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IMPACT OF THE HEAT CAPACITY OF ADSORBED PHASE ON PROCESS PERFORMANCE IN THE CAPTURE OF CO_2 FROM FLUE GAS USING PRESSURE SWING ADSORPTION

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The present study aims at demonstrating how important it is to include the substantial increase in CO_2 heat capacity around the critical temperature in the modelling of relevant PSA separations. It is shown that this parameter may considerably alter simulation results, especially in the cases when the adsorbed phase concentration is high, regeneration pressure is moderate and CO_2 content in the enriched stream is large.
Keywords: carbon dioxide abatement, flue gas, pressure swing adsorption, specific heat of adsorbed phase, critical temperature

Celem tej pracy jest zwrócenie uwagi na konieczność uwzględniania bardzo dużego wzrostu ciepła właściwego zaadsorbowanego ditlenku węgla w pobliżu temperatury krytycznej przy modelowaniu procesów wydzielania CO_2 ze spalin metodą adsorpcji zmiennociśnieniowej. Wykazano, że przyjmowana w obliczeniach symulacyjnych takich procesów wartość ciepła właściwego fazy zaadsorbowanej wpływa znacząco na wyniki symulacji w sytuacji, gdy na złożu utrzymuje się duże stężenie ditlenku węgla, stosowane są umiarkowane ciśnienia regeneracji oraz otrzymuje się duże stężenie CO_2 w gazie wzbogaconym.
Słowa kluczowe: ograniczanie emisji ditlenku węgla, spaliny, adsorpcja zmiennociśnieniowa, ciepło właściwe fazy zaadsorbowanej, temperatura krytyczna

1. INTRODUCTION

Any process design and optimisation should be based on sufficiently rigorous quantitative models. In developing such models we usually have to introduce certain simplifying assumptions and approximations that may have some effect upon the results and thus lead to deviations from the target product parameters or optimum

operating conditions. Commercial numerical simulators (e.g. ASPEN, gPROMS, MATLAB) provide useful tools in formulating mathematical description of a process under a range of conditions, as well as in its optimisation. However, the practical value of a given simulation package (i.e. model and simulator) depends on the extent to which it has been validated experimentally. Only such validation can safeguard the necessary accuracy of the package.

In the available literature a number of studies are presented concerning the removal of CO_2 from flue gas using various techniques (e.g. absorption, adsorption, membrane separation, or combinations of the individual methods). Whereas absorptive techniques are mature and extensively tested, the models for adsorptive and membrane separations of CO_2 from gas streams are still insufficiently verified. The majority of studies on post-combustion capture are either purely theoretical or predominantly experimental [1]. However, unwarranted simplifications may seriously distort both quantitative and qualitative conclusions. A case in point is the modelling of CO_2 capture from flue gas at temperatures around the critical value for CO_2 (304.13K). Large heat effects associated with CO_2 adsorption/desorption on a number of carbonaceous and zeolite materials, combined with the inherently cyclic nature of PSA processes lead to both bed and adsorbed phase temperatures oscillating around the critical value. This affects physicochemical parameters of the adsorbed phase and, especially, its heat capacity. The aim of the present paper is, therefore, to underline the importance of a considerable increase in the heat capacity of the adsorbed carbon dioxide in the vicinity of its critical temperature, and the impact of this increase on the modelling of the PSA separation of CO_2 from flue gas.

2. EFFECT OF ADSORBATE HEAT CAPACITY ON THE PARAMETERS OF ENRICHED GAS STREAMS

In theoretical analyses of PSA (or its special case – VSA, vacuum swing adsorption) separation of CO_2 from nitrogen/air mixtures it is usually assumed that the adsorbed phase heat capacity falls in the range $0 – 4$ J g^{-1} K^{-1} [2-7]. Numerical results were generally in good agreement with experimental data concerning CO_2 concentration in both enriched and purified gas streams, as well as regarding CO_2 recovery (e.g. Krishnamurthy et al. [5], Tanczyk et al. [7]). Krishnamurthy et al. [5] (who assumed a value of 0.7 J g^{-1} K^{-1} as the adsorbed phase heat capacity) note, however, a peculiarity appearing once the cyclic steady state has been attained: both the amplitude and average values of the temperatures calculated for the bottom and top of the bed were considerably higher than those measured experimentally. They suggest that this peculiarity "most likely arises from not fully capturing the dynamics of rapid pressurization from low vacuum pressure to atmospheric pressure at the entrance of the bed". A mathematical model and numerical simulator, which were successfully employed in the quantitative description of CO_2 separation in a two-column PSA installation (Tanczyk et al. [7]; adsorbate heat capacity = 0) failed

