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# ALUNITES IN THE RED BEDS OF THE "MARCEL" COAL MINE, UPPER SILESIAN COAL BASIN, POLAND

Abstract. Within the so-called red beds of the "Marcel" coal mine, Upper Silesian Coal Basin (USCB), the authors have recorded the presence of alunite and natroalunite using XRD, IR and SEM/EDS. Both of them contain probably isomorphic substitutions of barium, strontium, phosphorus and, possibly, the hydronium ion. These two minerals preferably occur at the bottom of the red beds, in clay laminae overlying a partly preserved coal seam; they are cryptocrystalline: their rhombohedral crystals, with a cube-like habit, are below 1 μm. The sulphates coexist mainly with clay minerals (illite, halloysite, kaolinite-D, smectite) and hematite, while quartz, siderite and sphalerite are subordinate or occur in traces. The genesis of the alunite and natroalunite has been linked to the final stage of the alteration of Carboniferous rocks and coal into the red beds in complex weathering and diagenetic-epigenetic processes. Both minerals must have been formed by metasomatosis of a clay precursor, affected by sulphuric acid resulting from supergenic oxidation of sulphides (mainly pyrite) dispersed in the Carboniferous strata.

*Key-words*: alunite, natroalunite, red beds, Upper Silesian Coal Basin

## INTRODUCTION

World occurrences and deposits of the alunite group minerals are mainly associated with young volcanic and pyroclastic rocks, particularly acid or intermediate in composition, altered (alunitized) by volcanogenic gases, vapours and solutions rich in sulphur. The occurrences of these minerals within other or genetically different rock types are less frequent and usually without any economic value (Kashkaï 1970).

The occurrences of the alunite group minerals in Poland are few and limited to sedimentary rocks. Alunite was identified without any doubts only in the non existing "Staszic" pyrite mine in Rudki near Nowa Słupia (Holy Cross Mts) by Stoch (1958) and Kubisz (1964) as well as in halite carnalitite in the salt mine "Kłodawa" in Kłodawa (Fijał 1973). The presence of alunite was mentioned by Morawiecki (1962) in veinlets intersecting refractory shales in the "Nowa Ruda" mine in Nowa Ruda (Lower Silesia),

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and also by Kuźniarowa and Strzyżewska (1963) in the weathering zone of the Menilite Beds of the Carpathians. Considering a lack of sound mineral identification, the findings of alunite in the last two papers are of a limited credibility. According to Kashkaï (1970), even less reliable are older reports of Kuhl (1931a, b) on the occurrence of alunite in the Cambrian shales from the vicinity of Sandomierz (Pieprzowe Góry Mts).

In the Czech part of the USCB, in the "Prezident Gottwald" and "Doubrava" mines, alunite was identified by Kralik (1982) in the so-called red beds, described by Kowalski (1977, 1979, 1982, 1983), Kralik (1982), Klika (1998) and Lipiarski et al. (1998). Kralik (*op. cit.*) identified alunite on the basis of X-ray and chemical analyses and suggested that it can be accompanied by gorceixite, a mineral of the crandallite group. A pos-

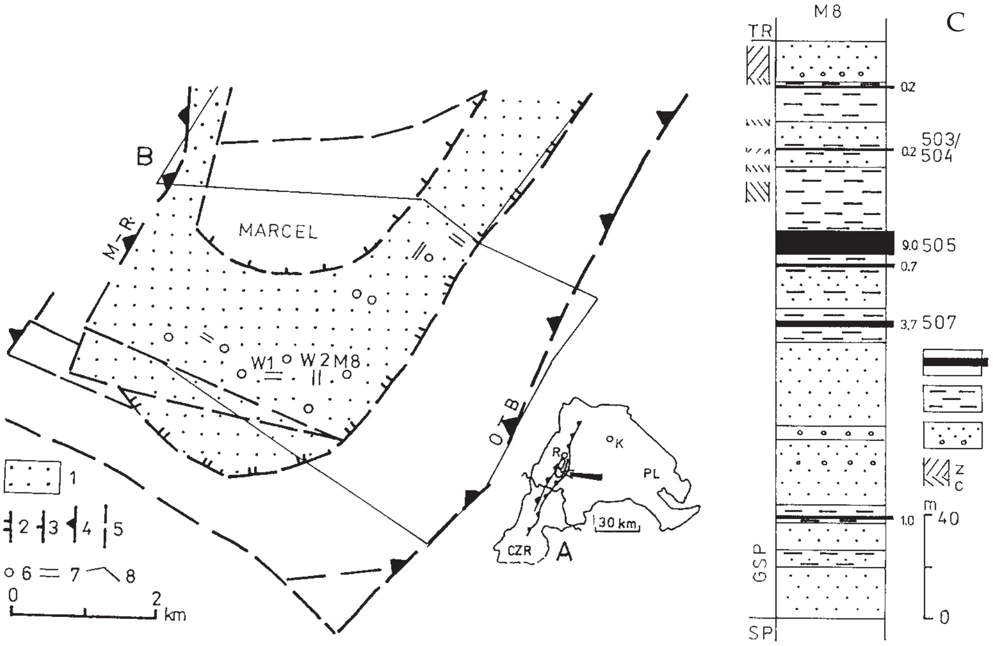

Fig. 1. A. Localization of the study area within the Upper Silesian Coal Basin (USCB).
The arrow shows the Chwałowice Trough; PL — Polish part of the USCB, CZR — Czech part of the USCB; towns: R — Rybnik, K — Katowice.
B. Localization of the boreholes and mine workings in the southern part of the Chwałowice Trough, in which red beds have been found. 1 — Upper Silesian Sandstone Series (Namurian), 2 — outcrops of the Upper Silesian Sandstone Series, 3 — outcrops of the Mudstone Series (Langsetian), 4 — overthrusts (O-B — Orłowa-Boguszowice, M-R — Michałowice-Rybnik), 5 — faults, 6 — boreholes (the profile of the M8 borehole is presented in Fig. 1C), 7 — mine working (sketches of the W1 and W2 exposures are shown in Fig. 2), 8 — boundaries of the "Marcel" colliery mine field.
C. Localization of the No. 505 seam within the Upper Silesian Sandstone Series in the borehole Marklowice-8. 1 — coal (thickness in meters and index of the seam are given on the right hand side); 2 — claystone, mudstone; 3 — sandstone, conglomerate; 4 — altered rocks of variegated colours: z — greenish, c — red or brown. Stratigraphy: SP — Paralic Series (Lower Namurian); GSP — lower section of the profile of the Upper Silesian Sandstone Series — the so-called Jejkowice Beds and Saddle Beds (Lower and Middle Namurian); Tr — Tertiary strata

sibility that alunite may be present in the red beds of the Polish part of the USCB, namely in the brecciated rocks overlying a disappeared 505/1 coal seam in the "Sośnica" mine, was suggested by Kowalski (1977); his supposition was based, however, on uncertain data, i.e. on a single DTA curve of a polymineral rock.

