Industrial mineralogy of the Polish fly ashes and their unique utilization

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Abstract

This study was undertaken to recognize sintering-, softening-, melting-, flow temperature, mineralogy, chemistry and prospects for utilization of the Polish fly ashes (FA, FAs). The study is metallurgy-foundry oriented, i.e. it regards the ashes as the (potential) charge material for production the chemical compounds, ceramics, metal-matrix composites (MMC) and ceramic-matrix composites (CMC) and as an item in new technologies. Moreover, definite ashes-derived compounds, e.g. cordierite have been shown to strengthen the metals. A comparison between the ashes and the rocks is drawn, and, comparison between the Polish ashes (type) and those from over-the-world ones is undertaken. The radioactivity of the ashes is addressed as well. 24 (25) samples can be classified into 'hybrid alumina' (close to F-class of the ashes), 'intermediate' (an Al-analogue to bottom ashes) and calcium-rich ones. Several unique samples, e.g. arcanite-calcite-ettringite- and a bottom ash are outside even this classification. The 'hybrid alumina' is knowable by Ca-silicates and Ca-aluminosilicates, the 'intermediate' is knowable by anorthite and amphiboles, whereas the calcium-rich ones is devoid of Ca-silicates. Enrichments in toxic elements is addressed and discussed. One of novelties of this paper is that we have encountered the amphiboles, leucite and Fe-Mn phosphates in the ashes – which cannot be regarded as accessory ones. Apart from the ash-Al-alloy pistons, metal-(cenosphere)-ash composites and intimately-intergrown-phase (IPC) composites, a FA-glass-armoured metal is also mentioned. Of the many technologies of the Institute the production of almost pure cordierite (indialite) from fly ash containing moderate amounts of CaO and SO_3 is worthy of note. Likewise, MMC- and CMC composites and ceramics thereof are also noteworthy.

Keywords: *composite, waste management, fly ash, ettringite, amphibole, cordierite*

1. Introduction

The hitherto mineralogy and chemistry of fly ashes (FAs) have been covered in, e.g. [1−14], whereas very odd FAs are examined by [15−16]. In these cases, the FA comprises, beside quartz, mackinawite ($FeS_{0.96}$), vaterite ($CaCO_3$), corundum, spinel, tricalcium silicate and magnetite [15] or the FA is solely composed of glass and carbon and practically devoid of spinel, quartz or mullite [16]. Moreover, diverse sulphides were also described [1−2]. Polish FA have been described by [17−20], among others. Of the Polish ashes, the following minerals have been mentioned by literature to date [17]: lime, portlandite, mullite, anhydrite, quartz, calcite, K-feldspar, plagioclase, haematite, magnetite, gypsum and accessory ones – spinel, wűstite, pyrrhotite, goethite, graphite and metallic iron (of hard coals). FA of brown coals contains: lime, mullite, anhydrite, quartz, plagioclase, haematite, magnetite, grossular, gypsum and glass [ibidem]. The authors of [18] have added: periclase, forsterite, muscovite, natrite and borax. Cf. also [20]. The author of [19] has described monazite, xenotime, zircon and the novel REE-oxides. Moreover, she connects U with decomposition of phosphates, e.g. rabdophane, whereas REE might have also occurred in glassy aluminosilicates (amorphous) masses [ibidem]. A part of the above-mentioned papers is of the local character (Silesia). The papers [21−22] are of solely building-ceramics-technological character. Chemical analyses (also trace elements) are also given by [23−25]. The other papers concerning trace elements are, e.g. [26−27]. The utilization of fly ashes (FAs) to diverse construction-materials purposes is dated since fifty's. This notwithstanding, the mining (stowing), cement-concrete- and building industry are still deemed to be the main user of the FA. Low CaO- (the F-type)- and high CaO- (the C-type) FAs are used by the cement

industry in a diverse manner [28] or not used (the C-type), due to lack of acceptance of the high-Ca materials by concrete industry, cf. [29]. Additionally, they are used as a leaning component. However, the materials from FA like geopolymers, cold-solidified FAs [29], or glass ceramics, e.g. [15] are used in technics and building (interior and exterior cladding). Geopolymers with a high carbon content, which challenge the definition of the geopolymer [30], are also produced. A review of mineralogy, chemistry, classification and diverse utilization goals of FA is given by [31], where zeolite production, agricultural purpose, the recycling of Fe, Al, Ga, Ge, Hg and diverse metallurgy-confined technologies, e.g. moulding sands are described. Materials made of FA can also be used as heat shields [32]. Commonly, FAs are classified as the F-type (with a high amount of silica and alumina but a low level of CaO (< 10%) or the C-type (>10% CaO) but the 'hybrid' samples are also frequently encountered. Diverse factors can contribute to the C-type character, and there are other classifications [31] as well. Glass ceramics and construction ceramics are made from diverse materials [33−36]. The synthesis of definite compounds from FAs, except zeolites [37−38], is less frequent. However, due to the use of diverse fuel in power plants, including biomass and, in general, low quality bituminous coal or lignite or the co-burning of the basic fuel with other materials, the number of compounds (minerals) to be found in FA is expanding extremely rapidly. Such the state of things is encouraging as regards synthesis from FA, but this may imply hazards. This paper is aimed at describing mineralogy of the Polish fly ashes and indicating their prospective, unique-foundry-directed utilization (composites, compounds, technologies). Particular kind of FA is well suited to particular technology. Owing to the unique character of some of FAs, (geo)chemical or technological aspects will also be addressed. *It should be stressed that the description of the formation (origin) of minerals (phases) and the problems of enrichment of elements – are generally beyond the scope and purpose of this paper.* This notwithstanding, several problems of the formation of definite minerals will be addressed. *In regard to the enrichments of elements, only comparisons with the world-wide average values for the ashes (and not for feed-coals) and with clarke values will be given.*

2. Materials and Methods

2.1. Materials

A total of twenty-four FAs were collected from twelve coal-fired power plants in Poland during 2010. The FAs are mainly fresh, and only a few (KL, Bi3s, Dos) originated from dumps; one of those being bottom ash (KWR). Additionally, one sample from Skawina has been collected [39] (Table 1). This sample was used for preliminary-technical-technological-model tests. Five modified samples (M7, Skt, Skpm, FLYASH and preheated EW-SKTT) – were analysed using powder X-ray diffraction (XRD). Fly ashes for the cenosphere utilization were collected separately, and, generally the cenosphere- technology is beyond the scope and purpose of this paper. Table 1 presents some traits of the investigated fly ashes.

2.2. Methods

Preliminary investigation of the FAs comprised: a). measurement of sintering-, softening-point-, melting-point- and flow temperature, b). leaching (rinsing out) by distilled water, c). magnetic separation by Ba-ferrite magnet, d). complete roasting in diverse gases, e). separation of cenospheres and f). radioactivity measurements. The above-mentioned temperature and radioactivity measurements covered all the samples, whereas only selected samples were model-targeted. All of these investigations are summed up in [39]. The temperatures discussed above were not only investigated (microscope with a heating stage), but a programme in C++ was devised which predicted the temperatures, based on correlations of refractoriness of groups of oxides such as $CaO + K_2O + Na_2O$, $Fe_2O_3 + FeO + MgO + Mn_3O_4$ and $SiO_2 + Al_2O_3 + TiO_2 + P_2O_5$ [ibidem]. Leaching was performed by triplicate mixing (10 min.) of FA and distilled water and rinsing out (13 min.). All of the processes were traced using XRF-WD analysis, XRD and pH measurement. Cenospheres were separated by the liquid method. Cenospheres have been used in diverse projects, and described in several papers, e.g. [40]. Radioactivity measurements of K, Ra, Th activity have been made using semiconducting γ-spectrometer with its on-line data-collecting- and computing programmes, Genie 2000. The IAEA standards K-40, Ra-226 and Th-228 were used as etalons. The measurements were made following the definite Standard (*see below*). The standardless quantitative energy-dispersive analysis (EDS) by electron microprobe (EPMA) has been used for several samples; with the grains being selected at random. X-ray fluorescence (XRF-WD) analysis was performed using an Axios Minerals (Pananalytical) spectrometer using the common mode, and the relative error should be deemed at 2−5%. X-ray powder diffraction patterns of the samples were recorded with PW 1710 (Philips, CoKα), D8Discover (Bruker, CoKα, CuKα) as well as by PW 1830 (Philips, CuKα). The range covered 10(3)-120° (90°) 2Θ; the step being 0.015 2Θ (CoKα and CuKα) and 0.05 2Θ (CuKα). The latter was intended to corroborate the presence of the main phases. For phase identification, the online programmes, diverse data bases, lexicons [41,42] and other materials were used. The recognized (matched) pattern demanded further analysis. The recorded patterns display frequently

