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Pilot scale testing of polymeric membranes for CO_2 capture from coal fired power plants

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Abstract

This paper summarizes the results obtained in Nanoglowa EU project using polymeric polyvinylamine fixed site carrier membranes developed at NTNU Norway for CO_2 removal from flue gas. The pilot scale testing using real flue gas was performed at Sines power plant of EDP in Portugal. The aim of the project was CO_2 separation from flue gas of coal fired power plants using membrane technology and involved several aspects: membrane up-scaling, material durability and pilot testing in a power plant. Gas permeation experiments and material analyses confirmed that the membrane material and separation performances were not affected negatively by exposure to synthetic and real flue gas contaminants. A pilot scale module having installed a 1.5 m^2 of NTNU membrane was tested continuously for 6,5 months. The membranes showed constant separation performances with a maximum content of 75% CO_2 in permeate and a permeate flow of 525 l/day. The performances were kept constant despite several challenges related to power plant operation such as high levels of NOx (600 mg/Nm^3) and 200 mg/Nm^3 SO_2, and frequent power plant outages.

Keywords: CO_2 capture, membrane, pilot scale, postcombustion, flue gas

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1. Introduction

The increasing consumption of fossil fuel such as coal, oil and natural gas and the effect of greenhouse gases on climate imposed immediate measures expressed on Kyoto Protocol: efficient energy conversion,

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efficient capture and safe disposal of CO_2. Among the possible options, CO_2 sequestration and subsequent disposal in aquifers or in exhausted gas or oil wells seems to be, at this time, one of the most mature technologies [1].

A wide range of technologies are being investigated as possible solutions, from the classical solution which implies high energy demand and solvent consumption - absorption by amino solutions in large columns, to new technology such as redesigned combustion processes, adsorbents, membrane contactors and hollow fibre or spiral wound membranes.

The intrinsic simplicity of a membrane separation process represents an unique advantage among the above mentioned separation processes because of relatively low energy consumption and no need for use of chemicals which may create an extra source of pollution [2]. The criteria for discerning between different types of membranes can be complex and has to take into account the balance of the overall process cost and membrane separation requirements: durability, selectivity and productivity [3].

CO_2 removal from flue gases represents a challenging task due to the very low CO_2 partial pressure and presence of water vapour. A series of studies reported a dramatically decrease on separation properties for solution-diffusion membranes based on polymers such as polyimide [4-6], due to a competitive sorption between water and permeating gases. A fixed site carrier membrane containing amino groups represents an optimum choice for humid gas streams such as flue gas, due to the reversible reaction mechanism of CO_2 with the amino groups in presence of water. A multitude of different membranes materials with functional groups as specific carriers for CO_2 were investigated [7-20], all of them having in common the CO_2 transport by facilitated transport in humid operating conditions rather than solution–diffusion mechanism.

Fixed site carrier membranes (FSC) combine the durability of a solid polymeric membrane with the selectivity of a supported liquid membrane (SLM) and at the same time overcome the limitation of SLM – the degradation due to the wash out of the carrier solution over time. The water in the swollen FSC membrane enhances the mobility of the fixed carrier and consequently the swollen FSC membrane shows CO_2 diffusivity between a fixed and a mobile carrier. The CO_2 molecules are transported both by facilitated transport and solution diffusion and the non–reactive gases such as N_2 and CH_4 are transported only via solution-diffusion mechanism [19].

2. Experimental

2.1 Materials

For the membrane selective layer preparation, polyvinylamine (PVAm) with Mw 340000 was kindly provided by BASF AG Germany. Other materials were: polysulfone (PSf) ultrafiltration membranes with 50000 MWCO from DSS Denmark. All the materials were used without further purification with the exception of PVAm 340 000 Mw from BASF. The PVAm polymer was purified in successive steps: re-precipitation in acetone and ethanol mixtures, washing, filtration, drying until constant weight, re-dissolution in distilled water as reported in [7].

2.2 Membrane preparation

The membranes used at NTNU for laboratory testing were produce manually having an area of 20 cm^2 [21]. PVAm/PSf flat sheet NTNU membranes were up-scaled for pilot testing from an area of 20 cm^2 to sheets of 900 cm^2 as reported in [22].

