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GRANULAR SORBENTS FROM HALLOYSITIC BASALT WEATHERING PRODUCTS (LOWER SILESIA) FOR REFINING OF PETROLEUM PRODUCTS

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Abstract: The porous structure, acidic and magnetic properties of granular sorbents produced from natural aluminosilicates have been investigated. The adsorption capacity of sorbents in a process of transformer's oil refining (percolation method) was compared revealing an effective performance of a sorbent with magnetic domains. Granular sorbents with magnetic domains and with a value of saturation magnetization 1.7 - 2.3 ($\sigma \cdot 10^{-7}$ Tm^3/kg, determined using the Faraday's method in 293 K) were prepared from halloysitic basalt weathering products, containing approx. 20 % of iron compounds. The produced halloysite sorbents, with a size of grains ranging 0.5 - 1.5 mm, possessed high mechanical strength and reveal adsorption properties which make them suitable for application in the refining percolation process of products of petrochemical or carbochemical origin.

Key words: granular sorbent, halloysitic basalt weathering products, refining of mineral oil.

Introduction

Producing sorbents from natural aluminosilicates constitutes an important field of application of clay minerals. Their diversity of composition, chemical structure and methods of processing create a possibility of producing a wide range of sorbents necessary for general application in adsorption processes.

In the refining-petrochemical industry sorbents obtained from natural aluminosilicates are used for purification of light petroleum products, lubricants, special purpose oils and paraffins. These refining treatments are described by Speight (1991) as clay processes. Depending on the type of petroleum products and the refining method (clay contacting or percolation method) powdery or granular sorbents are used. These are produced from various minerals and from clay minerals in particular.

Applied methods of production of mineral sorbents, i.e. the chemical or thermal activation of clay minerals, are aimed at removing water, exchanging ions of alkaline metals as well as aluminium and iron with H^+ or OH^- ions, and spreading of the porous structures of sorbents.

Powdery sorbents, described as "bleaching earths", are used in the clay contacting process.

Granular sorbents for the percolation method are produced by moulding activated powdery aluminosilicate materials. By applying a suitable forming method sorbents with the required grain size and mechanical strength are prepared.

In the percolation process it is possible to use mineral sorbents as thermally or chemically activated fine-grained fractions of some mineral raw materials (e.g. attapulgus clay products, bauxite).

The efficiency of granular mineral sorbents in the refining processes results from a multifunctional character of their surface, which is influenced by both the composition of the mineral material and the preparation methods.

Experimental

Principle

The experiments were carried out to determine the typical features of the surface of granular sorbents prepared from natural aluminosilicates (presented in Tab. 1), and to determine their influence on the adsorption capacity in the refining process of mineral oil. On the basis of the results mineral raw materials were selected, and a method to modify the preparation of granular sorbents for refining of oil products by the percolation method was developed.

In order to determine the adsorption capacities in the refining of mineral oils, and to compare the in-

Table 1: Chemical and mineralogical composition of clay raw materials.

Composition	Sample 1	2	3	4
SiO_2	33.65	61.68	48.60	60.70
Al_2O_3	26.20	17.67	16.29	10.71
Fe_2O_3	20.20	1.99	17.05	4.46
FeO	1.22	0.72	0.0	-
TiO_2	3.03	0.07	2.75	0.62
MgO	0.49	2.73	2.19	9.37
CaO	0.52	1.55	2.83	1.52
Na_2O	0.13	1.30	0.29	-
K_2O	0.10	2.30	0.23	0.89
H_2O^+	12.16	6.18	8.49	12.00
H_2O^-	1.78	3.74	5.10	2.20
main minerals:	halloysite	montmorillonite	beidellite	attapulgite
	hydrohalloysite	quartz	montmorillonite	
admixtures:	kaolinite Tc, D	kaolinite	nontronite	montmorillonite
	goethite	llite	goethite	sepiolite
	hematite		hematite	quartz
	magnetite		anataz	dolomite
	montmorillonite, quartz,		quartz	
	anataz			

1 - halloysitic basalt weathering product from the "Dunino" deposit (Lower Silesia, Poland)
2 - bentonitic clay from Upper Carboniferous deposit "Milowice" (Poland)
3 - smectitic basalt weathering product from deposit "Lesna" (Lower Silesia, Poland)
4 - attapulgus clay product from attapulgite deposit owned by Engelhard Minerals & Chemicals Corporation in Southern Georgia (USA) (used in the refining petrochemical industry)

fluence of typical features of sorbents' surfaces, granular sorbents from three natural aluminosilicates were prepared:

