A SELECTION OF AMINE SORBENTS FOR CO_2 CAPTURE FROM FLUE GASES

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Amine absorption processes are widely used in the industry to purify refinery gases, process gases or natural gas. Recently, amine absorption has also been considered for CO_2 removal from flue gases. It has a number of advantages, but there is one major disadvantage - high energy consumption. This can be reduced by using an appropriate sorbent. From a group of several dozen solutions, three amine sorbents were selected based on primary, tertiary and sterically hindered amines. The solutions were used to test CO_2 absorption capacity, absorption kinetics and heat of CO_2 absorption. Additional tests were performed on the actual absorber-desorber system to indicate the most appropriate sorbent for capturing CO_2 from flue gases.

Keywords: CCS, MEA, AMP

1. INTRODUCTION

The processes of removing acid components from gases are widely used in the industry for treating process gases, natural gas or refinery gases. The application of such processes to capture carbon dioxide from flue gas is also being considered. The most practicable processes in the power industry are those based on absorption, and among these the most studied and most widely applied in other industries for removing acid components is absorption in amine solutions. This process has a number of advantages, but there is one major drawback: it has high energy consumption. However, energy consumption can be reduced, either by optimising plant operation parameters (up to 10% energy consumption reduction) or by using an appropriate sorbent (up to 30% energy consumption reduction) (Chmielniak, 2010; Wang et al., 2011).

Carbon dioxide capture is possible using various types of amines, the first and most widely used being monoethanolamine (MEA). MEA is used in such processes as Econamine FG or Kerr-McGee/ABB Lummus Crest (Drage et al., 2007). It is characterized by a high absorption rate and a relatively low price. It does, however, have some disadvantages, such as high heat of desorption or high susceptibility to degradation.(Gouedard et al., 2012) For this reason other amines are increasingly used in the absorption process, for instance tertiary amines, incuding MDEA in the BASF aMDEA process, (Alvis et al., 2012; Optimize Gas Treating, Inc., 2008) amines with steric hindrance, e.g. in the KM-CDR Process, (Iijima et al., 2011; Kamijo et al., 2013; Mitchell, 2008) or polyamines. As part of the conducted studies a number of solutions were tested, ranging from 30% reference solution of MEA to systems based on amines with steric hindrance. The tests comprised determination of:

- absorption rate and absorption capacity,
- heat of CO_2 absorption,
- efficiency and energy absorption of the sorbent in the actual absorber-desorber system.

2. EXPERIMENTAL

Basic properties (absorption capacity, absorption rate) of potential sorbents were determined on stands designed for studying the equilibrium and kinetics of CO_2 absorption in mixtures of amines. The stand comprised a thermostated glass reactor, a cryostat for maintaining constant temperature and a hybrid vacuum pump for evacuating gases from the system. The setup also included a system for precise metering of liquid samples and for measuring and recording the pressure in the system. A diagram of the stand is shown in Figure 1. The stand was used for studying the kinetics of absorption, determining absorption isotherms and additionally for determining vapour pressures of amine mixtures.

Prior to investigating CO_2 absorption kinetics, the system was alternately evacuated and filled with carbon dioxide several times in order to remove air completely. Afterwards the reactor was filled with carbon dioxide to a set pressure. After the pressure and temperature in the system have stabilised, a single sample of sorbent was instilled. Upon introducing the solvent, pressure changes in time were measured. The adopted time interval enabled attaining a nearly equilibrium state of solution saturation, permitting thereby to determine not only basic data, such as the number of moles of CO_2 absorbed in a unit of time, but also data relating to the relationship between absorption rate and saturation ratio of the carbon dioxide solution. The results obtained were used to plot a carbon dioxide partial pressure vs. process duration time curve.
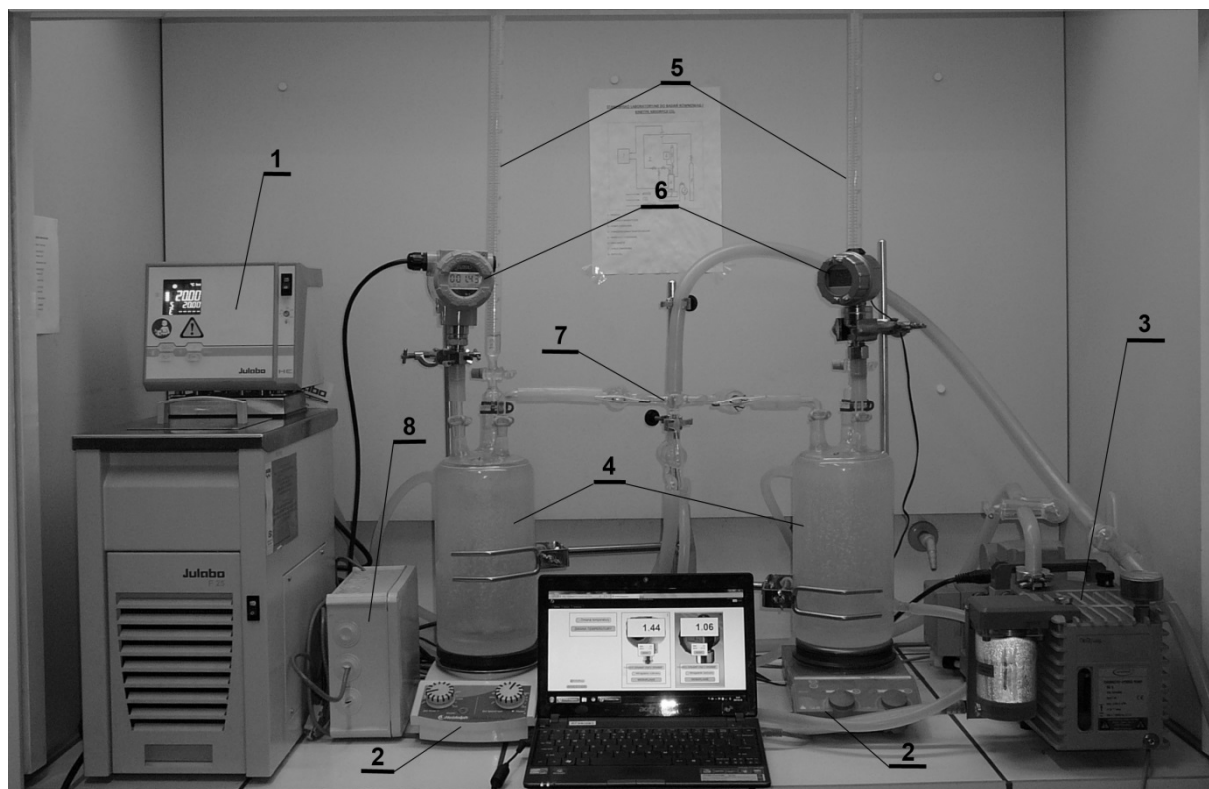