The authors of the current paper have managed to identify positively the presence of the alunite group minerals within the red beds of the Polish part of the USCB, found in the years 2000 (exposure W1) and 2001 (exposure W2) in the "Marcel" coal mine in the southern part of the Chwałowice Trough (Fig. 1, 2). Initially they were misinterpreted as the minerals of the crandallite group on the basis of XRD analyses of the enclosing rocks from the W1 exposure (Lipiarski, Muszyński 2001). This diagnosis has only been verified by additional, more detailed analyses (SEM/EDS, IR), providing proper mineral identification in the new samples from the W2 exposure. The mistake was due to a substantial similarity of X-ray patterns of alunites and isostructural with them minerals of the crandallite group, which — additionally — were previously described from the Upper Silesian Coal Basin (Gabzdyl, Ryszka 1995) and also from the Lublin Coal Basin (Muszyński, Wyszomirski 1982, 1998).

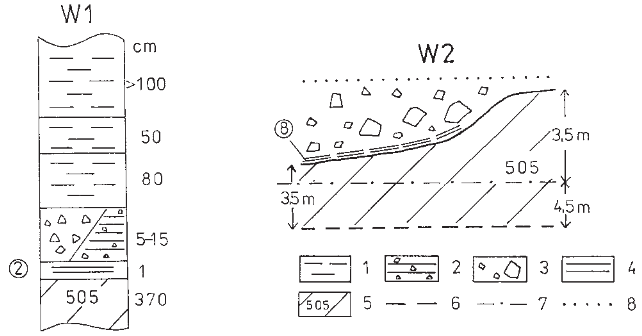

Fig. 2. Sketches (not to scale) of the exposures: W1 (pilot drift in the No. 505 seam at a depth of 200 m) and W2 (pilot cross-cut at a depth of 300 m), with the points of collecting the most alunite-rich samples 2 and 8; 1 — aleuritic claystones, variegated in places, 2 — collapse breccia with parallel structure, 3 — collapse breccia with random structure, 4 — variegated alunite claystone, 5 — coal, 6 — bottom of the No. 505 coal seam tapped with boreholes, 7 — bottom of the gallery, 8 — roof of the gallery

Laboratory investigations included optical microscopy, X-ray analysis (a Philips X'Pert APD diffractometer), infrared absorption spectroscopy (a BIO-RAD FTIR 165 spectrometer, samples as self-supporting films) and SEM/EDS (a HITACHI S-4700 microscope coupled to a NORAN Vantage spectrometer with a Si (Li) detector). The samples analysed using SEM/EDS were covered with carbon; the EDS chemical analyses were point-made.

## GENERAL CHARACTERISTICS OF THE RED BEDS OF THE "MARCEL" MINE

In the W1 exposure (Fig. 2), the lamina with a thickness of about 1 cm contacts directly with an underlying, partly preserved coal seam (an original thickness of the seam about 8 m has been reduced to 3.7 m) and is developed as creamy claystone with brownish red, parallel arranged streaks. Its main components include clay minerals (illite, halloysite, kaolinite-D, traces of smectite), minerals of the alunite group and hematite. Quartz is subordinate, and siderite and sphalerite occur locally as traces. The next layer is represented by brecciated and altered Carboniferous claystones, variegated (creamy-red-tan-brownish-yellow), with a diversified mineral composition. All of them contain clay minerals (illite, kaolinite-D, +/-smectite), detrital quartz, and subordinate alunites. In the red-coloured fragments hematite is the additional mineral, while in the yellow ones goethite accompanied by hematite; traces of boehmite and minerals of the hydrotalcite group cannot be excluded. Laminae and concretionary accumulations composed mainly of siderite and hematite also occur within these claystones. The claystone are overlain by silty claystones, weakly competent, structureless or bedded, grey but partly light grey, locally variegated. The main components, i.e. quartz, micas (illite, muscovite-hydromuscovite, sometimes biotite), kaolinite-D, are accompanied by traces or subordinate amounts of an alunite. Additional admixtures include heavy minerals (zircon, tourmaline, magnetite, leucoxene), goethite, pyrite, siderite and probable boehmite. In the red fragments hematite is the additional mineral, and the grey ones contain carbonized plant detritus. Medium-ordered kaolinite, siderite and traces of microcrystalline quartz line fracture surfaces.

In the W2 exposure (Fig. 2) variegated rocks are represented almost exclusively by collapse breccia*. Only in several places is the breccia separated from the preserved part of a coal seam, as it is in the W1 exposure, by a discontinuous, up to 0.5 cm thick, lamina of light rusty-red claystone. The rock is composed of a clay substance (smectite, illite), minerals of the alunite group, subordinate hematite and traces of quartz.

Clasts of the breccia have the sizes from a fraction of a millimetre up to above 50 cm, irregular, diversified shapes, and are represented by thermally and metasomatically altered Carboniferous claystones and mudstones. Also their mineral composition is diversified, as it depends on the composition of their parent rocks as well as intensity and character of the later alterations. They are composed most often of smectites, minerals of the kaolinite group (hydrohalloysite, halloysite and/or kaolinite-D), detrital quartz and neogenic microcrystalline quartz; additionally there appear zeolites, hematite, cristobalite, tridymite, illite and/or mixed-layer illite/smectite, mullite, calcite and siderite. In some of the clasts there occur detrital muscovite and/or hydromuscovite and a carbon substance.

The binding mass of the breccia is multicomponent, built of smectites, quartz, hematite, zeolites, minerals of the kaolinite group, goethite, illite, mullite, siderite and a mineral of the alunite group; in a single place chalcopyrite was found.

Numerous fractures and vesicle-like microcaverns (with a diameter up to 2–3 mm) are partly or completely filled with smectites, microcrystalline quartz, zeolites, siderite, minerals of the kaolinite group, illite and a mixed-layer illite/smectite, cristobalite, hematite and goethite.

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* Collapse breccia from the "Marcel" mine and zeolites occurring within it will be described separately.