Table 1. General description of the investigated ashes

Brand	Fuel	Samples	Traits/literature
Siekierki	bituminous coal as above + 10% biomass	Sz Sb	S-containig, unburned particles
Rzeszów	bituminous coal	Rp	
Połaniec	bituminous coal	P4 P8	4% unburned particles 8% unburned particles
Opole	bituminous coal	O2 O3 Oh	blended fly ashes
Bełchatów	lignite	B3z Bs	average LOI for both 2.7%; range: 1.43−4.99%
Kielce	bituminous coal bituminous coal biomass	KWP KWR KL	bottom ash from a dump
Białystok	bituminous coal	Bi1 Bi2 Bi3 Bi3s BiS	from a dump
Dolna Odra	bituminous coal	Dos	from a dump; 2.7% C
Szczecin	bituminous coal	Sze	
Wybrzeże	bituminous coal	Wy1 Wy2	
Poznań	bituminous coal	Poe	
Skawina	bituminous coal	Skp	4.0 and 4.0−5.0% unburned particles
Skawina	bituminous coal	EW-SKTT	[39]

coincided, and, there were also many peaks 'in the background' which only hardly can be estimated as the background itself. The diffractograms were interpreted while observing diversity of the standard patterns as well as by, e.g. picking over in text-files (tracing steps of the numerical outcome of the XRD pattern). Owing to the above-mentioned problems, the recognized phases were divided into main (certain), minor-accessory ones (their presence cannot be disregarded) and uncertain ones (recognition based, e.g. on a single reflection). In the latest case, it should be understood that the presence of the phase is supposed. Several samples created unique problems. For the purpose of the recognition of these samples, they were preheated at 800°C (16 h) and at 1200°C (5 h) to obtain definite products from the supposed minerals and to corroborate or discard the presence of the particular minerals which, into the bargain, were unlikely. One sample was intentionally melted, then X-rayed (XRD) – in order to trace the transformations. For the same purpose the infrared spectra (IR) of several problematical samples were recorded using a reflection spectrometer (Nicolet is10) of 8 cm^{-1} resolving power, in the range 450−4000 cm^{-1}, with KBr as a carrier. The bands of the range of 1882−2274 (2450) cm^{-1} are inherent of the mode of operation of the device, and, hence, not informative. The literature used for IR were, e.g. [43−52]. Monitoring chemical composition of the ashes of a few brands was also performed within the period of 5−6 months.

3. Results

3.1. Fly ashes characterization

The temperature traits of the FAs are presented below (Table 2).

One may observe (Table 2) that the highest melting temperatures (1460−1403°C) are attained by the samples Poe, B3z, Bs, Oh and KL, i.e. by both F-class- and C-class ashes. A similar phenomenon (the F- and C ashes) is observed at sintering temperature (1190−1110°C) for Bs, Dos, KWR, Oh, P4, Rp and Sz. The devised programme is capable of predicting all of the temperatures, if the sum of the silica and alumina is at and above 65 wt.%. Rinsing out the Skawina sample (outside the scope of the tables) gave pH 10.7, 10.48 and 10.13, after the first, second and the third cycle, respectively; the starting mix being pH 9.24. After leaching, Na (20.4%), K (29.4%), Ca (13.6%), Mg (10.7%) and minor amounts of Si and Al were rinsed out from the analysed FA. Simultaneously, amounts of Fe and Zn were enhanced from 4.37 to 5.35% and from 103 to 311 ppm, respectively. The ppm and ppb amounts of Cr,

Table 2. Sintering-, softening-point-, melting-point- and flow temperature of the fly ashes, °C; modified after [53]

Sample	Sintering temperature	Softening temperature	Melting temperature	Flow temperature
Sz	1110	1170	1207	1227
Sb	980	1240	1321	1353
Rp	1120	1230	1268	1331
P4	1140	1290	1309	1346
P8	905	1243	1321	1390
O2	981	1237	1383	1503
O3	985	1220	1395	1483
Oh	1150	1250	1403	1450
B3z	1080	1260	1431	1451
Bs	1190	1380	1409	1430
KWP	1050	1270	1316	1360
KWR	1160	1220	1283	1360
KL	870	1200	1460	1464
Bi1	992	1257	1304	1359
Bi2	906	1182	1312	1379
Bi3	960	1230	1288	1347
Bi3s	992	1239	1307	1362
BiS	-	-	-	-
Dos	1170	1260	1366	1442
Sze	1000	1230	1377	1479
Wy1	1060	1220	1310	1361
Wy2	1056	1237	1353	1389
Poe	1080	1260	1413	1452
Skp	-	-	-	-
Skp/EW-SKTT	990	1220	1399	1460
Range	870−1190	1170−1380	1207−1460	1227−1503
- No data.				

Cd and Pb are only leached within the error of analysis, e.g. Cr_2O_3 was reduced by 16 ppm (13.9%), whereas CdO was reduced by 44%. The primary amount of CdO was minute, i.e. 0.32 ppm. But PbO was depleted from 81 to 8 ppm. P_2O_5 and SO_3 were lost in the amounts of 10% and 20.90%, respectively. Following the leaching process, magnetite and illite were absent, but calcite has formed instead of them. Magnetic separation, especially – subsequent to leaching, was involved in the depletion of 25.7 wt.% Fe_2O_3, which was accompanied by depletion of the material in Al, Na, K, Ca. The authors of [39] claimed that no considerable changes in powder diffraction pattern took place after complete roasting, with the exception of, perhaps, increase of intensity of the haematite reflection and the emergence of albite (plagioclase). The separation of cenospheres in considerable amount (and showing high quality) was only possible from the samples Sze, Dos, O2, O3, Oh, P8, and P4, i.e. from the ashes close to the F-class. Radioactivity measurements were based on two coefficients, depending on $K + Ra + Th$ (f_1) and on Ra (f_2) specific activity, respectively. According to Polish radiation-protection regulations, the investigated ashes are generally safe. However, the activity of O2 and O3 is deemed on the limit or above the admitted activity (Table 2A). The values in the Table are given by way of example. The O2- and O3 sample are most radioactive of the set.

The EPMA analyses were performed on two Skawina samples (including Skp) and on B3z. Apart from glasses, the single point analyses determined the composition close to anorthite, anorthite + lime, alumoåkermanite (gehlenite) in B3z and the following ones in Skawina: quartz (silica), quartz + mullite, $Ca(ClO_3)_2 + Ca(OH)_2/CaO$ (interpretation), haematite-magnetite, supposed amphiboles and fayalite. The chemical WD-XRF analyses are presented below (Table 3).

Table 2A. Results of the radioactivity measurements; confidence level = 0.95; Bq/kg

Sample	Specific activity (Bq/kg)			f_1	f_2
	^{40}K	^{226}Ra	^{228}Th	(-)	(Bq/kg)
O2	861 ±42	143.6 ±6.0	114.0 ±5.7	1.336 ±0.054	143.6 ±6.0
O3	880 ±45	142.5 ±6.3	110.9 ±5.7	1.323 ±0.054	142.5 ±6.3
Oh	846 ±42	118.2 ±5.4	100.1 ±5.2	1.177 ±0.048	118.2 ±5.4
Rp	617 ±35	151.0 ±6.8	92.1 ±4.7	1.170 ±0.050	151.0 ±6.8
Admitted values (Standard)				<1.0−1.20	<200−240

Table 3. Bulk chemical composition of the fly ashes; wt.%; uncertainty 2−5%, relative

