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VERMICULITE FROM KOPAONIK (YUGOSLAVIA) CHARACTERIZATION AND PROCESSING

In the last few years, many nonmetallic minerals, including vermiculite, have been subject to geologic and mineral processing investigation in Yugoslavia. In this study, the identification of vermiculite from the Kusici–Kopaonik deposit (Yugoslavia) was carried out using microscopy, DTA, TGA, X-ray and IR spectroscopy methods. In addition, small amount of chlorite was identified in the examined sample by X-ray method. Expanding properties of different size fraction of vermiculite was performed, followed by the use of stereomicroscope and by measurement of the volumetric mass before and after the expansion. The maximum expansion was accomplished at 910–920 °C. The IR spectra showed that heating of vermiculite at this temperature (about 900 °C), for only 7 minutes, resulted in notable reduction of absorption bands characteristics for water, indicating the important water loss from the mineral.

INTRODUCTION

Vermiculite is a hydrated ferromagnesian aluminium silicate similar in texture to mica. Its major usable property is the ability to expand at high temperatures to 10–20 or even 40 times the original volume. Expanded vermiculite produces fire-resistant, sound-absorbent, and low-conductivity light-weight (filling mass of higher grade species 70–150, or lower grade 400–600 kg/m^3) material.

When ground, vermiculite is loose, grainy and porous, chemically inert, biologically stable and sterile. The high-grade vermiculite concentrate of various grain sizes is suitable for use in a number of products: as heat and sound insulator; as fire-fighting material; as light-weight concrete filler; as decorative element. Expanded vermiculite, as a nonhazardous raw material has a very important application in agriculture water-absorbent, ion-exchange, humidifier, soil conditioner, microelement soil enricher); as soil substrate in green-houses, as insecticide and herbicide filler; as litter in animal and poultry husbandry and secondary used as an organic material fertilizer (Kuzvart 1984). The heat-insulation property of vermiculite is very important in agricultural industry, as well as its biological stability sterility, chemical inertness (as a fruit-protecting material in log transport, etc.). Expanded vermiculite can also be used in waste water or air treatments. Expanded vermiculite has applications in agriculture, civil engineering, metallurgy and chemical industry (Vakanjac 1992).

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SAMPLES

Vermiculite was examined for identification and tested for separation of monomineral concentrations by different mineral processing techniques on four representative ore samples from vermiculite occurrences on the western slopes of Kopaonik Mt., NE of Kremić village. The occurrences are associated with a heterogeneous, altered ultramafite zone, in contact with granitoids on one and volcanic rocks on the other side. Vermiculite veins or lenses of up to metric size are localized in small fault and fracture structures in altered serpentinites.

Samples G-53a/91 and G-53b/91, from the salband part of the vermiculite vein were composited, for both preparation and testing, and taken for sample G. Another sample, slightly poorer and much finer-grained, had the symbol T-2. Soon after the initial operations, two more samples were collected, II and III. Sample III was relatively rich, composed of medium-grained vermiculite mineral and very coarse lumps of gangue. Sample IV, large aggregates of vermiculite crystals, was a specimen of 'pure vermiculite', used in many determinations of the mineral physical parameters.

EXPERIMENTAL METHODS

All raw material samples were analysed using stereoscopic microscope at small magnifications and mineral grains were generally characterized. The grain size composition was determined on standard laboratory sieves for each sample. Vermiculite was identified by spectrophotometry on the prepared thin sections, before and after the expansion by heating. For differential thermal analysis (DTA), apparatus AD 67, ADAMEL LHORMARGY was used, and for thermogravimetric analysis (TGA), thermobalance STANTON with heating rate 10 °C per minute in a 20–1000 °C range. The identification of vermiculite was verified by X-ray diffraction method on powder diffractometer Philips PW 1710. Finally, the separation of monomineral fractions, or vermiculite concentration, was tested using comminuted and classified ore.

DISCUSSION

X-ray powder diffraction revealed the monomineral character of the examined sample, corresponding to 14 layered silicate which could be vermiculite or chlorite (Dubyenetskiy, Pozhnin 1971) (Fig. 1a). For accurate identification of the mineral species, an oriented thin section was prepared from the sample. The reflection at 14 noted on the diffractograms was asymmetric, indicating the likely two-phase composition of the sample (Turkevitch 1971) (Fig. 1b). The reflection at about 14 remained generally unchanged for the thin section heat-treated at 480 °C. At higher temperatures, a broad reflection of the same intensity appeared at about 10 (Fig. 1c). All this verified the presence of two minerals: vermiculite and chlorite, in the sample. An X-ray diffractogram of oriented thin-section of the sample saturated with potassium ions showed thin-section of the sample saturated with potassium ions showed the presence of both vermiculite and chlorite, vermiculite prevailing over the very low chlorite (Dubyenetskiy, Pozhnin 1971; Yakovlev, Karpenko 1976; Turkevitch 1971) (Fig. 1d).