## CHARACTERISTICS OF ALUNITES

Alunites in both profiles characterized above (W1 and W2) occur mainly in the laminae of variegated claystones, directly overlying the preserved fragments of a coal seam. The alunite content, estimated from chemical analyses (Table 1), is *ca* 18 wt.% in

TABLE 1

Chemical compositions of alunite claystones from the red beds of the “Marcel” coal mine

| Component | Sample 2 | Sample 8 | Component | Sample 2 | Sample 8 |
|---|---|---|---|---|---|
| [wt.%] | | | [ppm] | | |
| $SiO_2$ | 32.53 | 30.03 | Sr | 2017 | 3140 |
| $TiO_2$ | 1.73 | 0.94 | Y | 37 | 36 |
| $Al_2O_3$ | 31.00 | 27.58 | Zr | 254 | 325 |
| $Fe_2O_3$ | 7.43 | 6..37 | Mo | 26 | 26 |
| MnO | 0.015 | 0.016 | Ag | 4.7 | 0.6 |
| MgO | 0.24 | 0.60 | Cd | <0.3 | <0.3 |
| CaO | 0.38 | 0.37 | Sb | 16.4 | 1.7 |
| $Na_2O$ | 2.48 | 1.46 | Cs | 7.0 | 309 |
| $K_2O$ | 1.15 | 3.79 | Ba | 3672 | 7957 |
| $P_2O_5$ | 0.32 | 0.67 | La | 140 | 220 |
| LOI | 21.29 | 25.34 | Ce | 186 | 409 |
| Total | 98.57 | 97.18 | Nd | 52 | 146 |
| $S_{total}$ | 2.84 | 3.99 | Sm | 9.4 | 19.6 |
| [ppm] | | | Eu | 1.8 | 4.5 |
| Be | 4 | 7 | Tb | <0.5 | <0.5 |
| Sc | 9.1 | 16.8 | Yb | 4.4 | 4 |
| V | 194 | 180 | Lu | 0.73 | 0.6 |
| Cr | 185 | 110 | Hf | 8.6 | 12.1 |
| Co | 9 | 8 | Ta | 3 | 4 |
| Ni | 25 | 27 | W | 8 | 6 |
| Cu | 342 | 293 | Ir | <5 | <5 |
| Zn | 262 | 70 | Au [ppb] | <5 | 19 |
| As | 24 | 61 | Pb | 420 | 173 |
| Se | <3 | 6 | Bi | <2 | 7 |
| Br | 8 | <1 | Th | 29 | <5 |
| Rb | 80 | 39 | U | 42.3 | 19.7 |

Analysed using ICP-AES and INAA at the Activation Laboratories Ltd (Canada).

sample 2 (W1) and *ca* 26 wt.% in sample 8 (W2), which classifies the rocks as alunite claystones. The alunites are also present as a constant, small admixture (exceptionally reaching several wt.%) in the remaining altered rocks of the W1 exposure, and as sporadic traces in the cement of the collapse breccia in the W2 exposure.

The alunites are cryptocrystalline and as such they are invisible in thin sections among dominating clay minerals and hematite. Their crystals, as indicated by SEM analyses (Phot. 1, 2), are as a rule smaller than 1 μm with a pseudocubic habit (rhombohedra appoximate the shape of the cube). The alunites form aggregates, in which they are to a different degree intergrown with other minerals, mainly with clay minerals and hematite. Due to that, it was impossible to separate a pure alunite fraction, and further phase and chemical examinations had to be carried out on natural samples.

In the X-ray patterns, the presence of the alunites is particularly revealed by the reflections around 5.73–5.75; 4.96–4.97; 3.51; 2.99–3.00; 2.81–2.88; 1.91 and 1.75–1.76 Å (Fig. 3, Table 2), as they do not coincide with the reflections of the accompanying minerals. The full set of the interplanar distances of the alunite in sample 8 is comparable with the literature data of potassium alunites (Table 2) and also approximates those of the alunite of the "Kłodawa" mine (Fijał 1973). On the other hand, the interplanar distances of the alunite in sample 2 are closer to those of the sodium and potassium-sodium alunites (Table 2). Particularly diagnostic is here the range of 006 and 107 the reflections (comp. also: Parker 1962; Kubisz 1964; Keller et al. 1967).

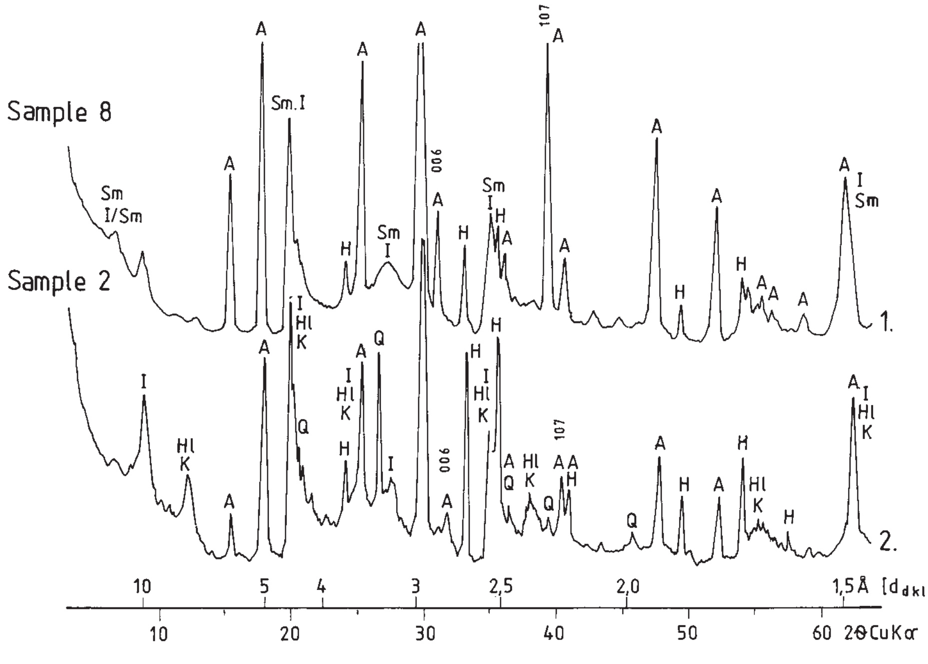

Fig. 3. X-ray patterns of the alunite claystones from the "Marcel" coal mine.
A — mineral of the alunite group, H — hematite, Hl — halloysite, I — illite,
I/Sm — mixed-layer illite/smectite mineral, K — kaolinite, Q — quartz, Sm — smectite