2.3 Membrane module for pilot testing

A pilot scale module having installed a 1.5 m^2 of membrane was fabricated by Yodfat, (Israel). The module was built in a "plate and frame" configuration consisting of 24 membrane sheets (25 cm x 25 cm) produced at NTNU, Norway. The module contained 12 sandwich membrane elements, having installed two membranes per element. Figure 1 shows the entire module with 12 elements and 24 membranes.

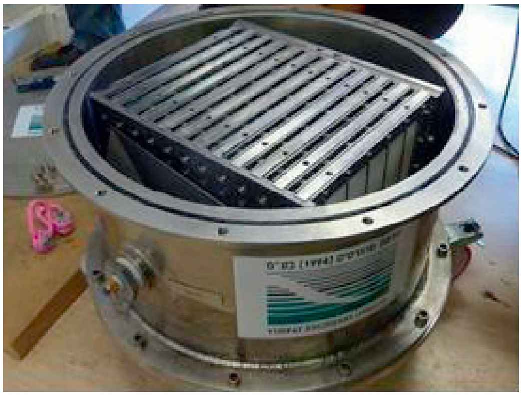

Fig. 1 Pilot scale membrane module

2.4 Permeation rig

Fig.2 shows the schematic drawing of the test rig.

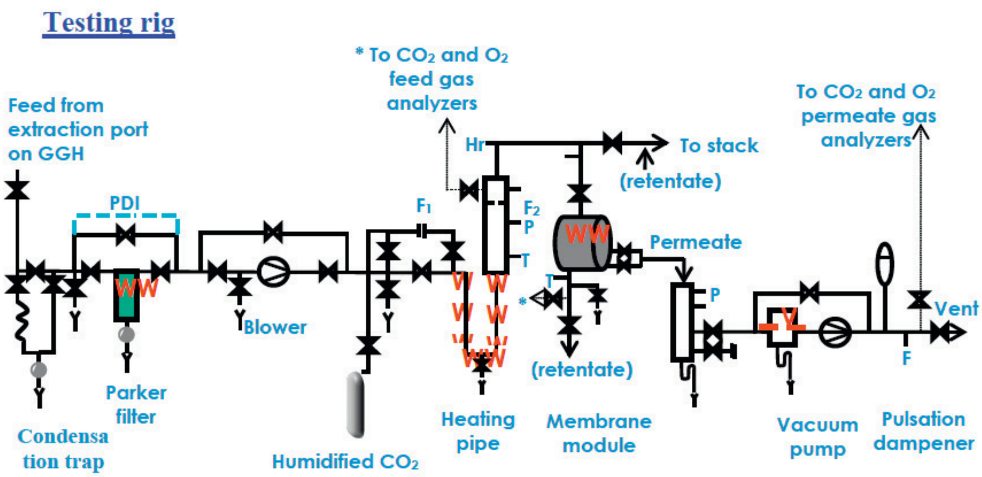

Fig. 2 Pilot scale testing rig at EDP, Sines, Portugal

The test rig was designed at EDP Portugal by António Ermida Mano and Manuela Berberan Santos based on previous experience of building and exploiting the rigs at NTNU Norway and ICHP Poland. All project partners were involved in the process of design: NTNU, (Norway), ICHP (Poland), Yodfat (Israel) and DNV- KEMA (The Netherlands).

3. Results and discussions

3.1 Location of permeation rig and summary of test parameters

The rig was situated close to the flue gas extraction point due to outdoor location. The location was at Unit No. 4 on the gas-gas heater inlet hood. Figure 3 shows the exact location of the test rig. The annotations in Fig. 3 stand for: FGD-flue gas desulphurization (SO_2 removal unit) and GGH gas-gas heater.

