Evaluation of different water vapor capture technologies and energy modeling results for membrane technology

Ludwin Daal, Hans Kamphuis, Arthur Stam, Ton Konings, Martijn Huibers, Sjoerd van Rijen & Jacques de Ruijter

DNV-KEMA the Netherlands, Department PGR-PCW, P.O. Box 9035, 6800 ET Arnhem, The Netherlands

Version March 30, 2012
Combined paper ID: 186 & 192

Abstract
One of the major challenges for power plant operators is the provision of water in arid areas. The shortage of water resources in these areas requires the availability of more efficient and cheaper water production processes. A large source of water is found in the form of evaporated water emitted from a power plant. Using selective membranes this evaporated water can be removed. The captured water is in a single step near demin water quality. The advantage of selectively removing water over condensing the entire flue gas stream is that less cooling energy demand is needed. Also the condensed water in this case would be of a corrosive nature. The objective within the European Integrated project CapWa www.watercapture.eu is to produce a membrane modular suitable for industrial applications within 3-4 years. The capture of evaporated water would increase the location flexibility of a plant. In order to evaluate this technology it has been compared with the two most promising alternatives. Parameters evaluated are among others the maturity of the technologies, performance, economic evaluation, water purity, operational aspects, health and safety. On the other hand questions are raised with respect to the energy demand and/or saving of the membrane technology. For the installation of membranes in a flue gas stream leads to a pressure drop that needs to be compensated with an ID-fan. For the driving force vacuum is needed. Also cooling energy is necessary to condense the captured evaporated water in often hot and dry regions. Therefore the energy consumption of Air Cooled Condensers has to be taken into account. At the same time the latent heat of water vapor can be reused to preheat condensate in the plant and thus create an energy saving. During the conference the outcome of the evaluation and the energy modeling results within SPENCE will be presented.

Keywords: Gas and vapor separation; Power generation; water capture; energy modeling;

1 INTRODUCTION

One of the major challenges for power plant operators is the provision of water in arid areas. The shortage of water resources in these areas requires the availability of more efficient and cheaper water production processes. A large source of water is found in the form of evaporated water emitted from a power plant. Using selective membranes this evaporated water can be removed. The captured water is in a single step near demin water quality. The advantage of selectively removing water over condensing the entire flue gas stream is that less cooling energy demand is needed. Also the condensed water in this case would be of a corrosive nature. The objective within the European Integrated project CapWa www.watercapture.eu is to produce a membrane modular suitable for industrial applications within 3-4 years. The capture of evaporated water would increase the location flexibility of a plant. In order to evaluate this technology it has been compared with the two most promising alternatives. Since the energy consumption and/or saving for the membrane technology plays a crucial role in operating costs, energy modeling has been conducted.

2 ALTERNATIVE WATER CAPTURE TECHNOLOGIES

In the first section a screening of alternative technologies for water vapor capture are assessed. The following capture technologies are reviewed: cryogenic separation, cooling with condensation, liquid and solid sorption

2.1 Liquid sorption

The principle of liquid sorption is the incorporation of a substance in one state (gas) into another substance of a different state (liquid). One component of the gas mixture is preferentially absorbed by the liquid. Sorption can be chemical (i.e. a chemical reaction, for example removal of acid gases by reaction with NaOH) or physical (i.e. dissolution, for instance removal of water from natural gas with glycol). In general, the partial pressure of the sorption material is very low and the vapor pressure of the solution is dominated by the partial pressure of the water. The difference between the partial pressure of water in the gas stream and partial pressure of water in the sorption material is the driving force for drying.

Folkedahl *et al*. (2006) report a literature study: the use of a liquid desiccant to strip water vapor from a flue gas stream appears to be a novel application based on the lack of literature found. Current applications for stripping water vapor from gasses are natural gas drying, building dehumidification and cooling. The application for removal of water from flue gas from coal-fired power plants was investigated and demonstrated by Folkedahl *et al*. (2006).

Water is removed from natural gas because it can impact on downstream equipment: formation of hydrates with CO_2 or hydrocarbons which can cause plugging, freezing of piping and low temperature corrosion by dissolved H_2S or CO_2. Natural gas dehydration with glycol is the most common and economic means of water removal. The types of glycol that are typically used for gas dehydration are triethylene glycol (TEG), diethylene glycol (DEG), ethylene glycol (MEG), and tetraethylene glycol (TREG), where TEG is most commonly used.

Building dehumidification is used for health reasons or for comfort, especially in humid areas. The liquid sorption material in dehumidification is called a desiccant. Commonly used liquid desiccants are aqueous solutions of two basic classes: inorganic salts (such as LiCl, LiBr or CaCl) and glycols (such as MEG, DEG, TEG or TREG).

Desiccant based water removal is currently not used in coal-fired power plants. By the high purity of the produced water, the possible application is water for the steam cycle, especially in areas where water is scarce and expensive. Desiccant technology employs chemical agents (i.e. desiccants) which possess a strong physicochemical affinity for water to extract water vapor. As in membrane technology, but unlike in condensation, water with a high purity can be obtained. A drawing of a flow sheet of a desiccant based scrubber plant is given in figure 1. Indicated is some typical operating data. The desiccant heater was added by the authors (Folkedahl *et al*. 2008). However, the authors expect that the heat of absorption can be used for desiccant heating, and no extra heater is needed.

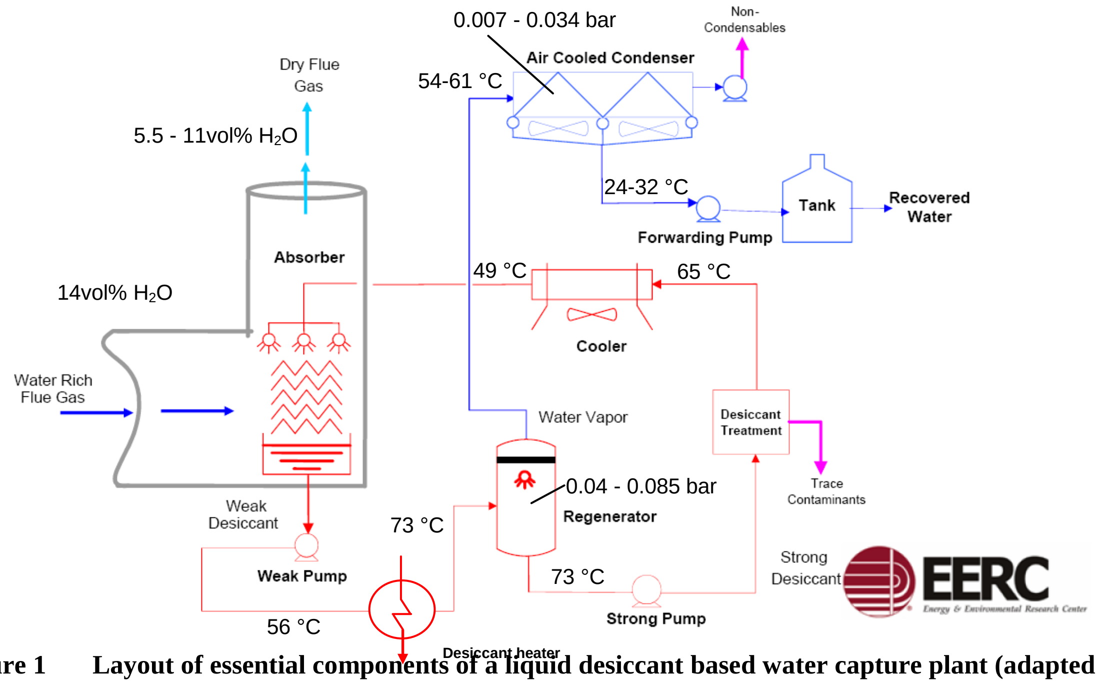

Figure 1 **Layout of essential components of a liquid desiccant based water capture plant (adapted from Folkedahl *et al*., 2006).**

Flue gas flows into the absorber column upwards while the desiccant (a 45% calcium chloride solution) flows downwards. Flue gas lean in water leaves the column at the top, passing a demister that removes any entrained desiccant droplets before flue gas is discharged through the stack. The water rich desiccant is pumped to the regenerator and heated to about 73 °C before entering the regenerator. The regenerator (also called flash drum) is a key component where water is separated from the desiccant solution as a result of differential pressure. This is accomplished by spraying the water rich desiccant solution into the flash drum volume, allowing the water to separate as a vapor and exit the top of the flash drum through a demister. The product water is then recovered in a downstream condenser. The condenser is kept at a low pressure (below 0.07 bar) using a vacuum pump. The desiccant solution leaving at the bottom of the regenerator, is pumped to a filtration system used for removal of insoluble contaminants. The desiccant solution is then cooled before entering the absorber.

