Study of sepiolite from Goleš (Kosovo, Yugoslavia). I. Sorption capacity

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The sorption of molecules of different size and polarity (water, *n*-hexane, isooctane, benzene, toluene, cyclohexane, carbon tetrachloride, isopropanol, isobutanol, methanol, ethanol) by sepiolite from Goleš, *i.e.* from the biggest to-date known Yugoslav deposit, was studied in this work. The BET surface area observed with different sorbates varied from 227 to 314 m^2/g, due to only partial migration of sorbate molecules into the pores or to imperfect packing of the sorbate molecules. The value of the outer surface area suggested that the average thickness of the fibers of Goleš sepiolite was approximately 15 nm.

Keywords: sepiolite, Goleš, sorption capacity, BET surface area, alcohols, alkanes, aromatics, carbon tetrachloride.

INTRODUCTION

The structure of sepiolite, a hydrated magnesium silicate, $Mg_8Si_{12}O_{30}(OH)_4(OH_2)_4 \cdot nH_2O$ ($n = 6$–8), was established by Nagy and Bradley,[1] and Brauner and Preisinger.[2] This mineral has a fibrous morphology. The fibers consist of talc-like ribbons alternated by channels along the fiber axes. Due to these channels, sepiolite is an important sorbent and molecular sieve.[3–7] Sepiolite has a high adsorptive capacity for many gases and vapours,[8–13] especially if the dimensions of the sorbate molecules enable their penetration into the sepiolite channels.

Sorption in sepiolites occurs in channels, as well as on its external crystallographic surface. Hence, the specific surface area, calculated from the adsorption isotherm, represents the sum of the outer and inner surface areas. Müller and Koltermann[14] have shown that much smaller surface area values were obtained when sorption data of some molecules, such as n-C_4H_{10} (of a cross-sectional area of 0.376 nm^2), were used, compared to the values obtained with CO_2 (0.169 nm^2) and SO_2 (0.244 nm^2) data. Barrer and Mackenzie[15] revealed that significant amounts of nitrogen, *n*-pentane and isopentane were sorbed

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by sepiolite at temperatures near their boiling points, in contrast to neopentane which was sorbed to a smaller extent. This was explained by the different migration of various sorbate molecules into the intercrystalline pores.

The adsorption properties of sepiolite change upon heating.[16] Sepiolite is transformed into an anhydride on heating at about 300 ºC (a phase without bound water). In the case of heating in vacuum, the transformation starts at lower temperatures.[17] On heating, the crystals fold,[18–20] so that the channels become inaccessible to sorbate molecules, resulting in a smaller surface area.

Hibbino *et al.*[21] proposed a method for the calculation of the surface area of sepiolite, based on the Brauner-Preisinger structural model. The values observed for five sepiolites originating from different deposits, varying in crystal sizes, were compared to experimental ones, calculated from adsorption isotherms. It was shown that the calculated values were often higher than the experimental ones. This was explained by the presence of closed channels, due to crystal defects, resulting in a smaller inner surface area. The outer surface area is a function of the thickness of the sepiolite crystals. Both the mentioned characteristics, which affect the sorption properties, are typical for sepiolites originating from different deposits.

There are several deposits of sepiolite in Yugoslavia: Trnava (Raška), Milićevci and Koviljača (Čačak),[22] as well as the deposit of palygorskite-sepiolite clays of the Pranjani Basin.[23] The biggest up-to-date known sepiolite deposit in Yugoslavia is at Goleš, located in southern Serbia.[24,25] Sepiolite occurs together with magnesite in veins in serpentinized peridotites.

In this paper, the sorption capacity of sepiolite from Goleš was studied. For this purpose molecules of different size and polarity were used. The results were expected to give information on the nature and availability of the surface of sepiolite from this deposit.

