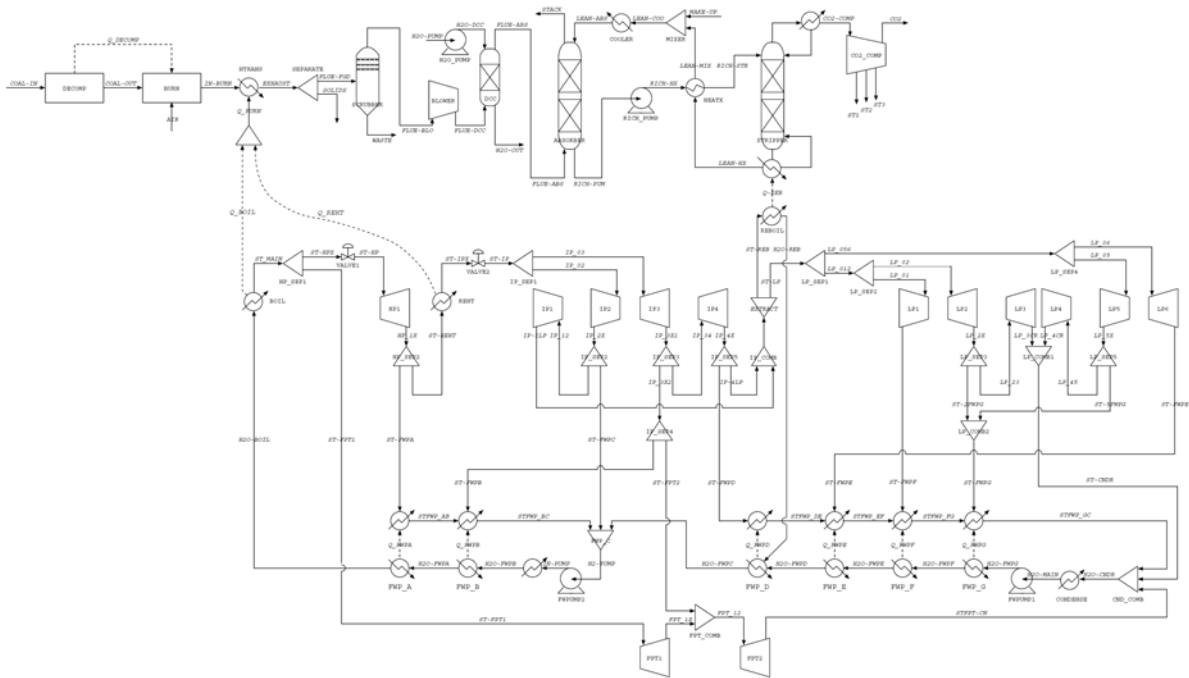
The simulation of a CO<sub>2</sub> scrubbing process offers the opportunity of predicting several variables that are important for the integration of the capture process with a power plant (**fig. 3.13**). For example, the energy requirements - both thermal and electrical - from the absorption process, which will have to be covered by the power plant itself. Another advantage is that in a simulation several scenarios can be analysed for both absorption and power generation process, thus customising current technologies. There are several simulation tools; Aspen Plus<sup>®</sup> is a widely used commercial software from AspenTech.

In order to get realistic results from simulations, it is important that variables like data on several chemical media are available and this is not always the case in modelling programs. One way of overcoming this issue would be by adjusting existing data, with the results from experiments. This would make the results more reliable. However, this is not always an option. This can only be

Another solvent that has been developed is KS-1 (**fig. 3.10**). This is a sterically hindered amine and can not only absorb more CO<sub>2</sub>, but also has a lower degradation rate than MEA. Furthermore, KS-1 would require about 25 % less energy for its regeneration [3.8] than MEA. Based on an IEA report [3.9], the energy penalty of using KS-1 is 1-2 percentage points lower than the one from Fluor, where MEA would be used as a solvent. However the capital costs are higher for KS-1, so the overall capture costs would be similar for both processes.