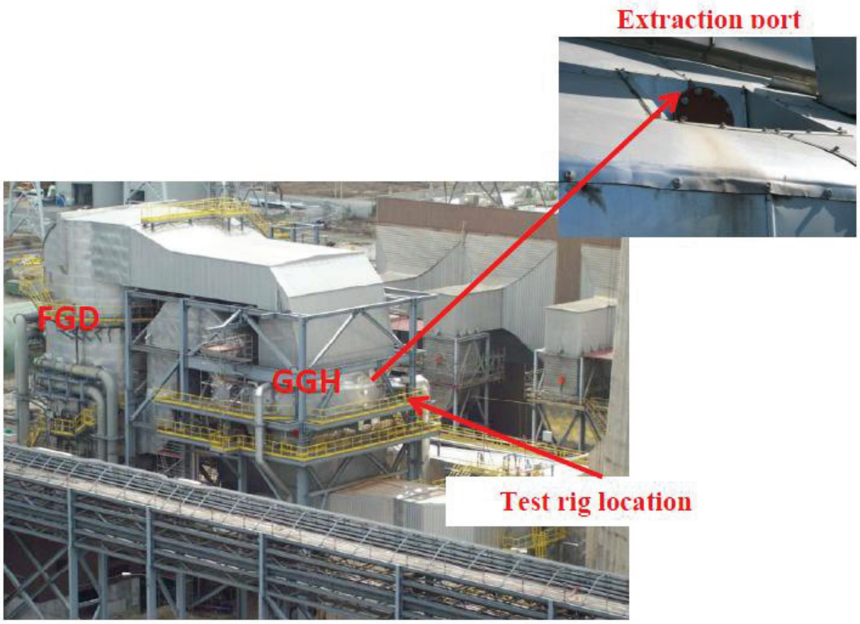

Fig. 3 Location of the pilot scale testing rig at EDP, Sines, Portugal

The test parameters and flue gas composition is presented in Figure 4. The figure indicates the unusual large amounts of SO_2, NOx present in flue gas in the first part of the test.

	From 23rd May until mid July	From 17th August to 2 Dec. 2011
Type of membranes (from NTNU)	FSC (Fixed-Site Carrier) flat sheet	
Membrane area in use	~ 0,25 m^2	~ 1,5 m^2
Membranes module (from Yodfat)	With 2 out of 12 elements (4 membranes)	With 12 elements (24 membranes)
Sines Power plant Unit 4	314 MWe, pulverised bituminous coal, flue gas cleaning (ESP, Wet FGD limestone-gypsum, SCR from mid August)	
Flue gas main composition:	Saturated gases at ~ 50 °C (~ 13% H_2O) Feed flow: 6-24 m^3/h, vacuum 100-200 mbar	
• **SO_2**	< 200 mg/Nm^3, 6%O_2, dry gas	
• **NOx**	500-600 mg/Nm^3, dry gas (SCR out of service)	< 200 mg/Nm^3, dry gas (SCR in service)
• **Dust (fly ashes)**	< 20 mg/Nm^3, 6% O_2, dry gas	
• **CO_2**	~ 12% vol. at MCR (lower at boiler low loads)	
• **O_2**	~ 6% vol. at MCR (higher at boiler low loads)	

Fig. 4 Test parameters and flue gas composition

The operating conditions are shown in Fig.4: feed gas flow was 6-24 Nm^3/h, feed pressure was atmospheric pressure, temperature was 45^0 C, vacuum pressure in permeate was 100-200 mbar (average 130 mbar). The gas leaks of the system were investigated and quantified. The internal leaks were impossible to determine and consequently were not accounted. The external leak, air in the system, was identified from mass balance to be 1.4 liters per hour (l/h) between August and October 2011 and 1.6 l/h between October and December 2011 due to vacuum pump replacement.

3.2 Permeate flow rate and permeate CO_2 concentration

Figure 5 shows raw data recorded between 17 of August and 6 October 2011 of CO_2 concentration in permeate and permeate flow rate. The membranes had constant separation performances for the entire period of testing. Variations of permeate flow rate and permeate content were observed and were attributed to fluctuating vacuum pump operation and fluctuating loading capacity of the power plant (Mw output). The periods with low power plant electrical output decreased considerably the CO_2 content and the relative humidity of the flue gas and this influenced the flow rate and CO_2 content of permeate The major fluctuations are attributed to power plant outages due to the replacement of SCR unit (de–NOx unit).

Prolonged outages of power plant produced a flue gas containing mostly air which decreased the CO_2 feed content to 5%, increased O_2 concentration up to 18% and decreased the relative humidity below 40% RH. There is a clear relation between flue gas low humidity and low CO_2 content and the decreases of permeate flow and CO_2 content.