- sorbent SH - prepared by hydrothermal modification (temperatures ranging 300 - 723 K) of the 0.5 - 1.2 mm grain fraction separated from a halloysitic basalt weathering product from the "Dunino" deposit (Lower Silesia);

- sorbent SM-20 - produced by moulding of granules of the "Miltar" bleaching earth (a bentonitic clay from the "Milowice" deposit, activated with a 20 % H_2SO_4) together with 20 wt. % of a non-activated bentonitic material and subsequent disintegration of the 0.5 - 1.2 mm grain size and subjection to hydrothermal processing as described above;

- sorbent Attapulgite - prepared from an American magnesium aluminosilicate "Attapulgus clay" used in the refining-petrochemical industry (the grain fraction 0.5 - 1.2 mm was separated).

Experimental conditions

The parameters of the porous structure were obtained from isotherms of benzene sorption in an apparatus for studying sorption by the gravimetric method (McBain - Bacra quartz spring balance) applied by Baldyga-Jankowska et al. (1977).

The acidity of the surface was measured by the IR spectroscopy on the basis of pyridine sorption on Brønsted and Lewis acid centers; applied by Datka (1985).

The thermo-magnetic properties of the sorbents were investigated using Faraday's method with a magnetic field strength $5.1725 x 10^5$ A/m.

The adsorption capacities of the sorbents were determined in the regeneration of a transformer oil with lowered exploitation properties. Refining of the oil was conducted in percolation columns at 323 - 328 K, with flow velocities through the bed equal to $1.h^{-1}$. Twenty

Table 2: Typical features and refining capacities of granular sorbents obtained from natural aluminosilicates.

DETERMINED PARAMETERS	Granular sorbents from natural aluminosilicates		
	SH	SM-20	Attapulgite
Porous structure:			
- surface of meso-, and micropores [m^2/g]	77.5	130	105.5
- volume of meso-, and micropores [cm^3/g]	0.25	0.26	0.39
- average radius of pores [nm]	6.8	4.1	7.1
Acidic properties by IR method:			
- Lewis centres [μmol/g]	108	98	253
- Brønsted centres [μmol/g]	126	355	62
Thermomagnetic properties:			
- value of magnetization saturation at 293 K [$\sigma \cdot 10^{-7} Tm^3/kg$]	1.72	0.10	0.026
- Curie Temp. T_c [K]	778	-	-
Refining properties: evaluation on the basis of changes of oil's properties after regeneration with 5 vol.% of sorbent*:			
- neutralization value [mg KOH/g]	0.020	0.020	0.015
- dielectric dissipation factor tgδ (at 363 K, 50 Hz)	0.001	0.003	0.003
- resistivity at 323 K [$\Omega \cdot cm$]	$5.4x10^{13}$	$2x10^{13}$	$5x10^{13}$

*properties of transformer oil before refining:
- neutralization value: 0.06 mg KOH/g
- dissipation factor tgδ: 0.010
- resistivity: $8x10^{11}$ $\Omega \cdot cm$

volumes of oil were regenerated by one volume of the bed. The sorbents' activity in the refining process was evaluated by determining the typical properties of the transformer oil, such as the neutralization value, resistivity and dissipation factor, which provide information on the oil's purity.

The neutralization value of the oil was determined according to the ISO 6618 standard indicating the amount of acidic compounds undesirable in the oil. Dielectric properties, such as the dielectric dissipation factor tgδ and the resistivity was determined according to the international IEC standards Publ. 296 (1982) and Publ. 247 (1978).These characteristic properties indicate that in the oil there are polar impurities with own or induced dipole moment, e.g. condensed aromatic compounds, resins, substances of acidic character, etc., which are particularly undesirable in mineral oils.

Typical surface properties of granular sorbents and their refining capabilities are presented in Tab. 2.

The obtained results show that during preparation of sorbents from natural aluminosilicates attention should be paid to their magnetic properties resulting from the presence of iron compounds in the mineral raw material (described by Bolewski et al. 1990). Magnetic domains in the sorbents prepared from clay minerals may play an important part in the process of adsorption of compounds with own or induced dipole moment where they are typically removed with the impurities during the oil's refining.