The technology can, in principle, be applied to a full size power plant. There is no technical limitation in scaling up of the absorber columns, which would be similar to an FGD. Folkedahl *et al*. (2006) proposed two types of full scale water capture plants, one for treating the complete flue gas stream, and one for treating a slipstream, dependent on the plant water needs.

Since an FGD and a CO_2 capture installation, which are technically quite alike to the proposed liquid sorption system, it is expected that load variations will pose no problem.

The technology of liquid sorption is widely used in gas dehydration and building dehumidification and cooling, but not in coal fired power plants. It can therefore be considered to be in the demonstration phase.

Process safety will be mainly be related to exposure of humans and environment to the desiccant. This is not expected to pose problems, such as experienced in amine based CO_2 capture, related to emission of carcinogenic solvent degradation products.

Energy is not saved but used to produce water. Reported capture rates (Folkedahl *et al*., 2006) are up to 70%, which can cover a fair amount of the required steam cycle water make-up. Energy costs and investment costs are economically viable, when the price of water is high, such as in dry areas. Folkedahl *et al*. (2006) report investment and operational costs for a desiccant based water removal plant for a 250 MW_e coal fired power plant of $5.8 mln and $500,000 per year, respectively.

2.2 Solid sorption

Solid desiccants can be either adsorbents or absorbents. Adsorbents, such as silica gel and activated alumina, undergo no chemical or physical change during the moisture removal process but hold a large amount of moisture on their particle surfaces. Absorbents, such as lithium chloride (LiCl), do change chemically and/or physically while picking up moisture. Selection of one desiccant over another depends on the environment being conditioned. Solid desiccants are usually held in a packed tower, rotary bed, or a rotary wheel.

Solid-desiccant dehydration is the primary form of dehydrating natural gas using adsorption, and usually consists of two or more adsorption towers, which are filled with a solid desiccant. Typical desiccants include activated alumina or a granular silica gel material. Wet natural gas is passed through these towers, from top to bottom. As the wet gas passes around the particles of desiccant material, water is retained on the surface of these desiccant particles. Passing through the entire desiccant bed, almost all of the water is adsorbed onto the desiccant material, leaving the dry gas to exit the bottom of the tower.

Solid-desiccant dehydrators are typically more effective than glycol dehydrators, and are usually installed as a type of straddle system along natural gas pipelines. These types of dehydration systems are best suited for large volumes of gas under very high pressure, and are thus usually located on a pipeline downstream of a compressor station. Two or more towers are required due to the fact that after a certain period of use, the desiccant in a particular tower becomes saturated with water. To 'regenerate' the desiccant, a high-temperature heater is used to heat gas to a high temperature (160 – 200 °C). Passing this heated gas through a saturated desiccant bed vaporizes the water in the desiccant tower, leaving it dry and allowing for further natural gas dehydration. Normally, the absorption/stripping cycle is used for removing large amounts of water, and adsorption is used for cryogenic systems to reach low moisture contents, i.e. low dew point. A graphical representation of natural gas drying processes is given in figure 2.

The gas drying process with solid desiccants is more expensive than glycol based drying, but lower dew points can be achieved. Since the objective is to remove a fair amount of water, rather than to 'clean' the flue gas against higher costs, solid sorption will always be economically less viable than liquid sorption. In addition, solid sorption is used for gas streams with low water content. Since with a water rich stream the solid sorbents will be soon saturated, i.e., the technology is not applicable. This technology will therefore not be discussed further.

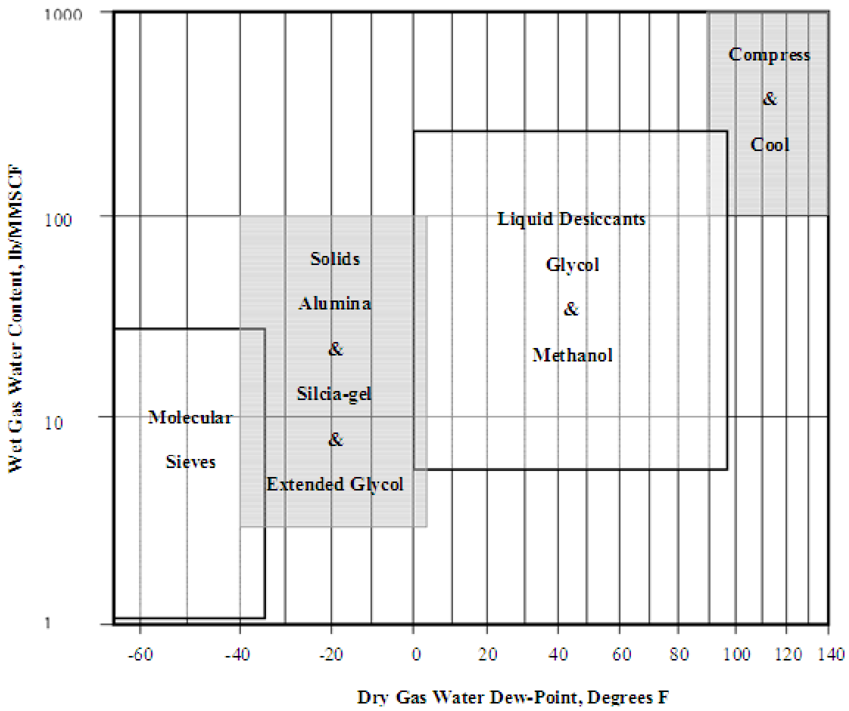

Figure 2 **Application of natural gas dehydration technologies (Huffmaster, 2004).**

2.3 Cooling with condensation

When flue gas is brought below the water dew point, water will condense. This straightforward physical phenomenon can be used to remove water from flue gas by installing heat exchangers in the flue gas ducts. A flow sheet diagram for a lay-out with and without FGD is given in figure 3.