	Bi1	KWP	Rp	B3z	KWR	Wy1	Dos	Sze	Bs	Sz	O3
MgO	3.74	2.36	2.87	0.94	2.93	2.13	2.60	2.14	0.87	1,48	1.94
Al_2O_3	2.60	17.94	17.97	21.50		23.94	28.68	27.55	20.12	15.72	27.84
SiO_2	25.95	41.98	31.16	32.21	38.20	49.99	47.23	50.30	34.20	28.77	49.69
CaO	40.98	4.44	9.00	29.09	13.76	5.25	5.88	4.77	28.12	25.13	4.38
MnO	1.61	0.28	0.25	0.03	0.41	0.14	0.10	0.08	0.06	0.08	0.07
P_2O_5	4.92	0.15	1.22	0.26	0.34	1.22	1.09	1.05	0.25	0.56	1.46
SO_3	5.58	4.22	10.40	5.94	5.93	1.13	1.45	1.15	5.83	15.04	0.71
Fe_2O_3	2.66	22.50	16.01	7.61	22.31	8.77	7.10	6.40	8.22	5.38	6.83
Co_3O_4			0.03		0.06		0.02	0.01			
NiO	0.02	0.07	0.10	0.01	0.22	0.02	0.03	0.04	0.01	0.03	0.03
TiO_2	0.32	1.04	1.53	1.54	3.32	1.35	1.40	1.43	1.53	1.08	1.55
CdO											
PbO	0.01	0.01	0.18	0.02	0.32	0.02	0.02	0.03	0.02	0.03	0.02
Cr_2O_3		0.09	0.08	0.05		0.03	0.04	0.04	0.03		0.04
CuO	0.02	0.07	0.08	0.02	0.27	0.04	0.03	0.02	0.02	0.02	0.03
Na_2O	0.56	0.57	4.16	0.12	4.13	1.63	0.74	1.33	0.13	0.99	1.16
K_2O	10.03	2.18	3.26	0.13	4.54	3.81	3.03	3.08	0.19	1.85	3.71
ZnO	0.20	0.03	0.54	0.04	0.72	0.03	0.03	0.04	0.04	0.09	0.02
BaO	0.17	0.08	0.50	0.10	0.66	0.20	0.27	0.28	0.10	0.18	0.26
Cl	0.50	1.59	0.14	0.05	1.09	0.06	0.01			3.17	0.02
SrO	0.08	0.04	0.30	0.15	0.33	0.12	0.16	0.15	0.16	0.12	0.16
ZrO_2	0.03	0.03	0.04	0.04	0.09	0.04	0.03	0.03	0.04	0.02	0.03
Br		0.03	x		0.04	0.01		x		0.03	
F		0.28		0.13						0.17	
As_2O_3	x	x	0.04	0.01		x	0.01	x	x	0.01	0.01
Rb_2O	0.03	0.01	0.03		0.06	0.02	0.03	0.03		0.02	0.03
Y_2O_3	x	x	0.02			0.01	0.01	0.01	0.01	0.01	x
Ga_2O_3			0.03	0.01	0.06	0.01	0.01	0.01	0.01		x
GeO_2			0.02								
SeO_2			0.02	x	0.03						
Sb_2O_3			0.02								
SnO_2			0.01								
Tl_2O_3			0.01								
Nb_2O_5				x	0.02	x	x	x	x		x
CeO_2							0.04		0.04		

Table 3. Bulk chemical composition of the fly ashes; wt.%; uncertainty 2−5%, relative – cntd

	Bi2	Bi3	O2	P4	KL	Sb	Skp	Poe	Wy2	BiS	P8	Oh	Bi3s
MgO	1.96	1.82	2.07	2.86	0.86	2.28	1.48	1.90	1.93	1.72	2.31	1.98	1.59
Al_2O_3	21.64	20.97	27.77	24.77	0.67	24.10	15.59	26.91	24.23	20.27	25.94	25.72	19.29
SiO_2	53.60	54.88	50.20	47.62	1.79	50.07	28.51	53.82	51.53	53.89	49.32	50.40	48.05
CaO	5.22	8.73	4.26	7.11	20.49	6.19	25.57	3.73	4.28	8.85	5.83	3.84	5.57
MnO	0.07	0.07	0.07	0.14	1.41	0.14	0.09	0.08	0.14	0.07	0.13	0.08	0.10
P_2O_5	0.98	0.91	1.74	0.68	1.10	0.77	0.56	0.57	0.69	0.93	0.89	1.09	0.90
SO_3	1.54	0.71	0.62	1.77	29.00	1.22	14.89	0.84	0.81	0.99	1.36	1.78	4.21
Fe_2O_3	9.18	6.85	6.27	8.17	1.56	8.89	5.55	6.48	9.46	7.94	7.68	6.83	15.60
Co_3O_4	0.01	0.01	0.01						0.01		0.02		0.02
NiO	0.03	0.02	0.03	0.03		0.02	0.03	0.02	0.03	0.03	0.03	0.01	0.02
TiO_2	1.00	1.11	1.54	1.45	0.09	1.41	1.04	1.36	1.29	1.20	1.46	1.38	0.91
CdO				0.05									
PbO	0.02	0.01	0.02	0.03	0.14	0.02	0.04	0.01	0.01	0.01	0.02	0.02	x
Cr_2O_3	0.01	0.03	0.05	0.04	0.05	0.04	0.03	0.04		0.03	0.04		0.02
CuO	0.02	0.02	0.03	0.02	0.05	0.03	0.03	0.02	0.03	0.02	0.03	0.02	0.02
Na_2O	1.55	1.04	1.16	1.79	0.35	1.31	0.96	0.84	1.48	0.96	1.41	1.26	1.04
K_2O	2.55	2.10	3.60	3.05	37.39	3.00	1.88	3.01	3.59	2.30	3.06	4.36	1.88
	Bi2	Bi3	O2	P4	KL	Sb	Skp	Poe	Wy2	BiS	P8	Oh	Bi3s
ZnO	0.08	0.03	0.03	0.07	2.02	0.06	0.09	0.03	0.03	0.04	0.06	0.04	0.04
BaO	0.28	0.35	0.28	0.17	0.19	0.23	0.19	0.18	0.23	0.37	0.17	0.23	0.22
Cl			0.02	0.05	2.43	0.02	3.07	0.01	0.03		0.04	0.78	0.02
SrO	0.18	0.24	0.16	0.09	0.11	0.12	0.12	0.09	0.10	0.28	0.11	0.12	0.20
ZrO_2	0.04	0.07	0.03	0.04	0.02	0.04	0.02	0.03	0.04	0.06	0.05	0.03	0.04
Br				x	0.04	x	0.03		x		x		
F							0.17						0.20
As_2O_3	0.01		0.01	0.01	x	x	0.01	x	x	0.01	0.01	x	x
Rb_2O	0.01	x	0.03	0.02	0.14	0.02	0.02	0.02	0.02	0.01	0.02	0.03	x
Y_2O_3	x	0.01	0.01		x	0.01	x	0.01	0.01	0.01	0.01	0.01	x
Ga_2O_3	x	0.01	0.01	x		0.01	x	x	x	x	x	x	x
GeO_2													
SeO_2	x												
Sb_2O_3													
SnO_2													
Tl_2O_3													
Nb_2O_5	x	x	x	x		x		x	x	x	x	x	x
CeO_2				0.03									

Explanations: (blanc) – not detected, x – below 0.01%. A partial analysis of a portion of the samples, cf. [53]. Additionally, for the EW-SKTT: 1.577 MgO, 6.690 Al_2O_3, 81.66 SiO_2, 4.293 CaO, 0.2552 P_2O_5, 0.2790 SO_3, 4.374 Fe_2O_3, $3.214 \cdot 10^{-5}$ CdO, 0.0081 PbO, 0.0115 Cr_2O_3, 0.2110 Na_2O, 0.4015 K_2O, 0.0103 ZnO and 0.0010 As_2O_3 (wt.%).

It is of interest that diverse fly ashes, i.e. Skp and Sz show the same amounts of elements, and, that all the investigated ashes cannot easily (in substance) be classified into C- and F-types. X-ray powder patterns, being assisted by recording the pattern of preheated and melted samples as well as by IR spectra revealed the crystalline phases of the fly ashes. The mineralogical composition of the ashes, based on XRD is presented below (Table 4). The crystalline character of a sample as well as the only *large amount* of glass (amorphous material) are also indicated in the Table 4. The crystalline phases in the Table 4 are ordered according to their content (intensity of reflections), i.e. the phases with the highest intensity – first, and so on. Please note that the classification in the Table is *not* based on quantitative analysis.

