Summary of doctoral dissertation

Title: **The use of solid polymeric membranes for the separation of carbon dioxide from flue gases**

Author: mgr inż. Aleksandra Janusz-Cygan

Promoter: prof. dr hab. inż. Krzysztof Warmuziński

The problem of reducing greenhouse gas emissions from anthropogenic sources is currently an issue of major social, political and scientific importance. The largest share in the generation of climate change is attributed to carbon dioxide. Actions taken in the EU to reduce CO_2 emissions are vital for this country, as the Polish energy sector is mostly based on coal. In the paper both methods of reducing CO_2 emissions from flue gases and methods of CO_2 separation were presented.

The basic aim of this study was to analyze the possibility of using commercial membrane modules to separate carbon dioxide from flue gases. Due to the absence of commercial membrane modules for the separation of CO_2 from flue gases, the study on the separation of CO_2/N_2 and $CO_2/N_2/O_2$ mixtures was conducted in the modules designed for purposes other than carbon dioxide capture. Evaluation of the separating possibilities of available modules was made in an experimental installation with hollow-fibre membrane modules. Extensive experimental studies of permeation of pure gases (in order to obtain data for the mathematical model) as well as a study of separation of binary and ternary gas mixtures containing the major components of the dry exhaust stream were made. Experimental tests were carried out both, in a membrane cell with the flat-sheet membrane made of polydimethylsiloxane, as well as in three commercial modules (an Air Products module PRISM PA1020 - wherein the active layer of the membrane is made of polysulfone, and in two UBE modules (CO–C05 and UMS–A5), in which a modified polyimide is an active layer). Basic research has shown that there are commercial materials that can be used to separate CO_2 from flue gases.

From the literature review and our own analysis it follows that for the capture of carbon dioxide after the combustion, it is not possible to obtain the assumed parameters of CO_2 stream purity (over 95%) and the recovery rate (not less than 90%) in a single-stage

installation. However, these parameters can be reached by using multi-stage membrane systems or hybrid installations. Therefore, an analysis of the use of commercial membrane modules in an adsorption-membrane installation for the high-efficiency separation of carbon dioxide from flue gases was proposed. The membrane modules would constitute the second stage of the installation, while the first stage of separation would be provided by pressure swing adsorption. Such a stage sequence in the hybrid installation will allow to minimize the energy required for the high-efficiency capture of CO_2.

Based on the results of numerical simulations of the PSA process, it was found that in the adsorption unit it is possible to increase the concentration of carbon dioxide from 13 vol.% to about 70 vol.%. Accordingly, the selection of the membrane module was based on the experimental evaluation of separation properties of the available modules, using gas mixtures containing 70 vol.% CO_2 at a flow rate of 0.05 kmol/h. In the experiments the Air Products module was used, which operates at a relatively low transmembrane pressure difference. Based on extensive experimental investigations of the separation of carbon dioxide from the synthetic dry flue gas in a demonstration hybrid installation it was found that 100% recovery of CO_2 and a rise of its concentration from about 12 vol.% to more than 95 vol.% are possible. The selected membrane module has therefore been positively verified in the experimental hybrid installation.

A modelling part of the work includes a mathematical description of the process of permeation of the main components of dry flue gases in the polymeric membranes. For simulation calculations two mathematical models were used:

- a model, in which perfect mixing of the gas phase on both sides of the membrane is assumed; the model is used to describe the separation process in the flat-sheet module;
- a model, in which a plug flow of the gas mixture on the feed side and the free flow of permeate is assumed; it is used to describe the separation process in hollow-fibre modules.

The numerical simulators developed were verified based on the results of the experimental CO_2 separation from binary and ternary mixtures, and can be used for both design and numerical simulations.