Fig. 1. Photo of the laboratory setup for studying absorption equilibria and kinetics of CO_2 absorption in mixtures of amines: 1 – cryostat, 2 – magnetic stirrer, 3 – vacuum pump, 4 – thermostated reactor, 5 – precise cylindrical separatory funnel with scale, 6 – vacuum meter, 7 – valves station, 8 – data acquisition systems

For studying CO_2 absorption equilibria, several samples of liquid solution were injected into the reactor at certain time intervals. After each sample injection and after some time required for establishing an equilibrium in the system, pressure was recorded and another sample was injected. The data obtained were used to determine the number of CO_2 moles absorbed in 1 dm³ of solution or by 1 mole of amine groups.

Absorption heat measurements were conducted in a CPA202 reaction calorimeter (Chemical Process Analyzer). The main component of the calorimeter was an isothermal stirred tank reactor. The reactor was provided with a temperature measurement system that ensured maintaining a constant temperature in the reactor with an accuracy of ±0.1 K. The reactor consisted of two glass cylinders that made up a side wall. A double glass layer and the air gap between the cylinders ensured good thermal insulation. Openings in the cover enabled feeding liquid and gaseous reagents, sampling and introducing appropriate measuring sensors. Heat exchange was effected mainly through the bottom of the reactor where a Peltier battery was installed which, depending on the need, acted as either a heater or a cooler. Thanks to a unique method of heat flux measurement, CPA did not require calibration before every measurement, which significantly shortened the time of measurement and its accuracy. The measuring system of the device enabled continuous recording of the pressure over the liquid surface, of the flux of heat evolved during the process, of the temperature in the reactor and the thermostat, of the stirrer speed, of the torque on the stirrer drive shaft, of the pressure and of the mass flow rate of the fed reagents.
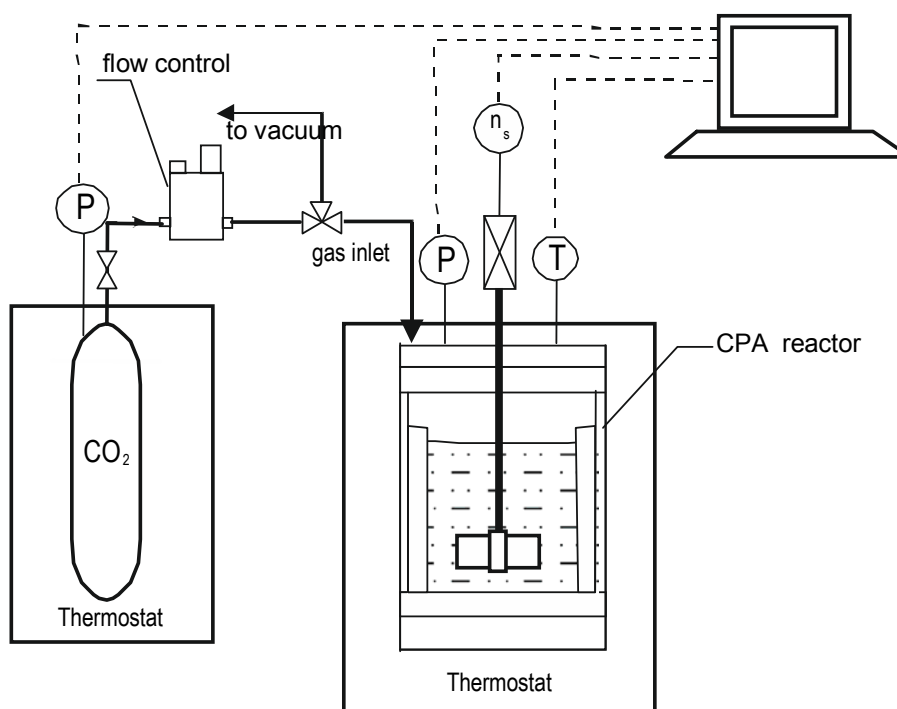