Table 4. Mineralogical composition of the fly ashes; CoKα, step = 0.015 2Θ

Sample	Main phases/minerals	Accessory, minor phases/minerals	Uncertain phases/minerals; notes
B3z[&]	quartz, alumoåkermanite[1], anorthite, anhydrite, lime	magnetite, haematite, melanterite[2]	mullite?
Bi1 crystalline	quartz, lime, haematite, enstatite	portlandite, bassanite, microcline (ordered), calcite, sanidine	apatite, halite ? lonsdaleite? = NiV_3?
Bi2[&]	quartz, mullite, haematite, magnetite	rutile, larnite, cristoballite	
Bi3	quartz, lime, mullite magnetite	haematite, apatite	
Bi3s	quartz, haematite, anhydrite, mullite	magnetite, wollastonite[3], alumoåkermanite	
BiS	quartz, mullite, lime, enstatite	sanidine, goethite, haematite, magnetite	muscovite
Bs	quartz, anorthite, anhydrite, lime, haematite, mullite		magnetite, Pt? = AlBeCu?
Dos[&] glass mainly	mullite, quartz, sillimanite, lime	magnetite, corundum, metahalloyisite[4], carpathite[5], haematite, illite	
O2 glass mainly	quartz, mullite, haematite, lime	magnetite, apatite, halite, tridymite	pargasite, paragonite
P8	quartz, mullite, haematite	magnetite, anhydrite, lepidocrocrocite, pyrite	pargasite?, mordenite?
Poe[&]	quartz, mullite, haematite	gypsum, epidote, lime, hydromagnesite, hercynite	illite-2M$_2$?
Sb	quartz, mullite, lime, magnetite	anhydrite, haematite	$NaPd_3O_4$?
Wy2	quartz, mullite	haematite, magnetite, maghaemite, anhydrite, lime, lepidocrocite	
O3	mullite, quartz, haematite	magnetite, anhydrite, diaspore, stilpnomelane	
KL[&] crystalline	arcanite[6], calcite, ettringite, hureaulite[7]/gatehouseite[8]	bassanite, sylvite	FZR419[*]
KWP[&] crystalline	quartz, gypsum, mullite	haematite, hercynite	gibbsite
Oh	quartz, mullite, haematite		rutile = microcline, gypsum, anhydrite
P4	quartz, mullite, lime, anhydrite	maghaemite, metahalloyisite, carpathite, hercynite	

Table 4. Mineralogical composition of the fly ashes; CoKα, step = 0.015 2Θ – cndt

Sample	Main phases/minerals	Accessory, minor phases/minerals	Uncertain phases/minerals; notes
Rp	quartz, anorthite, anhydrite, haematite, lime, mullite	alumoåkermanite, xonotlite	
KWR glass, mainly	quartz, haematite, magnetite, anhydrite	calcite	richterite, hedenbergite?, narsarsukite[9] *see the text!*
Skpm	quartz, mullite, anhydrite, richterite, leucite, grossular, rokuhnite[10], hydromolysite[11]	arfvedsonite, anorthite, haematite, fluorite	
Skp	quartz, anhydrite, mullite, rokuhnite, hydromolysite, leucite, hastingsite-dashkesanite[#], richterite, portlandite	$Fe_{0.64}Ni_{0.36}$, hartite[12], gypsum, fluorite, haematite	scolecite, winchite?[13]
Skt	quartz, anorthite, haematite, mullite, maghaemite	tridymite, hercynite	aegirine
Sz[&]	quartz, anhydrite, mullite, leucite, diverse hastingsites-solid solution, e.g. potassic magnesiohastingsite[14], dashkesanite[#], richterite, hydromolysite, rokuhnite, brownmillerite	magnetite, hartite, fluorite	haematite, gypsum
Sze	quartz, mullite, anhydrite, maghaemite	haematite, stilpnomelane	
Wy1	quartz, mullite, lime	magnetite, sillimanite	anhydrite, haematite, gypsum?
M7[16] [&]	anorthite, diopside	åkermanite, hoelite[15]	labradorite, fluororichterite, fluorophlogopite
FLYASH[&] glass			anorthite, oligoclase, åkermanite, diopside, spinel
EW-SKTT; Skawina cf. [39] preheated	quartz, mullite	haematite, albite-low, illite-2M$_1$	after 12-h heating at 800°C, enhancement of the haematite- and plagioclase reflections are the only change; CuKα

*Explanations: nine samples from the table – cf. [53]; KWR – bottom ash; Skp is an original FA, whereas Skpm and Skt represent the Skp sample after magnetic separation and heat (800°C) treatment, respectively; M7 and FLYASH represent the sample Sz after heat (1200°) treatment and pouring the melt of it (1460°C) and quenching, respectively; [&] – after [53]; * – FZR419 – ferrous-zincian rhodochrosite, $(Mn,Fe,Zn)CO_3$ No. 419 of [41]; [#] – potassic-chlorohastingsite (amphibole, dashkesanite is a synonym): $KCa_2Fe_3MgFe[Si_6Al_2O_{22}]Cl_2$; [1] – $(Ca,Na)_2(Al,Mg,Fe)Si_2O_7$; [2] – $FeSO_4 \cdot 7H_2O$; [3] – PDF 19-249; [4] – i.e. halloyisite-7Å (PDF 9-453); [5] – $C_{24}H_{12}$ (coronene, PDF 21-1577); [6] – K_2SO_4 (PDF 5-613); [7] – $(Mn,Fe)_5(PO_3OH)_2(PO_4)_2 \cdot 4H_2O$ (PDF 34-146); [8] – $Mn_5(PO_4)_2(OH)_4$ (PDF 47-1822); [9] – $Na_2(Ti,Fe)Si_4O_{11}$; [10] – $FeCl_2 \cdot H_2O$; [11] – $FeCl_3 \cdot 6H_2O$; [12] – $C_{20}H_{34}$ (α-phyllocladene, PDF 01-076-8626); [13] – amphibole, $(Ca,Na)Mg_4(Al,Fe)Si_8O_{22}(OH)_2$ (PDF 20-1390); [14] – amphibole, contains Cl; [15] – antraquinone, $C_{12}H_8C_2O_2$; [16] – diverse pyroxenes (diopsides) can be matched there as well, e.g. a synthetic Al-Ti tschermakite-diopside (PDF 01-089-1410).*

Most of the analysed ashes are a hybrid Al-Si type, close to the common ashes. In the review of the XRD powder patterns of FAs (below), *only selected reflections of the selected crystalline phases are given*. The powder pattern (Fig. 1) is quite representative for the majority of the ashes, the main minerals being mullite, quartz, sulphates and/or Fe oxides.

