

## ADSORBENTS FOR CO<sub>2</sub> SEPARATION FROM FLUE GAS

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The purpose of this paper is to determine the maximum adsorption capacity and the stability of impregnation agent ethanolamine to enhanced samples of activated carbon. Samples were characterized using BET surface analysis, BJH pore distribution and elemental analysis. Adsorption capacity was studied in a static regime in the pure CO<sub>2</sub> atmosphere at the atmospheric pressure and at 30 °C and 50 °C. Stability of the impregnating agent bound to solid surface was studied by means of elemental analysis to specify the changes in nitrogen content before and after adsorption and before and after FID analysis. Flame-ionization detector was used to estimate the sum of organic compounds that were released from the solid surface at a given temperature. The results show that the best maximum adsorption capacity and impregnating agent stability among samples impregnated with MEA was for the molecular sieve 13X.

**Key words:** activated carbon, adsorption, carbon dioxide, ethanolamine.

**Adsorbensi za izdvajanje CO<sub>2</sub> iz dimnog plina.** Cilj ovog rada je odrediti maksimalni kapacitet adsorpcije i stabilnost impregnacijskog sredstva etanolamin za poboljšanje uzoraka aktivnog ugljena. Uzorci su karakterizirani analizom površine BET metodom, analizom distribucije pora BJH metodom i elementarnom analizom. Adsorpcijski kapacitet je proučavana statičkim postupkom u atmosferi čistog CO<sub>2</sub> pri atmosferskom tlaku i temperaturi 30 °C i 50 °C. Stabilnost impregnacijskog sredstva vezanog na čvrstu površinu je proučavano elementarnom analize s ciljem određivanja promjene u sadržaju dušika prije i nakon adsorpcije te prije i poslije FID analize. Plameno - ionizacijski detektor je korišten za procjenu sume organskih spojeva koji su oslobođeni s čvrste površine na određenoj temperaturi. Rezultati pokazuju da je najbolji maksimalni kapacitet adsorpcije i stabilnosti impregnacijskog sredstva među uzorcima impregniranim s MEA na 13X molekularnom situ.

**Ključne riječi:** aktivni ugljen, adsorpcija, ugljični dioksid, etanolamin.

### INTRODUCTION

Adsorption process is one of the commonly used methods of gas mixture separation. As regards issues related to carbon dioxide capture and storage (CCS), it is supposed to be an option for CO<sub>2</sub> capture from flue gas. [1] Considering the flue gas conditions after desulfurization, e.g. high moisture content, presence of SO<sub>x</sub>, NO<sub>x</sub> and other impurities, solid sorbent should have good CO<sub>2</sub> selectivity, sufficient CO<sub>2</sub> adsorption capacity and significant regeneration efficiency. One of the ways of increasing the selectivity of adsorbents in

given conditions is enhancing a solid surface with a CO<sub>2</sub> selectively-reacting compound via impregnation. Ammonia, polyethyleneamine, metal oxides or various amines are amongst the commonly used impregnating agents in case of activated carbon. The surface of zeolitic molecular sieves can be modified by alkali metal hydroxides (CaOH, NaOH) or by functionalization using amines. [2 - 5] This article is primarily focused on describing and preparing the activated-carbon-based and molecular-sieve-based adsorbent samples, testing their maximum

adsorption capacity at elevated temperature and estimating the stability of impregnating agent to assess the utility of the adsorbent

samples prepared by a certain impregnation method.

## EXPERIMENTAL

### Materials and impregnation method

Microporous/mezoporous activated carbon Envirocarb AP4-50 (Chemviron Carbon), in the form of cylindrically-shaped particles, was used to prepare five samples with a different amount of nitrogen. Molecular sieve 13X (Sigma-Aldrich), in the form of spherically-shaped particles, was chosen to prepare one sample with a specified amount of nitrogen. Solutions of various concentrations of ethanolamine in methanol were used for the impregnation. Ethanolamine (MEA), NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH, M=61.08 g/mol, 98% purity, was supplied by Sigma-Aldrich. The impregnation was

carried out following the methods in [6], which was slightly modified: First, the adsorbent samples were outgassed at 150 °C for 2h. Then, each sample was treated by methanol at least once, preferably twice. Outgassed and methanol-treated samples were washed for 15 minutes in impregnating solution of ethanolamine and methanol. After impregnation, some samples were air-dried overnight at ambient temperature (samples APMEA00, 11 and 20) and some at 120 °C (samples APMEA50 and 13XMEA50).

### Adsorbent samples characterisation

Samples of adsorbents were examined by means of BET surface analysis, BJH pore distribution analysis and t-plot analysis using SA 3100 (Beckman Coulter). Surface area of each adsorbent sample was estimated by BET surface analysis. Total pore volume was evaluated from adsorption isotherm of helium at -196 °C and micropore volume was determined by t-plot analysis. Samples

were analyzed before and after impregnation.