Fig. 2. Diagram of the measuring setup applied in absorption heat investigations (Kierzkowska-Pawlak and Chacuk, 2010; Kierzkowska-Pawlak and Chacuk, 2011)

Measurements were made in a semi-periodical manner under isothermal conditions. The gas was metered into the reactor by means of a flow controller at an interval range of 150 to 300 seconds. CO_2 feeding rate was set at 150 to 200 mg/min. Feeding the gas to the reactor caused an increase of the gas pressure in the reactor which reached its maximum at the moment of stopping the gas inflow. After gas inflow was stopped, the pressure decreased as a result of CO_2 absorption by the liquid, until a physical/chemical equilibrium was established. The flux of evolved heat was measured from the start of gas feeding (start of absorption) until a physical/chemical equilibrium was established. This was followed by a subsequent gas feeding stage. The entire process was conducted under stirring at continuous speed, which is particularly important from the point of view of establishing heat flux

baseline. The measurement consisted in determining 3-4 values of absorption heat (differential and integral heat of absorption) for the increasing ratio of solution carbonation.

CO_2 removal from flue gas was investigated on a laboratory scale on a dedicated stand. The main components of the setup included an absorption column (absorber), a desorption column (regenerator) and a main heat exchanger. The columns had a randomly filled packing of glass Raschig rings 6x6x0.5mm with an option to replace the packing with another type. Glass walls of the columns enabled to observe liquid flow distribution over the packing. The task of the main heat exchanger was heat exchange between the hot regenerated solution and saturated solution. The regenerated solution was pre-cooled in the main heat exchanger. When necessary, the solution could be cooled to a lower temperature in a final cooler. The saturated solution was pre-heated while passing through the main heat exchanger, which reduced the amount of heat required to regenerate the solution in the desorption column. The sorbent was additionally filtered on a bed of activated carbon to remove solid contaminants and some of the products of amine degradation. Heat necessary to regenerate the solution was provided in the desorber by means of an electric heater with adjustable output. The components of the regenerator, sorbent piping and the main heat exchanger were thermally insulated to reduce heat losses. The gas mixture was homogenised in a mixer to which gas cylinders and an air compressor were connected. The gas mixture was subsequently transferred to the absorption column where CO_2 capture proceeded.
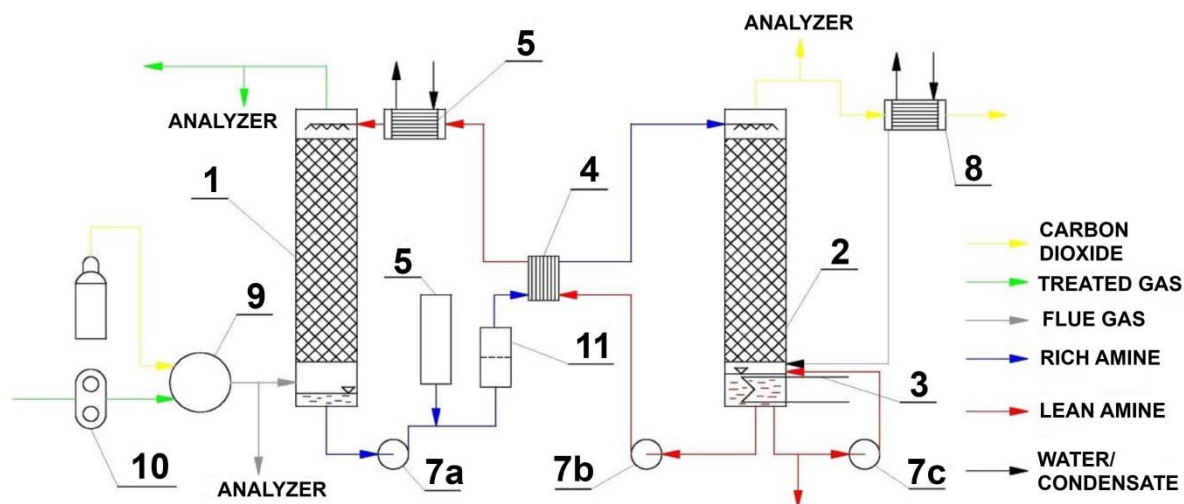