Remarkable, the permeate flow rate and CO_2 concentration recovered to initial values when the power plant was operated at normal loading capacity and under constant conditions.

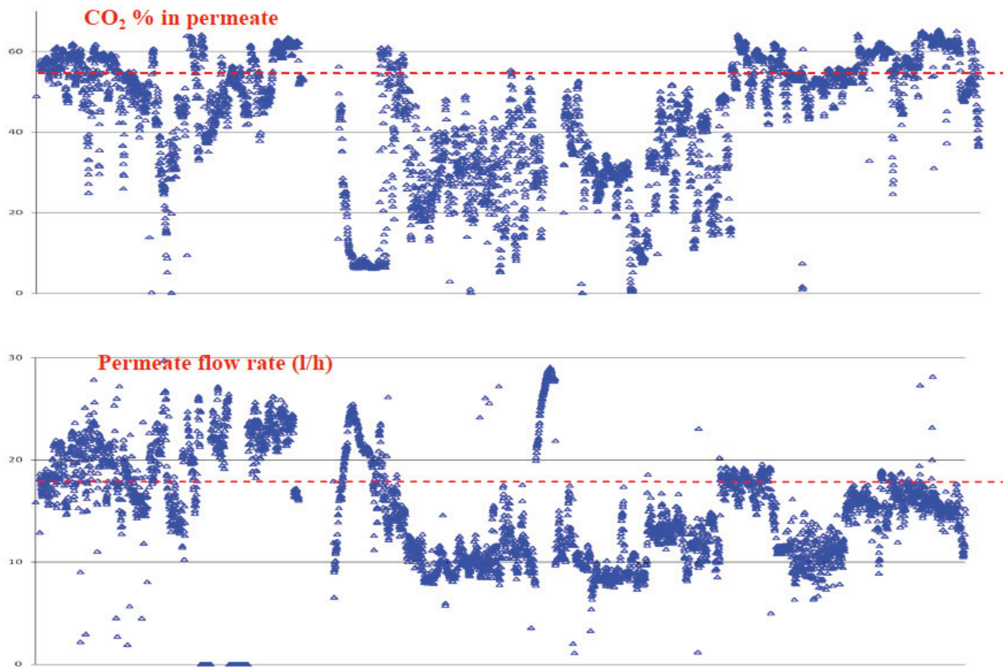

Fig. 5 Raw data for permeate flow rate and CO_2 content measured from 17 August to 6 October 2011

The membranes showed constant separation performances with a maximum of 75% CO_2 content in permeate and a permeate flow of 525 l/day. The raw results were used to calculate the CO_2 permeance and CO_2/N_2 selectivity using the complete mixing model [7]. During periods of constant power plant operation the values of CO_2 permeance and CO_2/N_2 selectivity were similar to values obtained in the laboratory at NTNU. Both CO_2 permeance and CO_2/N_2 selectivity were constant for the entire testing period. CO_2 permeances between 0.2 and 0.6 m^3 (STP)/(m^2 bar h) and CO_2/N_2 selectivity between 80 and 300 were obtained during periods of constant operation of power plant.

Several studies for different flue gas sources pointed out that by an innovative membrane process design and using high performance membranes, the separation with membranes can compete with absorption in terms of costs and efficiency without adding an extra pollution by use of toxic chemicals [22-27].

4. Conclusion

The separation performances of the membranes produced at NTNU were confirmed by independent testing from laboratory scale to pilot scale testing despite differences in testing equipment among project partners. The results showed that using large area of module membranes instead small membranes can be more beneficial in terms of accuracy testing. The membranes did not lose the separation performances during more than six months continuous operation in very harsh and challenging conditions: frequent plant outages, high concentration of NOx and SO_2 and various technical problems. During periods of constant power plant operation, the values of CO_2 permeance and CO_2/N_2 selectivity were similar to values obtained in the laboratory at NTNU. Both CO_2 permeance and CO_2/N_2 selectivity were constant for the entire testing period. CO_2 permeances between 0.2 and 0.6 m^3 (STP)/(m^2 bar h) and CO_2/N_2 selectivity between 80 and 300 were obtained during periods of constant operation of power plant.

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