EXPERIMENTAL

A sample of white sepiolite was taken from horizon 10 in the Magura magnesite mine (Goleš Mt.). After drying for six hours at 100 ºC, the sample was ground and sieved through a 2 mm–size sieve. The sample was treated at room temperature (20 ºC) with 4 M HCl. The XRD pattern of the original sample is presented in Fig. 1. It is clear that only sepiolite is present in the studied sample. An 18.23 % loss of mass was registered after DT-TG analysis due to presence of a small amount of magnesite as an impurity.[26] In the critical region 400–700 ºC, where magnesite decomposes, a 2.83 % loss mass, very close to the theoretical value of sepiolite, was found. This is one more proof of the high purity of the sepiolite (with traces of magnesite).
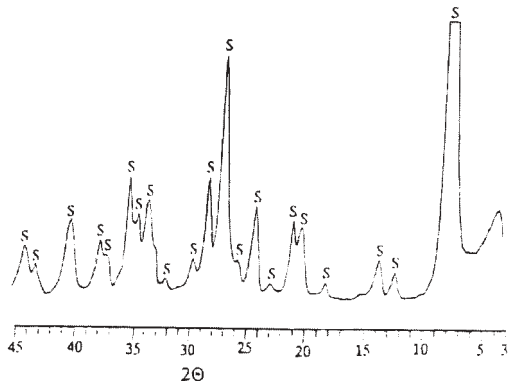

Fig. 1. XRD pattern of the studied sample of the Goleš sepiolite.

Chemical analyses of the sample began with three acid treatments, followed by gravimetric determination of SiO_2. In the remaining liquid phase, the cations were determined by atomic absorption spectrophotometry (Varian 775). The investigated sample of Goleš sepiolite consisted of 53.72 % SiO_2, 0.05 % Fe_2O_3, 0.13 % CaO, 25.26 % MgO, 0.03 % NiO and 0.24 % Na_2O. Its ignition loss was 21.03 %. The sample prepared by drying at 105 °C and hand grinding – 0.75 mm was assumed as the original one. In addition to the original sample, the same sample preheated at 400 °C for six hours was examined.

The nitrogen adsorption isotherm was measured at – 197 °C, using an Autosorb 6-Quantchrome instrument. Prior to the measurements, the samples were outgased under vacuum ($p = 1 \times 10^{-4}$ mm Hg) at 100 °C.

The sorption of condensable vapours at 20 °C was estimated using a McBain spring balance. The corresponding samples were also pretreated by outgasing under vacuum ($p = 1 \times 10^{-4}$ mm Hg) at 100 °C.

RESULTS AND DISCUSSION

Nitrogen adsorption measurements

Accoring to BDDT classification,[27] the nitrogen adsorption-desorption isotherm of the Goleš sepiolite had the characteristic shape of type II isotherms (Fig. 2). The corresponding surface area was calculated using the BET method,[28] assuming the cross-sectional area of a N_2 molecule to be 0.162 nm^2. The BET surface area was shown to be rather high, 334 m^2/g. Nevertheless, it was smaller than the one observed for Amboseli sepiolite, $S_{BET} = 364$ m^2/g,[29] but higher than the corresponding surface areas of Toledo sepiolite, $S_{BET} = 321$ m^2/g[30,31] and Turkish sepiolite (from the central Anatolia deposit), $S_{BET} = 290$ m^2/g.[10] The values of different samples from Goleš varied from 199 to 344 m^2/g depending on the presence of magnesite and the degree of crystallinity of the sepiolite.[26] The highest values of the BET surface area, determined by nitrogen, were exhibited by samples with the lowest content of magnesite and the highest crystallinity.