The KWR-bottom-ash (BASH) sample (Fig. 2), is apparently composed of amorphous phase (glass), but the powder pattern shows definite peaks and 'protuberances' or 'steps' which cannot be disregarded. Such a pattern can equally be created by a glass and crystalline material or by disordered crystals. Definite standard patterns of aluminosilicates, Al-silicates or oxides of Si
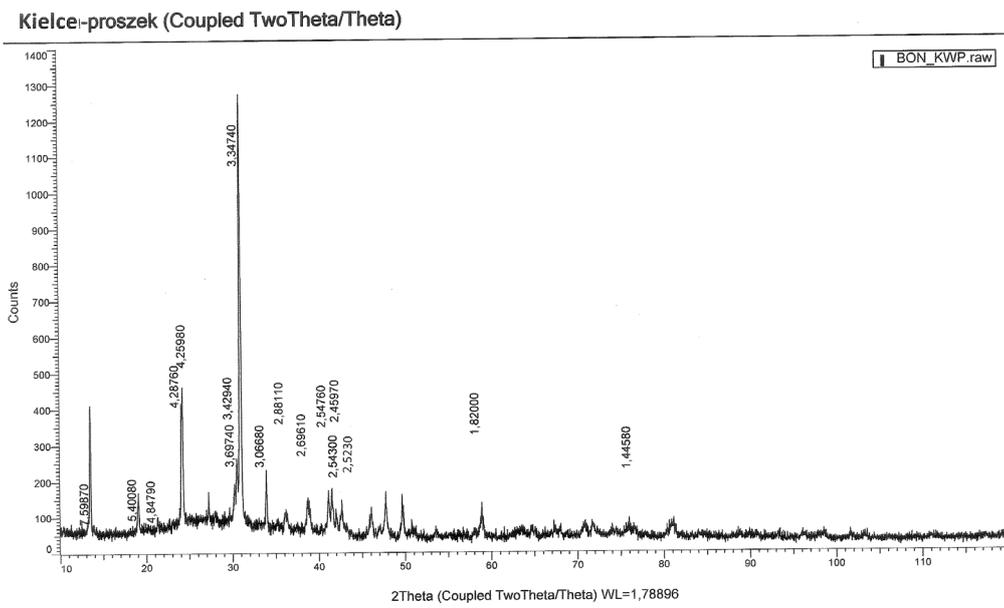
Fig. 1. The XRD powder pattern of the KWP-sample (Å): quartz (4.2598, 3.3474, 1.8200), gypsum (7.5987, 4.2876, 3.0668), mullite (5.4008, 3.4294, 2.5476), haematite (3.6974, 2.6961, 2.5230), hercynite (2.8811, 2.4597, 1.4458), gibbsite (4.8479) [53]
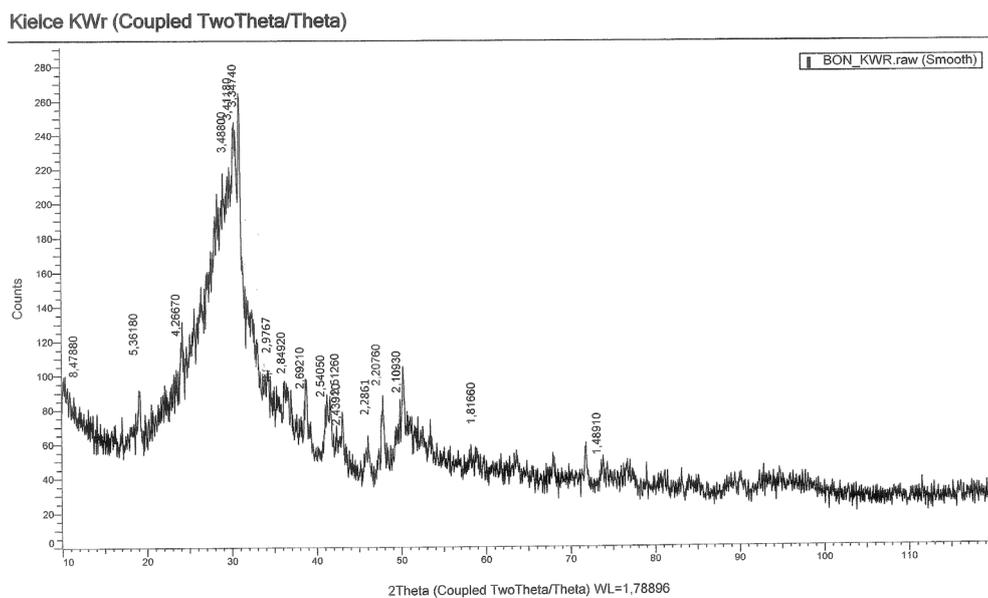
Fig. 2. The XRD powder pattern of the KWR-sample (Å): quartz (4.2667, 3.3474, 1.8166), anhydrite (3.4880, 2.8492, 2.2076), magnetite (2.5405, 2.1093, 1.4891), haematite (2.6921, 2.5126, 2.2076), richterite (8.4788, 3.4118, 2.9767 + steps on the largest quartz-glass 'reflection', narsarsukite (5.3618), calcite (2.2861)

and Al can be matched to the pattern, but there is no Al (Table 3). This cannot be explained except, by unhomogeneity of the sample (quite unlikely). Consequently, the pattern is interpreted without taking Al into account.

The XRD powder pattern of the KL-sample (Fig. 3) has a very distinctive appearance. This sample is a prod-

uct of the sole deflagration of biomass and comprising arcanite, calcite and ettringite – as the main minerals.

The powder pattern of B3z is in a class of its own (Fig. 4); the B3z is mainly composed of alumoåkermanite, anorthite, lime and quartz.
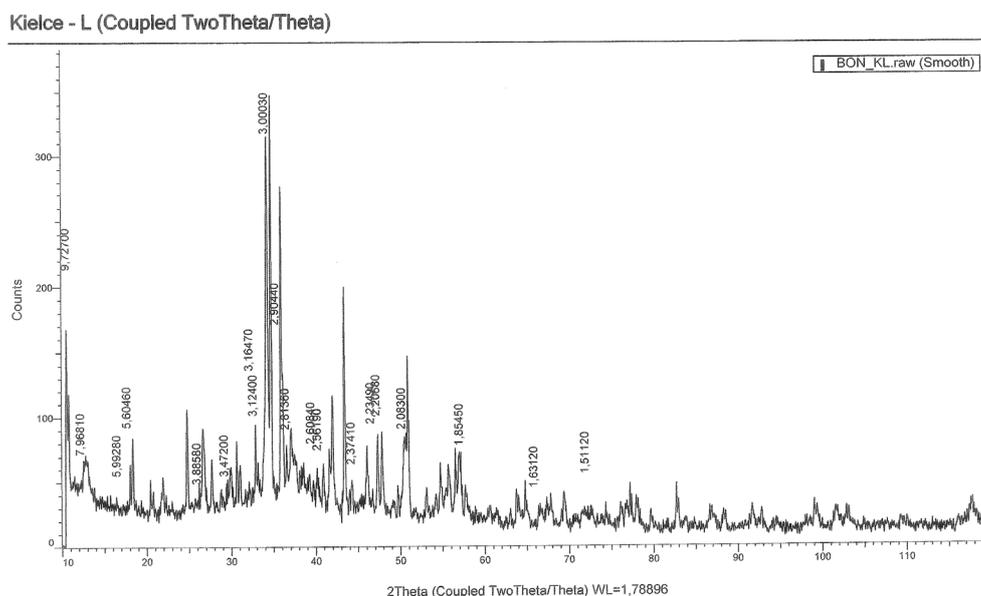
Fig. 3. The XRD powder pattern of the KL-sample (Å): ettringite (9.7270, 5.6046, 3.8858, 2.5619, 2.2068), arcanite (3.0003, 2.9044, 2.0830), hureaulite (7.9681, 3.1240, 2.6084, 1.6312), bassanite (5.9928, 3.4720, 2.8136, 1.8545), sylwinite (3.1647, 2.2349), FZR419 (2.3741, 1.5112); calcite, gatehouseite – no marks [53]
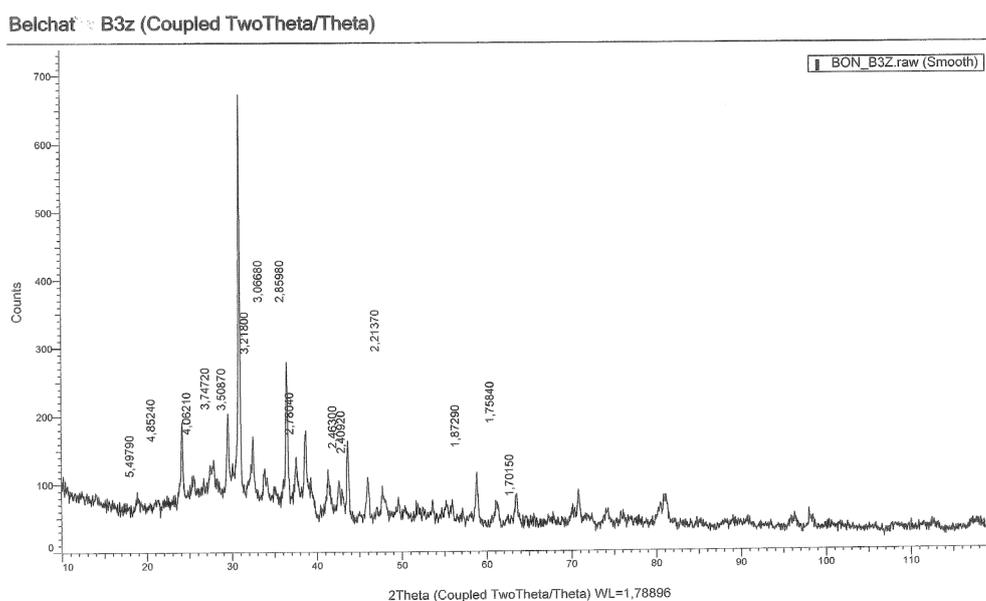
Fig. 4. The XRD powder pattern of the B3z-sample (Å): alumoåkermanite (3.7472, 3.0668, 2.8598, 2.4630, 1.7584), anorthite (4.0621, 3.2180, 1.8729), anhydrite (3.5087, 2.2137), lime (2.7804, 2.4092, 1.7015), melanterite (5.4979, 4.8524); the other ones (quartz mainly) – no marks