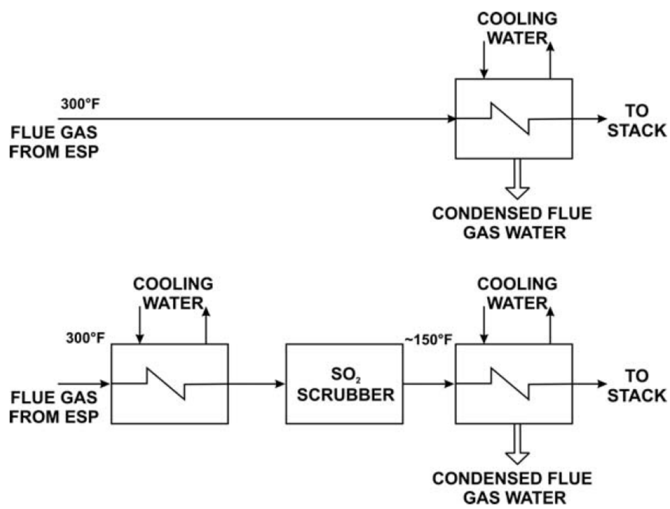

Figure 3 **Flow sheet of condensing heat exchangers in flue gas duct, without FGD (top) and with FGD (bottom). (Levy *et al.*, 2008).**

Advantages of recovery of water with heat exchangers, as mentioned by Levy *et al.* (2008) are the use of captured water as make up water for a cooling tower, the increased efficiency by using exchanged heat for boiler feed water preheating and by decreased load of ID fan and an emission co-benefit (capture of Hg, SO_3, NO_x, HCl along with water). Also potential application in CCS is mentioned: water needs to be separated before transport anyway, and, amine and ammonia based scrubbers require inlet temperatures of < 40 °C.

Application of cooling with condensation for water recovery from coal combustion flue gas is a rather novel technology which is under development. Recovery of heat is a comparable technology which has been demonstrated by Babcock Borsig in 2002, Michels *et al*., 2004. Capture efficiencies between 10 and > 80% can be obtained, while producing lower grade water (acids condense along with water). The produced water can be used as make up water for the cooling tower, but likely not for the steam water cycle. Process safety and control do not imply any hurdles to apply the technology. Condensation of acids (H_2SO_4, HCl, HF, HNO_3) form a severe risk on low temperature corrosion, and application of plastic coatings or alloyed steels will increase investment costs. Environmental benefits are mainly in the increase of the plant efficiency when the recovered heat is used for e.g. combustion air and/or feed water preheating. No auxiliary materials would be needed for the process. The process can due economically viable due to the efficiency increase.

2.4 Cryogenic separation

Cryogenic separation is a technology to separate gasses with very low boiling points. An example is air separation. This technology is applied, for example, in the production of oxygen used for coal gasification. With respect to cooling of flue gasses, the only application that has been investigated is the capture of CO_2 from flue gasses. This is, however, a very energy intensive process, requiring very large heat exchangers with high investment costs. A acceptable water recovery rate can be achieved by cooling of flue gasses to ~ 40 °C. Cryogenic separation - which is applied to obtain high purity gasses - is not a likely application, since the objective is not to purify the flue gas, but to recover a reasonable percentage of water. Compared to condensation cooling, cryogenic separation will have higher investment and operating costs, and offers no additional advantages. This technology will therefore not be investigated further.

2.5 Technology screening

A comparison of the technologies under discussion is given in table 1. It shows possible application, possible scale up, water purity, safety and environmental risks, economic viability and concludes if any further study is needed. This is summarized here below.

Liquid sorption, e.g. glycol or $CaCl_2$ based separation, is a technology that can be applied for removal of water from flue gasses. The application of this technology for water removal from coal combustion flue gas has been investigated in a DOE funded project. Large scale applications already exist. High purity water can be obtained thus permitting use of the water in the water steam cycle. Economic viability is, because the use of energy in the stripper, dependent on the price of purified water, i.e. water availability. This technology is therefore further investigated in section 3.

Solid sorption is used to reach low dew points, e.g. in drying natural gas for obtaining certain transportation standards. For removal of water from flue gasses, this technology seems unsuited and it will be economically less viable than liquid sorption. This technology is therefore not investigated any further.

Cooling with condensation is a suitable technology for separation of water from flue gasses. The application of this technology for water removal from coal combustion flue gasses has been researched in a DOE funded project. The water purity will be less than separation with liquid sorption or membrane separation. However, it can be used as make up water for cooling towers directly. Furthermore, the purification of water may be worthwhile to investigate further, also because the process is economically viable with the reuse of heat for feedwater or combustion air preheating. This technology is therefore further investigated in section 4.

Table 1 Comparison of water removal technologies for recovery of water from flue gas from a coal fired power plant

	Liquid sorption	Solid sorption	Cryogenic separation	Condensation cooling
Application for capture of water from flue gas	yes	no, used for reaching low dew points rather than bulk separation	no, used for reaching purification rather than bulk separation	yes
Possibility for scale up	yes	yes	yes	yes
Water purity	sufficient for boilerfeed water	sufficient for boilerfeed water	Unclear, but no selective separation	sufficient for cooling tower make up, not as boilerfeed
Safety and environmental risks	no	no	yes (cold)	No
Economic viability	yes, but water needed	Always less than liquid sorption	Always less than condensation cooling	yes
Further study	yes	no	no	yes

Cryogenic separation is normally applied for separation of gasses with very low boiling points, e.g. in air separation, while the objective in this project is to recover a substantial percentage of water, with no particular interest to obtain low water concentrations in the flue gas. Compared to condensation cooling, cryogenic separation will have higher investment and operating costs, offers no additional advantages and is a technology suited for purification rather than bulk separation. This technology will therefore not be investigated further.

3 DESICCANT BASED WATER REMOVAL

3.1 Maturity of technology

Desiccant based water capture has been researched as funded by the US Department of Energy (DOE) during 2003 – 2006. Both bench scale and pilot scale tests have been performed. The technology has been successfully demonstrated, but is under development. In order to select a suitable desiccant for the demonstration project, Folkedahl *et al*. (2006) report a literature study: the use of a liquid desiccant to strip water vapor from a flue gas stream appears to be a novel application based on the lack of literature found. Other applications for stripping water vapor from gasses are natural gas drying, building dehumidification and cooling.

3.2 Technology performance

Water recovery: In the pilot scale testing, as described by Folkedahl *et al*., 2006, the amount of captured water is a function of several variables including desiccant temperature, desiccant concentration, circulation rate, desiccant/gas contact method (spray tower versus packed bed) and flash drum pressure. The water recovery fraction as measured in a test series with flue gas from natural gas and coal combustion, ranged from 22 to 62% of the available water in the flue gas stream. Measured water concentrations at the inlet and outlet of the absorber ranged from 11.8 to 14.9 vol% and 5.5 to 10.9 vol% respectively with typical standard deviations of $\leq$ 0.2 vol%.

Water purity: As in membrane based water vapor separation, the obtained product is very pure. The results from the test series with natural gas only and natural gas with a large share of coal, were comparable. The pH of the produced water with the coal series was lower (3 to 4 instead of 4 to 5) but this was attributed to problems experienced with the regenerator, causing contamination of the produced water with desiccant solution.

Looking at the natural gas test series only, the produced water is of the same quality, or better, as produced by reverse osmosis technology, which is normally used to produce boiler make-up water. A small exception is calcium as $CaCO_3$, see figure 4. It is expected by Folkedahl *et al*. (2006) that water produced from flue gas for both natural gas and coal firing would need only minimal upgrading before use in a utility steam cycle.

