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METHOD OF EFFECTIVE USE OF METHANE AND NITROGEN SEPARATED FROM NATURAL GASES

METODY EFEKTYWNEGO WYKORZYSTANIA METANU I AZOTU Z NATURALNYCH GAZÓW

A mature concept of separation of natural gases, which usually contain methane and nitrogen, is the presented in the paper. As a result of ion-exchange with metal cations: Na, K, Mg followed by high-temperature roasting, clinoptilolite becomes a zeolite molecular sieve, that has kinetic diameter of 3.7 Å. As a result high-methane gas can be obtained 95 vol% methane, that can be directly sent to the gas network. The methane recovery exceeds 95%, whereas the outlet methane in nitrided gas losses are below 3 vol%. An idea was put forward to use the obtained nitrogen in enhanced oil recovery technology.

Keywords: natural gas separation, methane, nitrogen, clinoptilolite

W zaazotowanych złożach gazu ziemnego występują też takie, w których zawartość azotu nie przekracza 35% vol. Zatem przeważa w nich metan, który jednak nie może być wykorzystany jako gaz opałowy (handlowy), a tym bardziej jako gaz przesyłowy do sieci. Podniesienie koncentracji metanu w tych zaazotowanych gazach staje się możliwe wskutek opracowania odpowiednio efektywnej metody odseparowania metanu z mieszaniny gazów.

W artykule prezentowana jest dojrzała koncepcja takiej technologii, która umożliwia zarówno wykorzystanie metanu, jaki i azotu pochodzących z odwiertów zaazotowanego gazu. Bazowym materiałem używanym w tej technologii jest klinoptylolit jako glinokrzemian wydobywany ze złóż naturalnych np. na Słowacji. Z materiału tego wskutek dokonania wymiany jonowej kationów metali: Na, K, Mg oraz wysokotemperaturowego spiekania, można wytworzyć specyficzne zeolitowe sito molekularne (ZMS). Cechuje się ono bardzo korzystną właściwością, a mianowicie wysoką kinetyczną selektywnością rozdziału mieszaniny gazów.

Sito to dobrze adsorbuje azot, a wydajnie przepuszcza metan wraz z wyższymi węglowodorami, których molekuły mają średnicę większą od 3,7 angstrema. Proponuje się wykonanie na takim adsorberze względnie prostych cykli operacji próżniowej zmiennociśnieniowej adsorpcji (VPSA). Są to przede wszystkim operacje: wysokociśnieniowej adsorpcji, dwustopniowej desorpcji oraz wyrównywania ciśnień między adsorberami. Są one poprzedzone wykonaniem oczyszczania i przygotowania mieszaniny gazów we wstępnym segmencie instalacji. Taka kilkuadsorberowa instalacja VPSA jest korzystnie jednomodułowa. Może ona przerabiać od 1 tys. m^3 na godzinę do 10 tys. m^3 na godzinę gazu zaazotowanego (o zawartości azotu mniejszej od 35% vol).

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Produkt tej instalacji będzie się cechował dobrymi parametrami. Mianowicie będzie to gaz wysoko-metanowy o zawartości powyżej 95% vol CH$_4$ pod wysokim ciśnieniem. Natomiast strata metanu w azocie (jako w gazie inertnym) będzie mała, bo niższa od 3% vol CH$_4$. Produkt o takim stopniu czystości może być podawany bezpośrednio do sieci gazu. Ponadto sprawność uzysku metanu w tej instalacji będzie wyższa od 90%.

Przedstawione okoliczności będą pozytywnie oddziaływać na aspekt ekonomiczny praktycznego zastosowania prezentowanej koncepcji. Co więcej w sytuacji, gdy taka instalacja będzie posadowiona na złożu ropno – gazowym o obniżającym się już wydobyciu ropy, może być wykorzystany również azot pochodzący z tej instalacji. Zaproponowano zatłaczanie tego azotu z powrotem do złoża celem wspomagania wydobycia ropy w technologii EOR.

Słowa kluczowe: separacja gazu naturalnego, metan, azot, klinoptylolit

1. Introduction

One of earlier papers on the use of clinoptilolite with ion-exchange method to the separation of hydrocarbons was a patent (Chao & Rastelli, 1990). The PSA method involving clinoptilolite is useful not only for natural gases separation but also hydrogen production (Sawda et al., 2002). For removing nitrogen and carbon dioxide from methane gases, the Engelhard Corporation worked out titanium silicate molecular sieves (Mitarinen, 2004). However, the proposed use of modified natural zeolite is more advantageous economically. According to the presented concept, methane separated from the low-methane natural gas in the installation with the VPSA method can be used both as commercial fuel gas or be enriched to the high-methane gas quality. The removed nitrogen can be used for enhancing oil production in oil fields.