completely in the case of a four-column VSA system (Warmuzinski et al. [8]; heat capacity $= 0 - 4$ J g^{-1} K^{-1}). The latter case is illustrated in Fig. 1 which shows CO_2 content in the enriched stream. The experimental points, represented by solid diamonds, correspond to Cases $1 - 3$ in Warmuzinski et al.'s [8] study and deviate considerably from the values predicted using the model developed by Tanczyk et al. [7] for the heat capacity of the adsorbed phase ranging between 0 and 4 J g^{-1} K^{-1}. However, when the heat capacity is raised to a value of 60 J g^{-1} K^{-1}, the agreement becomes much better. The increase in the heat capacity was justified by the fact that all the other key physical and process parameters were carefully tested and verified using various approaches. Moreover, this increase simultaneously improved the agreement between the experimental and predicted temperatures (concerning both their absolute values along the bed and the amplitudes of temperature variation).
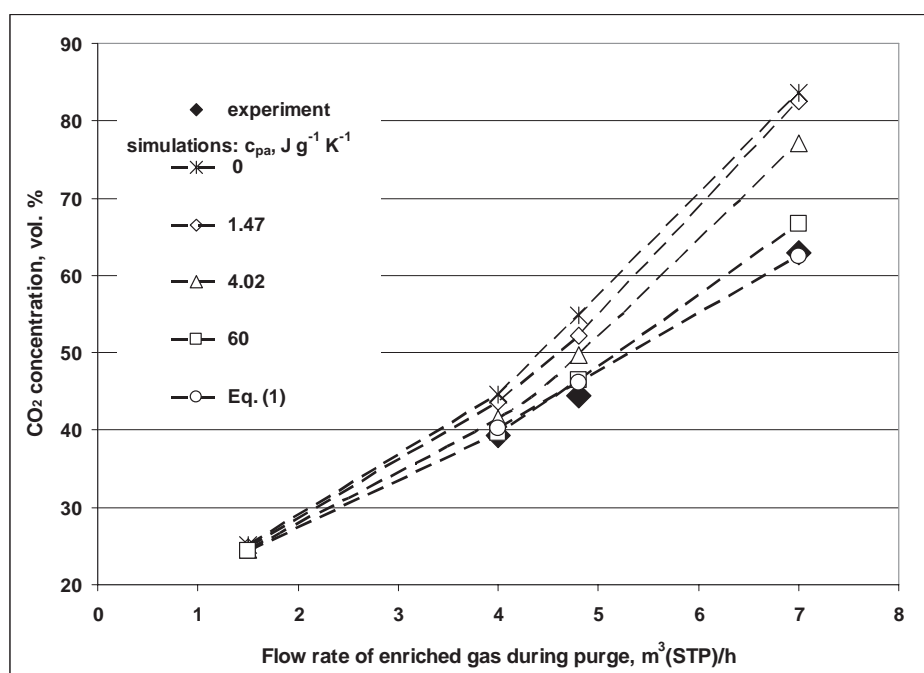

Fig. 1. CO_2 concentration in the enriched gas as a function of the enriched stream flow rate during purge (experiment: Cases 1-3, Warmuzinski et al. [8])
Rys. 1. Stężenie CO_2 w gazie wzbogaconym w zależności od natężenia przepływu gazu wzbogaconego w kroku płukania (eksperymenty: przypadki 1-3, Warmuzinski i in. [8])