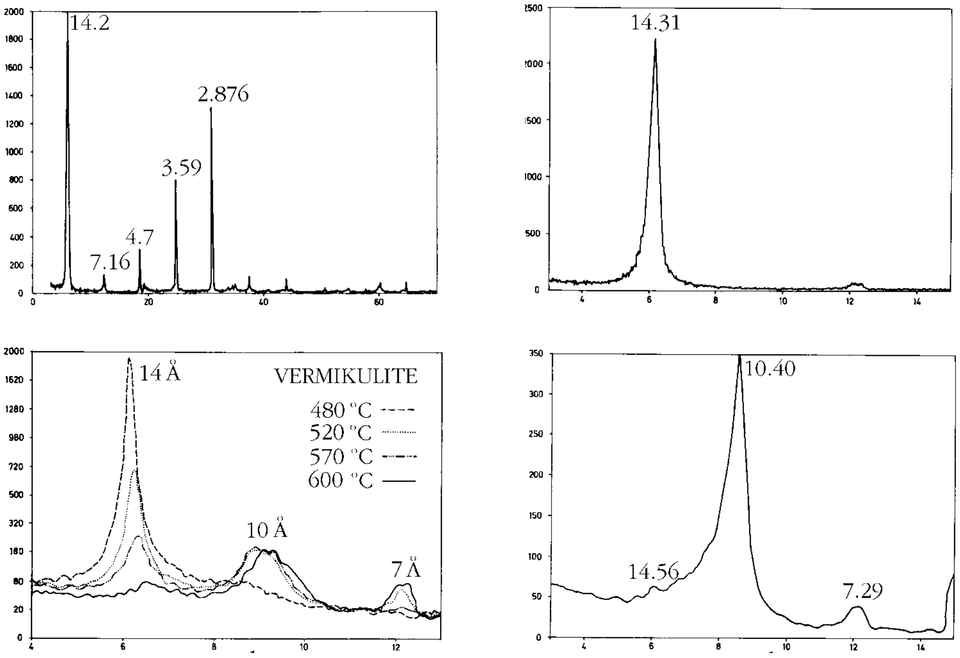

Fig. 1 X-ray diffractograms of: a) investigated sample in the powder, b) oriented thin section, c) thermally treated thin section with two present minerals: chlorite and vermiculite, d) oriented thin section of the sample saturated with potassium ions, with dominant mass rate of vermiculite and negligent chlorite

Vermiculite expansion experiments. The examinations included a number of vermiculite expansion experiments for establishing the optimum temperature range and the time of residence in the oven. Different size fractions were tested. The expanding was viewed in a stereomicroscope and the volumetric mass measured before and after the expansion. Best product of maximum expansion was obtained at temperatures of 910–920 °C and the shortest residence in the over of seven minutes. The minimum volumetric masses or maximum expansions were the main parameters determining the heating time (Dubyenetskiy, Pozhnin 1971).

Infrared spectrum of the examined sample (composites III and IV) showed a broad band in the wave numbers range from 3700 to 3000 cm^{-1}, as well as the band at 1630 cm^{-1}, both characteristic of molecular water (Fig. 2). The presented spectrum also shows bands at about 1000 cm^{-1} and about 640 cm^{-1}, which correspond to stretching vibrations of Si–O bond. Spectrum 1 suggests the presence of vermiculite in the examined sample.

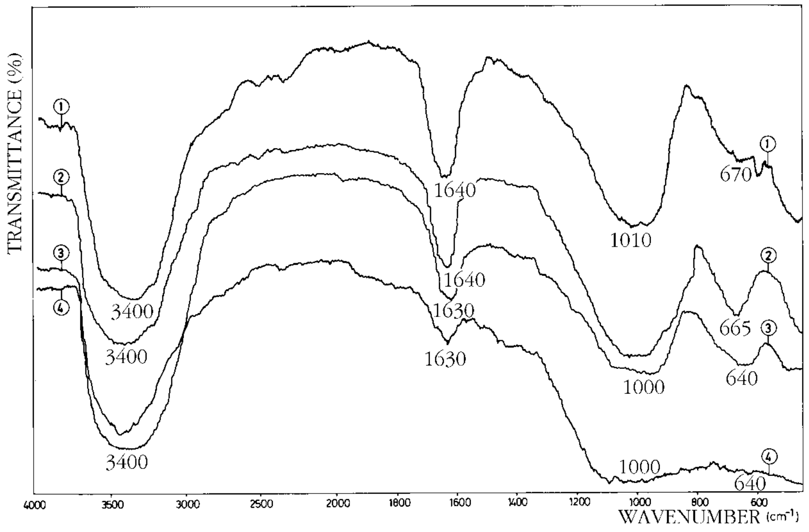

Fig. 2. Infrared spectra of 'row' and expanded vermiculite;
1 – vermiculite samples III and IV, *2* – expanded vermiculite samples III and IV,
3 – vermiculite samples G and T-2, *4* – expanded vermiculite samples G and T-2