TABLE 2

X-ray data of alunites from the “Marcel” coal mine compared to literature data

| “Marcel” mine, sample 2 | | Natroalunite (Menchetti, Sabelli 1976) | | Natroalunite (Chitale, Güven 1987) | | K-Na-alunite (Goldbery 1980) | | “Marcel” mine, sample 8 | | Alunite (Kubisz 1964) | | Alunite (Menchetti, Sabelli 1976) | | hkl[1] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| d[Å] | I | d[Å] | I | d[Å] | I | d[Å] | I | d[Å] | I | d[Å] | I | d[Å] | I | |
| 5.73 | 15 | 5.73 | 2 | 5.68 | 2 | 5.673 | 10 | 5.75 | 17 | — | — | 5.76 | 9 | 101 |
| | | 5.60 | 2 | 5.55 | 2 | — | — | | | 5.742 | 4 | | | 003 |
| 4.96 | 67 | 4.93 | 100 | 4.90 | 55 | 4.923 | 55 | 4.97 | 36 | 4.951 | 7 | 4.98 | 45 | 012 |
| 3.510 | 56 | 3.52 | 15 | 3.49 | 23 | 3.488 | 31 | 3.510 | 27 | — | — | 3.52 | 28 | 110 |
| | | 3.46 | 2 | 3.44 | 1 | — | — | | | 3.498 | 6 | — | — | 104 |
| 2.991 | 100 | 2.992 | 20 | 2.969 | 60 | — | — | 2.997 | 100 | — | — | 3.00 | 100 | 021 |
| | | 2.997 | 40 | 2.960 | 100 | 2.969 | 100 | | | 2.990 | 10 | | | 113 |
| — | — | 2.935 | 10 | 2.929 | 12 | — | — | — | — | — | — | — | — | 015 |
| 2.811 | 8 | 2.796 | 8 | 2.790 | 7 | 2.814 | 4 | 2.881 | 13 | 2.879 | 4 | 2.880 | 5 | 006 |
| 2.452 | 5 | 2.459 | 3 | 2.449 | 2 | 2.458 | 2 | 2.485 | 8 | 2.481 | 2 | 2.488 | 2 | 024 |
| 2.229 | 23 | 2.255 | 2 | 2.242 | 2 | 2.243 | 16 | 2.286 | 32 | — | — | 2.284 | 25 | 205 |
| | | 2.228 | 20 | 2.221 | 39 | 2.209 | 8 | | | 2.286 | 8 | | | 107 |
| 2.210 | 18 | 2.214 | 2 | — | — | — | — | 2.217 | 8 | 2.215 | 4 | 2.221 | 5 | 122 |
| — | — | — | — | — | — | — | — | — | — | — | — | 2.027 | 2 | 214 |
| — | — | — | — | — | — | — | — | — | — | — | — | | | 018 |
| 1.910 | 22 | 1.903 | 20 | — | — | — | — | 1.907 | 33 | — | — | 1.920 | 25 | 033 |
| | | | | 1.896 | 41 | 1.896 | 29 | | | — | — | | | 303 |
| | | 1.861 | 5 | 1.857 | 5 | — | — | | | 1.9189 | 2 | | | 009 |
| | | 1.879 | 1 | 1.875 | 2 | — | — | | | 1.9071 | 9 | — | — | 027 |
| 1.755 | 23 | 1.754 | 10 | 1.747 | 32 | 1.748 | 21 | 1.753 | 14 | 1.7494 | 8 | 1.755 | 12 | 220 |
| — | — | — | — | — | — | — | — | — | — | — | — | 1.760 | 1 | 208 |
| 1.657 | 11 | 1.651 | 2 | 1.645 | 7 | — | — | 1.683 | 4b | 1.6821 | 2 | — | — | 217 |
| | | | | | | 1.646 | 3 | | | 1.6490 | 2 | — | — | 312 |
| — | — | — | — | — | — | — | — | 1.655 | 2b | — | — | 1.655 | 2 | 312 |
| — | — | — | — | — | — | — | — | | | — | — | | | 306 |
| — | — | — | — | — | — | — | — | | | — | — | | | 036 |
| — | — | 1.616 | 1 | — | — | — | — | | | — | — | | | 1010 |
| 1.569 | 5 | 1.562 | 2 | 1.558 | 4 | 1.559 | 2 | 1.572 | 1b | — | — | 1.567 | 1 | 134 |
| | | 1.546 | 3 | 1.542 | 6 | 1.549 | 2 | | | 1.5708 | 1 | 1.571 | 2 | 128 |
| 1.488 | 55 | 1.512 | 1 | — | — | — | — | 1.497 | 17b | 1.5087 | 8 | 1.514 | 3 | 401 |
| | | 1.504 | 1 | 1.500 | 2 | 1.505 | 3 | | | — | — | | | 315 |
| | | 1.493 | 1 | — | — | — | — | | | — | — | — | — | 042 |
| | | 1.484 | 4 | 1.480 | 8 | 1.483 | 7 | | | 1.4948 | 7 | 1.498 | 11 | 226 |
| — | — | 1.466 | 9 | 1.463 | 20 | 1.472 | 6 | — | — | — | — | | | 0210 |

[1] — hkl indexing after Menchetti and Sabelli (1976).

b — diffused reflection.

Infrared absorption spectroscopy has provided better spectrum in the case of sample 8 as it contains a higher amount of alunites in comparison with sample 2. Diagnostic for the alunites in this spectrum (Fig. 4), not coinciding with the bands of the accompanying minerals, are the bands at 595, 623, 681, 1027, 1087, 1165, 1238, 3486 and 3510 cm$^{-1}$ (Moenke 1962; Kubisz 1972; Fijał 1973; Farmer 1974, Wilkins et al. 1974, Serna et al. 1986). According to Fijał (1973), the sharp band 1027 cm$^{-1}$ is attributable to the $\nu_1$ vibrations, the bands at 595, 623 and 681 cm$^{-1}$ to the $\nu_3$ vibrations, and the bands a 1087, 1165 and 1238 cm$^{-1}$ to the $\nu_4$ vibrations of the $SO_4^{2}$ tetrahedra. A different interpretation of the alunite IR spectrum gave Serna et al. (1986), who attributed two bands in the range 630–690 cm$^{-1}$ to the $\nu_4$ vibrations. Characteristic also of alunites bands around 430, 470 and 525 cm$^{-1}$, being $\nu_2$ vibrations, are in the spectrum discussed completely hidden within the infrared bands of clay minerals. The strong maximum at 3486 cm$^{-1}$ and a weak deflection at 3510 cm$^{-1}$, corresponding to valance vibrations of hydroxyl groups, prove the alunite of sample 8 to be of the potassium type (comp. Serna et al. 1986). In the case of the sodium variety of alunite, these bands are shifted to the