2. Specification of natural zeolite as zeolite molecular sieve (ZMS)

Attention was paid to clinoptilolite as natural zeolite of volcanic origin, made of alkali metals hydrated aluminasilicate (Ca, K, Na, Mg). It has an interesting crystalline structure with a free space in the form of micropores and microcanals, fraction of nanometer in size. The sorptive properties of clinoptilolite are modified by: surface adhesion, Van der Vaals forces and electromagnetic forces. The inlet diameters of microperes (microcanals) depend on the type of constituent ions, including those from the ion exchange process. Clinoptilolite favours ion exchange and has great sorption ability. Those physicochemical properties make clinoptilolite stand out among other zeolites.

The specified clinoptilolite was exported by PRO-ZEO company from the deposit Humenne, Slovakia. The natural zeolite was modified: first Na$^+$ and K$^+$ ions were exchanged with Mg^{2+} and Na$^+$ ions, then the material was roasted at 350°C. Over 75% Na$^+$ and K$^+$ ions were exchanged in equal gram-atom quantities to Mg^{2+} and Na$^+$ ions. The Mg^{2+} and Na$^+$ ions were located in proper places in the crystalline structure as a result of which molecular gates were formed in that micro-porous (microcanal) structure, 3.7 Å in size. The diameter of the molecules was the following: 3.6 Å for nitrogen, 3.4 Å for carbon dioxide. Hydrogen sulfide and water also have diameters lower than 3.7 Å, unlike methane and higher hydrocarbons which have 3.8 Å. Thus modified clinoptilolite reveals adsorption selectivity of N$_2$, CO$_2$, H$_2$S and H$_2$O against methane.

The increased sorption capacity was obtained by using higher purity clinoptilolite with almost zero montmorillonite content.

Then, sorption isotherms were experimentally investigated for modified sorbent at temperature 298 K, Fig. 1.
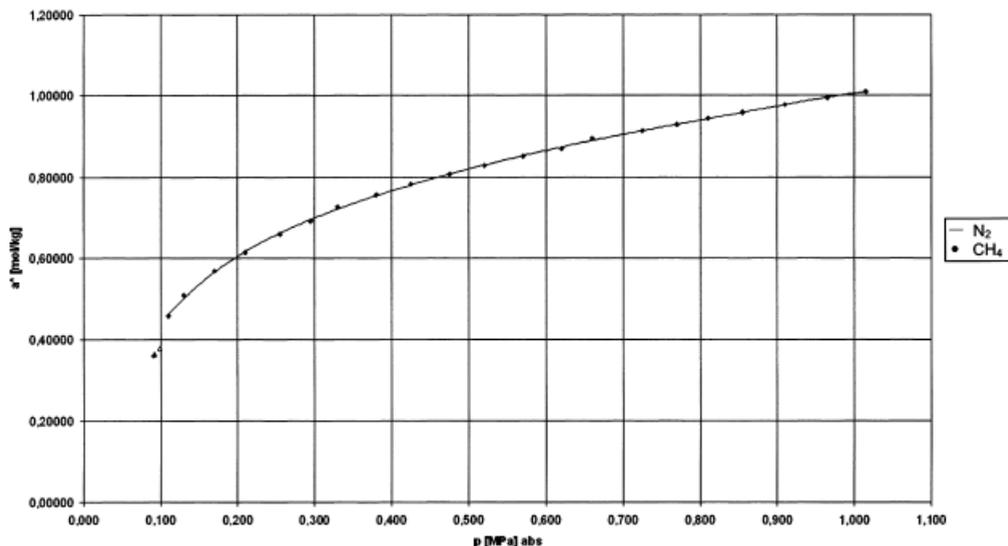

Fig. 1. Isotherm of adsorption of N_2 and CH_4 (Mg, Na – Clino) 298K

The isotherms for nitrogen turned out to be identical with methane isotherms, creating a line well described with the equation:

$$a_i = a^{\infty} \frac{bc_i}{1 + bc_i} \qquad (1)$$

where:

$$a^{\infty} = a^{\infty}_{CH_4} = a^{\infty}_{N_2} = 1.2 \; \frac{mol}{kg}$$

$$b = b_{CH_4} = b_{N_2} = 12.1 \cdot 10^{-3} \; \frac{m^3}{mol}$$

Adsorption kinetics $a = f(t)$ was also experimentally measured at temperature of 298 K and atmospheric pressure for nitrogen and methane, Fig. 2.