Figure 2 shows infrared spectra of vermiculites – natural and thermally treated ones to a temperature of 920 °C for seven minutes. Compared spectra 1 and 2 show a loss of water between the layers in vermiculite structure during the thermal treatment. This is indicated by the weaker intensities of the bands at about 3400 cm^{-1} and about 1640 cm^{-1}, which represent stretching and bending vibrations of OH group from water molecule, respectively (Dubyenetskiy, Pozhnin 1971; Shandrik 1977; Turkevitch 1971). However, vermiculite structure retained an appreciable amount of OH even at this high temperature. The likely explanation is the short (7 min) residence of vermiculite at the highest temperature of 920 °C and the other thermal treatment conditions. Reference literature ((Dubyenetskiy, Pozhnin 1971; Shandrik 1977) mentions 850 °C as sufficiently high temperature for a virtually complete and irreversible water elimination from natural (Mg) vermiculite during a thirty-minute heating. Vermiculite of G and S-2 samples is represented in the same figure by infrared spectrum 3. It does not show substantial difference compared with the preceding sample. Heated for seven minutes at the same temperature of 920 °C, this vermiculite sample (spectrum 4) shows notably reduced bands (at 3400 cm^{-1} and 1630 cm^{-1}) which suggest a significant water loss from the mineral. However, neither this vermiculite sample had complete loss of water by thermal treatment under the mentioned conditions.

Differential thermal analysis revealed two strong endothermic reactions: in range 50–230 °C with maxima at 110 and 120 °C and in range 230–300 °C with maximum at 260 °C, typical of vermiculite (Fig.3).

Thermogravimetric analysis also indicated vermiculite: at 20–200 °C loss of 12.11%; at 200–400 °C loss of 3.02%; at 400–700 °C loss of 1.84%; at 700–1000 °C loss of 3.36%; the former two corresponding to water and the latter two to OH group losses (Fig.4).

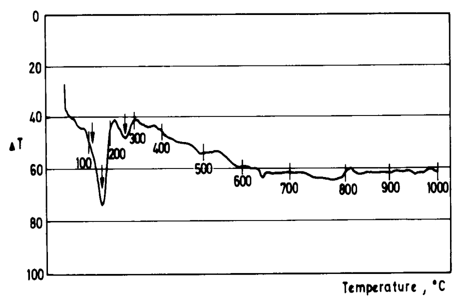

Fig. 3. DTA curve of vermermiculite

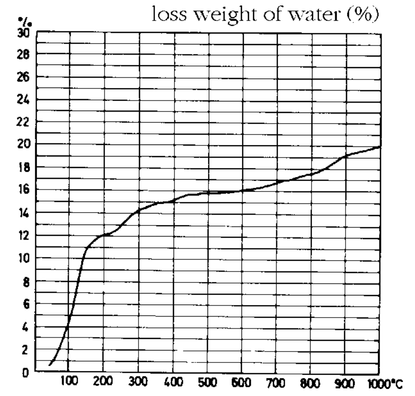

Fig. 4. Thermogravimetric curve of vermiculite

Vermiculite concentration (after grinding and/or classification) was performed with a pneumatic shaking table for coarser fraction, and using air-eluviator for finer fraction (Table 1). Concentration by dry electromagnetic separation was also tested. Magnetic separation gave very high recoveries, but low-grade concentrates. Sample G gave excellent concentration and high recoveries. Sample T-2, with much lower average vermiculite rate, gave lower recovery and poorer quality. Similar behaviour was that of sample III. Sample IV was a monomineral ore.

CONCLUSION

It was verified that the raw material contained two minerals: vermiculite and chlorite. X-ray diffractograms of oriented thin section saturated with potassium ions showed the presence of vermiculite and chlorite in the material. Vermiculite far prevals in mass rate over the very low chlorite. Thermogravimetric analysis confirmed the presence of vermiculite. The same findings were in a way confirmed by IR spectra of vermiculite, before and after expansion by heating to 920 °C for 7 minutes. Microscopy, spectrophotometric IR spectra, DTA, TGA, density, expansion quality, and other properties indicated a high grade vermiculite. Vermiculite raw material is easy to process including crushing, classifying, elutriation, gravity concentration, electromagnetic separation, and gives high grade concentrates at high recoveries.

