MINERALOGIA POLONICA
Vol. 35, No 2, 2004
PL ISSN 0032-6267

Wojciech FRANUS[1,2], *Jerzy KLINIK*[3], *Małgorzata FRANUS*[1]

MINERALOGICAL CHARACTERISTICS AND TEXTURAL PROPERTIES OF ACID-ACTIVATED GLAUCONITE

Abstract. The authors activated glauconite from the Lubartowska Lowland (E Poland) in 3M HCl for 1, 3, 4 and 7h at 100°C and studied impact of the activation on mineralogical and textural features (specific surface area, porosity and microporosity) of the mineral. Acid activation does not destroy the glauconite: its layer structure has been preserved despite leaching a considerable number (about 60%) of octahedral cations. The activation has significantly increased major textural parameters of the glauconite, i.e. its specific surface, porosity and microporosity.

Key-words: glauconite, acid activation, surface area, microporosity

INTRODUCTION

Acid activation of clay minerals has been a subject of many papers. The process has been studied mainly on the minerals of the smectite group as potential mineral materials for manufacturing of bleaching earths (e.g. Fijał et al. 1975a, b; Kheok et al. 1982; Christidis et al. 1997). Much less such data have been published for glauconite.

Glauconite is a common mineral in widespread clayey-sandy rocks in the vicinity of Lubartów (Krzowski 1995; Gazda et al. 2001), so the authors carried out basic investigations aimed at testing of the effects of acid activation on the structure and textural parameters of the glauconite as a possible mineral raw material in environmental engineering technologies. This mineral, with many applications outside our country (Smith et al. 1996; Baker, Uwins 1997; Kuusik, Viisimaa 1999; Stefanova 1999; Srasra, Trabelsi-Ayedi 2000; Griffioen 2001), in Poland has not been frequently utilized so far. As glauconites are strongly diversified in their mineral and chemical com-

---

[1] Lublin University of Technology, Faculty of Civil and Sanitary Engineering, Department of Geotechnics, ul. Nadbystrzycka 40, 20-618 Lublin, Poland; e-mail: wfranus@akropolis.pol.lublin.pl

[2] A scholarship holder of the Foundation Supporting Polish Science, the program Domestic Outgoing Scholarship.

[3] AGH, University of Science and Technology, Faculty of Fuels and Energy, al. Mickiewicza 30, 30-059 Kraków, Poland.

positions, the results obtained by different authors are not directly comparable. The investigations presented here were to determine industrial potential of the Tertiary glauconite from the vicinity of Nowodwór.

MATERIALS AND METHODS

Glauconite

The glauconite studied was collected from Tertiary sands of the Lubartowska Lowland near Nowodwór. Its average content in these sediments varies between 20 and 30% (Gazda et al. 2001). The sands were washed on the 63 μm sieve; then, from the glauconite-quartz concentrate left on the sieve the glauconite was magnetically separated.

Acid activation

Activation was carried out using 3M HCl for 1, 3, 4 and 7h, boiling samples of the glauconite concentrate on the water bath at 100°C. The glauconite samples were also activated at 60°C in 3M HCl for 3h using a magnetic stirrer. After acid treatment, the samples were washed with distilled water until the Cl^- ion disappeared, and dried at 80°C.

Methods of mineralogical and chemical investigations

The mode of the glauconite occurrence was studied using a JEOL 5200 scanning electron microscope with an EDS attachment for chemical analyses in microareas. Samples were covered with graphite.

A mineralogical type of the glauconite was determined using the X-ray method with a TUR-M62 diffractometer (CoK_α radiation).

The composition of the natural glauconite as well as the degree of degradation of its octahedral layer due to acid activation were analysed using a Perkin-Elmer Plasma 40 ICP–AES analyser.