It can be expected that considerable differences between courses of those plots also appear at higher pressures. For this reason, two results following from the interpretation of Fig. 2 should be confronted. After 90 seconds the adsorption capacity of nitrogen reaches 0.28 mol/kg, being 70% the balance adsorption capacity. After the same time, the adsorption capacity of methane
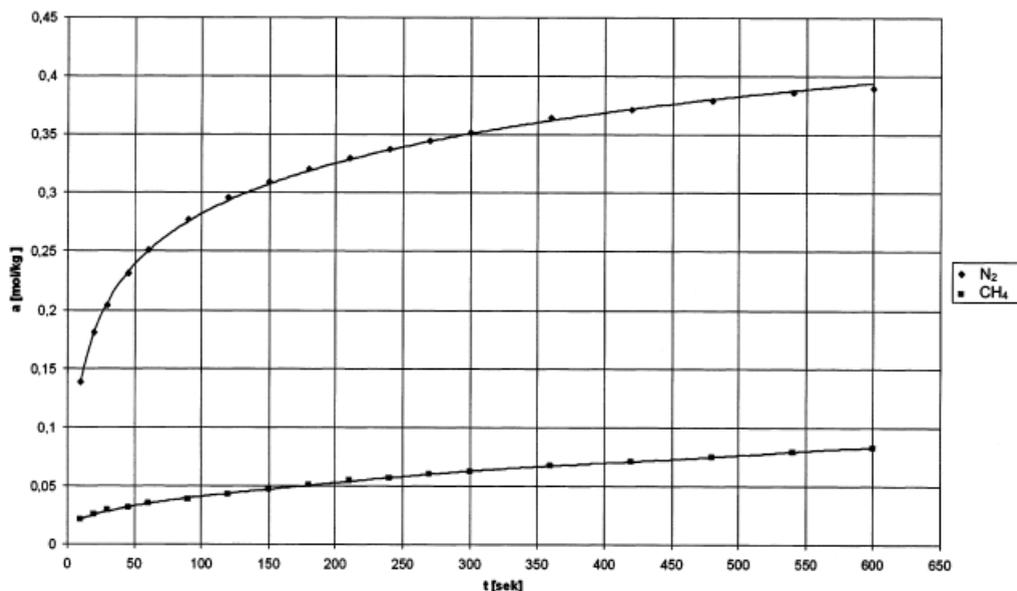
Fig. 2. Kinetics of adsorption of methane and nitrogen (Mg, Na – Clino) 298K

reaches 0.04 mol/kg, being less than 10% the balance adsorption capacity. This signifies that nitrogen is adsorbed in that modified adsorbent much faster than methane; the latter easily penetrates the sorbent deposit. This was also confirmed by further analysis of adsorption kinetics of nitrogen and methane.

Here the point is to describe the kinetics with slightly different kinetics equations than those presented in literature so far, i.e.:

$$\frac{da_i}{dt} = k_i \left[bc_i \left(a^\infty - a_i \right) - \left(a_{N_2} + a_{CH_4} \right) \right] \tag{2}$$

Then the LDF procedure of vacuum swing adsorption theory was used (Ruthven et al., 1993), where the values of transport coefficient k_i of two components of the nitrogen-and-methane mixture were determined on the basis of experimental data. As a result of the estimation, the following values of those coefficients were obtained:

$$k_{N_2} = 1.2 \cdot 10^{-2} \, s^{-1} \qquad k_{CH_4} = 2.7 \cdot 10^{-4} \, s^{-1}$$

and the following value of kinetic selectivity of nitrogen vs. methane: K = 44.4.

3. The model and computer software

The assumed mathematical model of natural gases separation with the VPSA method referred to the nitrogen-methane system. The natural gases mixture was expected to reach such a bi-

component state. In the case of very high sulfur content in high-nitrogen gas, hydrogen sulfide should be removed with unconventional methods, e.g. Claus method, before the entry to the gas separation installation. Otherwise, when the hydrogen sulfide content was low and resembled that of carbon dioxide, those gases could be removed with nitrogen in the VPSA installation.

Without going into detail, the most important model equations were (1) and (2) as well as transport equation of i-*th* component ($i = 1, 2$) and mass balance equation. Moreover, there were also some equations needed for determining coefficients of the model.