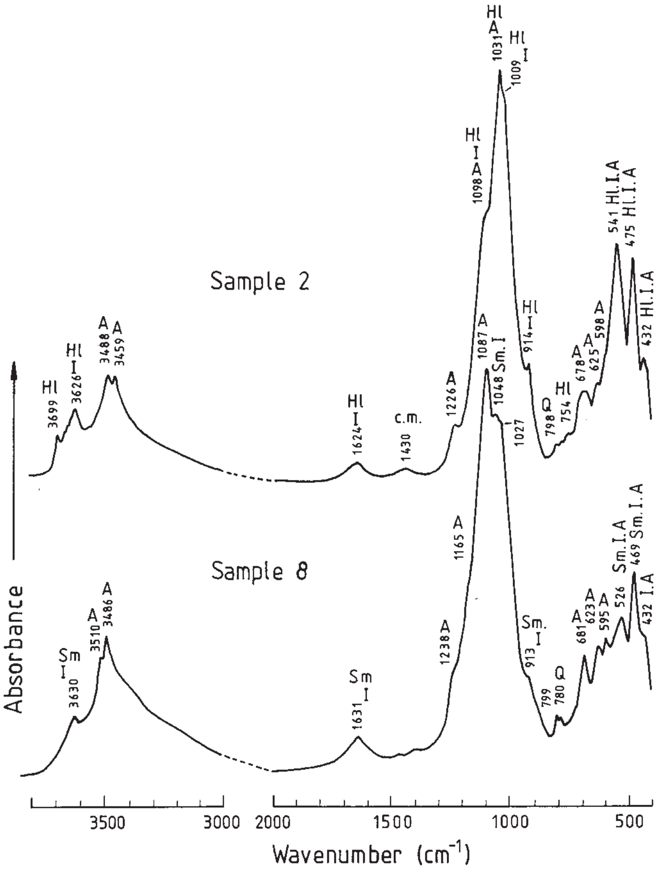

Fig. 4. Infrared absorption spectra of the alunite claystones from the "Marcel" coal mine. A — mineral of the alunite group, Hl — halloysite, I — illite, Q — quartz, Sm — smectite

values 3459 and 3488 cm$^{-1}$, respectively; such a shift can be observed in the spectrum of sample 2 (Fig. 4). In the latter sample, in which its content of an alunite mineral is lower than in sample 8, this mineral gives rise only to distinct $\nu_3$ bands with the maxima at 598, 625, 678 cm$^{-1}$ and the $\nu_4$ band at 1226 cm$^{-1}$, all of them caused by vibrations of the $SO_4^{2}$ ion. In the spectra of both samples there are no bands that could be attributed to either $H_3O^+$ ion (comp. Kubisz 1972; Wilkins et al. 1974) or $NH_4$ ion (comp. Altaner et al. 1988), i.e. the ions that can replace other monovalent ions (mainly $K^+$ and $Na^+$) in the structure of alunites (Kubisz 1964, Ripmeester et al. 1986). According to some authors (e.g. Serna et al. 1986), it is even uncertain whether distinct absorption due to the presence of the $H_3O^+$ ions exists at all. The detection of the absorption bands characteristic of this ion is difficult if occurs in sulphate minerals, as more pronounced $H_3O^+$ bands ($\nu_2$) occur in the same range (950–1175 cm$^{-1}$) as the bands of S-O vibrations. In our samples that are polymineral in their composition, in the range discussed there also appear the absorption bands of clay minerals (halloysite, illite, smectite). Other authors (Altaner et al. 1988) point to the band at around 1650 cm$^{-1}$ as caused by $H_2O$ or $H_3O^+$ contained in the structure of alunite. In the samples analysed this band cannot identify alunite because of coincidence with vibrations of water molecules present in clay minerals.

The minerals coexisting with the alunites studied are in sample 2 clay substance (illite, halloysite, kaolinite-D and traces of smectite), hematite, subordinate quartz and traces of siderite, while in sample 8 smectite, illite, hematite and traces of quartz (Fig. 3, 4). In addition, in sample 2 studied using the SEM/EDS method, a single grain of zinc sulphide (sphalerite?) has been found within an aggregate of microcrystalline Ti-bearing hematite (Ti is most probably incorporated in the structure of hematite).

Considering very small sizes of the alunite crystals studied, it has not been possible to avoid in the EDS point analyses effects of some of these admixtures in the chemical results (Table 3) or to determine chemical formulae of the alunites. But, mainly on the basis of sulphur and alkali contents, an overall chemical composition of the alunites has been established and these minerals have been chemically classified. The results of the analyses, particularly after recalculation into molecular contents, have revealed differences in the amount of alkalis (K, Na). These elements occur first of all in the structure of alunites and decide upon the type of these minerals, but — considering their excess in relation to sulphur — must also be present (one or both) in the accompanying illite and, probably, in smectite. The $K_2O/Na_2O$ molar ratio in the analytical points 1–5 in sample 8 is generally high and indicates that the alunite of this sample represents a potassium variety; the same ratio in sample 2 is low and indicates the presence of a sodic variety. The analytical points 6–8 in sample 8 can correspond to both, sodic and potassic alunite, the latter interpretation being more probable by analogy with the remaining samples. Comparing the $SO_3/(K_2O + Na_2O)$ molar ratio in the points 1–5 in sample 8 with the respective stoichiometric ratio of the alunite group of minerals with the formula $AR_3(SO_4)_2(OH)_6$, a deficit of alkalis can be seen. It must be accepted, then, that the A site is occupied not only by alkali ions (K, Na), but also by some other cations. Among possible substitutions ($H_3O^+$, $NH_4$, $Pb^+$, $Ag^+$, $Ca^{2+}$, $Ba^{2+}$, $Sr^{2+}$, $Ce^{2+}$, $Rb^+$, $Hg^{2+}$, $Tl^+$ — e.g. Scott 1987; Rudolph et al. 2003), the hydronium ion

TABLE 3

Chemical point analyses (EDS method) of alunite aggregates contained in alunite claystones from the red beds of the "Marcel" coal mine [in wt.%]

| Component | Sample 2 | | | Sample 8 | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1* | 2 | 3 | 1* | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| $SiO_2$ | 24.29 | 41.75 | 50.28 | 9.84 | 9.22 | 12.17 | 10.81 | 22.23 | 46.39 | 49.33 | 49.01 |
| $TiO_2$ | 0.84 | 1.20 | — | 1.67 | 1.82 | 2.26 | 2.66 | 4.14 | 0.68 | 2.10 | 2.54 |
| $Al_2O_3$ | 41.50 | 40.10 | 39.08 | 37.88 | 35.80 | 37.10 | 36.70 | 33.18 | 36.51 | 36.56 | 36.41 |
| $Fe_2O_3$ | 2.72 | 2.40 | 1.82 | 5.53 | 7.18 | 5.58 | 6.20 | 4.59 | 2.74 | 1.92 | 1.68 |
| CaO | — | — | — | — | 0.72 | — | — | — | — | — | — |
| $K_2O$ | 1.01 | 0.89 | 0.77 | 7.61 | 8.04 | 7.72 | 7.77 | 5.90 | 3.85 | 2.82 | 2.62 |
| $Na_2O$ | 5.06 | 2.89 | 4.14 | 0.96 | 1.30 | 1.03 | 1.06 | 0.81 | 1.99 | 3.46 | 3.36 |
| $P_2O_5$ | 0.82 | — | — | 1.66 | 1.63 | 1.55 | 0.98 | — | — | — | — |
| $ZrO_2$ | — | — | — | — | — | — | | 1.53 | — | — | — |
| $SO_3$ | 23.75 | 10.78 | 3.91 | 34.85 | 34.27 | 32.59 | 33.82 | 27.61 | 7.83 | 3.81 | 4.38 |
| Total | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

* Numbers of the analyses correspond to the EDS spectra presented in Figure 5.