Methods of textural investigations

Sorption and desorption isotherms were determined using a sorption manostate (Ciembroniewicz, Lasoń 1972) with argon vapours at a temperature of liquid nitrogen (–195.5°C) after degassing of the samples to the pressure around 10^{-5} mm Hg. The specific surface was calculated applying the theory of multilayer vapour adsorption of Brunauer, Emmett and Teller (BET) (Brunauer et al. 1938; Ościk 1979; Klinik 2000). The specific volume of micropores was determined with Dubinin-Radushkievitch equation (Ościk 1979). The specific surface of mesopores and their specific volume were calculated applying the II variant of Dubinin method (Dubinin 1956; Ościk 1979; Klinik 2000).

RESULTS OF MINERALOGICAL AND CHEMICAL ANALYSES

The glauconite separated from the glauconite sands of the Nowodwór area is developed as spherical, loaf-like or ellipsoidal, grass green aggregates (pellets) characteristic of this mineral, with prevalent diameters between 0.12 and 0.25 mm (Fig. 1). A heterogeneous nature of platy glauconite accumulations can be seen under the scanning microscope in the fractures of its grains (Phot. 2). Acid activation affects only the outermost glauconite surfaces, resulting in distinct corrosion along these fractures (Phot. 3).

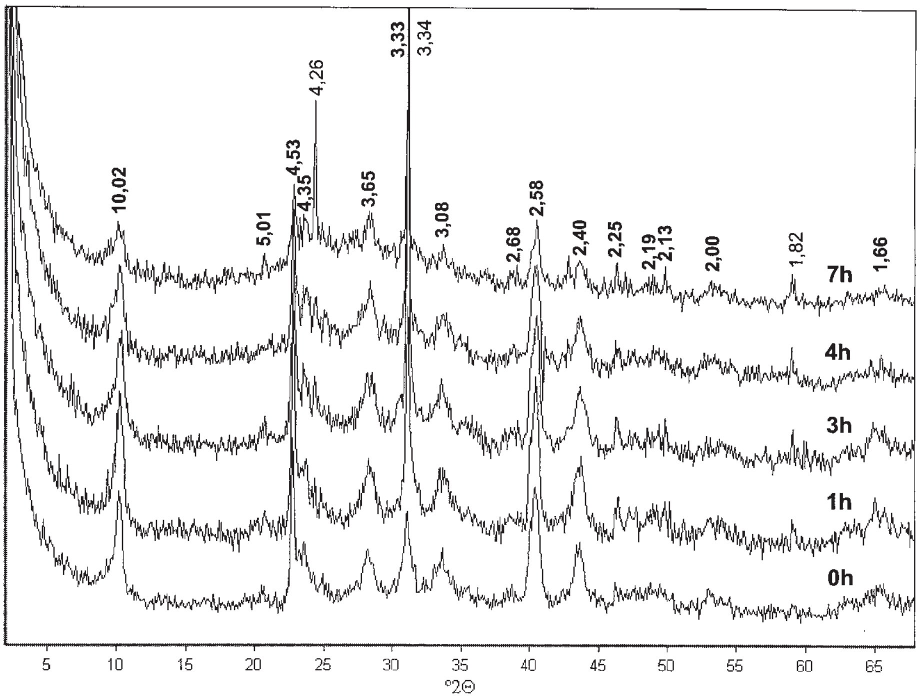


Fig. 1. X-ray patterns of the glauconite samples

The results of XRD investigations provide an almost complete set of d_{hkl} reflections, characteristic of the 1M-glauconite polytype (Fig. 1, sample 0h). The X-ray patterns of the oriented, air-dry samples and the samples saturated with ethylene glycol indicate that the glauconite studied contains about 10% of smectite layers, possessing thus the structure with an ordered arrangement of interstratifications of the IISI type (Środoń, Gaweł 1988).