After heating at 400 °C for six hours, the BET surface area with N_2 was determined. Comparing the value of outer surface, it could be seen that these values are practically identi-
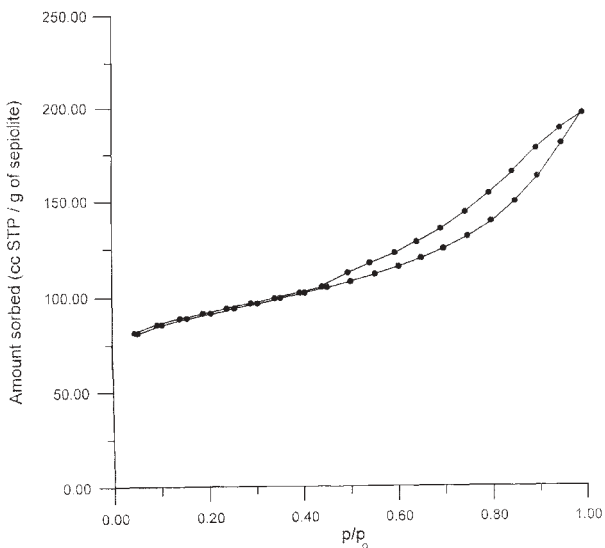

Fig. 2. Adsorption-desorption isotherm of nitrogen on the Goleš sepioltie.

cal.[26] This means that by heating to 400 ºC, half of the bound water was released and the crystals bent, resulting in the non-availability of micropores to sorbate molecules. As a result of this fact, the BET surface area corresponds to the outer surface area of a sample.

The t – plot method[32] was used for the qualitative assessment of the microporosity. The observed micropore area, having a value of 207 m^2/g, was much higher than the external surface area (128 m^2/g). The ratio between the inner and outer surface areas depended on the thickness of the sepiolite crystals. According to the method of Hibbino *et al.*,[21] the average width of the fibers of the Goleš sepiolite was estimated to be 15 nm (more than the Spanish sepiolite but less than the Turkish one). Sepiolite with shorter fibers is characterized by a larger number of silanol groups on the surface which is important in its use as a rheologic additive. The micropore volume, calculated from the *V-t* curve,[32] was 0.09 cm^3/g, and the total pore volume, based on the amount of adsorbed nitrogen, at a relative pressure of 0.98 was 0.31 cm^3/g.

Sorption of linear and branched hydrocarbons

The selectivity of sepiolite for the sorption of *n*-hydrocarbons is well known. It is proportional to the ratio between the inner and outer surface areas. Several authors considered it unlikely that the sepiolite channels were available for intercrystalline sorption of branched hydrocarbons.[3,8,10] The adsorption isotherms of *n*-hexane and isooctane on sepiolite from Goleš are shown in Fig. 3. Apparently *n*-hexane showed a greater affinity for the adsorbent, especially at lower relative pressures. Assuming that the cross-sectional area of an isooctane molecule is 0.54 nm^2, a BET surface area of 194 m^2/g was calculated. Comparing this value with the value based on *n*-hexane adsorption (260 m^2/g), as well as with the value observed by the *t*-method with nitrogen measurements (128 m^2/g), it may be concluded that the sorption of isooctane was not confined to the external surface. The dif-
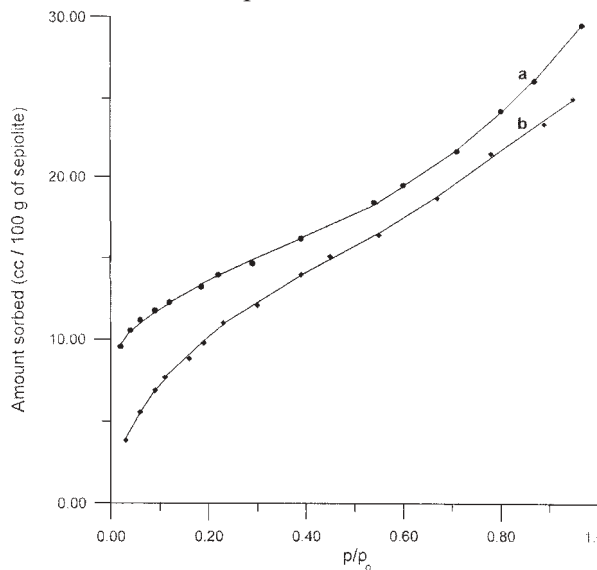