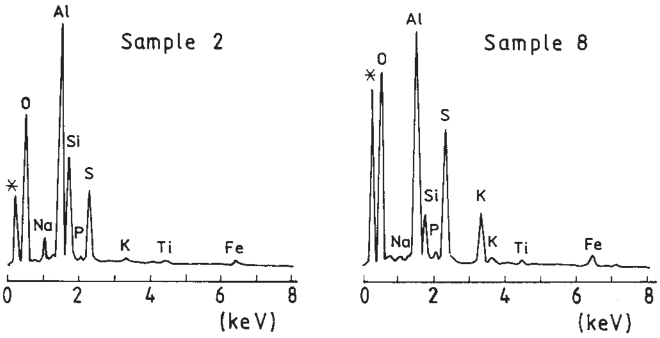

Fig. 5. EDS spectra (point analyses) of alunite aggregates with subordinate admixtures of clay minerals and hematite in the alunite claystones from the "Marcel" coal mine
* — peak of surface-deposited carbon (sample preparation)

($H_3O^+$) can be considered first. However its content would have been low, below the detection limit using absorption infrared spectroscopy; the presence of this ion has not been recorded in the spectra obtained (see discussion above and Fig. 4). In the alunites of both samples analysed, substitutions of Pb, Ba, Sr ions at the A site and replacement of the $SO_4^{2}$ by $PO_4^{3}$ ions are also possible, which are suggested by positive correlation between the contents of the elements mentioned and the sulphur content (Table 1, 3).

An excessive amount of sodium in respect to sulphur established in sample 2 and in the analytical points 6–8 in sample 8 suggests the presence of a sodic variety of illite (brammalite), expected previously by Kowalski (1977) in the red beds of the USCB.

## SUMMARY AND CONCLUSIONS

The occurrence of alunites in the "Marcel" mine is one of few recorded in Poland (Morawiecki 1962; Kuźniarowa, Strzyżewska 1963; Kubisz 1964; Fijał 1973) and, simultaneously, a single site within the so-called red beds of the Polish part of the Upper Silesian Coal Basin. Similar occurrences in the Czech part of the USCB were earlier described by Kralik (1982) and Klika (1998).

The alunites of the "Marcel" mine are represented by two varieties: potassic (alunite, potassium alunite) and, less frequent in the nature, sodic (natroalunite, sodium alunite), both probably containing substitutions of barium, strontium, phosphorus and, possibly, the hydronium ion. The following features characterize the alunites:

1 — cryptocrystalline development (rhombohedral crystals, approximating cube in their habit, the sizes below 1 μm);

2 — the presence in higher amounts (up to about 26 wt.%) at the bottom of red beds, in thin discontinuous layers of claystone, directly overlying the preserved fragments of oxidized (burnt out) coal of the seam No. 505;

3 — coexistence mainly with clay minerals (illite, halloysite, kaolinite-D, smectite) and hematite; subordinately or in traces the alunites are accompanied by quartz, siderite and sphalerite.

The red beds of the Upper Silesian Coal Basin are products of a long-lasting, post-Carboniferous but pre-Miocene, supergenic weathering of clastic and clay rocks as well as coals of the Carboniferous age. During the weathering, the outcropping coal seams underwent local, temporary, endogenic fires and later, after burial by Miocene strata, diagenetic-epigenetic alterations began (Kowalski 1977, 1979, 1982, 1983; Kralik 1982; 1984; Klika 1998; Lipiarski et al. 1998). The formation of a range of neogenic minerals: mullite, tridymite, cristobalite, microcrystalline quartz, smectites, halloysite, hydrohalloysite, kaolinite, illite, hematite, zeolites, goethite, siderite, calcite and alunite, and sporadically occurring chalcopyrite and sphalerite was an effect of these processes.

The alunites could have only formed after partial burning of coal seams, in a successive stage of supergenic weathering but probably prior to shallow burial (about 200 m) under clay sediments of the Miocene sea, because these minerals can form only in a strongly oxygenating environment (Kashkaï 1970). It is worthy mentioning that similar, hydrated, basic aluminium sulphates (probably of the basaluminite or hydrobasaluminite type) originate at present in mine workings of the USCB (Gabzdyl, Kopiec 1970).

The conditions favouring the formation the alunites studied were locally met mainly at the bottom of red beds, along their contact with the remaining fragment of the coal seam that probably shielded underlying strata from the descending solutions. The alunites may have formed in two ways: either 1 — by direct crystallization in open space from a conveyed acid solution that contained all necessary elements in the form of ions (reaction I), or 2 — by metasomatosis, in reaction of descending solution of sulphuric acid with earlier formed, crystalline or amorphous aluminosilicates that were weathering products of Carboniferous rocks and/or residuum left behind after coal (according to reactions II and III). The second process seems to be more probable. The source of sulphuric acid solutions, the carriers of sulphate ions, is seen most probably in oxidation of iron sulphides (pyrite, subordinate marcasite; reaction IV), common minerals both in the coals and the rocks of the USCB (e.g. Ratajczak 1989; Parzętny 1995; Kucha, Lipiarski 1998). Contemporary waters rich in sulphate ions, noted in the Upper Carboniferous of the USCB by Pałys (1966a, b) and Gabzdyl and Kopiec (1970), are just examples of such solutions.

I. $3Al^{3+}_{(aq)} + K^{+}_{(aq)} + 2SO_4^{2}{}_{(aq)} + 6H_2O_{(aq)} \rightleftarrows \underset{\text{alunite}}{KAl_3(SO_4)_2(OH)_{6\,(s)}} + 6H^{+}_{(aq)}$

(source: Evans et al. 2003)

II. $\underset{\text{illite}}{KAl_2[(OH)_2Al_2Si_3O_{10}]} + 4H^{+} + 2SO_4^{2} \rightleftarrows 3SiO_2 + \underset{\text{alunite}}{KAl_3(SO_4)_2(OH)_6}$

(source: Goldbery 1980)

III. $\underset{\text{kaolinite}}{Al_4[(OH)_8Si_4O_{10}]} + 2Na^{+} + 4SO_4^{2} + 9H_2O = \underset{\text{sodium alunite}}{2\ Na\ Al_3(SO_4)_2(OH)_6} + 6H_4SiO_4$

(source: Chitale, Güven 1987)

IV. $FeS_{2\,(s)} + 7/2O_{2(aq)} + H_2O_{(aq)} \rightarrow Fe^{2+}_{(aq)} + 2SO_4^{2}{}_{(aq)} + 2H^{+}_{(aq)}$

(source: Evans et al. 2003)

The temperature of alunite formation in hipergenic processes (in the core of weathering) is suggested to be at about 20–50°C (Kashkaï 1970). In the case of the occurrence described, the temperature could have been higher, as the descending solutions could be heated up by oxigenating or even glowing coal substance; such a processis similar to those observed currently in coal waste dumps (Wagner 1980). The maximum temperature of alunite formation, determined experimentally and deduced from field observations, is around 500°C (Kashkaï 1970).