Unique cognition problems were created by the Skp- and Sz-samples, the chemical analysis of which match one another, the crystalline phases are similar. However, the samples originate from diverse plants which use diverse bituminous coals. Owing to the rejecting the computer recognition of cordierite in the XRD powder pattern by one of us (especially, PDF 048-1600) [54], it was decided to analyse the samples by recording and recognition of the patterns of the preheated samples and making the IR spectra of the raw and preheated samples. The Skp-sample (Table 4, Fig. 5) is especially knowable by its amphibole and leucite content, accompanied e.g. by portlandite, $Fe_{0.64}Ni_{0.36}$ and, certainly, hartite, i.e. $C_{20}H_{34}$ (α-phyllocladene), (Table 4). The Sz sample (Table 4, Fig. 7) displays a very similar phase composition to the Skp sample. However, Sz sample contains a series of hastingsites (amphiboles) and magnetite, whereas portlandite is not detected by XRD (Table 4). Following magnetic separation (Skpm), grossular was identified in XRD pattern. To corroborate the presence/absence of amphiboles or cordierite, it was decided to overheat the samples which should lead to pyroxenes. After heating the Skp-sample (800°C, 16 h, Skt, Fig. 6), anorthite dominates the pattern, accompanied by minor amounts of e.g. haematite, maghaemite and, certainly, aegirine (pyroxene). After heat treatment of the Sz sample (M7, 1200°C, 5 h, Fig. 8), anorthite and a series of diopsides (pyroxenes) are the main species.

Hoelite, a native antraquinone, cannot be disregarded in the pattern. The heating of Sz above the melting temperature (1460°C, 5 h) and quenching in air, a part of a new technology [39], produced glass with a trace of feldspars – the FLYASH-sample (Table 4). Moreover, the amount of carbon and non-deflagrated particles of the raw ashes (Table 1) seem to partially corroborate conjecture regarding the presence of coke-like substance. This conjecture is based on 'peaks in the background', especially in the samples P4, Bs, Wy2, Oh, KWR and Sz, where the unburned particles are present (Table 1, except the KWR).