Fig. 3. Adsorption isotherms of: a) *n*-hexane, and b) isooctane on the Goleš sepiolite.

ference in the surface areas originating from nitrogen and isooctane isotherms can be attributed to imperfect packing of the large isooctane molecules on corrugations of the surface, as in the case of palygorskite.[15]

Finally, the question of whether this molecule is sorbed on the internal surface of sepiolite was answered by investigating its sorption on sepiolite preheated at 400 ºC, for which XRD analysis confirmed that it had been transformed into an anhydride (sepiolite without bound water). From the t – plot which passess through the intersection of the coordinate axes it was proved that there was no more sorption in the micropores. The BET surface area based on nitrogen adsorption isotherms was almost equal to the external surface area. Consequently, the results suggested that sorption, in this case, occurred only on the external surface. The adsorption isotherm obtained with isooctane for the same sample, was compared with the corresponding isotherm of the original sample (Fig. 4).
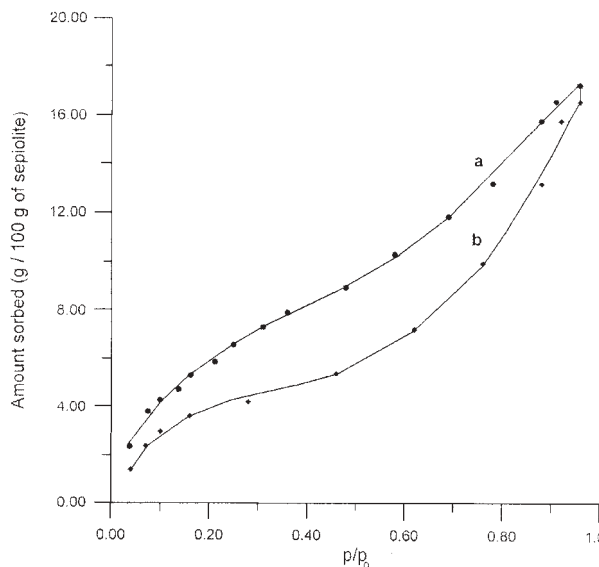

Fig. 4. Adsorption isotherms of isooctane on the Goleš sepiolite: a) original sample, and b) a sample preheated at 400 ºC.

It was clear that the sorption was higher in the case of the untreated sample, especially at low relative pressures. The surface area of the treated sample based on isooctane sorption was 132 m^2/g, which is quite similar to the value observed with nitrogen. Therefore, the observed low value of the surface area of the original sample did not result from imperfection of the packing at the external surface, but was due to the limited access of isooctane to the sepiolite channels. Consequently, it seems as though adsorption of isooctane, albeit a limited one does occur in the micropores of sepiolite.

Sorption of molecules of different polarity

It is not clear from the literature whether polar or nonpolar molecules have a greater affinity to sorption on sepiolite. Adsorption isotherms for the adsorption of several non-polar molecules on Goleš sepiolite are shown in Fig. 5. The benzene, toluene and cyclohexane isotherms

were very similar. Using the cross-sectional areas given by McClellan and Harnsberger,[33] the following BET surface areas were calculated: with benzene 268 m²/g ($A_m = 0.4$ nm²), cyclohexane 273 m²/g ($A_m = 0.45$ nm²), and with toluene 302 m²/g ($A_m = 0.46$ nm²). The different values were due to imperfect packing of the molecules of different size in the channels. A much lower value (219 m²/g) was obtained with carbon tetrachloride ($A_m = 0.4$ nm²). The access of this molecule to the micropores of the sepiolite was limited.
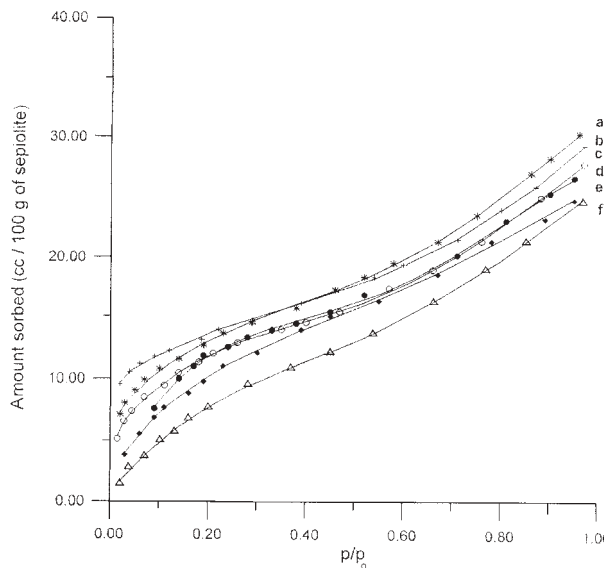