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# REFERENCES

ALTANER S.P., FITZPATRICK J.J., DENNIS KROHN M., BETHKE P.M., HAYBA D.O., GOSS J.A., ZOE ANN BROWN, 1988: Ammonium alunites. *Amer. Miner*. 73, 145–152.

BROPHY G.P., SCOTT E.S., SNELLGROVE R.A., 1962: Solid solution between alunite and jarosite. *Amer. Miner*. 47, 112–126.

CHITALE D.V., GÜVEN N., 1987: Natroalunite in a laterite profile over Deccan Trap basalts at Matanuamad, Kutch, India. *Clays Clay Miner*. 35, 3, 196–202.

EVANS K.A., GANDY C.J., BANWART S.A., 2003: Mineralogical, numerical and analytical studies of the coupled oxidation of pyrite and coal. *Miner. Magaz*. 67, 2, 381–398.

FARMER V.C. (Ed.), 1974: The infrared spectra of minerals. *Miner. Soc. Monogr*. 4. London.

FIJAŁ J., 1973: Studium mało rozpowszechnionych minerałów kujawskich złóż soli. *Prace Miner. PAN* 33, 1–56.

GABZDYL W., KOPIEC A., 1970: O produktach działalności siarczanowych wód karbońskich w kopalni „Prezydent". *Przegl. Geol*. 11, 508–510.

GABZDYL W., RYSZKA J., 1995: Phosphorus-rich coaly tonsteins and coal seams in Silesia. XIII Int. Congr. on Carbo-Perm. Book of Abstracts. 28.08.–2.09.1995. Kraków, Poland.

GOLDBERY R., 1980: Early diagenetic, Na-alunites in Miocene algal mat intertidal facies, Ras Sudar, Sinai. *Sediment*. 27, 189–198.

HALL A.J., FALLICK A.E., PERDIKATSIS V., PHOTOS-JONES E., 2003: A model for the origin of Al-rich efflorescences near fumaroles, Melos, Greece: enhanced weathering in a geothermal setting. *Miner. Magaz*. 67, 2, 363–367.

KASHKAÏ M.A., 1970: Alunity, ikh genezis i ispol'zovanie. T. I–II. Moskva, Izd. "Nedra".

KELLER W.D., GENTILE R.J., REESMAN A.L., 1967: Allophane and Na-rich alunite from kaolinitic nodules in shale. *Journ. Sedim. Petrol*. 37, 1, 215–220.

KLIKA Z., 1998: Geochemistry of coal from region of the red beds bodies of the Upper Silesian Coal Basin. VŠB — Technical University Ostrava. 1–85.

KOWALSKI W.M., 1977: Petrografia pstrych utworów górnośląskiej serii piaskowcowej (namur górny) Rybnickiego Okręgu Węglowego. *Kwart. Akad. Górn.-Hutn. — Geologia*, 3, 1–61.

KOWALSKI W.M., 1979: Rozmieszczenie pstrych utworów na podmioceńskich wychodniach skał karbońskich w pónocno-wschodniej części Rybnickiego Okręgu Węglowego. *Annales UMCS*, Sect. B, Geogr. Geol., 34, 113–122.

KOWALSKI W.M., 1982: Przedmioceńska strefa wietrzenia w stropie warstw załęskich (pstre utwory) Rybnickiego Okręgu Węglowego. *Kwart. Geol*. 26, 1, 59–70.

KOWALSKI W.M., 1983: Procesy wietrzeniowe i epigenetyczne w obrębie pstrych utworów Rybnickiego Okręgu Węglowego. *Przegl. Geol*. 31, 11, 591–595.

KRALIK J., 1982: Mineralogie pestrých vrstev v ostravsko-karvinské cernouhelné pánvi. *Cas. Slez. Muz.* Opava [A], 31, 149–171.

KRALIK J., 1984: Tepelné změny uhlonosných sedimentů při požárech důlních odvalů a přírodním hoření uhelných slojí. *Sbor. véd. Prací Vys. Šk. báň.* Ostrava, 30, 171–198.

KUBISZ J., 1964: Studium siarczanowych minerałów hipergenicznych Polski. *Prace Geol. PAN* 26, 1–93.

KUBISZ J., 1972: Studies on synthetic alkali-hydronium jarosites III. Infrared absorption study. *Miner. Polon*. 3, 23–37.

KUCHA H., LIPIARSKI I., 1998: Mineralogy and geochemistry of sulphides from coal seams, Upper Silesian Coal Basin, Poland. *Miner. Polon*. 29, 2, 23–40.

KUHL J., 1931 a: O tworzeniu się kaolinu i ałunitów we wschodniej części Gór Świętokrzyskich (Góry Pieprzowe) koło Sandomierza. *Spraw. z Czyn. i Pos. PAU* 36, Kraków.

KUHL J., 1931 b: Zur Bildung des Kaolins und der Alunite in östlichen Teil des polnischen Mittelgebirges (Góry Pieprzowe) in der Umgebung von Sandomierz. *Bull. Intern. de l'Acad. Polonaise Sc. Lett.* Sér. A: Sc. Mat., 665–675.

KUŹNIAROWA A., STRZYŻEWSKA A., 1963: Minerały i niektóre własności techniczne łupków menilitowych w Bieszczadach. *Kwart. Geol*. 7, 4, 653–654.

LIPIARSKI I., MUSZYŃSKI M., 2001: Wtórne iłowce crandallitonośne ze zmienionych utworów środkowego namuru w KWK "Marcel" w GZW. *Kwart. Akad. Górn. Hutn. — Geologia* 27, 2–4, 315–327.

LIPIARSKI I., PRASNOWSKI M., SZREDER M., 1998: Objawy fosylnego wietrzenia węglonośnych utworów dolnego i środkowego namuru w niecce chwałowickiej koło Rybnika w zachodniej części GZW. Mat. 21. Symp. „Geol. form. węglonośnych Polski". Wyd. Geol. Akad. Górn. Hutn. Kraków, 37–42.

MENCHETTI S., SABELLI C., 1976: Crystal chemistry of alunite series: crystal structure refinement of alunite and synthetic jarosite. *Neus. Jahrb. Miner. Monath.* 9, 406–417.