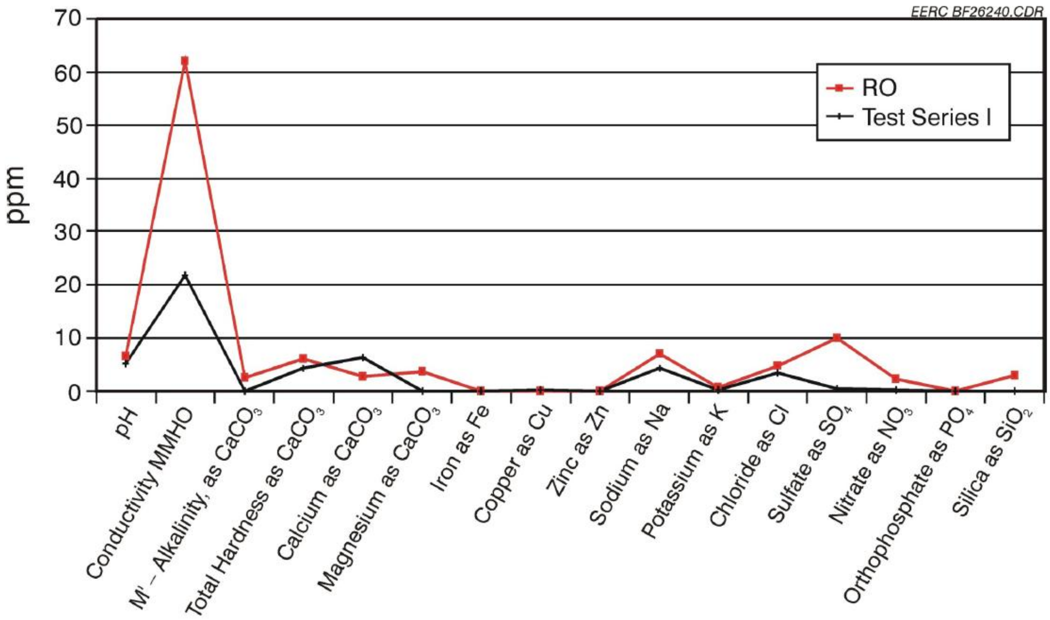

Figure 4 Pilot scale test results on water purity. Test results compared with water quality produced by a reverse osmosis (RO)-plant which is normally used to produce boiler make-up water.

3.3 Operational aspects

Process safety and control: The process control of the pilot scale unit included temperature control of the heat exchangers and control of the desiccant flow rate. The process control schematics do not imply apparent safety risks in case of failure.

The desiccant solution is a 45% $CaCl_2$ solution. According DOW (Dow, 2006) calcium chloride can act as an irritant by desiccating moist skin. Solid calcium chloride dissolves exothermically and burns can result in the mouth and esophagus if calcium chloride is ingested. Ingestion of concentrated solutions or solid calcium chloride products may cause gastrointestinal irritation or ulceration.

Maintenance and durability: Two points are of main interest with respect to maintenance and durability: corrosion and crystallization. It was mentioned by Folkedahl *et al*. (2006) that corrosion is a major design stumbling block in the proposed design. Most of the salt-based desiccants (such as calcium chloride) are highly corrosive to steel and most other common metals. Corrosion inhibitors will not be very helpful since oxygen is present in the flue gas. Coating with or use of complete polymer components may be the only solution.

Environmental aspects: Emissions will be reduced, as was measured, especially SO_x, Hg and also particulates, although the capture rates were very variable. However, small amount of calcium chloride carry-over from the absorber was detected. NO_x emissions were not affected. CO_2 emissions will increase due to a decrease in power plant efficiency.

Auxiliary materials: Aside from the desiccant, no auxiliary materials are needed.

3.4 Economic evaluation

Investment costs: are estimated by Folkedahl *et al*. (2006) as 5.8 mln USD (2006) for a turn key installation. This includes equipment cost (4.7 mln USD) and installation cost (1.1 mln USD). The prices are based on vendor data. Assuming an interest rate of 4%, this results in capital cost of 200.000 USD/year.

Energy costs / benefits: The power use for a 250 MW_e coal fired power plant was estimated to be about 1,150 kW which is the sum of the desiccant pump power (400 kW), air fans of condenser and desiccant cooling (500 kW), and the vacuum pump (250 kW). At a price of 0,01 USD/kWh and 24 hours per day operation, this results in about 100.000 USD/year.

Cost of auxiliary materials and operation: Whether desiccant degrades is not explicitly mentioned by Folkedahl *et al*. (2006). The operational costs include desiccant costs and are estimated for a 250 MW_e coal fired plant to be about 200.000 USD/year.

Economical viability: The total annual costs were estimated to be about 500.000 USD, resulting in a price of 0,02 USD per gallon of pure water (4,4 USD/m^3). Whether this is economical viable depends very much on the location of the plant; in areas where water is scarce this may be the case.

4 CONDENSING HEAT EXCHANGERS

4.1 Maturity of technology

The technology to use condensing heat exchangers to recover water from flue gas, has been subject of research for more than five years. Levy *et al*. (2008) report a US DOE funded research program, researching water recovery from flue gasses using heat exchangers. Heat exchangers to cool flue gasses, with the objective to recover the heat for feed water preheating, have been investigated for a longer time. As an example, Babcock Borsig has installed a flue gas cooler in 2003 in the Mehrum power plant in Germany (refer to Michels *et al*., 2004). A condensing heat exchanger, however, has a lower operating temperature to condense moisture from the flue gasses. This may impose extra demands on corrosion resistance.

Condensing moisture from flue gasses with heat exchangers is a technology that is under development. It has been demonstrated on pilot scale (heat exchanger surface area approximately 7 m^2). The project report by Levy *et al*. (2008) does not describe any disadvantages of the technology. However, the condensation of acids and mercury will impose demands on corrosion resistance of materials used and constraints on further use as working medium in the power plant.

4.2 Technology performance

Water recovery: The capture efficiency depends on various factors such as flue gas water content (i.e. presence of wet FGD, type of fuel), cooling water inlet temperature, heat exchanger design and flue gas and cooling water flow rates. Levy *et al*. (2008) suggest that water capture efficiencies greater than 70 percent will be possible. However, for cooling water flow rates down to 50%, capture level can drop to 10 – 30%. Theoretical model considerations with the use Aspen process simulation software indicated capture efficiencies for different options, a heat exchanger efficiency of 85% and with varying flue gas moisture fraction. With cold boiler feed water as heat sink capture efficiency lies between 0 - 10% (supercritical plant) and 0 - 4% (subcritical plant). When using inlet combustion air as heat sink, efficiencies lie between 20 - 25% (winter) and 10 - 18% (summer). When additional ambient air is used, capture efficiencies lie between 80 - 87% (winter) and 48 - 72% (summer).

Water purity: will affect possible application of the captured water, based on the application process requirements. Use of water as a substitute for demineralized water, will have stricter demands than e.g. for cooling tower make-up water.

Different compounds present in the flue gas will condense along with water. Levy *et al*. (2008) investigated the co-capture of acids and mercury by measurements in a pilot scale plant. The sulfate concentration dropped from 19 to 7.5 ppm, wet (test 1) and from 12.5 to 3 ppm, wet (test 2). If sulfate means sulfuric acid is not clear. Anyway, based on some assumptions, this would result in a concentration of about 900 ppm of H_2SO_4 in the captured water. Chloride and nitrate concentrations in the condensed water were measured and ranged from 10 to 100 and 0.2 to 2.2 mg/liter, respectively, dependent on the heat exchanger (highest values for the hottest heat exchangers at flue gas temperatures of about 75 °C and lowest values for the coolest heat exchanger at 40 °C). HF was not considered. For mercury, it was very difficult to determine the Hg concentration in the water since the mass balance measured Hg in flue gas and measured Hg in condensed water did not close and the difference was several orders of magnitude.

4.3 Operational aspects

Process safety and control: is not investigated or described in Levy *et al*., 2008. Points of attention will be leakage of diluted acids (emission to the environment). The application of the recovered water will largely influence any post-cleaning step. When water is applied as source for demineralized water (assuming this will be economically viable), the water quality needs attention.

Michels *et al*. (2004) mention several options for heat recovery such as condensate preheating, combined condensate and air preheating (with one or two heat transfer cycles) and only air preheating. Condensate preheating can be run continuously. However, the other options have a discontinuous performance because of the cyclic load of the air preheaters.