Fig. 5. Sorption of non-polar molecules on the Goleš sepiolite: a) cyclohexane, b) hexane, c) benzene, d) toluene, e) isooctane, and f) carbon tetrachloride.

The adsorption isotherms obtained with water, isopropanol and isobutanol, as polar adsorbates, and the Goleš sepiolite as adsorbent are plotted in Fig. 6. The BET surface ar-
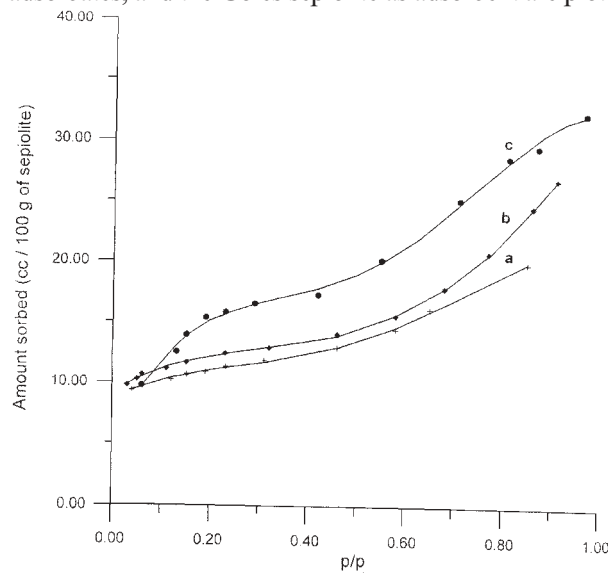

Fig. 6. Adsorption isotherms of: a) water, b) isopropanol, and c) isobutanol on the Goleš sepiolite.

eas obtained with water 335 m^2/g (A_m = 0.108 nm^2), isopropanol 301 m^2/g (A_m = 0.388 nm^2) and isobutanol 346 m^2/g (A_m = 0.394 nm^2), indicate a significant penetration of these molecules into the channels of the adsorbent. Figures 5 and 6 show that Goleš sepiolite sorbed polar as well as nonpolar molecules. The different obtained surface area values may primarily be attributed to imperfect packing of the different molecules in the pores.