MOENKE H., 1962: Mineralspektren. Berlin.

MORAWIECKI A., 1962: β-alumohydrokalcyt z Nowej Rudy. *Kwart. Geol.* 6, 4, 539–566.

MUSZYŃSKI M., WYSZOMIRSKI P., 1982: Minerals of crandallite group in some tonsteins of the Lublin Coal Basin. *Miner. Polon.* 13, 1, 17–24.

MUSZYSKI M., WYSZOMIRSKI P., 1998: New occurrences of the crandallite group minerals in sedimentary rocks of Poland. *Miner. Polon.* 29, 1, 19–27.

PAŁYS J., 1966 a: O genezie solanek w górnym karbonie na Górnym Śląsku. *Rocz. Pol. Tow. Geol.* 36, 2,121–154.

PAŁYS J., 1966 b: Wody typu siarczanowo-sodowego i węglanowo-sodowego na Górnym Śląsku. *Przegl. Geol.* 5, 229–232.

PARKER R.L., 1962: Isomorphous substitution in natural and synthetic alunite. *Amer. Miner*. 47, 127–136.

PARZENTNY H.R., 1995: Wpływ nieorganicznej substancji mineralnej na zawartość niektórych pierwiastków śladowych w węglu Górnośląskiego Zagłębia Węglowego. *Pr. Nauk. Uniw. Śl.* 1460, 1–88.

POBORSKI J., 1947: Złoże i kopalnia rud „Staszic" w Rudkach, w Górach Świętokrzyskich. *Przegl. Górn.* 34, 4, 26–33.

RATAJCZAK T., 1989: Charakterystyka mineralogiczno-petrograficzna oraz niektóre własności fizykochemiczne piaskowców i łupków rejonu kopalni „Jaworzno". *Kwart. Akad. Górn.-Hutn. — Geologia* 15, 3, 41–60.

RIPMEESTER J.A., RATCLIFFE C.I., DUTRIZAC J.E., JAMBOR J.L., 1986: Hydronium ion in the alunite-jarosite group. *Canad. Miner.* 24, 435–447.

RUDOLPH W.W., MASON R., SCHMIDT P., 2003: Synthetic alunites of the potassium-oxonium solid solution series and some other members of the group; synthesis, thermal and X-ray characterization. *Europ. Jour. Mineral.* 15, 913–924.

SCOTT K. M., 1987: Solid solution in, and classification of, gossan-derived members of the alunite-jarosite family, northwest Queensland, Australia. *Amer. Miner.* 72, 178–187.

SERNA C.J., PARADA CORTINA C., GARCIA RAMOS J.V., 1986: Infrared and Raman study of alunite-jarosite compounds. *Spectrochim. Acta* 42A, 6, 729–734.

STOCH L., 1958: Niektóre zagadnienia analizy termicznej różnicowej minerałów. *Arch. Miner.* 21, 2, 185–228.

WAGNER M., 1980: Przemiany termiczne węgla kamiennego w strefach pożarów hałd kopalnianych. *Zesz. Nauk. AGH — Geologia* 6, 2, 5–14.

WILKINS R.W.T., MATEEN A., WEST G.W., 1974: The spectroscopic study of oxonium ions in minerals. *Amer. Miner.* 59, 811–819.

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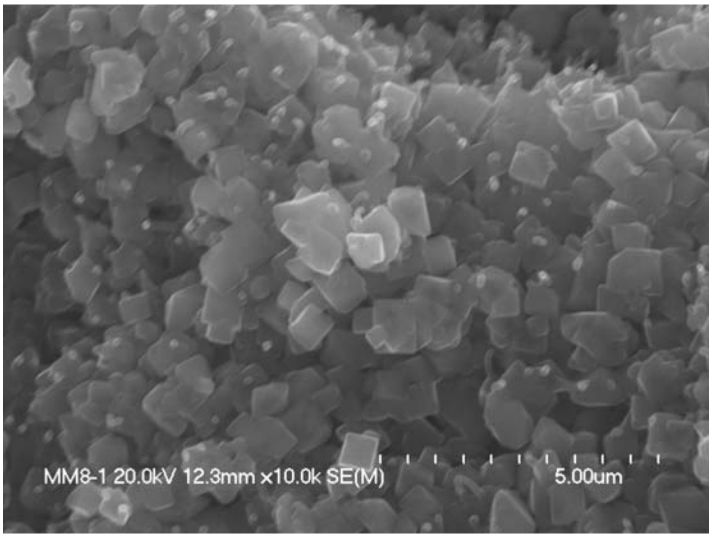
# AŁUNIT W tzw. PSTRYCH UTWORACH Z KOPALNI WĘGLA KAMIENNEGO „MARCEL", GÓRNOŚLĄSKIE ZAGŁĘBIE WĘGLOWE, POLSKA

## Streszczenie

Wśród tzw. pstrych utworów w kopalni węgla kamiennego „Marcel" (GZW) (Fig. 1, 2) udokumentowano metodami XRD, IR, SEM/EDS (Fig. 3–5, Table 1–3, Phot. 1, 2) obecność ałunitu (odsłonięcie W2) i natroałunitu (odsłonięcie W1). Minerały te występują zwłaszcza w spągu pstrych utworów, w laminach iłowców kontaktujących z częściowo zachowanym pokładem węgla (Fig. 2). Są wykształcone kryptokrystalicznie; ich romboedryczne kryształy, o pokroju zbliżonym do sześcianu, mają wielkość poniżej 1 μm (Phot. 1, 2). Prawdopodobnie zawierają one podstawienia diadochowe baru, strontu, fosforu i ew. jonu hydroniowego w strukturze. Współwystępują głównie z minerałami ilastymi (illit, haloizyt, kaolinit-D, smektyt) i hematytem; podrzędnie lub śladowo towarzyszą im kwarc, syderyt i sfaleryt. Ich genezę należy wiązać z końcowym etapem formowania się pstrych utworów ze skał i węgla karbonu, w złożonych procesach: wietrzennych, a następnie diagenetyczno-epigenetycznych. Bezpośrednio ałunity powstały zapewne metasomatycznie, przez oddziaływanie na ilasty prekursor roztworów kwasu siarkowego, związany z supergenicznym utlenianiem siarczków (głównie pirytu), rozproszonych w utworach karbonu.

Phot. 1. SEM. An aggregate of rhombohedral (cube-like) crystals of alunite, almost without an admixture of associated minerals. Alunite claystone from the “Marcel” coal mine, sample 8



Phot. 2. SEM. An aggregate of rhombohedral (cube-like) crystals of alunite, with numerous inclusions and intergrowths of associated minerals (isometric or elongated grains <0.25 µm in size). Alunite claystone from the “Marcel” coal mine, sample 8

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