Fig. 3. Schematic diagram of the laboratory stand for investigating the CO_2 removal process (Śpiewak et al., 2014a): 1–absorption column, 2–desorption column, 3–electric heater, 4–heat exchanger, 5–solution cooler, 6–absorbent tank, 7a–rich amine pump, 7b-lean amine pump, 7c–circulation pump, 8–gas cooler, 9–gas mixing chamber, 10–air blower, 11–solution filter

3. RESULTS

From a group of several dozen solutions, three were selected (Wilk et al. 2012; Wilk et al., 2013b). These were characterised by relatively good availability, low price and advantageous properties, both in terms of absorption kinetics and absorption heat. All data available for these sorbents were compared, ranging from basic parameters to energy absorption and efficiency attained in the actual CO2 capture process effected in an absorber-desorber system. The sorbents included: 30%MEA – as the standard reference solution, which is the solution of the first and most often used amine for removing acidic components in the industry, 30%MDEA + 10%PZ (Wilk et al., 2013a) which is a system of activated tertiary amine having a potentially low absorption heat and high resistance to degradation, and 30%AMP + 10%PZ which is a system of an amine with steric hindrance with an addition of a

polyamine that reacts readily with CO_2, the system potentially combining the advantageous features of primary and tertiary amines.

The results of carbon dioxide absorption equilibria in the solutions show that under low partial pressures, the activated N-methyldiethanolamine solution provided results much inferior to those of the other amines. However, with increasing CO_2 partial pressure, the absorption capacity of the MDEA-containing solution approaches that of the monoethanolamine solution. The best parameters were obtained for the solution of the amine with steric hindrance (2-amine-2-methyl-1-propanol) containing an activator. In this case the absorption capacities were significantly higher than those of both the MEA solution as well as of the MDEA solution. The data obtained on equilibrium absorption capacities and on carbonation ratios are presented in graphs in Figures 4 and 5 and in Table 1. The data presented in the Table 1 compare the equilibrium absorption capacities of solutions for the carbon dioxide partial pressure that corresponds to a typical CO_2 content in flue gases from coal fired power generating units. These show that the absorption capacity of the 30%MDEA+10%PZ solution is by ca. 25% lower than that of the 30% monoethanolamine solution, and that the 30%AMP+10%PZ has a capacity by ca. 15% higher than that of the MEA solution.

Table 1. Comparison of the equilibrium absorptive capacities of the studied solutions at CO_2 partial pressure of 12 kPa

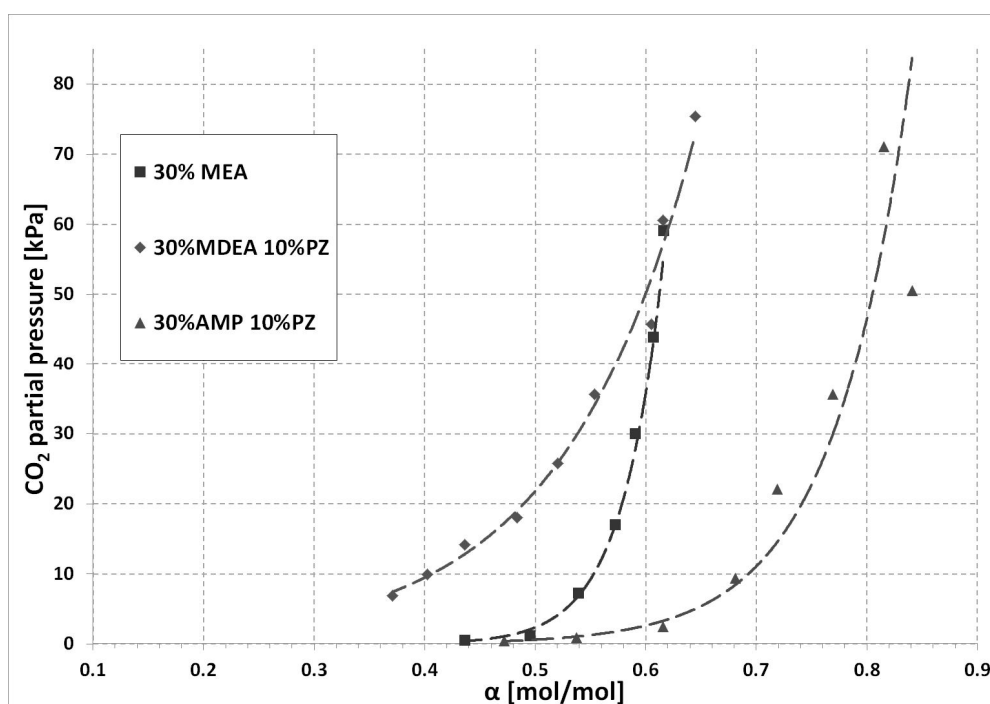| Solution	30% MEA	30% MDEA 10% PZ	30% AMP 10% PZ
Absorption capacity for pCO_2 = 12 kPa [mole/dm^3]	2.73	2.03	3.12