Maintenance and durability: A significant section of the flue gas coolers will operate below the acid dew points (H_2SO_4, HCl, HNO_3, HF). For example, sulfuric acid condenses on surfaces of the heat exchanger, forming a thin layer of diluted sulfuric acid that attracts fly ash and forms deposits. The deposits, forming on vertical heat transfer tubes, may be washed away using a pre-installed washing system. Where deposits are not removed, corrosion can be a continuous process. Dew point graphs of H_2SO_4, HCl and HNO_3 are given in figure 5.

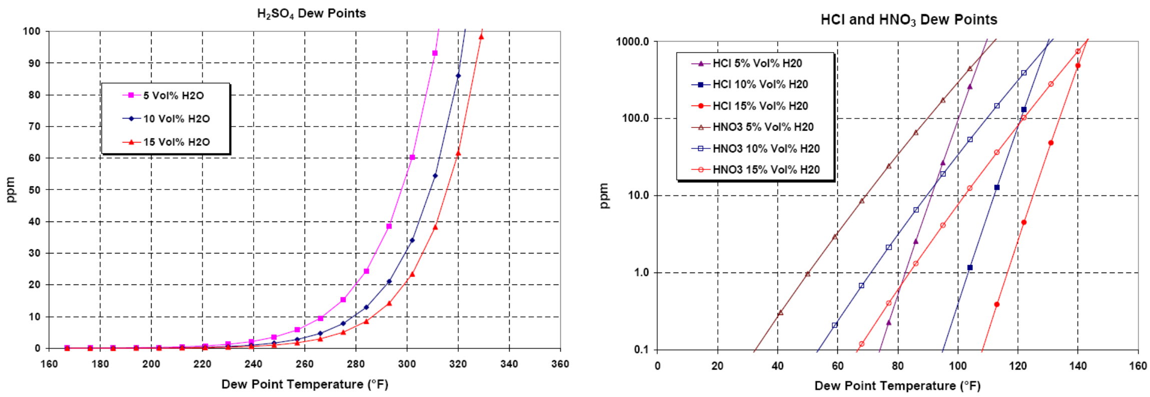

Figure 5 Acid dew points (H_2SO_4, HCl and HNO_3), as function of acid and moisture concentration (Levy *et al*., 2008).

It is clear that the heat exchanging surfaces need to be constructed from corrosion resistant materials such as alloys, carbon steel with coatings, plastic tubing or borosilicate glass, (Sarunac, 2010). Babcock Borsig mentions fluoroplastic G-FLON ® for a heat exchanger installed for heat recovery only (Michels *et al*., 2004). According to Sarunac (2010) this material features high resistance to corrosion and reasonable heat conduction transfer characteristics.

Environmental aspects: Levy *et al*. (2008) present the co-capture of acids and mercury as an environmental profit. This remains questionable, since many analyses do not include a wet FGD. With such a system, emission limits can be met and sulfur emissions do not provide a problem. An exception could be SO_3 which is not captured very effectively by a wet FGD. Also NO_x emissions do not provide a problem in Europe, since in many countries $DeNO_x$ installations are common technology. The benefits of co-capturing NO_x in the US (where DeNOx systems are not as common as in Europe) may not be valued equally in Europe. A second question is the clean-up of the captured water. Is it cleaned, and if so, how is the S, N, Cl, F and Hg emitted?

The fuel savings will result in a decrease of carbon (and other) emissions. In a project with heat recovery only, a number of 31,000 t/a of avoided CO_2 avoided is mentioned for a 750 MW_e lignite fired power plant (Michels, 2004).

Auxiliary materials: The process itself will not need auxiliary materials. Dependent on the application for the recovered water, such as demineralized water, auxiliary equipment will be needed to clean up the water.

4.4 Economic evaluation

Investment costs: The turn-key project cost for a 30 MW_{th} fluoroplastic heat exchanger that replaces a steam air preheater amounted EUR 4.7 million (Michels, 2004). Corrected for inflation this would translate to EUR 6.4 million (price level mid 2011). However, this project is special since due to the low quality coal the steam air preheater is operational 90 percent of the time. The overall efficiency increase was 0.37 percent point for a 750 MW_e lignite fired power plant.

KEMA also studied the use of plastic heat exchangers for heat recovery from flue gas (KEMA, 1997). Several options were studied for a 652 MW_e net bituminous coal-fired power station Table 2 shows the electric efficiency improvement and the associated capital investment cost (corrected for inflation).

Table 2 Heat recovery from flue gas, electric efficiency improvement and CapEx

Case	Efficiency improvement (percent point)	Capital investment cost (million EUR, 2011)		
		Minimum	Maximum	Average
A	0.75	15.24	20.79	18.02
B	0.85	16.63	22.87	19.75
C	1.10	26.33	36.73	31.53

Based on these capital cost estimates pay-back times ranging from 9.5 – 19 years have been calculated. Only energy savings have been considered in this evaluation. Water recovery has not been taken into account since the minimum temperature considered was still above the water dew point.

Energy costs / benefits: Energy (i.e. work) is not consumed, but gained in this process. Theoretical analyses using Aspen Plus process simulation software on four different types of US coals resulted in an increase of net power output of 1.25 to 1.77%. The heat rate improved with improving water capture efficiency, and both increased with increasing inlet flue gas moisture concentration, decreasing inlet combustion air temperature and increasing heat exchanger effectiveness.

Cost of auxiliary materials and operation: Cost of demin water production via reverse osmosis (RO) or ion exchange (IX) technology is estimated to be 1.5 – 2 EUR/m^3 (KEMA, 2010).

5 TECHNOLOGY BENCHMARK

Technologies to recover water from flue gas are benchmarked on the quality of the recovered water, associated energy consumption or energy savings, capital investment, operational cost and maturity of technology. The performance of the technologies described in this report with respect to these indicators varies considerably.

Due to the influence of local circumstances (wet or arid climate conditions) only a qualitative ranking can be performed (see table 4).

Table 3 Qualitative benchmark water recovery from flue gas technologies

	Liquid dehydration	Condensation cooling	Membranes
Water quality	++	-	++
Energy consumption / savings	-	++	+
CapEx	to be determined in separate study		
OPEX	to be determined in separate study		
Technology maturity	+	+	-

Water quality: of the membrane process technology is supposed to be of boiler feed water quality. Probably it is acceptable without further treatment. The water quality of liquid dehydration can also be of very good quality depending on the performance of the demister in the stripper column. Water from condensation cooling of flue gas from coal combustion will be contaminated with acids such as H_2SO_4, HNO_3, HCl, HF. Depending on the application treatment will be necessary.

Energy consumption: The primary goal of condensation cooling processes is energy recovery from flue gas. Depending on the heat exchanger lay-out and power plant characteristics the net electric efficiency can be improved with 0,4 – 1,8 percent point according to values reported in literature. Liquid sorption requires energy input.

The major energy requirement for liquid dehydration processes is heat input for stripping the enriched liquid. For this purpose steam has to be extracted from the turbine.

For membrane technology the major energy input is electricity for vacuum pumps. Depending on the heat exchanger lay-out and power plant characteristics the net electric efficiency can decrease with 0,1 – 1,1 percent point, these calculations are given in this paper.

CapEx and OPEX: Sources for information with respect to CapEx are diverse and difficult to compare. All numbers have been corrected to standard conditions:

- flue gas from a 600 MW_e bituminous coal fired power plant with wet FGD
- water recovery plant designed for 20 or 40% water recovery
- cost of electricity 50 EUR/MWh
- CapEx is installed cost.