After activation in 3M HCl the structure of the glauconite remains generally unchanged. In all X-ray patterns the major reflections of glauconite have the same *d* values (10.02; 5.53; 3.33; 2.58 Å). The time of activation affects, however, the intensity of the glauconite reflections: in the sample activated for 7h it is two times lower than in the sample not activated. It can be explained by formation of amorphous reaction products when the structure of glauconite is leached of some elements but does not collapse. The presence of the amorphous substance also explains a distinctly elevated background of the X-ray pattern in the range 20–40°(2Θ) in the sample activated for 7h.

TABLE 1

Chemical composition of the glauconite (sample hand-picked under the binocular)

Component [wt.%]	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	H_2O
	49.70	5.36	24.44	4.06	0.36	0.08	7.83	8.39

The chemical composition of the glauconite studied (Table 1), and particularly its $Fe_2O_3>Al_2O_3$ ratio, classifies it as a ferruginous glauconite (Krzowski 1995). Recalculation of the chemical composition into the formal unit according to the respective crystallochemical rule (22 charges of anions in a half of the formal unit) gives the following formula:

$$(K_{0.74}Na_{0.01}Ca_{0.03})[(Fe^{3}_{1.37}Al_{0.16}Mg_{0.45})(Al_{0.31}Si_{3.69}O_{10})(OH)_2]$$

Acid activation affects mainly chemical composition of the octahedral layer, while the tetrahedral layer is less prone to it because of strong bonds among silicon and oxygen ions. The amount of major ions of the octahedral layer removed is presented in Table 2 and Figure 2, while Figure 3 shows the range of damage of this layer. This damage increases with activation time and after 7 h reaches 63%.

TABLE 2

Content [wt.%] of the main octahedral cations of the glauconite samples
(bulk samples after magnetic separation)

Activation time	Fe_2O_3	Al_2O_3	MgO
0 h	22.67	4.34	4.25
1 h	19.73	3.97	3.68
3 h	18.57	3.02	3.43
4 h	11.99	2.16	2.33
7 h	7.98	1.61	1.68

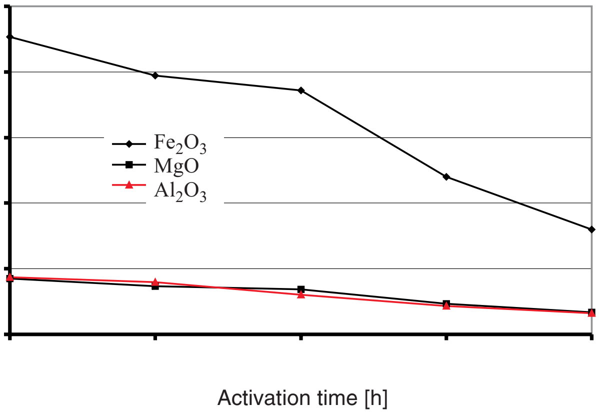


Fig. 2. Change of the amount of main octahedral cations of the glauconite samples due to acid activation

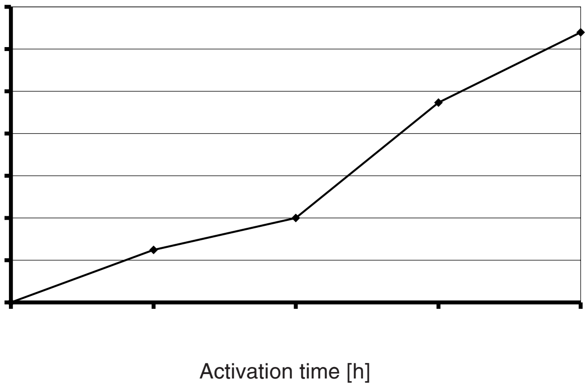


Fig. 3. The total of the main octahedral cations removed from the glauconite samples during acid activation

RESULTS OF TEXTURAL ANALYSES

Isotherms of argon sorption and desorption at the temperature of liquid nitrogen prior and after activation are presented in Figure 4. The activation does not change their character and the curves correspond to the type I of the BET isotherm (Brunauer et al. 1938; Ościk 1979; Klinik 2000), being equivalent of the type I according to the IUPC classification (Gregg, Sing 1982; Sing et al. 1985). The hysteresis loop corresponds to the loop H4 in the IUPC classification and indicates that the pores in the material studied are developed as narrow slits between two surfaces (in the case of clay minerals these are interlayers).