Fig. 4. Comparison of the absorption capacities of the studied solutions

The obtained kinetic data show similar relations as those of the equilibrium data. Under the same conditions the highest carbon dioxide absorption rate was provided by the solution based on 2-amine-2-methyl-1-propanol with an addition of piperazine. It may be assumed that the high absorption rate by this solution results from the application of a system of a fast reacting amine with steric hindrance with an addition of piperazine, the reaction rate of which is nearly 10-fold higher than that of

monoethanolamine (Bishnoi et al., 2000; Derks et al., 2006). It can also be seen that despite the addition of 10% piperazine, the rate of absorption of carbon dioxide in the tertiary amine (MDEA) solution is substantially lower than that in the 30% MEA solution. Experimental data on absorption rates are presented in Fig. 8 and Table 2.
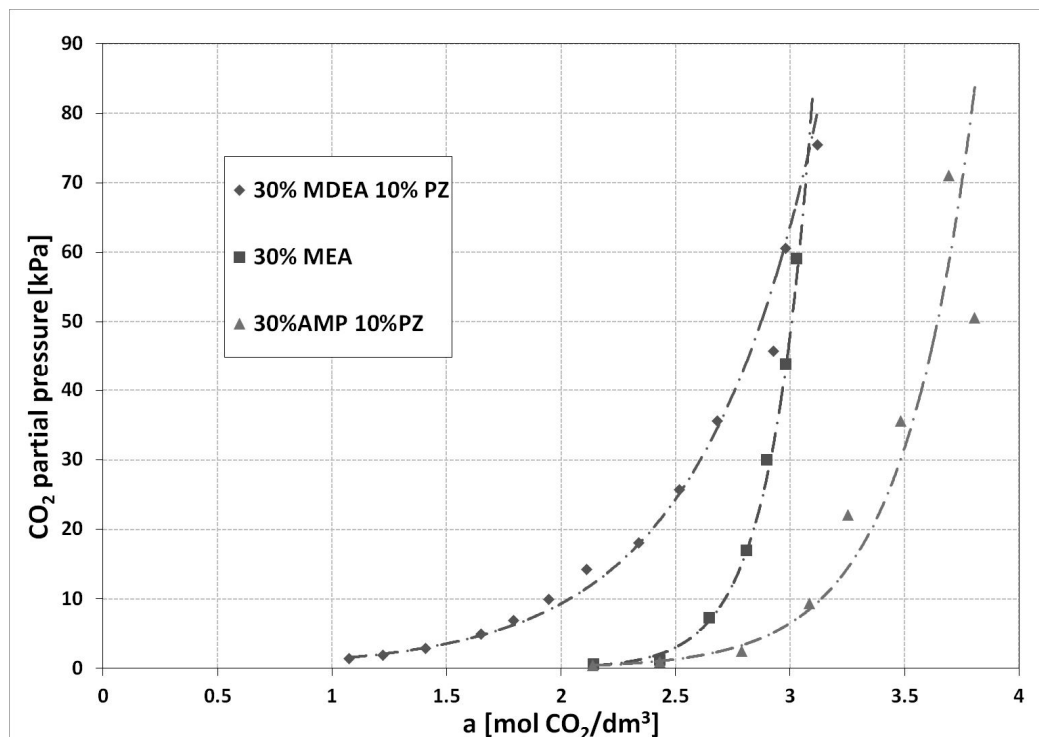

Fig. 5. Comparison of degree of carbonisation of the studied solutions
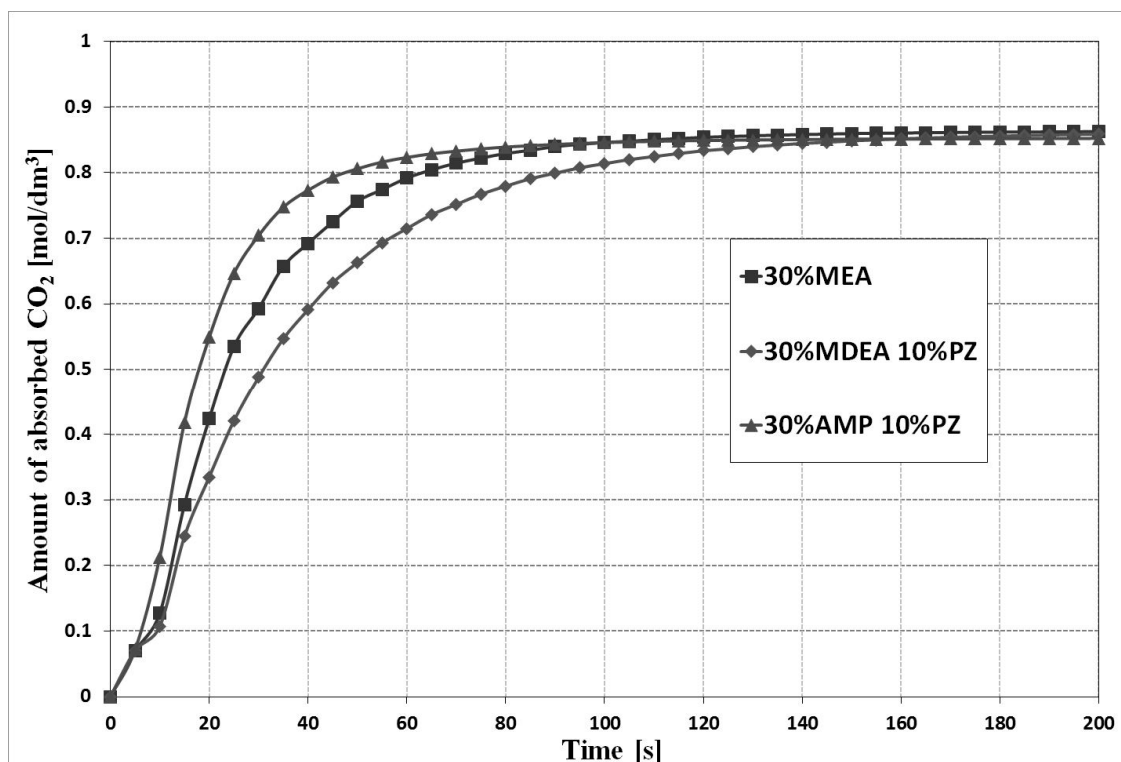