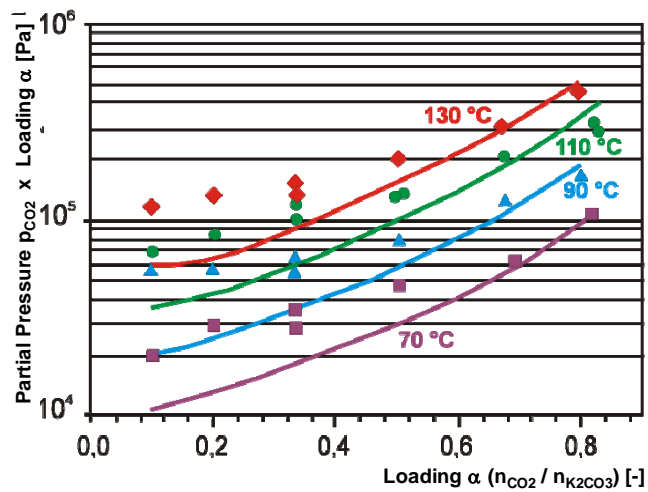
The amount of energy required for the regeneration of the solvent in the chemical absorption represents a major draw back for this technology.

According to [3.11] the CO<sub>2</sub>-capture with chemical absorption would implicate losses in the range of 15-25 % efficiency points from the power plants, depending on the original efficiency of the plant to be retrofitted. Nevertheless some studies [3.9], [3.12], revealed that research has been making rapid progress in this matter, so that the forecasts for this technology look better than first anticipated.



**Fig. 3.13:** Simplified scheme for a power plant with a post-combustion carbon capture plant [3.13]

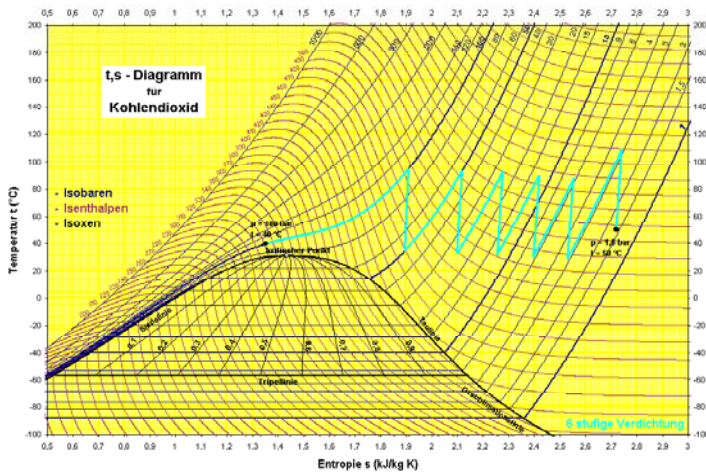
undertaken if the solvent to be tested is considered by the simulation program. Several research projects focus on the development of new solvents to be used for CO<sub>2</sub>-capture from fossil fuel power plants. Especially these solvents would not be available to analyse their performance with new process design concepts.



**Fig. 3.14:** Measured and calculated data for aqueous carbonate solution (calc. with ASPEN+ data bank)

## 4 CO<sub>2</sub>-Transport and Storage

### 4.1 CO<sub>2</sub>-Transport



**Fig. 4.1** : T-s-diagram for CO<sub>2</sub>-compression with a 6-stages compression (green lines)

To transport the captured CO<sub>2</sub> from the power plant to a storage site it has to be compressed to pressures of 120-200 bars. Compression and liquification is done in several stages (**fig. 4.1** with 6 stages) to reduce the energy demand. As shown in fig. 4.1 the CO<sub>2</sub> in this state is near the critical point. The CO<sub>2</sub>-concentration should be above 95 % and trace elements like SO<sub>2</sub>, H<sub>2</sub>S, O<sub>2</sub>, N<sub>2</sub> and others should be below 4 % to avoid cavitation and corrosion. Unsolved water is to be limited to 500 ppm. Otherwise ice formation is to be expected. This can be realised by drying processes.

To realize the transport of CO<sub>2</sub> over a larger distance the acceptance by the population is a very important aspect in this context. A lot of legal and psychological questions have to be answered.

### 4.2 CO<sub>2</sub>-Storage

The storage of the captured CO<sub>2</sub> can be realised onshore or offshore, generally. **Fig. 4.1** shows some worldwide storage projects. Onshore-sites need an acceptance from the local population. For that reason it is very important to demonstrate reliability and safety of such sites.

**Fig. 4.3:** CO<sub>2</sub>-storage projects worldwide. In Europe the onshore project in Ketzin, offshore the project in the Sleipner oil field have to be mentioned.