Textural parameters of the natural and activated glauconite are shown in Table 3 and Figure 5. All these parameters increase with the activation time: for instance the specific surface from 78 m^2/g in natural glauconite to 329 m^2/g after 7-hour activation

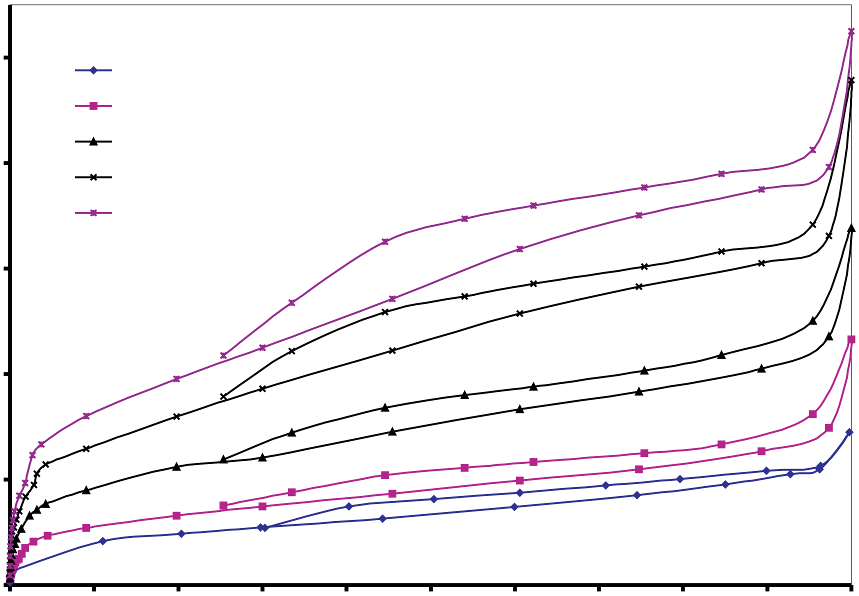


Fig. 4. Isotherms of sorption and desorption of argon on the natural and activated glauconite samples

TABLE 3

Textural properties of the glauconite

Time and temperature of activation	S_{BET} [m^2/g]	V_{mic} [mm^3/g]	S_{mes} [m^2/g]	V_{mes} [mm^3/g]
0h	78.0	21	33.1	44
1 h — 100°C	106.1	25	35.3	63
3 h — 60°C	131.0	27	46.1	77
3 h — 100°C	186.7	40	53.6	90
4 h — 100°C	269.8	58	73.6	104
7 h — 100°C	324.1	72	104.0	128

S_{BET} — specific surface [m^2/g],
V_{mic} — specific volume of micropores [mm^3/g] calculated from Dubinin- Radushkievitch equation,
S_{mes} — specific surface of mesopores [m^2/g] calculated according to variant II of Dubinin method,
V_{mes} — specific volume of mesopores [m^2/g] calculated according to variant II of Dubinin method.