Fig. 6. Comparison of rates of CO_2 absorption in the studied solutions

Table 2. Comparison of the amounts of CO2 absorbed by the studied sorbents during 20, 40 and 60 s

Time [s]	30% MEA	30% MDEA 10% PZ	30% AMP 10% PZ
	Amount of absorbed CO_2 [mol/dm^3]		
20	0.423	0.335	0.549
40	0.692	0.591	0.773
60	0.792	0.715	0.823

The heat of absorption depends on the carbon dioxide saturation ratio of the solution. The larger the amount of CO_2 absorbed in the system, the lower is the absorption heat. This is particularly evident in the case of primary amines: up to the saturation ratio of 0.5, carbon dioxide reacts mainly to form a carbamate and the values of absorption heat change only slightly. At α higher than 0.5, CO_2 reacts mainly to form a bicarbonate and the absorption heat is significantly reduced. In the case of amines that do not form carbamates, such as MDEA, reduction of absorption heat is observed from the start of solution saturation, with no abrupt drops as in the case of, for instance, MEA (Kohl and Nielsen, 1997).

The data gathered shows, as expected, the lowest absorption heat for N-methyldiethanolamine activated with piperazine. The mean CO_2 absorption heat of this solution is by ca. 8% lower than that of the 30% MEA solution. The AMP solution with piperazine showed only a slightly lower absorption heat than the ethanolamine solution. Data on absorption heat are presented in Table 3 and Fig. 7.
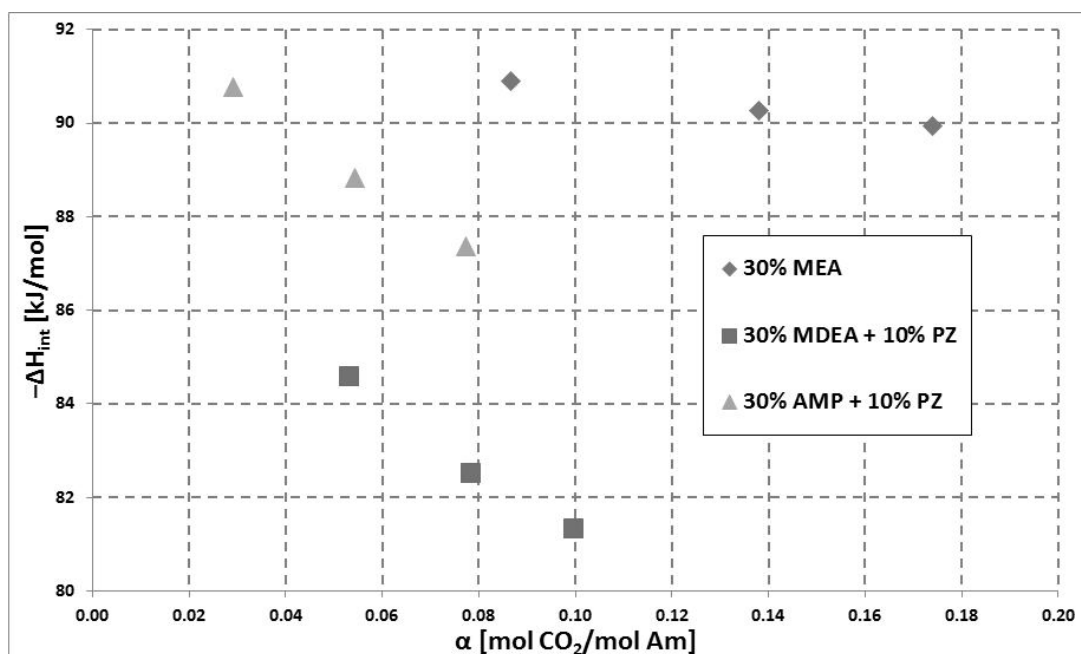

Fig. 7. Comparison of the absorption heat of the studied solutions (Kierzkowska-Pawlak, et al. 2013)

Table 3. Mean values of the heat of CO_2 absorption in the studied solutions

Solution	$-\Delta H$ (kJ/mole)
30% MEA	90.37
30% MDEA + 10% PZ	82.81
30% AMP + 10% PZ	88.99

In addition to equilibrium, kinetic and absorption heat investigations, tests were performed on the actual absorber-desorber system to indicate the most appropriate sorbent for capturing CO_2 from flue gases (Śpiewak et al., 2014a, b). Figure 8 presents a comparison of test results of the studied sorbents.