This can be seen in Figs. 2 and 3 which show the temperature variation in subsequent VSA cycles at distances of 0.1 and 1.4 m from the bed inlet. It may be noted that, for a low value of the heat capacity (4.02 J g^{-1} K^{-1}), the calculated temperature front appears at the bed outlet, contrary to the experimental data (Fig.3). Another important characteristic can be seen in Fig. 1: the differences between the measured values and those predicted using the model tend to disappear with

a decrease in the inlet flow rate of the enriched gas during purge, irrespective of the value assumed for the heat capacity of the adsorbed phase. This is due to a decrease in the portion of the bed saturated with CO_2-rich gas, and thus, a much weaker effect of the adsorbate heat capacity upon the overall heat capacity of the system. The phenomenon observed would also explain why the simulation tool that yielded quite accurate results for the system with a low degree of CO_2 enrichment [7], failed in the case when more concentrated streams of CO_2 were obtained [8].
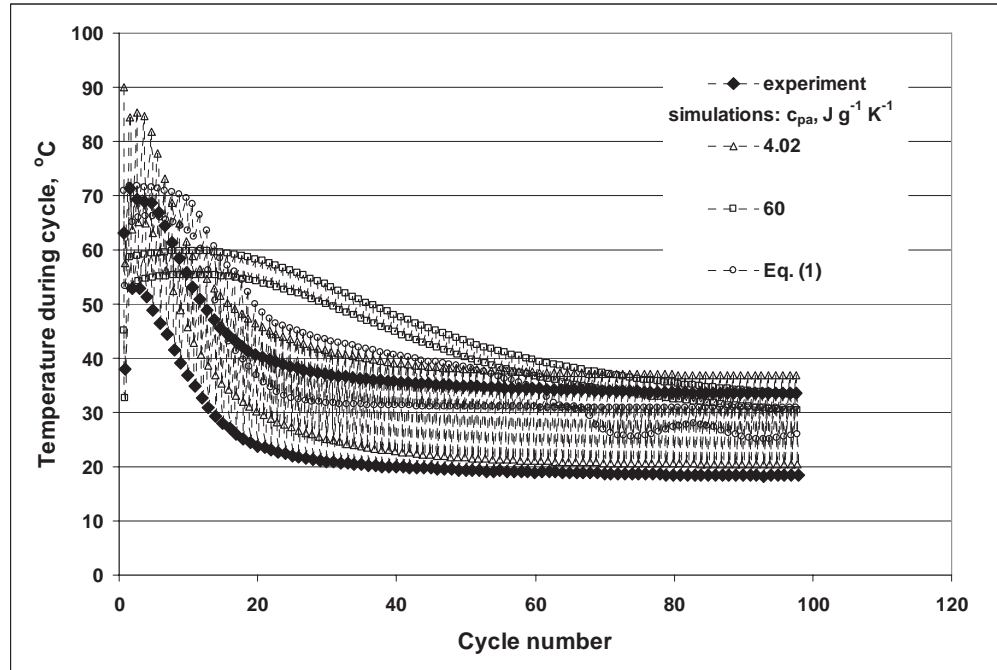

Fig. 2. Temperature variation over VSA cycles at a distance of 0.1 m from the bed inlet (experiment: Case 4, Warmuzinski et al. [8])

Rys.2. Zmiany temperatury w cyklu VSA w odległości 0,1 m od początku złoża (eksperyment: przypadek 4, Warmuzinski et al. [8])

Fig. 4 shows the dependence of CO_2 concentration in the enriched stream upon the regeneration pressure. Again, the agreement between simulations and experiment (Case 4, Warmuzinski et al. [8]) becomes satisfactory only after the value of the heat capacity of the adsorbed phase has been raised to 60 J g^{-1} K^{-1}. It may also be noted that a decrease in the regeneration pressure leads to a better agreement between the values calculated for the different heat capacities. The lower regeneration pressure results in a decreased CO_2 concentration in the adsorbed phase, and thus, limits the effect of the adsorbate heat capacity on the overall heat capacity of the system. It is worth noting that the regeneration pressure reported by Krishnamurthy et al. [5] (0.009 – 0.025 bar) was notably lower than that employed by Warmuzinski et al. [8] (0.151 – 0.198 bar). This was probably one of the reasons why Krishnamurthy et al. [5] obtained a good agreement between their predictions and the experimental results