The amount of nitrogen was measured by elemental analysis using Flash EA 1112 NC (Thermo Fisher Scientific Laboratory). The samples were analyzed before and after impregnation and some also after FID analysis, except the untreated adsorbents and a sample APMEA00, which was treated only by pure methanol.

### Static adsorption study

Static adsorption capacity test was designed to evaluate gravimetrically the maximum adsorption capacity of selected samples. First, approximately 1 g of each adsorbent was put into a desiccator which was sealed and evacuated. After that, a balloon was evacuated and filled up with pure CO<sub>2</sub>, then it was connected with the

desiccator and the samples were surrounded by pure CO<sub>2</sub> atmosphere. The desiccator with the balloon was put into an oven which was heated up to 30 °C or 50 °C. After the adsorption equilibrium was reached (approximately 4 days), the samples were weighed and the adsorption capacity at a particular temperature was estimated.

## Stability of impregnating agent

Using the flame ionization detector, we were able to quantify the sum of organic compounds leaving solid surface at specific temperature. Samples were put into a glass column and placed into an oven heated to 30 °C or 50 °C. Flame-ionization detector was

used to specify the maximum sum of organic compounds released from the surface. To depict the changes in nitrogen content after FID analysis and to complement the stability tests, elemental analysis was carried out.

## RESULTS AND DISCUSSION

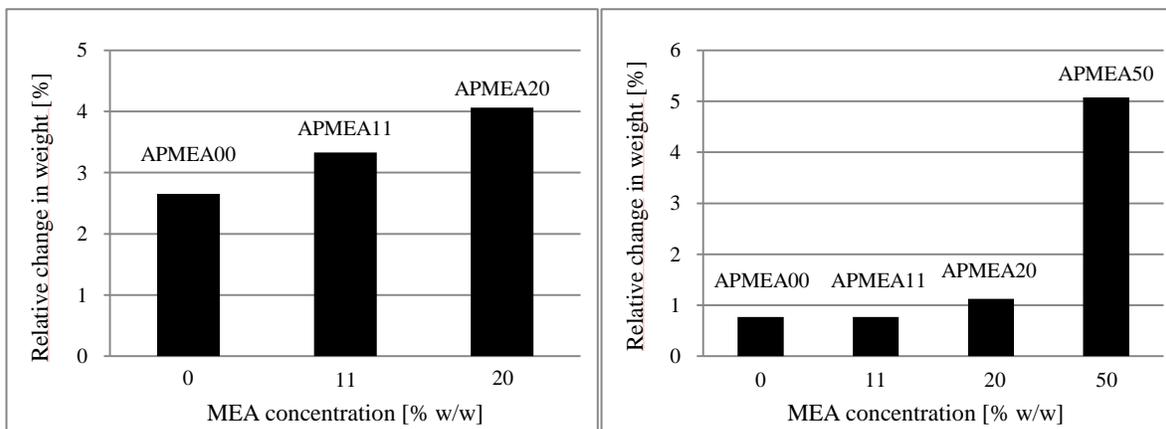
By examining the samples via surface and pore volume analysis, we can show the difference in surface characteristics between untreated and impregnated samples. Samples APMEA50 and 13XMEA50 were prepared especially to see if there is any difference in adsorption capacity and impregnating agent stability between samples that were dried at elevated temperature and samples dried at ambient temperature and also if there is a difference in these characteristics between the sample based on activated carbon and that based on molecular sieve.

Table 1 shows the description of prepared samples including their maximum adsorption capacity at 30 °C and 50 °C. As

can be seen in Table 1, in case of impregnated samples, the maximum capacity at 50 °C is not better than in case of tests running at 30 °C. Only impregnated samples were tested to prove a correlation between nitrogen content and maximum adsorption capacity. At higher temperature, the sample 13XMEA50 showed the best adsorption capacity of 7.2% w/w (see Figure 1), and in the series of carbon-based adsorbents, the sample APMEA50 proved the highest adsorption capacity of 5.1% w/w. In case of carbon-based samples, there is an evident increase in adsorption capacity according to nitrogen content, except the APMEA77 sample.