The IR spectra were also used, to corroborate or discard definite conclusions drawn from the XRD patterns. KL, Skp, Skt and Sz were analysed using IR spectra. The spectrum of KL (Fig. 9) wholly corroborated the findings of the XRD analysis, and namely, by displaying absorption bands at 1094, 662 (656) cm^{-1} (bassanite), 1094 (arcanite), 1641, 956 (1040, no marks) cm^{-1} (ettringite) and 1411, 872, 708 cm^{-1} (calcite/carbonates). The 3410 cm^{-1} band of water and OH$^-$ from ettringite is surely being hidden under extremely broad band peaking at 3362−3318 cm^{-1} band. The 1017 cm^{-1} (no marks) band is due to hureaulite (ν3), whereas that of the 1193 cm^{-1} band may tentatively be ascribed to the stretching of P-O (or silica) – (Fig. 9).
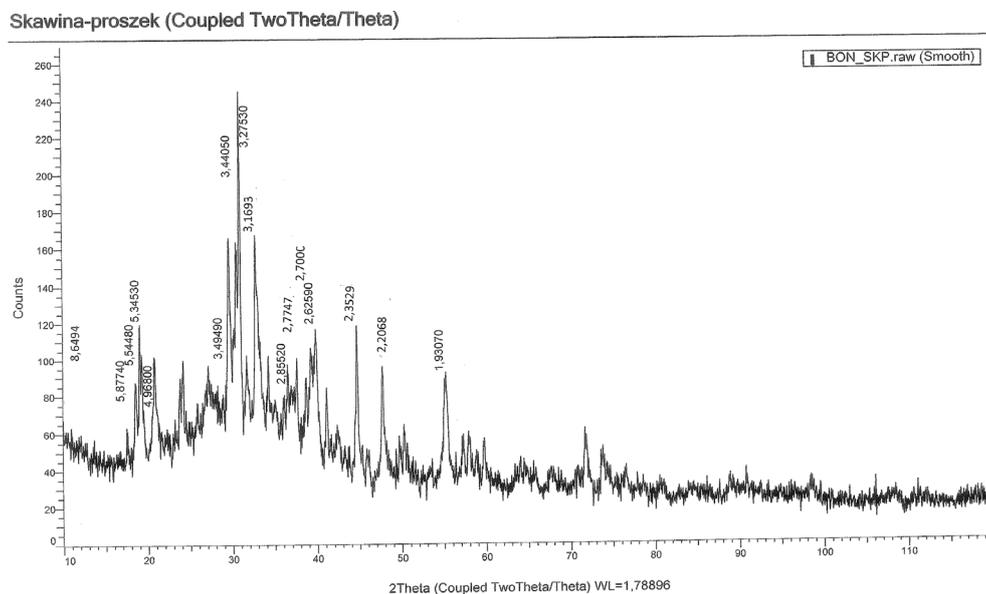
Fig. 5. The XRD powder pattern of the Skp-sample (Å): leucite (5.5448, 5.3453, 3.4405, 3.2753), portlandite (4.9680, 2.6259, 1.9307), anhydrite (3.4949, 2.8552); amphiboles – mainly dashkesanite and richterite, but also common richterite (PDF 00-0230667) and hastingsite (PDF 20-378) can be matched (8.6494, 3.2753, 3.1693, 2.7747, 2.7000, 2.3529, 2.2068), hydromolysite (5.8774)
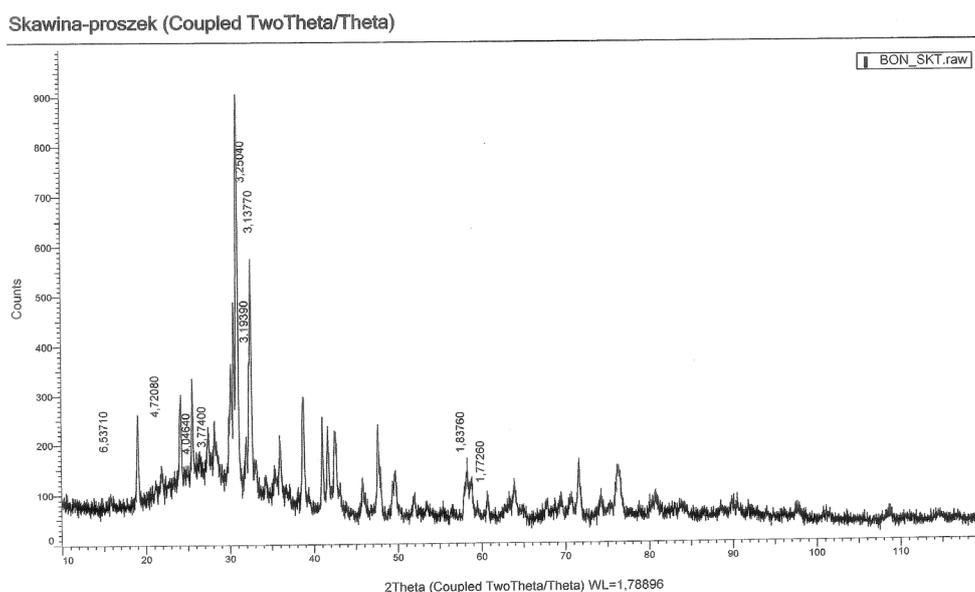
Fig. 6. The XRD powder pattern of the SKt-sample. Besides quartz and mullite, the pattern is dominated by anorthite (the only numbers, Å); aegirine or kushiroite (Al-diopside) is only a conjecture
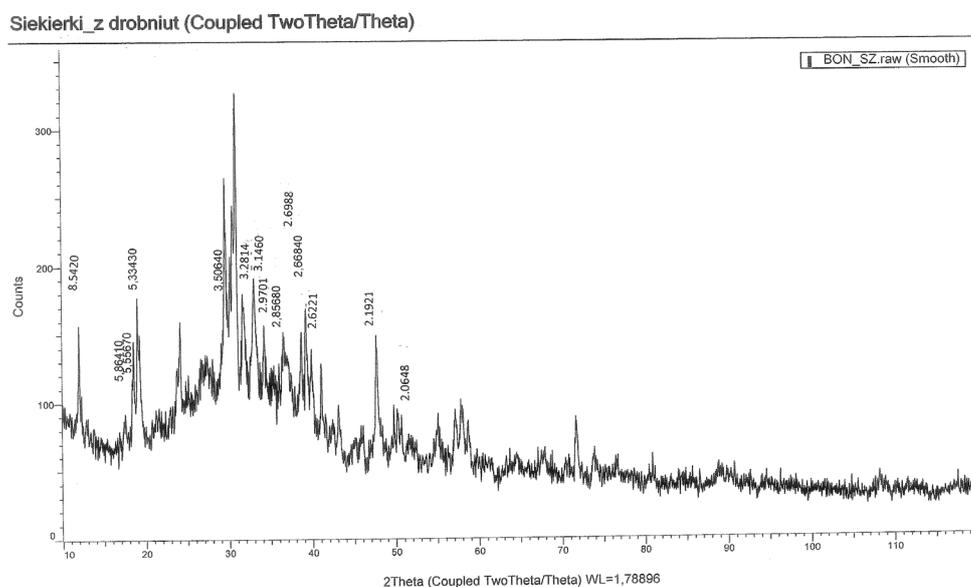
Fig. 7. The XRD powder pattern of the Sz-sample (Å): leucite (5.5567, 5.3343, 2.6684), hydromolysite (5.8641), anhydrite (3.5064, 2.8568); amphiboles: potassic chlorohastingsite (dashkesanite), potassic magnesiohastingsite and richterite. Common hastingsite (PDF 20-378) can be matched as well. (8.5420, 3.2814, 3.1460, 2.9701, 2.8568, 2.6988, 2.6221, 2.1921, 2.0648). The other ones – quartz and mullite – no marks [53]
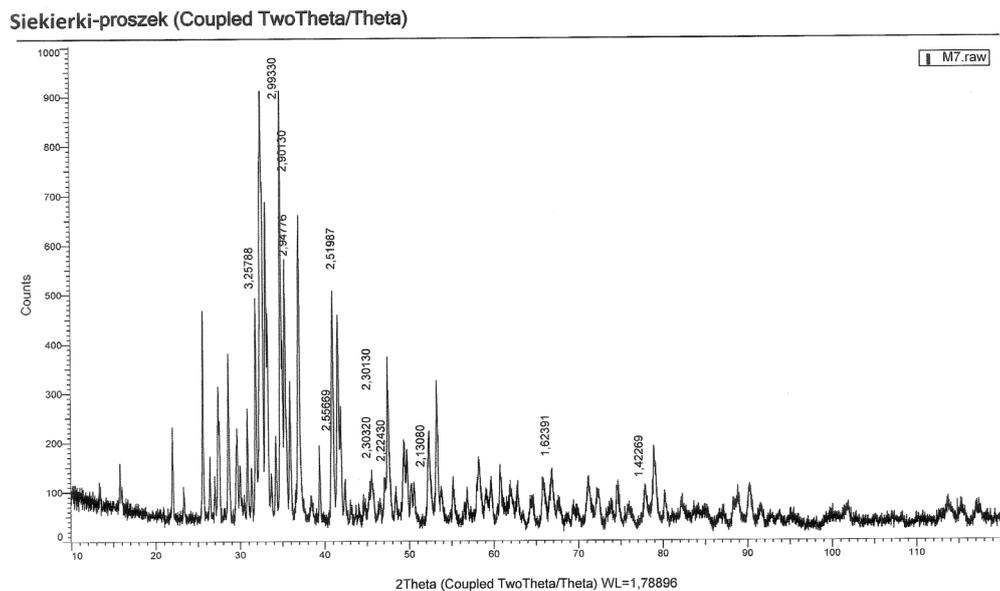
Fig. 8. The XRD powder pattern of the M7-sample (Å): Diopside (3.25788-coincide with several ones, 2.9933, 2.94776, 2.9013, 2.55669, 2.51987, 2.3032, 2.3013, 2.2243, 2.1308, 1.62391, 1.42269). The other ones – mainly anorthite – no marks
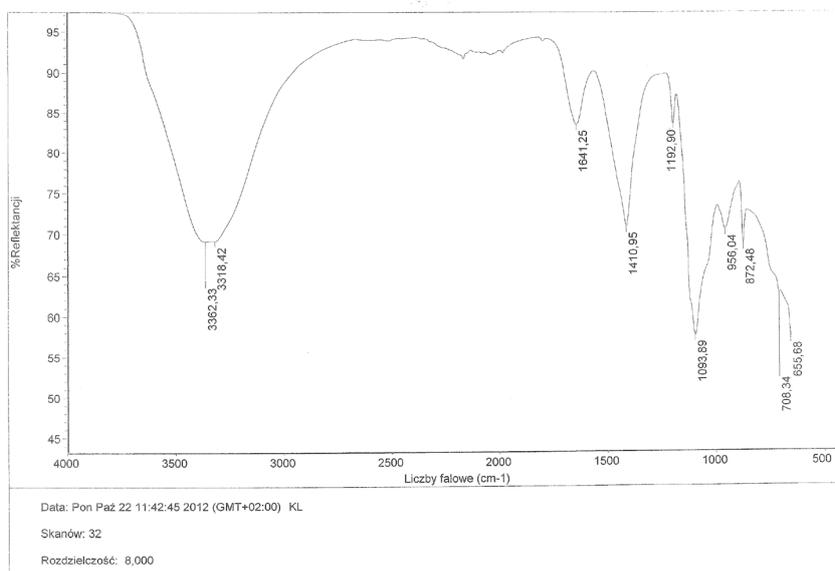
Fig. 9. The IR spectrum of the KL-sample

There are unique methods for careful identification and interpretation of the spectra of amphiboles, e.g. [43,44], but they concern the >3000 cm^{-1} region. However, the amphiboles are practically always solid solutions, and the absorption bands in that region are frequently of low or zero intensity! Hence, in spite of general similarity of the spectra of the pure amphiboles, the exact values at lower energies of the definite absorption bands of a given solid-solution sample can hardly be given, but rather they can be estimated or even matched to definite etalon-amphibole. In our case (Sz, Skp), the IR pattern is obliterated by the presence of the other hydrated phases. With regard to the Sz-sample (Fig. 10), one can say that the *spectra of Skp (Fig. 11) and Sz are extremely similar*, but that of Sz shows more hydroxyl and water – which can be in relationship with the higher amount of amphiboles in the Sz, as proven by XRD and the higher intensity bands, 936, 979 cm^{-1} of this sample. The spectra of SKp and Sz are almost identical. One may easily ascribe, especially 674, 775, 793, 875, 936(938), 979 (982), and 1098 cm^{-1} bands and all those above 3000 cm^{-1} to amphiboles. But the bands above 3000 cm^{-1} are also related to other hydrated phases like portlandite. It should be emphasized that we are dealing with F- and Cl-amphiboles, i.e. with the amphiboles where the OH^{-} groups are at least partially replaced with Cl^{-} or F^{-}. *Hence, the above-3000-cm^{-1} band need not be intensive. Finally, the spectra exactly match those of chloropotassic hastingsite, hastingsite (magnesio)hastingsite, and partly of fluororichterite –* cf. *[50−52]*. Several bands can solely be ascribed to silica (861 cm^{-1}), whereas 1098 cm^{-1} may also point to amorphous silica, cf., e.g. [49]. Several sulphate's bands may coincide with those of amphiboles, e.g. 674 cm^{-1} of anhydrite, *but general appearance of the spectra is that of amphibole-material*. The band at 1419 cm^{-1} may be due to both sulphates and carbonates, whereas