concerning CO_2 concentration and recovery, despite using a similar numerical tool and a low value of the heat capacity.
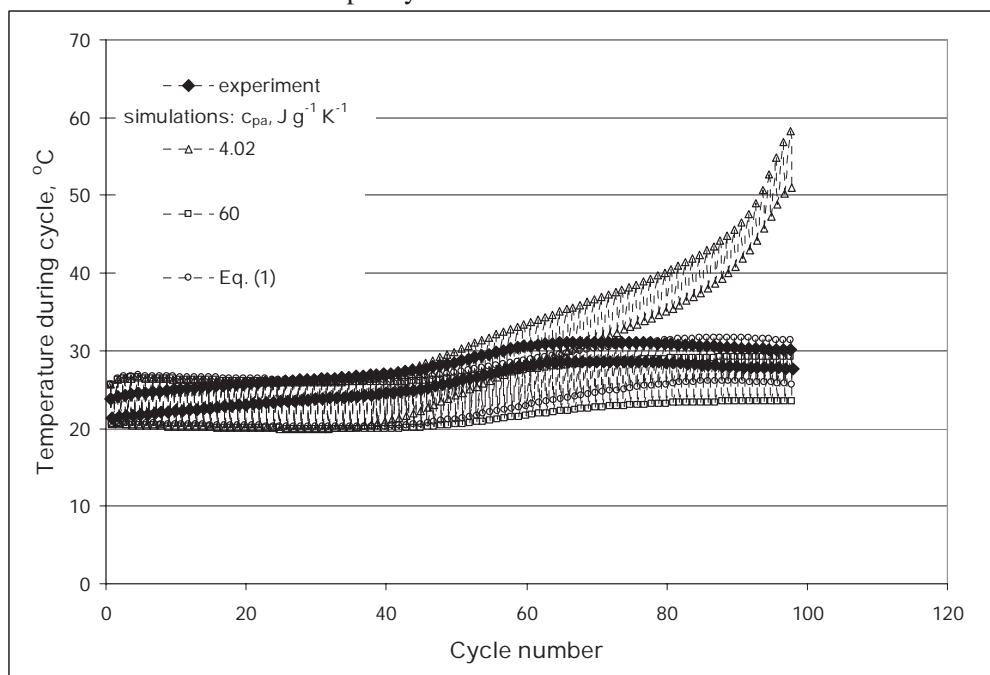

Fig. 3. Temperature variation over VSA cycles at a distance of 1.4 m from the bed inlet (experiment: Case 4, Warmuzinski et al. [8])

Rys.3. Zmiany temperatury w cyklu VSA w odległości 1,4 m od początku złoża (eksperyment: przypadek 4, Warmuzinski et al. [8])

It remains to be demonstrated, however, that the use of increased heat capacities for the adsorbed phase has a sound physical justification. One such reason may be the strong, nonlinear rise in c_p for fluids around critical temperatures. For CO_2 at 304 K the isobaric heat capacity may reach 386.9 J g^{-1} K^{-1} (saturated liquid) or 555.6 J g^{-1} K^{-1} (saturated dry vapour) [9]. In the case of the adsorbed phase a similar phenomenon was observed by Rahman et al. [10] who derive a thermodynamic relation to predict the heat capacity and then use it to model the behaviour of the system methane – activated carbons. This relation has, however, to be further verified [11] and cannot be directly extended onto CO_2 – ZMS 13X systems. It may be concluded from the study of Rahman et al. [10] that at temperatures below the critical temperature the heat capacity of the adsorbed phase virtually coincides with the values for the saturated liquid. The assumption that the adsorbed phase may, under such conditions, be treated as a saturated liquid is also suggested by, among others, Critoph [12]. Moreover, the cyclic nature of PSA processes that are based on rapidly alternating steps of adsorption and desorption leads to concomitant phase changes of the adsorbate. We may thus infer that at temperatures below the critical temperature the