The adsorbed bed was divided into N elements of the same volume. The number of time intervals was calculated separately for each process VPSA operation, under equal residence time for unit volumes of gas in unit volumes of the bed. The parameters of unit volume of bed were calculated for the defined initial and boundary conditions, and for a given unit volume of the bed in a given time interval. The equation system was solved by the finite difference method and the iterative calculations method.

The results of solutions obtained in that numerical model enabled one to work out a scheme of the flux of gas streams in specific operations of gas separation process. Therefore, the numeric simulation was indicative of the way in which the VPSA method should be realized in the installation where nitrogen other components was separated from methane or methane and higher hydrocarbons.

4. Methods of natural gases preliminary washing and drying

This paper is devoted to nitrided natural gases to 35% vol% N_2, mainly composed of methane and possibly higher hydrocarbons, but which can have hydrogen sulfide and carbon dioxide in their composition. The ceasure of 35 vol% N_2 content results from the tendency to avoid excessive development of multi module installations based on VPSA method, and so the increased capital costs. Natural gas may contain condensates, in that light gasoline (C_3, C_4), the separation of which is economically justified. It is necessary to dry the natural gas deeply of H_2O and make sure there is no mercury in it. The mixture of gases directed to the VPSA module should have properties of the N_2-CH_4 system; it may contain CO_2 and small quantities of H_2S as well as higher hydrocarbons (in gaseous phase).

In the section preceding the entry to the VPSA, the module gas is dehydrated in separators and cleaned of solid particles on filters. Neither traditional drying with the glycol nor alcoa method will be used here. Instead the vortex method for gas drying is proposed. It can be simultaneously used for gasoline separation. This method is a reasonable alternative of gas decompression process in the de Laval nozzle.

The vortex device makes use of the separation effect of gas particles, which differ in temperature, i.e. kinetic energy in the whirl motion. Two whirls can be formed in the vortex pipe: an outer, warm whirl passing towards the warm end of the pipe, and the inner, cold one transporting particles to the cold end of the pipe. Prior to this, the condensate $CH_3OH + H_2O$ and gasoline condensate NGL are separated from gas running to the vortex at temperature –25°C. Once having passed through the vortex, the gas is collected at the cold end (-55°C) and directed to another separator, where light gasoline (C_3, C_4) is separated. Afterwards, the obtained condensate is stabilized.

Such devices as vortex enable deep drying and simultaneous separation of condensates from natural gases. Ready solutions for this type of technology are offered by, e.g. UVI Vortex Inc., RWE Germany, Tractebel.

5. Concept of nitrogen and methane separation and use

The VPSA method of separating natural gas is technically and economically justified for gas quantities to 10,000 m^3/h (in standard pressure and temperature conditions), especially when nitrogen content does not exceed 35 vol% N_2. Then, apart from a preliminary section plus 4 to 7 adsorbers filled mainly with modified clinoptilolite, the one-module VPSA installation can be composed of ceramic granulate and alcoa. The VPSA module is fed with dried and degasolined (if needed) gas at the wellhead pressure. The following technological operations are realized on each adsorber with the use of a programmed controller:

- Adsorption (A): nitrogen is withheld in the sorbent deposit, whereas methane, which adsorbs to a minimum degree, passes through the deposit;
- Lowering (E↓) of pressure after adsorption, and increasing (E↑) of pressure: for making pressure between adsorbers equal;
- Concurrent desorption (BD): pressure is lowered to a higher value than atmospheric pressure;
- Vacuum desorption (D) at lowest possible pressure;
- Gas filling (RR).

Those operations can be performed at temperature of 293 K.
The scheme of separation processes is given in Table 1.

TABLE 1

Scheme of separation processes
Symbols of technological operations are described in the text

1	A	E↓	BD	D	E↑	RR
2	RR	A	E↓	BD	D	E↑
3	E↑	RR	A	E↓	BD	D
4	D	E↑	RR	A	E↓	BD
5	BD	D	E↑	RR	A	E↓
6	E↓	BD	D	E↑	RR	A

Those operations create a sequence of a short 90-sec-period cycle. Attempts should be made to minimize the losses of methane enclosed in nitrided gas after vacuum desorption operation (D). This has an influence on the quality of high-methane gas and efficiency of methane recovery in the installation. Moreover, for technological reasons, methane contained in gas after desorption operation (BD) should be utilized.