Table 1. Vermiculite concentration test data

Size fractions mm	wt %	Concentration		
		in size fraction	wt % of feed	
		C_1 = 44.15	12.83	25.36
		C_2 = 43.14	12.53	
		T = 12.71	3.69	3.69
+ 6.680	29.05*	100.00	29.05	29.05
		C_1 = 45.16	5.96	8.83
		C_2 = 21.77	2.87	
		T = 33.07	4.37	4.37
–6.680 + 4.699	13.20*	100.00	13.20	13.20
		C_1 = 35.62	3.33	5.41
		C_2 = 22.32	2.08	
		T = 42.06	3.92	3.92
–4.699 + 3.327	9.33*	100.00	9.33	9.33
		C_1 = 31.18	3.24	6.38
		C_2 = 30.20	3.14	
		T = 38.62	4.01	4.01
–3.327 + 2.326	10.39*	100.00	10.39	10.39
		C_1 = 27.43	2.17	6.03
		C_2 = 48.68	3.86	
		T = 23.89	1.89	1.89
–2.326 + 1.651	7.92*	100.00	7.92	7.92
		C_1 = 33.65	2.25	4.50
		C_2 = 33.66	2.25	
		T = 32.69	2.19	2.19
–1.651 + 1.168	6.69*	100.00	6.69	6.69
		C_1 = 30.46	1.66	3.44
		C_2 = 32.48	1.78	
		T = 37.01	2.02	2.02
–1.168 + 0.833	5.46*	100.00	5.46	5.46
		C_1 = 52.79	2.14	2.66
		C_2 = 12.95	0.52	
		T = 34.26	1.39	1.39
–0.833 + 0.589	4.05**	100.00	4.05	4.05
–0.589 + 0.000	13.91	T = 13.91	13.91	13.91
Ore feed:	100.00		100.00	100.00

[*] Pneumatic table,

[**] Cyclone – dust classifier 'Bacho', C_1, C_2, – concentrates, T – tailing.

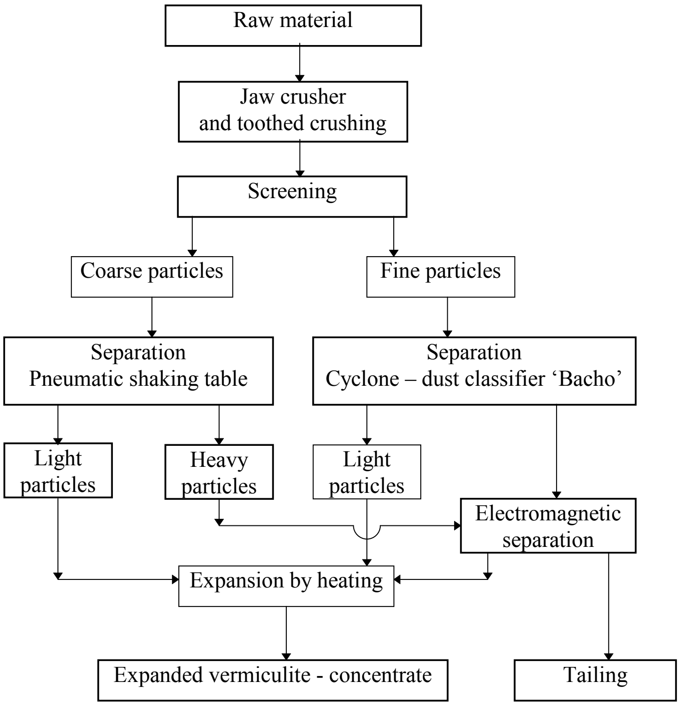

Fig. 5. Schematic flowsheet for vermiculite concentration

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Wermikulit, jak wiele innych surowców niemetalicznych, jest w ostatnich latach przedmiotem szerokich badań geologicznych i przeróbczych w Jugosławii W pracy zbadano próbki surowca wermikulitowego ze złoża Kisic-Kopaonik, stosując techniki spektroskopii rentgenowskiej i w podczerwieni oraz DTA i TGA. Za pomocą metod rentgenowskich stwierdzono, że badany surowiec zawiera głównie wermikulit oraz niewielkie ilości chlorytu. Badany materiał poddano klasyfikacji (separacji) powietrzno-grawitacyjnej, wydzielając lekkie frakcje wzbogacone w wermikulit. Określono rozszerzalność objętościową różnych klas ziarnowych badanego materiału oraz stwierdzono, że maksimum pęcznienia osiąga się w temperaturze 910–920 °C. Widma IR pokazały, że w tych temperaturach już po 7 minutach zanika pasmo charakterystyczne dla wody, co świadczy jej zaniku w strukturze minerału.