It is concluded that a separate study is necessary to assess CapEx and OpEx cost of the three technologies considered on an equal basis.

Maturity of technology: Liquid dehydration process technology (scrubbers) is mature technology and used in flue gas treatment for desulfurization (sorption of sulfur dioxide in a suspension of lime or limestone) on large scale. Sorption of water vapor from flue gas is, however, a novel application but no major problems are expected. Choice of construction materials to avoid corrosion problems requires attention.

Cooling of flue gas from coal combustion below the dew point of water and therefore also below the dew point of acids has been demonstrated. Fluoroplastic or fluoroplastic coated heat exchangers are necessary. Optimization of process lay-out, operating conditions and equipment design will be necessary.

Membrane technology for water recovery from coal combustion flue gas has been tested on small scale only. This technology is considered to be the least mature. Demonstrations are planned in the near future.

6 ENERGY MODELLING

6.1 Introduction

It is clear that OPEX will play an important role in the water capture technology choice. Since the membrane technology is under development, an estimation of energy requirements and savings should be made. For this purpose energy modelling is used. An important step in the development of the membrane technology is to determine a configuration to generate the driving force over the membrane with the lowest energy demand. To this end two studies were done in the EU funded CapWa project:

- *decision tool for single-stage or multistage gas-gas separation*
- *water and energy savings per separation system*

This chapter gives a brief summary of these studies.

Concerning single-stage or multistage operation, from other membrane development programmes (e.g. in EU FP6 IP NanoGLOWA, and commercial research by MTR) it is already clear which concepts for driving force generation exist, as shown in the figure below. From research by (among others) RWTH it became clear that permeate suction was the best option in terms of energy efficiency. Feed compression would have the benefit of relative reduction of required membrane area, but for application in power plant flue gas this is not considered desirable and/or feasible due to the large amount of flue gases. Also, for water capture as opposed to CO_2 capture, membrane area is much less of an issue due to orders of magnitude higher permeability of the respective membranes for water and CO_2. Hence, for the work described in this joint deliverable, only permeate suction was considered. Subsequently and looking at one stage water vapour recovery and purity, it can be deduced that one membrane stage should suffice. A second stage would not add improvements in captured water amount that could not be achieved by simply increasing membrane area.

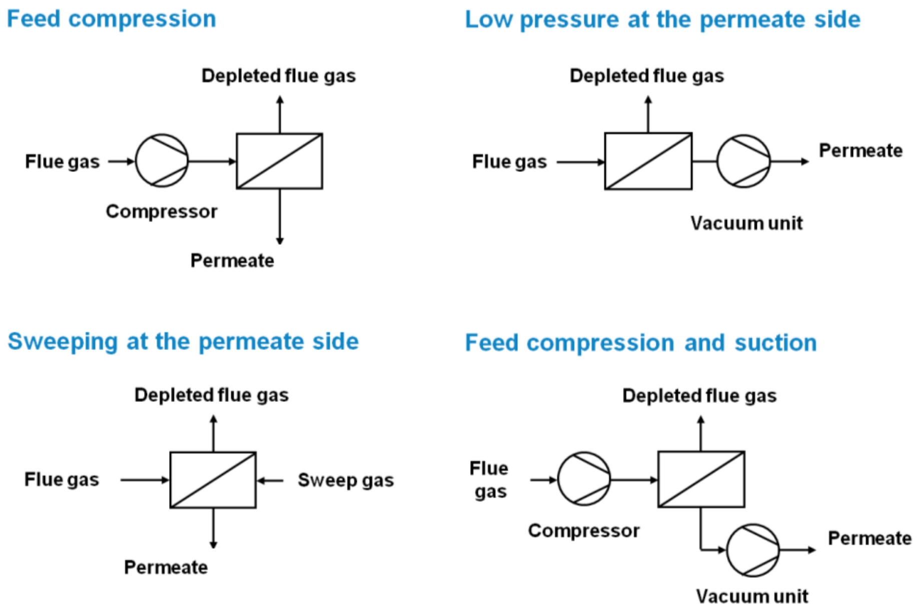

Figure 6 Membrane separation driving force concepts (source: RWTH, within NanoGLOWA).

6.2 Pre-modelling considerations and case definition

A very large array of possible process and system configurations of the membrane water capture process exists within a power plant (gas or coal fired). Setting up well-defined cases is a necessity to limit the number of scenarios to a manageable / calculable amount, but within those cases (see further on in this report) there is still considerable space for optimisation and variation. Therefore, as usual, efficient and meaningful modelling commences with charting and selecting variables and parameters, and defining cases.

An indicative list of factors that play a role are:

- Application-dependent (fixed external) factors:

Feed gas flow; Gas composition; Relative humidity of flue gas; Feed temperature; Interaction with up- and downstream processes (e.g. FGD, reheater, ID fan);

- Location-dependent (variable external) factors:

Cooling water availability; Cooling water temperature; Air temperature

- Membrane process factors:

Process layout: connectivity, stages, etc.; Pressure drop over membrane unit; Permeate pressure; vacuum pump type and efficiency; Water capture efficiency

Membrane process factors: The amount of captured water is assumed fixed, and for both applications two recovery values are used. The lower percentage value – 20% wt. – corresponds roughly to the amount of water needed for a coal plant in general, so the plant can be self-sufficient with respect to water in this case. The higher value – 40% – corresponds to about double that value, making the plant a water producer. Respectively 33 and 66 m^3/hr of water is produced. In case of a gas-fired power plant, the water content in the flue gas stream is lower than that of a coal fired plant. Fortunately less water is needed for a gas fired combined cycle (GTCC). State of the art GTCC or HRSG's are designed to utilize either 0.5 or 1.0 m^3/hr.

The pressure drop from feed to retentate over the membranes is assumed to have a constant value of 10 mbar. While this value obviously depends on parameters such as membrane area, configuration, and of course the set water recovery, the order of magnitude is known to be acceptable for ID fans (in existing coal fired plants) to overcome the pressure drop. This simplification seems justifiable for the detail level required for this report.

Permeate composition is considered fixed as well, and set to 99% H_2O plus 1% non-condesables (mostly CO_2). In reality there is a dependence on vacuum pressure and membrane area, but based on both membrane modelling and pilot experiments this seems an acceptable value. These values are from field measurements from a coal fired plant in the NanoGLOWA project and a measurement done at DNV-KEMA (gasfired). Ideally you would have the amount of non-condensables reduced to zero, theoretically you would be able to use the condensation power of the evaporated water to maintain the vacuum pressure. The lower the non-condesables content the lower the vacuum energy required.

The membrane area is not explicitly defined. Given the other assumptions, is not directly necessary: the derivative key parameters of recovery and pressure drop are explicitly defined and fixed, making defining membrane area obsolete for this modelling work.

Vacuum techniques: The driving force for flow of H_2O through a membrane is created by creating a partial pressure difference between the feed gas and permeate flow. Two variants are used of creating this partial pressure difference a steam Jet Vacuum Pump and A liquid ring pump.

Cases: Parameters like flue gas properties reflect the conditions of a 550 MWe unit of IEC's Ruthenberg power plant as much as possible. For the coal-fired power plant two cases are defined for each method of vacuum generation, with each having a recovery of either 20% (plant self-sufficiency) or 40% (plant as a water producer). This gives a total of 4 cases, from each of these cases each will be cooled at two different temperatures using Air Cooled Condensers (ACC). In addition a reference case with cooling water of 12ºC applying a liquid ring pump is also modelled. This gives a total of 9 cases for coal. For gas 8 cases are used, here cooling water case is not used. For the gas fired plant the conditions of the Gas Natural's 380MW Combined Cycle power plant (with GE9FA gas turbine) are used. As mentioned previously the flue gas conditions and physical properties are different to the coal fired i.e. temperature, CO_2 and water content.