**Table 1.** Characterization of adsorbent samples  
**Tablica 1.** Karakterizacija uzoraka adsorbensa

Sample	MEA conc. [% w/w]	BET surface area [m <sup>2</sup> /g]	Pore volume [ml/g]	Micropore volume [ml/g]	Maximum adsorption capacity at 30 °C [% w/w]	Maximum adsorption capacity at 50 °C [% w/w]
AP4-50	0	873	0.47	0.21	-	-
APMEA00	0	1192	0.6	0.13	2.7	0.8
APMEA77	7.7	998	0.49	0.18	3.4	-5.9
APMEA11	11	965	0.47	0.23	3.3	0.8
APMEA20	20	1031	0.52	0.14	4	1.1
APMEA50	50	971	0.48	0.13	-	5.1
13X	0	533	0.35	0.22	-	-
13XMEA50	50	23.5	0.11	0	-	7.2



**Figure 1.** Maximal sorption capacity at 30 °C (left) and 50 °C (right) of some samples of activated carbon

**Slika 1.** Maksimalni sorpcijski kapacitet pri 30 °C (lijevo) i 50°C (desno) nekih uzoraka aktivnog ugljena

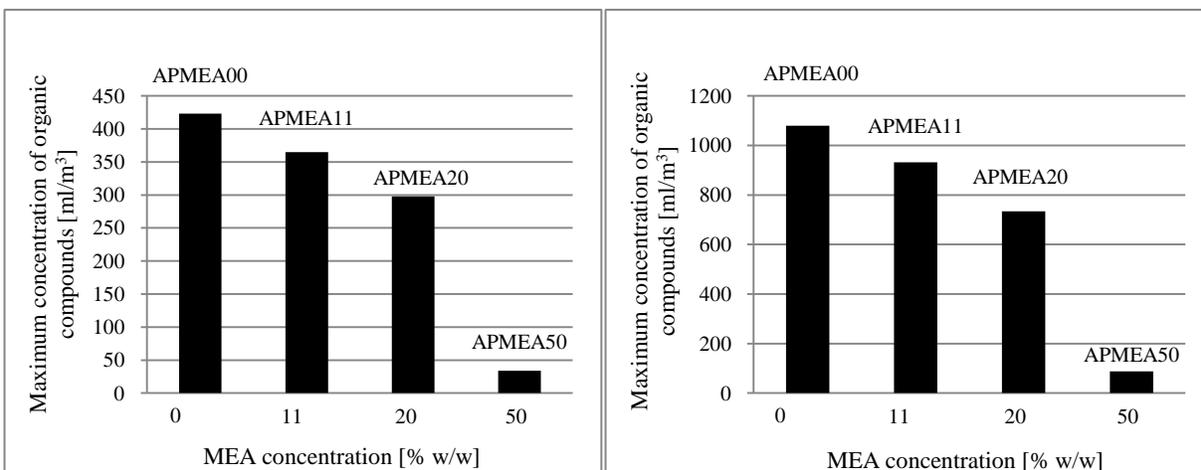
We assume that these results could have been misrepresented because of the insufficient drying of carbon-based samples APMEA00 –APMEA20. This way, residual

methanol was probably released from solid surface during the tests (see also Table 2 and Figure 2 to compare).

**Table 2.** Comparison of nitrogen content before and after FID analysis at 50 °C

**Tablica 2.** Usporedba sadržaja dušika prije i nakon FID analize pri 50 °C

Sample	Nitrogen content before FID analysis [% w/w]	Nitrogen content after FID analysis [% w/w]
AP4-50	0.2	-
APMEA00	0.2	-
APMEA77	1.1	1.1
APMEA11	1.3	1.2
APMEA20	1.7	1.9
APMEA50	4.9	4.2
13X	0	-
13XMEA50	4.1	3.9



**Figure 2.** Maximum concentration of organic compounds released from solid surface during FID analysis at 30 °C (left) and 50 °C (right)

**Slika 2.** Maksimalna koncentracija organskih komponenti otpuštenih s čvrste površine za vrijeme FID analize pri 30 °C (lijevo) i 50 °C (desno)

Where as the carbon-based adsorbents, which were just air-dried, showed a massive release of organic compounds especially at 50 °C, molecular sieve 13X with MEA released a maximum of only 6.5 ml/m<sup>3</sup> organic compounds at 30 °C and 9.2 ml/m<sup>3</sup> at 50 °C. Maximum concentration of released organic compounds was lowest in case of APMEA50 sample (88 ml/m<sup>3</sup> at 50 °C, 34 ml/m<sup>3</sup> at 30 °C), considering only carbon-based samples. In comparison, untreated adsorbent AP4-50 released only 2.4 ml/m<sup>3</sup> at 30 °C.

## CONCLUSION

As a conclusion, we may see that the maximum concentration of organic compounds depends on the amount of methanol present in samples. The amount of fixed nitrogen, which was in accordance with MEA concentration of impregnating solution, did not change significantly after FID analysis. Yet, the difference increased with an increasing amount of nitrogen in samples after impregnation. Considering the prepared samples, the best adsorption

capacity and good amine stability was found in 13XMEA50 sample.

These experiments were carried out to assess the characteristics of adsorbents prepared by impregnation, considering impregnation method, maximum adsorption capacity and impregnating agent stability at elevated temperature. The testing will continue and will be further extended by focusing on modification of the impregnation method, dynamic adsorption tests and regeneration capability.

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