Accordingly, the following variants of operation in the VPSA module are possible:

Variant I. The lean-methane gas containing, e.g. about 50 vol% CH_4 is exploited from production wells in an area having industrial (fuel) gas demand. In that situation 1/4th input gas going to the VPSA module can be directed to desorption operation (BD), where the methane content is increased to the level of industrial (fuel) gas. Simulations realized in this approach reveal that 95.5 vol% methane content and 91% methane recovery efficiency can be reached in that variant. The cost of investment in this approach is lower than in the following and other variants.

Variant II. Moderate methane content gas is produced from the wells. However, despite the closeness of a high-methane gas network in the neighbourhood, the CH_4 content is too low in the gas to make it fit for direct pipeline transport. Therefore, after the desorption stage (BD) 75% CH_4 gas should be re-circulated in a quantity corresponding to the $1/5^{th}$ input gas to the VPSA module. Then the gas should be compressed to the wellhead pressure value and directed to the main entry stream. For instance, for dried entry gas containing 74% CH_4 one can obtain gas with 98% CH_4 content and 92.5% recovery efficiency (calculated for pure methane). Then the methane losses mainly caused by its low concentration in nitrided gas after desorption operation (D) shall not exceed 2 vol% CH_4. Though the percentage values are better than in the previous variant, the capital cost is higher because a compressor has to be used for gas re-circulation purposes. Still higher values can be obtained in both variants, when pressure is equalized in three stages, instead of one stage.

There is still another variant that can be considered here, though it is slightly impractical. It lies in supplying the installation with a gas engine. The motor could be fed with gas from the desorption operation (BD) and used for generating electrical energy and heat. The bidding action revealed that the cost of such a gas engine and its mounting would exceed the investment cost of the VPSA installation.

No matter which of the variants of gas separation based on the VPSA method has been selected, nitrogen from the installation has to be utilized somehow. Frequently natural gas production is realized jointly with or close to oil exploitation, the rate of which usually significantly decreases with time. In this case nitrogen can be used for enhancing oil production.

6. Use of nitrogen in some EOR operations

The secondary recovery processes in oil reservoirs may be performed using various techniques, e.g. conventional waterflooding, water alternating gas injection or double displacement process. One of the forms of enhanced oil recovery (EOR) methods is injection of lean gas into reservoir. Displacing of oil from porous medium through the fluids mixing with oil found application in the technologies of secondary oil reservoir exploitation methods (EOR). Those methods include: injection of gases like CO_2, N_2 or other natural gas. Gas injection reduces the pressure decline connected with the production of oil from the reservoir. Miscibility at the first contact occurs in the reservoir if the original reservoir fluid and injected gas are miscible. This means that all possible mixtures for initial compositions lead to forming of a single-phase system.

The most important parameters having direct influence on mixing of the reservoir fluid with nitrogen or the natural gas are: content of intermediate pseudo-components (hydrocarbons C_2-C_6, CO_2, H_2S), molecular weight of heavy fractions M_{C7+} and temperature.

Fluid displacing should always be realized as the miscible process because of low resistances caused by decreasing effective permeability as a result of changes of saturation, viscosity and surface tension between two phases.

In a number of papers, e.g. (Sanger et al., 1994) the authors state that the process of displacing of oil/condensate by nitrogen is less efficient than displacing by carbon dioxide or another gas containing fumes.

This is caused by the increase of the minimum mixing pressure in comparison with carbon dioxide, or combustion gases. Owing to its availability, the use of nitrogen for injection resulting

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in the increase of oil reservoir pressure is beneficial. Nitrogen from the VPSA installation may be used for this purpose.

The CO_2 injection may be used in a future EOR sequestration project. At the first stage CO_2 can injected, then classical nitrogen injection may be considered (Nagy & Olajossy, 2007, 2008, 2010).

7. Summary

The use of methane retrieved from moderate high-nitrogen natural gases is presented in the paper. Nitrogen removed from the VPSA installation can be also utilized. According to the presented concept the separation of nitrogen from methane first takes place in adsorbers mainly filled with modified clinoptilolite as natural molecular sieve. The coefficient of N_2 selectivity from methane is so high that the successive cyclic operations in the VPSA method are efficient enough to produce a gas having lower-parameters, which corresponds to industrial (fuel) or to produce high-methane gas, which can be directed to the gas network at high pressure. In this case no expensive gas compressor has to be involved for pumping the gas. It is advantageous if the VPSA installation is located close to the oil wells with dropping production rate. Then the nitrogen from the installation can be injected to the deposit to enhance the oil production (EOR technology), in line with respective procedure.

8. Acknowledgements

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