Modelling tool: The calculations have been made using a DNV-KEMA's proprietary **SPENCE®** process modelling software package. This is a known energy calculating software program which has been updated with market and field data from DNV-KEMA.

6.3 Energy calculation results

Coal: In Figure 7 an overview is given of main heat consumption, power consumption and cooling water of a coal fired power plant of all 9 cases. Here the cases are:

- Reference case with cooling temperature at 12 °C and 20% capture rate
- Two cooling temperatures 20 ºC and 50 ºC
- Two vacuum methods: steam jet and liquid ring
- Two recoveries: 20 and 40% which correspond to 33 m^3/hr and 66 m^3/hr

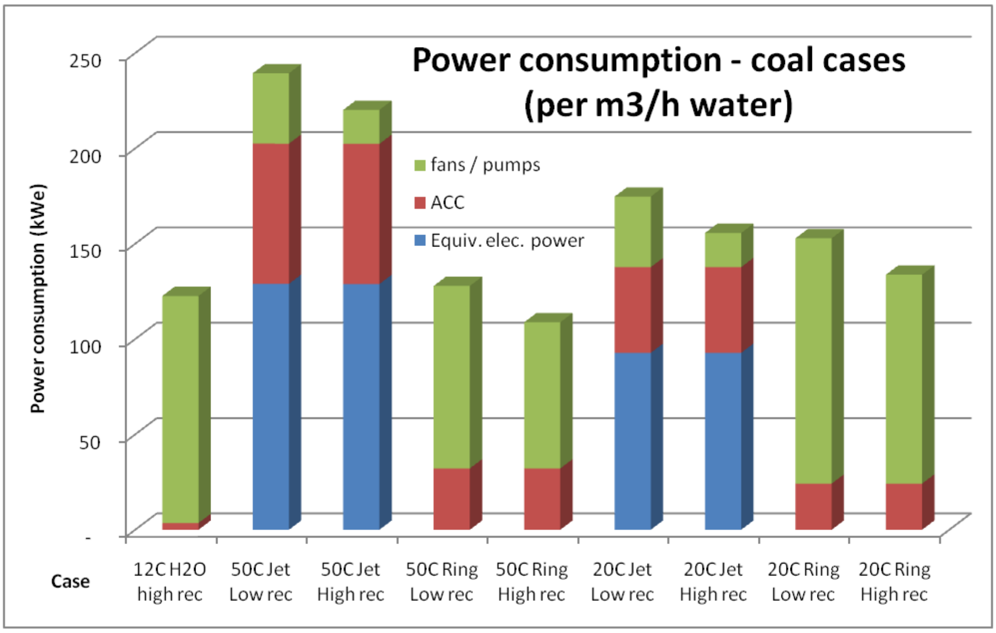

Figure 7 Results of energy calculations for all 9 coal cases

The figure shows that the OPEX is primarily influenced by the energy consumption of the vacuum pump, or the equivalent thereof by the steam jet. Prior to the modelling results one could have concluded that a lower ambient temperature would lead to less overall power consumption. However the figure shows that the vacuum energy required (liquid ring or steam jet) is the energy determining consuming step, since less vacuum energy is needed at a higher condensating pressure 125 mbar (50 ºC) versus 25 mbar (20 ºC).

Gas: The energy calculations show a similar trend as shown in figure 5 for the 8 cases:

- Two cooling temperatures 20 ºC and 50 ºC
- Two vacuum methods: steam jet and liquid ring
- Two recoveries: 0.5 and 1.0 m^3/hr (20% and 40% capture rate)

6.4 Improved vacuum – compression cases

In this paragraph three cases are recalculated with an improved vacuum and compression set-up. The three cases are the coal case with cooling water cooling at 12ºC, and the gas and coal case with 40% capture rate and ACC cooling at 50ºC with liquid ring. The latter two were shown as having the lowest energy consumption from the 8 cases (see figure 7).

Calculation results: are shown in the following table. With an electricity price of €0.05 per kWh, costs of water are €0.70, €2.21 and €1.87 per m^3 water respectively for each case.

Table 4 Capture rate at 40% with different optimized cases

Case	Power cons. water or ACC cooling [kWe]	Power con fans / pumps [kWe]	Total power cons. [kWe]	Captured water [kg/h]	Energy Cons. [kWh/m3]
COAL with 12°C	208	734	942	67222	14.01
COAL with ACC at 50°C	2029	941	2970	67222	44.18
GAS with ACC at 50°C	15	20	35	935	37.43

6.5 Energy savings in gas fired plants

For the gas turbine based power plants, no energy savings can be reported if water from the flue gas is captured. This is due to the fact that all heat for preheating condensate/feed water is done by waste heat from the gas turbine and no extraction steam from the steam turbine is used for this purpose. Heat for preheating of condensate/feed water/make up water is taken after the pinch and can’t be used to produce steam (and thus power). Also there is no reheating of flue gas necessary because the flue gas temperature is already high enough. Heat from condensation of captured water is at a low level and can’t be used useful in a gas turbine based power plant.

6.6 Energy savings in coal fired plants

The majority of the boiler type power plants are coal fired and often equipped with a FGD (Flue Gas Desulphurisation unit) which saturates the flue gas with water in removing a certain amount of SO_2 (gas fired boilers are not common equipped with an FGD because the sulphur content of the fuel is normally low if any). Water recovery will take place after the FGD. The flue gas at this point is saturated with water and should be heated up to prevent condensation in the stack and/or to ensure that the plume exits the stack.

For heating up the flue gas two systems are available: regenerative heating (heating up ’cleaned’ flue gas by cooling down ‘dirty’ flue gas before it enters the FGD) and heating up ‘clean’ flue gas by low pressure steam.
If regenerative heating is used, no direct energy savings are expected. If steam reheating is used, direct savings on steam consumption are possible. This steam can than be expanded in the steam turbine and generates extra electricity.
An increasing amount of power plants operate in wet stack mode where the stack is lined with rubber and condensation of water from the flue gas is normal operation. Heating the flue gas is in this case not necessary. However water and energy can be captured from the flue gas and used in the steam system.

The big advantage when enough water is removed from the flue gas after the FGD is that the water dew point decreases and reheating is not necessary anymore to prevent water condensation. For systems with regenerative reheating, the regenerative heat exchanger can be removed if enough water is removed from the flue gas. An advantage of removing the regenerative heat exchanger is that the emissions will improve because the leakage from ‘dirty’ to ‘clean’ flue gas is not possible any more. The flue gas side inlet temperature of the FGD will however increase and the FGD should be able to operate with this higher temperature (max. 120 °C) or the flue gas should be quenched to an acceptable temperature. The water consumption will increase in both cases because the entering flue gas contains more heat.
The water capture membranes that are used in the CapWa technology are able to operate at a temperature lower than 100 °C. At higher temperatures the reliability is not guaranteed. For power plants with a FGD, this temperature is not reached. Depending on the type of coal (and the water content of the coal) the typical flue gas temperature after the FGD[1] is:

- ±50 °C which is a low water content, for example with hard coal burning
- ±70 °C which corresponds to a high water content, for example: lignite burning.