physical properties of the adsorbed CO_2 are close to those of the liquid CO_2 on the liquid-vapour saturation line.
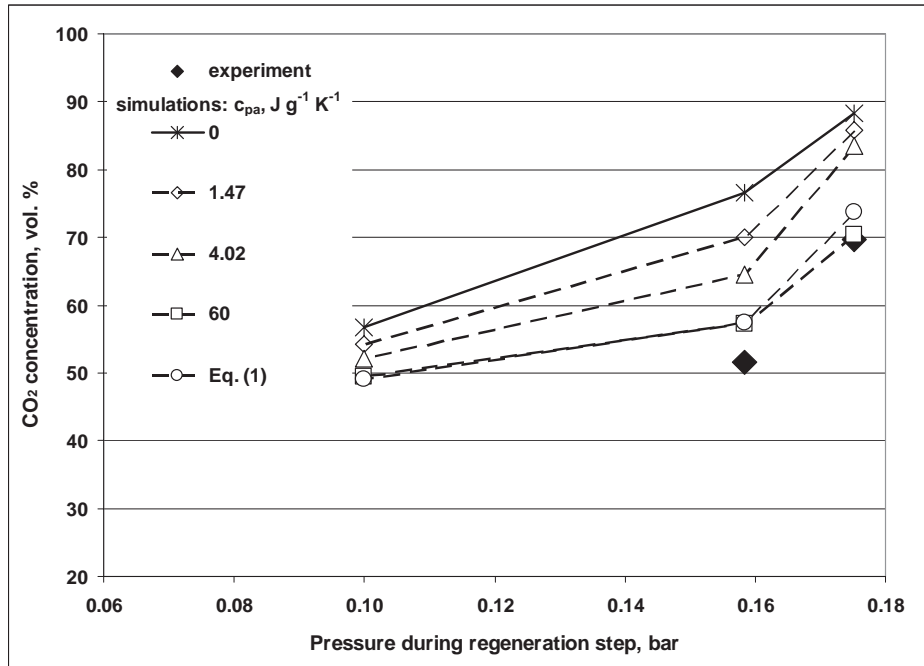

Fig. 4. CO_2 concentration in the enriched gas as a function of the regeneration pressure (experiment: Case 4, Warmuzinski et al. [8])

Rys. 4. Stężenie CO_2 w gazie wzbogaconym w zależności od ciśnienia regeneracji (eksperyment: przypadek 4, Warmuzinski i in. [8])

Therefore, for the cases shown in Figs. 1-4 simulations were done using heat capacities of the adsorbed phase (c_{pa}) calculated from the equation proposed by Grønvold [13], with the relevant coefficients evaluated based on the study of Span and Wagner [9]:

$$c_{pa} = \frac{367.17}{0.125} \cdot \left(\left(\frac{|T - T_C|}{T_C} \right)^{-0.125} - 1 \right) \left(1 + 14.01 \cdot \left(\frac{|T - T_C|}{T_C} \right)^{0.38} \right) - 7968.6 + 12951.4 \cdot \left(\frac{|T - T_C|}{T_C} \right) \quad (1)$$

where T and T_c denote, respectively, the actual temperature and the critical temperature. In the analysis, the concentrations of nitrogen and oxygen in the adsorbed phase were neglected as negligibly low compared with that of carbon dioxide. As may be seen from Figs. 1 and 4, the concentrations of CO_2 in the enriched gas stream essentially coincide with the results obtained using a constant value of 60 J g^{-1} K^{-1} for the adsorbed phase heat capacity. However, the use of Eq. (1) leads to

even further improvement, both qualitative and quantitative, in temperature profiles relative to the measured values (Figs.2,3).

3. CONCLUSIONS

In the present paper several clues were highlighted, that suggest a substantial increase, under certain conditions, in the heat capacity of the adsorbed CO_2. These include much lower experimental temperature amplitudes compared with simulations and a sharp rise in the heat capacity around critical temperatures for both fluids in general (among others, CO_2) and adsorbed phases (e.g. CH_4 – see Rahman et al. [10]). It was concluded that the commonly assumed values of the heat capacity of the adsorbed phase may seriously affect the results predicted for the removal of CO_2 from flue gas via pressure swing adsorption under such circumstances as elevated CO_2 concentrations over the adsorbent (as is the case when zeolite adsorbents are used), moderate regeneration pressures and high CO_2 content in the enriched stream. It was also shown that, even if the model itself is firmly based on a sound physical representation of the process, unrealistic values of this single parameter may, under certain circumstances, jeopardize the quality of the conclusions thus obtained. Consequently, the numerical optimization of the process (leading to the maximization of CO_2 recovery and concentration in the enriched stream and/or to lowering the energy demand by increasing the regeneration pressure) may yield unreliable or confusing results.