Sorption of n-alcohols

The adsorption isotherms obtained with *n*-alcohols of different chain lengths (Fig. 7) were not in agreement with the presumption that adsorption by sepiolite is independent of the polarity of the adsorbate. The BET surface area obtained with methanol was 227 m^2/g (A_m = 0.180 nm^2), *i.e.* smaller than the area obtained with ethanol, 273 m^2/g (A_m = 0.230 nm^2), or *n*-butanol, 298 m^2/g (A_m = 0.354 nm^2). The fact that the lowest value was obtained when methanol was the adsorbate and that the sorption was proportional to the non-polar chain length indicates that non-polar molecules have a greater affinity to sepiolite. However, such an assumption is tentative, firstly because if that were true then water would be expected to give rise to a smaller value of the surface area than methanol, which is not the case. Secondly, the possibility of the replacement of one of the two coordinated structural water molecules in sepiolite by one molecule of alcohol has been suggested by Serna and Van Scoyoc[9] and Dandy and Nadiye-Tabbiruka.[34] If such a replacement would occur then gravimetric measurements underestimate the amount of adsorbed alcohol by the amount of water replaced. The discrepancy was shown to be the greater, the smaller difference in molecular weight of the alcohol and water was. This explains the fact that methanol was apparently sorbed to lesser extent than the higher alcohols. This is one more proof for the theory of replacement, which has also been explained by IR spectroscopy (Trifunović, 1999).[26]
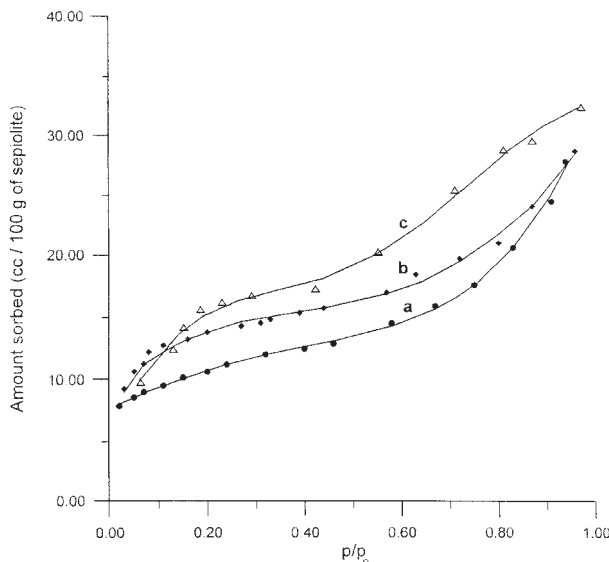

Fig. 7. Adosrption isotherms of: a) me-thanol, b) ethanol, and c) *n*-butanol on the Goleš sepiolite.

CONCLUSIONS

The specific surface area of the sepiolite from Goleš, obtained from nitrogen adsorption isotherm, was high compared to sepiolites from other known world deposits. The Goleš sepiolite has a greater sorption affinity to n- than to branched hydrocarbons, primarily due to the fact that its inner surface area is larger than its outer surface area. The inner/outer surface area ratio was found to be approximately 1.6, which suggests that the average thickness of the Goleš sepiolite fibre is about 15 nm. The sorption did not depend on the polarity of the adsorbate molecules. The different surface areas observed by using different sorbates results from partial migration into the sepiolite channels or from imperfect packing of sorbate molecules on the surface. The sorption of different chain length n- alcohols confirmed the theory of replacement of molecules of coordinated water by molecules of alcohol.

ИЗВОД

ИСПИТИВАЊЕ СЕПИОЛИТА СА ГОЛЕША (КОСОВО, ЈУГОСЛАВИЈА)
I СОРПЦИОНЕ ОСОБИНЕ

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У овом раду испитивана је сорпција молекула различите величине и поларности (вода, n-хексан, изооктан, бензен, толуен, циклохексан, угљен-тетрахлорид, изопропанол, изобутанол, метанол, етанол) на сепиолиту са Голеша, до сада највећег познатог лежишта сепиолита у Југославији. Измерена ВЕТ-површина за различите сорбате била је у опсегу 227–314 m^2/g, што је последица само делимичне миграције молекула сорбата у поре или пак несавршеног паковања молекула сорбата. Вредност спољашње површине је указивала на просечну дебљину влакана голешког сепиолита око 15 nm.