It shows distinct differences in the course of CO_2 removal from flue gas of elevated CO_2 content for the various sorbents used. The best results were obtained in the case of the AMP/PZ system. This sorbent is characterised by the highest efficiency of CO_2 removal and the lowest energy consumption for solution regeneration. Under identical conditions, due to poor kinetic properties, similar efficiencies are not attainable in the case of MDEA/PZ solution. Low efficiency translates into a low amount of CO_2 separated from the gas stream, which is reflected in the regeneration energy related to the unit of mass of the removed CO_2. Therefore, the low absorption heat of the MDEA/PZ solution is of no significance for the studied system, the kinetics of absorption being more important. The MDEA/PZ sorbent provided good results only in the case of low gas flow rates, that is for tests with longer gas-liquid contact time. The MEA solution, on the other hand, requires a higher heating output to attain satisfactory efficiency (85%). The process where MEA is used is characterised by higher energy consumption as compared to the AMP/PZ solution (4.59MJ/kg CO_2 for MEA, 4.23 MJ/kg CO_2 for AMP/PZ).
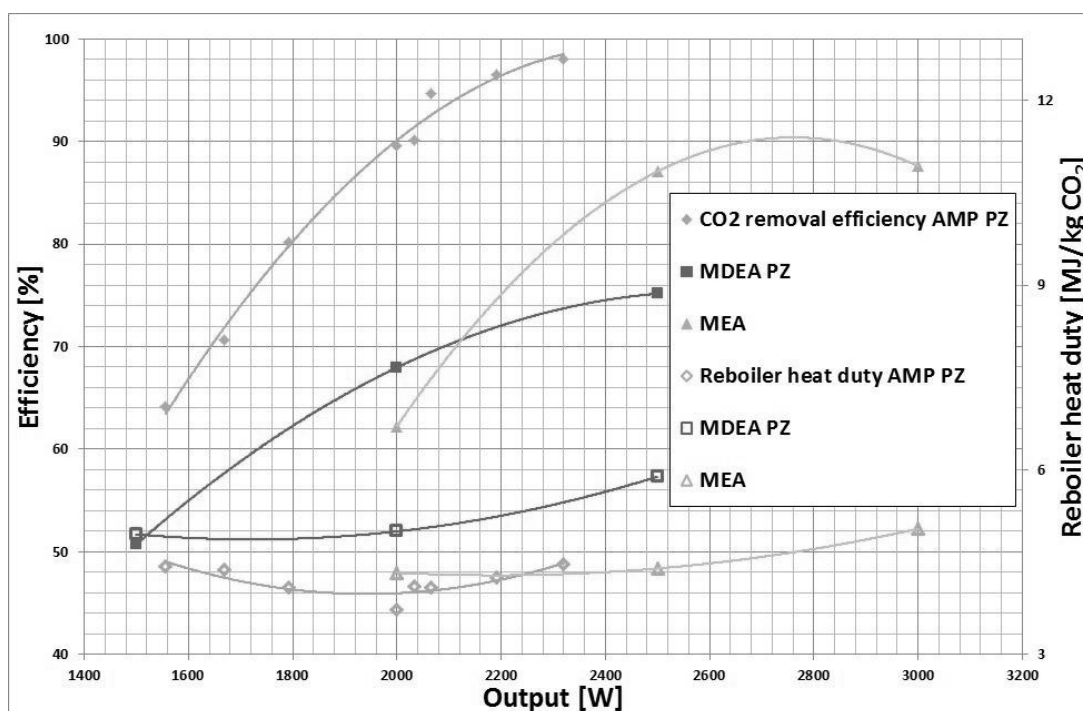

Fig. 8. Comparison of test results for solutions of MEA, MDEA+PZ, AMP+PZ (Wilk et al., 2014)

4. CONCLUSION

The results show that it is possible to prepare solutions that feature lower heat of carbon dioxide absorption and higher CO_2 capture efficiency and lower energy consumption per kg of captured CO_2 as compared to the 30% solution of monoethanolamine that is now most widely used for CO_2 capture. The AMP solution showed the most advantageous parameters in terms of absorptive capacity and CO_2 absorption kinetics, even in comparison with the ethanolamine solution, while also being characterised by lower heat of absorption (89 kJ/mole). The process tests have shown that the application of the AMP/PZ system substantially improves the efficiency of CO_2 capture and decreases by 8% the energy consumption calculated for every kilogram of captured CO_2.

efficient zero-emission coal-fired power units integrated with CO$_2$ capture and in the framework of Contract SP/E/2/66420/10 - Strategic Research Programme - Advanced Technologies for Energy Generation: Developing a technology of oxyfuel combustion for pulverized fuel and fluidized-bed furnaces integrated with CO$_2$ capture system.