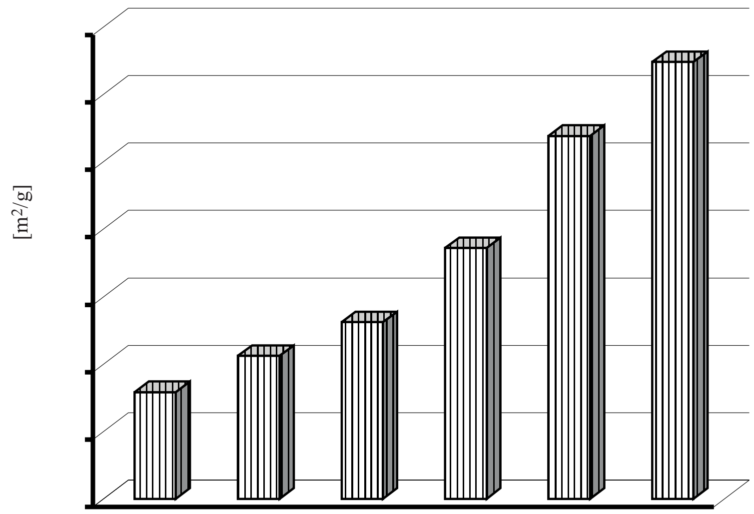


Fig. 5. Specific surface area of the natural and activated glauconite samples

in 3M HCl. Specific surface of activated glauconite depends also on activation temperature, being 131 m^2/g after 3-hour activation at 60°C and 186 m^2/g after 3-hour activation at 100°C. The volume of micropores and mesopores as well as the surface of the latter also follow this trend.

SUMMARY

Activation of the glauconite separated from Tertiary sands of the Lubartowska Lowland was carried out in 3M HCl for 1, 3, 4 and 7 h at 100°C. The investigations have shown that after the acid activation the mineral phase still represents glauconite despite a strong damage of its structure resulting from leaching of major elements of the octahedral layer. Almost all the X-ray reflections from the interplanar surfaces of the mineral have been recorded after acid activation, although of considerable lower intensity. It can be explained as an effect of formation of amorphous reaction products of the silica gel type (the same process also takes place in the case of acid activation of montmorillonite) and has been proved particularly by increases in the volume and specific surface of mesopores. The structure of these products assumes most probably a globular character, and micropores must be developed as empty spaces among the newly formed, gel-type silica molecules.

Applying chemical treatment it is possible to change the mineralogical character and textural properties of glauconite, so these procedures are perspective in utilization of glauconite as a bleaching agent.

Acknowledgements. The study was supported by KBN (Warsaw), Grant no. 4 T09D 029 22; and AGH — University of Science and Technology (Cracow), Faculty of Fuels and Energy, Scientific Project No. 10.10.210.52.

REFERENCES

BAKER J.C., UWINS P.J.R. 1997: Freshwater sensitivity of glauconitic hydrocarbon reservoirs. *J. Petrol. Sci. Eng*. 18, 83–91.

BRUNAUER. S., EMMETT P.H., TELLER E. 1938: Adsorption of gases in multimolecular layers. *Jour. Am. Chem. Soc.* 60, 309–319.

CHRISTIDIS G.E., SCOTT P.W., DURHAM A.C. 1997: Acid activation and bleaching capacity of bentonites from the islands of Milos and Chios, Aegean, Greece. *Appl. Clay Sci.* 12, 329–347.

CIEMBRONIEWICZ A., LASOŃ M. 1972: Manostat sorpcyjny — półautomatyczny aparat do badań sorpcyjnych. *Roczn. Chemii* 46, 703 (in Polish).

DUBININ M.M. 1956: Issliedowanije poristoj struktury twierdych tieł sorbcjonnymi mietodami. *Zh. Fiz. Khim.* 30. 1652 (in Russian).

FIJAŁ J., KŁAPYTA Z., ZIĘTKIEWICZ J., ŻYŁA M. 1975a: On the mechanism of the montmorillonite acid activation. Part I. Degradation of Ca-montmorillonite structure. *Miner. Polon.* 6, 1, 29–43.

FIJAŁ J., KŁAPYTA Z., KWIECIŃSKA B., ZIĘTKIEWICZ J., ŻYŁA M. 1975b: On mechanism of acid activation of montmorillonite. Part II. Changes in the morphology and porosity in the light of electron microscopic and adsorption investigations. *Miner. Polon.* 6, 2, 49–57.