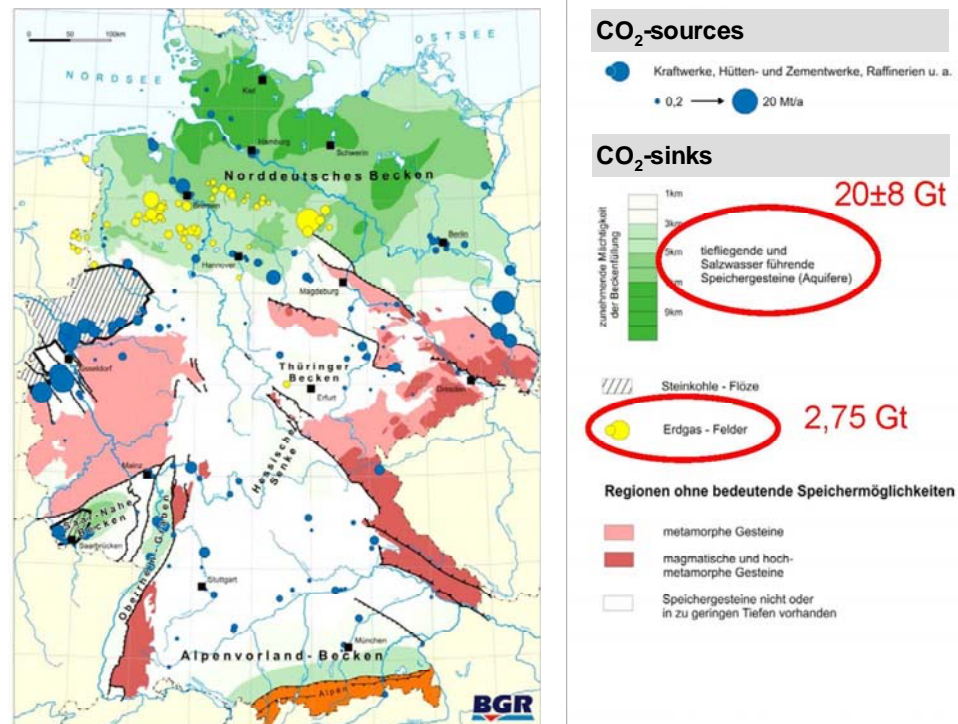


In Germany a big project call CO<sub>2</sub>SINK [4.] is running in Ketzin near Berlin. In a saline aquifer storage and migration behaviour is investigated. Specially CO<sub>2</sub>-leakage rates are measured. This has to be done individually at each location because the tectonic situation is different.

An other question is the storage capacity related to the amount of CO<sub>2</sub> over the power plant running time. If there is no storage capacity near the plant location long pipeline distances are the consequence. The situation in Germany had been investigated by the BGR (Bundesanstalt für

Geowissenschaften und Rohstoffe, Germany, [4.1, 4.2], see fig. 4.2). The map shows the big emission points (blue dots). Just in the northern parts of Germany bigger storage sites are available with a total capacity of 16-30 Gt of CO<sub>2</sub>. The distance in between are some 100 kilometers.

**Fig. 4.4:** Sources of CO<sub>2</sub> (blue dots) and areas, suitable for CO<sub>2</sub>-storage (mainly in the northern regions of Germany). The yellow dots indicate depleted gas fields which are also suitable for storage. ([4.2])



In North Sea oil and gas fields CO<sub>2</sub> can be used for enhanced recovery of oil (EOR) and gas. The injection of CO<sub>2</sub> increases the yield directly. STATOIL tests this method since 10 years in the Sleipner oil field, which is situated west of Norway.

## 5 Conclusion

In power generation carbon capture and storage will come more and more into the focus. The practical application of CCS-technologies has to solve problems in the area of CO<sub>2</sub>-capture in the plant, the transport of the CO<sub>2</sub> from the plant to a storage location and the storage itself.

Carbon capture for existing power plant can be realised by post-combustion carbon capture methods. Organic or inorganic solvents like amines, ammonia, carbonates and others are used. Problems in this area are corrosion of materials and degradation of the washing medium. Also safety questions have to be taken into account. The biggest disadvantage is the high energy consumption for the regeneration of the washing medium. It is realized by steam from the power plant which can not be used for power generation and is reducing the plant efficiency.

Oxy-combustion carbon capture uses combustion with pure oxygen and a flue gas recirculation to stabilise the combustion temperature. Costs for the air separation are dominating in this technology. With some restrictions it can be used for retrofit of existing plants.

Pre-combustion carbon capture is based on coal gasification. The synthesis gas is conditioned, shifted and the CO<sub>2</sub> separated. For this is done for a much smaller gas stream the separation is cheaper. Also less O<sub>2</sub> is needed for gasification in relation to oxy-combustion.

Nevertheless, reduction of power plant efficiency between 6-14 %-Pts. is the most dominating problem and all efforts try to reduce this.

Transportation and storage are problems which can be solved technically. This area is dominated by legal and psychological questions.

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