REFERENCES

Alvis R.S., Hatcher N.A., Weiland R.H., 2012. CO$_2$ removal from syngas using piperazine - activated MDEA and potassium dimethyl glycinate. *Nitrogen+Syngas 2012*. Athens, Greece, 20–23 February 2012.

Bishnoi S., Rochelle G.T., 2000. Absorption of carbon dioxide into aqueous piperazine: reaction kinetics, mass transfer and solubility. *Chem. Eng. Sci.*, 55, 5531-5543. DOI: 10.1016/S0009-2509(00)00182-2.

Chmielniak T., 2010. Węglowe technologie energetyczne 2020+. *Polityka Energetyczna*. 13, 77-89.

Derks P.W.J., Kleingeld T., van Aken C., Hogendoorn J.A., Versteeg G.F., 2006. Kinetics of absorption of carbon dioxide in aqueous piperazine solutions. *Chem. Eng. Sci.*, 61, 6837–6854. DOI: 10.1016/j.ces.2006.07.009.

Drage T.C., Arenillas A., Smith K.M., Pevida C., Piippo S., Snape C.E., 2007. Preparation of carbon dioxide adsorbents from the chemical activation of urea–formaldehyde and melamine–formaldehyde resins. *Fuel.* 86, 22-31. DOI: 10.1016/j.fuel.2006.07.003.

Gouedard C., Picq D., Launay F., Carrette P.-L., 2012. Amine degradation in CO$_2$ capture. I. A review. *Int. J. Greenhouse Gas Control*, 10, 244-270. DOI: 10.1016/j.ijggc.2012.06.015.

Iijima M., Nagayasu T., Kamijyo T., Nakatani S., 2011. MHI's energy efficient flue gas CO$_2$ capture technology and large scale ccs demonstration test at coal-fired power plants in USA. *Mitsubishi Heavy Industries Technical Review*. 48, 26-32.

Kamijo T., Kajiya Y., Endo T., Nagayasu H., Tanaka H., Hirata T., Yonekawa T., Tsujiuchi T., 2013. SO$_3$ impact on amine emission and emission reduction technology. *Energy Procedia.* 37, 1793–1796. DOI: 10.1016/j.egypro.2013.06.056.

Kierzkowska-Pawlak H., Chacuk A., 2010. Carbon dioxide removal from flue gases by absorption/desorption in aqueous diethanolamine solutions. *J. Air Waste Manage. Assoc.,* 60, 925–931. DOI: 10.3155/1047-3289.60.8.925.

Kierzkowska-Pawlak H., Chacuk A., 2011. Kinetics of CO$_2$ desorption from aqueous N-methyldiethanolamine solutions. *Chem. Eng. J.*, 168, 367–375. DOI: 10.1016/j.cej.2011.01.039.

Kohl A., Nielsen R., 1997. *Gas Purication*. Gulf Publishing Co., Houston.

Optimize Gas Treating, Inc. 2008. Piperazine – Why It's Used and How It Works. 2008, *The Contactor*, 4 (2).

Mitchell R., 2008. Mitsubishi Heavy Industries Carbon Capture Technology. *Carbon Capture J.*, 1, 3-5.

Śpiewak D., Krótki A., Tatarczuk A., L. Więcław-Solny L., Wilk A., 2014. Badania procesu usuwania CO$_2$ za pomocą wieloskładnikowych sorbentów aminowych. *Inż. Ap. Chem.*, 53, 182-184.

Śpiewak D., Krótki A., Spietz T., Więcław-Solny L. Wilk A., 2014. Porównanie wyników badań procesu usuwania CO$_2$ z mieszanin gazów dla sorbentów aminowych. *Inż. Ap. Chem.*, 53, 2014, 308-310.

Wang M., Lawal A., Stephenson P., Sidders, J., Ramshaw C., 2011. Post-combustion CO$_2$ capture with chemical absorption: A state-of-the-art review. *Chem. Eng. Res. Des.* 89, 1609-1624. DOI: 10.1016/j.cherd.2010.11.005.

Wilk A., Więcław-Solny L., Dreszer K., Tatarczuk A., Krótki A., 2012. Wpływ dodatków aktywujących na zdolności sorpcyjne mieszanin aminowych opartych na N-metylodietanoloaminie – MDEA. *Karbo*, 57, 123-130.

Wilk A., Więcław-Solny L., Krótki A., Śpiewak D., 2013. Impact of the composition of absorption blend on the efficiency of CO$_2$ removal. *Chemik*, 67, 399-406.

Wilk A., Więcław-Solny L., Śpiewak D., Spietz T., 2014. Badania laboratoryjne nad doborem optymalnych warunków pracy instalacji separacji CO$_2$. *Polityka Energetyczna*, 17, 339-350.

Wilk A., Więcław-Solny L., Tatarczuk A., Śpiewak D., Krótki A., 2013. Effect of composition of absorption solution on carbon dioxide removal efficiency. *Przem. Chem.,* 92, 1000-1005.