GAZDA L., FRANUS M., FRANUS W., KRZOWSKI Z. 2001: Mineralogical and crystallochemical characteristic of glauconite from Gawłówka (Lublin Upland, Poland). *Miner. Slov*. 33, 2, 16.

GRIFFIOEN J. 2001: Potassium adsorption ratios as an indicator for the fate of agricultural potassium in groundwater. *J. Hydrogeol*. 254, 244–254.

GREGG S.J., SING K.S.W. 1982: Adsorption, surface area and porosity (2nd ed.). Academic Press, London.

KHEOK S.C., LIM E.E. 1982: Mechanism of palm oil bleaching by montmorillonite clay activated at various acid concentrations. *J. Am. Oil Chem. Soc*. 59, 129–131.

KLINIK J. 2000: Tekstura porowatych ciał stałych. Wyd. AGH, Kraków, 125 pp. (in Polish).

KRZOWSKI Z. 1995: Glaukonit z osadów trzeciorzędowych regionu lubelskiego i możliwości jego wykorzystania do analiz geochronologicznych. *Prace Nauk. Polit. Lub*. (rozpr. habilit.), 9–133 (in Polish).

KUUSIK R., VIISIMAA L. 1999: A new dual coagulant for water purification. *Wat. Res*. 33/9, 2075–2082.

OŚCIK J. 1979: Adsorpcja. PWN, Warszawa (in Polish).

SING K.S.W., EVERETT D.H., HAUL R.A.W., MOSCOU L., PIEROTTI R.A., ROUQUÉROL J., SIEMIENIEWSKA T. 1985: Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure Appl. Chem.* 57, 4, 603–619.

SMITH E.H., LU W., VENGRIS T., BINKIENE R. 1996: Sorption of heavy metals on Lithuanian glauconite. *Water Res*. 12, 2883–2892.

SRASRA E., TRABELSI-AYEDI M. 2000: Textural properties of activated glauconite. *Appl. Clay Sci.* 17, 71–84.

STEFANOVA I.G. 1999: Natural sorbents as barriers against migration of radionuclides from radioactive waste repositories. In: P. Misaelides et al. (eds.) *Natural Microporous Materials in Environ. Techn., Ser. E — Applied Sci.* 362, 371–379.

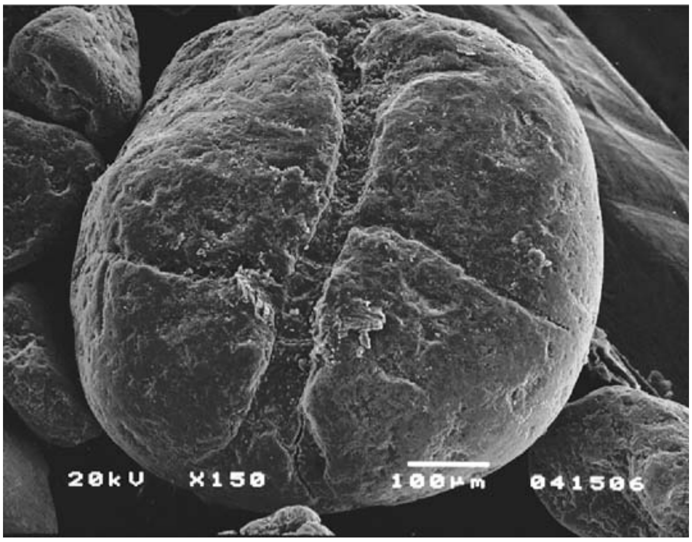
ŚRODOŃ J., GAWEŁ A. 1988: Identyfikacja rentgenowska mieszanopakietowych krzemianów warstwowych. In: A. Bolewski. W. Żabiński (eds.) Metody badań minerałów i skał, 290–307 (in Polish).