The products of basalt weathering from Lower Silesia are among the clay minerals useful for the preparation of sorbents with magnetic domains. They are characterized by a high content of iron and titanium compounds. Particulary interesting properties were revealed by the aluminosilicate material from the "Dunino" deposit near Legnica (described by Dyjor et al. 1991). Its main components are halloysite (a mineral of the kaolinite group) and large amounts of iron oxides (magnetite, hematite and goethite). The same mineral raw material was used by Drag (1991) for the production of zeolithic sorbents.

According to the patent (Rutkowski et al. 1993), sorbents, using halloysitic basalt weathering products containing over 20 wt. % of iron compounds as raw material, were prepared by different preparation methods to produce granular sorbents for refining of mineral oils.

The preparation was conducted in such a way that magnetic domains present in the sorbents should be preserved:

SH sorbent - Prepared from a dried, crushed and averaged sample of the halloysitic basalt weathering products from which the grain fraction 0.5 - 1.5 mm was

Table 3: Results of investigations of sorbents from halloysitic basalt weathering products.

DETERMINED PARAMETERS	Sorbent type		
	SH	SHL	SMH
Bulk density [g/dm^3]	880	830	750
Grain size [mm]	0.5-1.5	0.5-1.5	0.5-1.5
Moisture content [wt.%]	<1	<1	<1
Mechanical strength (Polish standard PN-81/L-04533) [wt.%]	96	98	99
Thermomagnetic properties:			
value of magnetization saturation at 293 K [$\sigma \cdot 10^{-7} Tm^3/kg$]	1.72	2.3	2.0
Refining properties in the percolation process, on the basis of changes of:			
a) properties* of transformer oil:			
-decrease of neutralization value [%]	65	50	60
-decrease of dielectric dissipation factor tgδ [%]	90	70	90
b) properties* of used turbine oil:			
-decrease of acidity [%]	60	65	50
-decrease of content of oil deterioration products, determined by IR method [%]	50	55	60

*calculations of change of property: $[(X_1 - X_2)/X_1]x100\%$
X_1 - value determined before refining
X_2 - value determined after refining

separated and processed hydrothermally at temperatures ranging 300 - 723 K.

SHL sorbent - Prepared from the same raw material which was first ground, tossed and after drying moulded together with a 20 wt. % addition of smectitic basalt weathering products from the "Lesna" deposit (Lower Silesia). The obtained granules were dried and crushed to the 0.5 - 1.5 mm fraction and processed hydrothermally at 300 - 723 K.

SMH sorbent - Obtained by moulding of 50 wt. % of tossed halloysitic material with 50 wt. % of "Miltar" bleaching earth (bentonitic clay activated with 20 % H_2SO_4). The obtained grain fraction 0.5 - 1.5 mm was hydrothermally activated at the same conditions as the SH and the SHL sorbents.

Tab. 3 presents selected properties of the granular sorbents prepared from the halloysitic basalt weathering products.

Results and discussion

By comparing the porous structure and acidic properties of sorbents used in the refining process (Tab. 2), it can be shown that the SH sorbent gave the best results in the refining of transformer oil. Effective performance of the SH sorbent prepared from the halloysitic basalt weathering products should be related to the magnetic properties which are absent in the "Attapulgite" sorbent as well as in the SM-20 sorbent.

The adsorption of compounds with own or induced dipole moment, removed from oil during the refining process, is influenced not only by the developed structure and acid centers on the surface of sorbents, but also by the presence of domains with own magnetic moments in the sorbent's structure.

SH granular sorbent (Tabs. 2, 3) represents the easiest waste-free way of preparing an effective sorbent by hydrothermally activating separated grain fractions. By moulding other mineral raw materials together with the halloysitic basalt weathering products (Tab. 3 SHL and SMH sorbents) SH granular sorbent products can also be prepared. Sorbents prepared in such a way reveal (due to the preservation of iron compounds) saturation magnetization values ranging 1.7 - 2.3x10^{-7} Tm^3/kg at 293 K, which certifies the presence of magnetic domains.

Sorbents with grain sizes of 0.5 - 1.5 mm, are characterized by the high mechanical strength required in the process of refining by the percolation method.

Conclusion

It was found that the magnetic domains in the granular sorbents prepared from clay raw materials may play an important part in the process of adsorption of compounds with own or induced dipole moment. Granular sorbents that contain magnetic domains can be prepared by means of waste-free methods using halloysitic basalt weathering products from Lower Silesia which contain approx. 20 wt. % of iron compounds. Adsorption capacity and high mechanical strength of the sorbents make them suitable for application in the refining of products of petrochemical and carbochemical origin.

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