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REFERENCES

1. B. Nagy, W. F. Bradley, *Am. Miner.* **40** (1955) 885
2. K. Brauner, A. Preisinger, *Tschermaks Miner. Petr. Mitt.* **6** (1956) 120
3. A. J. Dandy, *J. Phys. Chem.* **72** (1968) 334
4. J. M. Serratosa, *Proc. Int. Clay Conf. Oxford* (1979) 99
5. B. F. Jones, E. Galan, in: *Hydrous Phyllosilicates*. Reviews in Mineralogy, 19, S. W. Bailey Ed., Mineralogical Society of America, Washington, 1988, p. 631
6. J. Santaren, *Ind. Miner.* **304** (1993) 35
7. E. Galan, *Clay Miner.* **31** (1996) 443
8. R. M. Barrer, N. Mackenzie, D. M. MacLeod, *J. Phys. Chem.* **58** (1954) 568
9. C. J. Serna, G. E. VanScoyoc, *Proc. Int. Clay Conf. Oxford* (1979) 197
10. S. Inagaki, Y. Fukushima, H. Doi, O. Kamigaito, *Clay Miner.* **25** (1990) 99
11. M. Suguira, H. Hayashi, T. Suzuki, *Clay Sci.* **8** (1991) 87
12. M. P. Bernal, J. M. Lopez-Real, *Bioresource Technol.* **43** (1993) 27
13. H. I. Ünal, B. Erdoan, *Appl. Clay Sci.* **12** (1998) 419
14. K. P. Muller, M. Koltermann, *Z. Anorg. Allgem. Chem.* **341** (1965) 36
15. R. M. Barrer, N. Mackenzie, *J. Phys. Chem.* **58** (1954) 560
16. Y. Grillet, J. M. Francois, J. Rouquerol, J. E. Poirier, *Clays Clay Miner.* **36** (1988) 233

17. A. J. Dandy, M. S. Nadiye-Tabbiruka, *Clays Clay Miner.* **23** (1975) 428
18. H. Nagata, S. Shimoda, T. Sudo, *Clays Clay Miner.* **22** (1974) 285
19. C. Serna, J. L. Alrichs, J. M. Serratosa, *Clays Clay Miner.* **23** (1975) 452
20. T. Kiyohiro, R. Otsuka, *Thermochim. Acta* **147** (1989) 127
21. T. Hibbino, A. Tsunashima, A. Yamazaki, R. Otsuka, *Clays Clay Miner.* **43** (1995) 391
22. M. Ilić, M. Bačanac, Z. Miladinović, *Tehnika* **52** (1997) 150 (in Serbian)
23. V. Jović, M. Kovačević, S. Djurić, M. Ršumović, V. Poharc-Logar, *Vatrostalni materijali* **24** (1994) 7 (in Serbian with English summary)
24. Z. Maksimović, G. Radukić, *Geološki anali Balkanskog poluostrva* **28** (1961) 309 (in Serbian)
25. M. Radojević, M. Dojčinović, D. Simić, V. Vučelić, O. Kovačević, *J. Serb. Chem. Soc.* **64** (1999) 131
26. M. Trifunović, "Characterization of sepiolite from the Goleš deposit. Sorption properties and an estimation of the possibility of its application". *M. Sc. Thesis*, University of Belgrade (1999) (in Serbian)
27. S. Brunauer, L. S. Deming, W. E. Deming, E. Teller, *J. Am. Chem. Soc.* **62** (1940) 1723
28. S. Brunauer, P. Emmett, E. Teller, *J. Am. Chem. Soc.* **60** (1938) 309
29. A. J. Dandy, *J. Chem. Soc. (A)* (1971) 2383
30. J. L. Bonilla, J. de D. López Gonzalez, A. Ramirez Saez, F. Rodriguez Reinoso, C. Valenzuela Calahorro, *Clay Miner.* **16** (1981) 173
31. F. Rodriquez Reinoso, A. Ramirez Saez, J. de D. López Gonzalez, C. Valenzuela Calahorro, L. Zurita Herrera, *Clay Miner.* **16** (1981) 315
32. J. H. De Boer, B. C. Lippens, B. G. Linsen, J. C. P. Broekhoff, A. van den Heuval, Th. J. Osinga, *J. Coll. Interf. Sci.* **21** (1966) 405
33. A. L. McClellan, H. F. Harnsberger, *J. Coll. Interf. Sci.* **23** (1967) 577
34. A. J. Dandy, M. S. Nadiye-Tabbiruka, *Clays Clay Miner.* **30** (1982) 347.