Wojciech FRANUS, Jerzy KLINIK, Małgorzata FRANUS

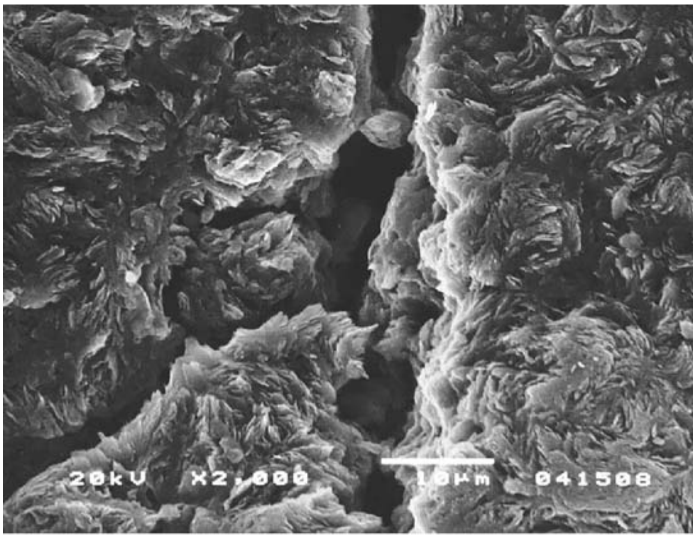
CHARAKTERYSTYKA MINERALOGICZNA I WŁAŚCIWOŚCI TEKSTURALNE AKTYWOWANEGO KWASOWO GLAUKONITU

Streszczenie

Badaniom poddano próbki glaukonitów aktywowanych 3M HCl przez okres 1, 3, 4 i 7 godzin w temperaturze 100°C. Studiowano wpływ aktywacji na zmianę charakteru mineralogicznego, jak również właściwości teksturalne glaukonitu (powierzchnia właściwa, porowatość i mikroporowatość). Badania mineralogiczne wykazały, że aktywacja kwasowa nie wpłynęła w sposób znaczący na strukturę glaukonitu (budowa pakietowa została zachowana) pomimo wyługowania z warstwy oktaedrycznej znacznej ilości (nieco ponad 60%) kationów ją budujących. Wyraźnie zaznaczyła się także tendencja wzrostowa głównych parametrów teksturalnych badanych glaukonitów, tj.: powierzchni właściwej (4-krotnie), porowatości (3-krotnie) i mikroporowatości (3,5-krotnie).

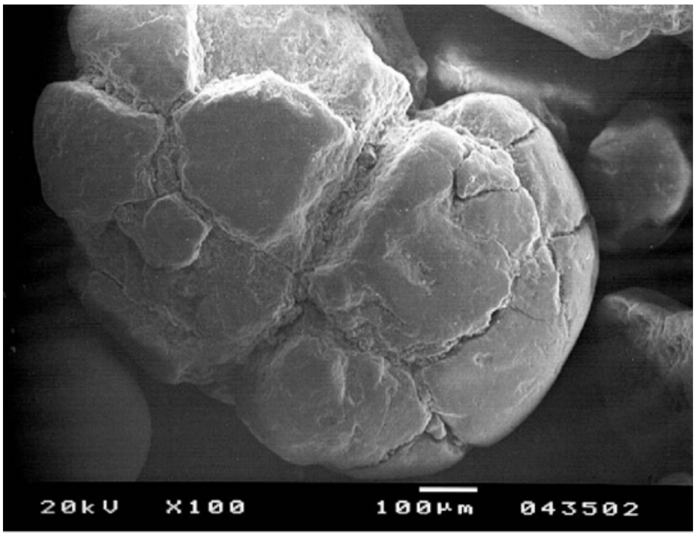


Phot. 1. Glauconite. A SEM image



Phot. 2. A close-up of the Photo 1

W. FRANUS, J. KLINIK, M. FRANUS — Mineralogical characteristics and textural propertie of acid-activated glauconite



Phot. 3. Glauconite activated for 7h. A SEM image