Table 5 Summary of energy savings when water vapor capture with membranes is used after FGD of a 600 MWe coal fired plant in a WET (cold) region

Description	Saved [kWe]	Capture rate	Remarks	Likelyhood
No reheating of flue gas by low pressure steam	3300	>70%	Additional water loss at FGD due to high inlet temperatures	NO, hardly any cases like this, increase use of wet stack
Energy recovery before FGD - 3rd condensate preheater	6960	70%?	High CapEx and OPEX for plastic / ceramic heat exchanger	NO, new power plants are not built this way due to poor payback time, see also 4.4
Condensate preheating	924	>12%	In wet cold area's, if accessible by piping	YES, can be combined with additional savings described here

For wet (cold) regions an energy saving of 924 kWe can be achieved regardless of 20% or 40% water capture, this is equal to EUR 369,600[2]. This is €1.25 per m^3 @ 20% water

[1] The lower the water content of the flue gas, the lower the temperature directly after the FGD. When the water content of the coal is low, the partial pressure of the water in the flue gas is low and more water can be evaporated to reach saturation in the FGD. Evaporating water will cool down the flue gas temperature resulting in a lower outlet temperature of the FGD.
[2] Assuming 8000 hours at EUR 50 per MW

recovery and € 0.62 per m^3 @ 40% water recovery. There are configurations possible to achieve a much higher energy recovery but this is based on a site-by-site basis and the necessary investments in example a plastic heat exchanger needs to be determined. If carbon credits are awarded to the energy savings then the savings can amount to €1.51 per m^3 @ 20% recovery.

For dry regions there are no energy savings to be expected.

7 CONCLUSIONS & DISCUSSION

Alternatives for water capture: Solid desiccants such as silica, alumina and molecular sieves and cryogenic cooling can obtain lower dew points than dehydration by liquid scrubbing and condensation cooling but are more expensive. Since the purpose of water recovery from flue gas is not to obtain an extreme low dew point but to produce water in the most economic way the first two technologies have been discarded.

Dehydration of flue gas by scrubbing with a concentrated aqueous salt solution with low water activity (such as LiBr, LiCl, $LiNO_3$, or $CaCl_2$) or glycol (such as MEG, DEG or TEG) is not commercially used but has been tested on pilot plant scale. The technology is used on a large scale for dehydration of air (air conditioning systems) and natural gas conditioning. Glycol based systems have the disadvantage of atmospheric losses with the flue gas whereas salt solution based systems can be very corrosive. The advantage is the production of high purity water but the energy demand for heating and cooling is high.

Cooling of flue gas below the dew point of water with the objective to recover water is not practiced commercially. All efforts in this area are focused on efficiency improvement of the power plant. A demonstration project has been executed in a German lignite fired power plant. The main disadvantage of this technology is the condensation of acids (sulfuric acid, nitric acid, hydrochloric acid, hydrofluoric acid) present in the flue gas. Therefore the heat exchanger needs to be coated or be manufactured completely from plastic (such as G-FLON a fluoroplastic) making it expensive. The water that is produced will be contaminated and needs further treatment.

Dehydration by liquid scrubbing and condensation cooling can be considered as being more conventional and more mature than membrane technology for water recovery. However, for a proper comparison of investment and operational cost a separate study is necessary since data found in literature are difficult to compare.

Energy calculations First and foremost, one key assumption in the energy modelling calculations turns out not to be valid, being that a fixed amount of water is captured, independent of cooling or vacuum pump settings (20 °C or 50 °C cooling yields a vacuum of 125 or 23 mbar respectively, while with 12 °C cooling water 14 mbar is achieved). These are vastly different numbers, that could cause a water capture yield increase of up to a factor of four (source: DNV-KEMA in-house membrane permeation modelling and field results). In turn, absolute energy use will change because of a different permeate flow (and composition, to a small extent), and energy consumption per unit water will obviously change as well.

An approach to circumvent the effects described above is to reduce membrane area in correlation with pressure. In other words: the deeper the vacuum, the smaller the membrane area used, to precisely that extent that the amount of captured water remains the same as used for the model input. What does change, however, is the pressure drop over the membrane area (now assumed constant), and hence the ID fan power. The implications of the invalid assumption described here are very important to keep in mind when looking at the current modelling results, and can be of sufficiently large impact to require a refinement of the modelling. One example is that now more cooling apparently and paradoxically leads to higher (electrical) power use, because a deeper vacuum needs to be recompressed to ambient pressure.

From the figures and tables the following can be concluded:

- The relative order (pattern of energy consumption per unit water) of each of the cases is the same for the coal-fired and gas-fired power plant cases
- The energy consumption of the vacuum pump outweighs the energy consumption of air cooled condensers and other units combined; in the optimized conditions they come closer to each other
- Steam jet compression is not an energy-efficient vacuum option for the studied applications, unless low pressure steam is available at a site
- Of any set of two cases with high and low relative recovery, high recovery is always more energy-efficient per unit captured water than low recovery.

Preliminary recommendations resulting from the modelling work are:

- to minimize the amount of non-condensables in the permeate. Here a **high selectivity of the membranes for water vapour is essential**
- Another recommendation is to further investigation is to refine modelling by making water recovery dependent on vacuum pressure, and/or by adjusting membrane area and related pressure drop to maintain the set recovery rate.

A general conclusion that can be drawn from the modelling work, in particular the optimized cases, the operating costs for water production (assuming €0.05 per kWh) end up in an interesting price range of well below €10 per cubic meter in the hot DRY regions. According to the market demin water prices in these area's as a worst-case are around €10 per cubic meter. In WET regions, where cooling water is available, additional energy savings can be achieved which correspond to €1.51 per m^3 savings which should be subtracted on the consumption.

Lastly, a truth that should be obvious and is commonly applicable to modelling work, is still stated here: in interpreting these results, the model assumptions should be kept in mind, as well as the fact that care should be taken in comparing these general results to specific cases (i.e. specific power plants with a specific and unique parameter set).

The research has been made possible by funding from the Dutch Government, EU sixth and seventh framework under contract number CP-FP 246074 and in cooperation with our partners and the Dutch Power industry. For more information on the CapWa project please go to www.watercapture.eu

REFERENCES

DOW, 2006 Product Safety Assessment (PSA): Calcium Chloride. Dow Chemical Company. May 2, 2006. http://www.dow.com/productsafety/finder/cacl_2.htm.

Folkedahl, 2006. Folkedahl, B., Weber, G.F., Collings, M.E. Water extraction from coal-fired power plant flue gas. Final report. DOE Cooperative Agreement No. DE-FC26-03NT41907. December 2006.

Huffmaster, 2004 Huffmaster, M.A. Gas dehydration fundamentals introduction. Laurance Reid Gas Conditioning Conference 2004. http://www.scribd.com/doc/6784934/Gas-Dehydration-Basics

KEMA, 1997 (Vlist, D. van, Wichern, P.H.M.). Kunststof warmtewisselaar voor rendements-verbetering in poederkoolgestookte ketels. Report no. 95101-KPG/PEN 97-2758.

KEMA, 2010 (Baron, V.). Demin water production versus capture of evaporated water from a water rich air stream. Report no. 55108009-TOS/PCW 10-4820.

Kohl, 1997. Kohl, A.L., Nielsen, R.B., Gas purification, Fifth Edition. ISBN 0-88415-220-0, Gulf Publishing Company, Houston Texas.

Levy, 2008. Levy, E. Bilirgen, H. Jeong, K., Kessen, M., Samuelson, C. Whitcombe, C. Recovery of water from boiler flue gas. Final Technical report. DOE Award Number DE-FC26-06NT42727. Energy Research Center, Lehigh University. December 2008.

Michels, 2004. Michels, B., Adamczyk, F., Koch, J. Retrofit of a flue gas heat recovery system at the Mehrum power plant. An example of power plant lifetime evaluation in practice. VGB PowerTech, Nr. 10, 2004.

Sarunac, 2010. Sarunac, N. Flue gas heat recovery in power plants, part III. Coal Power. August 2010.