SYMBOLS - OZNACZENIA

c_{pa} –   heat capacity of adsorbed phase, J g^{-1} K^{-1}
            ciepło właściwe fazy zaadsorbowanej

T –   temperature, K
            temperatura

T_C –   critical temperature, K
            temperatura krytyczna

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WPŁYW CIEPŁA WŁAŚCIWEGO FAZY ZAADSORBOWANEJ NA PROCES WYDZIELANIA CO_2 ZE SPALIN METODĄ ADSORPCJI ZMIENNOCIŚNIENIOWEJ

Większość publikacji dotyczących adsorpcyjnego wydzielania CO_2 po procesach spalania to prace bądź tylko teoretyczne bądź   tylko doświadczalne [1]. Tymczasem zastosowanie w modelowaniu pewnych założeń upraszczających może w istotny sposób wpływać na wyniki obliczeń i poprawność wysnuwanych na ich podstawie wniosków. Z taką sytuacją mamy do czynienia przy modelowaniu adsorpcyjnego procesu wydzielania ditlenku węgla ze spalin w zakresie temperatur bliskich temperaturze krytycznej CO_2 (304,13 K). Duże efekty termiczne towarzyszące adsorpcji/desorpcji CO_2 na wielu adsorbentach węglowych i zeolitowych oraz cykliczność procesu adsorpcji zmiennociśnieniowej (PSA) prowadzą do tego, że temperatura złoża i fazy zaadsorbowanej stale przekracza granicę wyznaczaną przez temperaturę krytyczną. Ma to wpływ na właściwości fizyczne fazy zaadsorbowanej, a w szczególności na jej ciepło właściwe, które w pobliżu temperatury krytycznej podlega istotnym zmianom.

W publikacjach dotyczących teoretycznej analizy procesu zatężania CO_2 w mieszaninach z tlenem i powietrzem metodą adsorpcji zmiennociśnieniowej w bilansie cieplnym układu gaz/adsorbent/adsorbat przyjmuje się zazwyczaj wartości ciepła właściwego fazy zaadsorbowanej z zakresu 0–4 $J\ g^{-1}\ K^{-1}$ [3-7]. Tam, gdzie możliwa jest eksperymentalna weryfikacja modelu obserwowane są w pewnych przypadkach rozbieżności między wynikami doświadczeń i obliczeń. I tak na przykład w pracy Krishnamurthy'ego

i in. [5] (ciepło właściwe fazy zaadsorbowanej: 0,7 J g^{-1} K^{-1}) stwierdzono, że po osiągnięciu cyklicznego stanu ustalonego obliczeniowa amplituda i średnie wartości temperatury na początku i końcu złoża były w kolejnych cyklach znacząco wyższe niż wartości eksperymentalne. Z kolei model matematyczny i symulator numeryczny, które z powodzeniem zastosowano do opisu wydzielania CO_2 w dwukolumnowej instalacji PSA ([7], ciepło właściwe adsorbatu: 0 J g^{-1} K^{-1}) zupełnie zawodziły w przypadku opisu pracy czterokolumnowej instalacji VSA ([8], 2015, ciepło właściwe adsorbatu: 0–4 J g^{-1} K^{-1}), rys. 1-4.

Według Spana i Wagnera [9] w najbliższym otoczeniu temperatury krytycznej ma miejsce radykalny, silnie nieliniowy wzrost wartości izobarycznego ciepła właściwego płynów, sięgającego w przypadku CO_2 w temperaturze 304 K pułapu 386,9 J g^{-1} K^{-1} (ciecz nasycona). Zależność tę można opisać równaniem (1), którego ogólna postać została zaproponowana przez Grønvolda [13]. Jej zastosowanie prowadzi do znaczącej jakościowej oraz ilościowej poprawy obliczeniowego przebiegu zmian parametrów procesu w stosunku do wartości zmierzonych (rys. 1-4).

W pracy wykazano, że przyjmowana w obliczeniach wartość ciepła właściwego fazy zaadsorbowanej wpływa znacząco na wyniki symulacji procesu zatężania CO_2 w strumieniu spalin metodą adsorpcji zmiennociśnieniowej w sytuacji, gdy na złożu utrzymuje się duże stężenie ditlenku węgla, stosowane są umiarkowane ciśnienia regeneracji oraz otrzymuje się duże stężenia CO_2 w gazie wzbogaconym.