775 cm^{-1} – is due to mullite. In the water-hydroxyl region the bands at 3398 and 3567 cm^{-1} can be ascribed to gypsum in spite of little amount of the latter – anhydrite can also acquire water upon drying, from the other phases. The haematite increment (973 – no marks, 1098 and 1620 cm^{-1}). As one may observe, all of these considerations were directed towards accepting or rejecting the presence of diverse kinds of cordierites in the samples. It may be stated that *there is no cordierite type* in the Skp- and Sz sample, i.e. as based on the XRD powder pattern-, the powder pattern of preheated samples and IR analysis. The spectra *do not match* the spectrum of any kind of cordierite of [55,50−52]. Likewise, the characteristic, intensive band of 770−800 cm^{-1} of ring silicates [56] or, rather, 780−810 cm^{-1} [46] is practically absent. In the spectra of the Sz and Skp, there are none of the following bands: 906−909 cm^{-1}, 955−958 cm^{-1}, 1139−1143 cm^{-1} and 1171−1173 cm^{-1}. These bands are also the strongest bands of the diverse type of cordierites, cf. [50−52,55]. Moreover, only trace amounts of sekaninaite (low temperature Fe-cordierite) could be conceivable, *but such a conjecture can by no means be drawn from the analyses*. The spectrum of Skt (Fig. 12), a preheated Skp-sample, is dominated by anorthite bands (1024, 941, 777, 728 and 694 cm^{-1}). However, the 949 cm^{-1} band may be ascribed to labradorite, 694 cm^{-1} to maghaemite, whereas that of 794 cm^{-1} is surely due to tridymite. Besides, the band at 728 cm^{-1} could be due to leucite, whereas that of 943 cm^{-1} (coincidence with 941 cm^{-1}) is the only intensive band of aegirine – cf. [52]. As noted above, the bands in the region 1882−2274 (2450) cm^{-1} are inherent in the mode of operation of the spectrometer. This notwithstanding, the enhancement of the bands in that region may or may not point to definite C=C-, C≡C- or C–P-containing compounds.
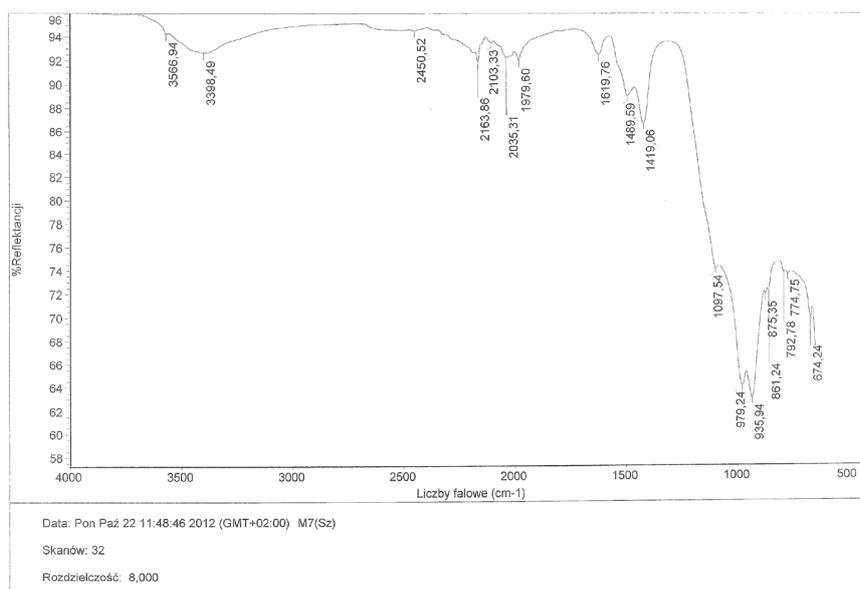
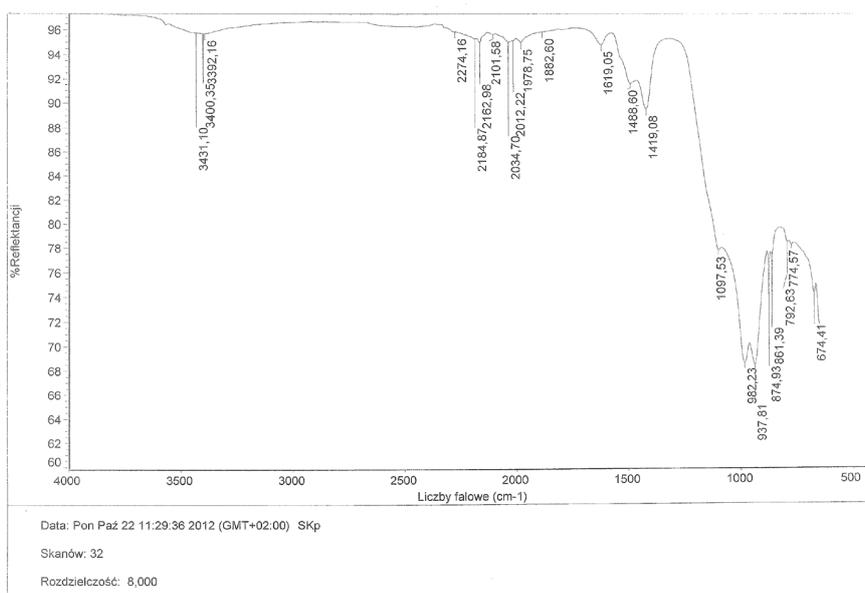*Fig. 10. The IR spectrum of the Sz-sample [53]*
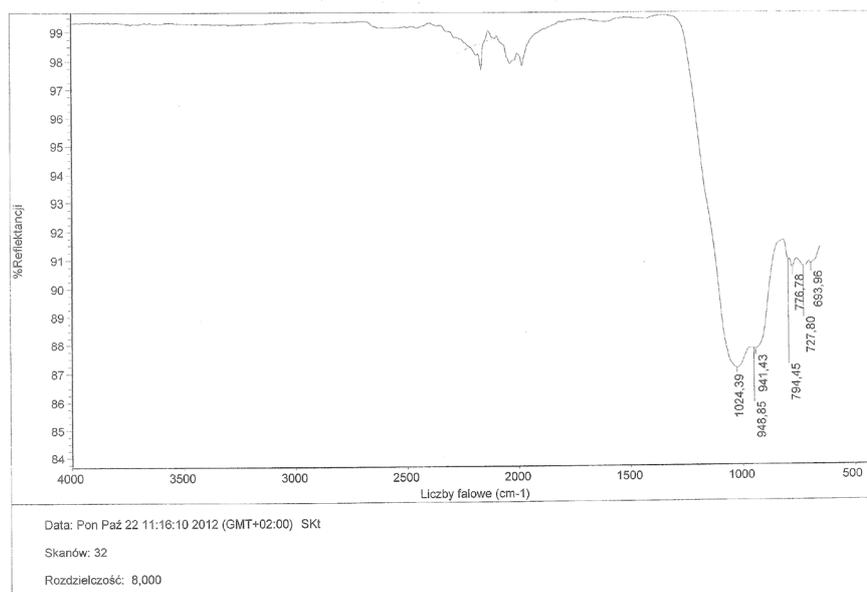

Fig. 11. The IR spectrum of the Skp-sample

Fig. 12. The IR spectrum of the Skt-sample

4. Discussion

4.1. The fly ashes in general

It should be stressed that definite utilization of FA demands the monitoring of, at least, its chemical and mineralogical composition. Therefore, the long-lasting usage of FAs in defined technology is theoretically possible, provided a betterment of the composition of ash by small additions and the composition should be monitored over time. There is not much to add on the preliminary investigation of Polish ashes. However, lowering pH values after consecutive rinsing-out cycles of FAs may be a sign that the Skawina-FA [39] possess Levis-acid surfaces, e.g. framework silicates or silica. Furthermore, the 'depletion pattern' points to depletion of elements from glass and/or illite, for the most part. Owing to the lack of standardization in leaching procedures of FA, there is no way to compare the papers of [57−60]. Authors of [57] claim that the following elution Ca>Na>K, Mg and no elution of Mn, Fe took place. The amounts of Zn and Cr were 7.2 ppm and 19.2 ppm, respectively. Cadmium, Pb, Co, Ni and Cu being below the detection limit of ICP-AES, whereas all the anions except SO_4^{2-} and Cl^- were below the detection limit of chromatography. Our sequence of elution of the EW-SKTT sample was Na>K>Ca>Mg, whereas Fe and Zn were enhanced in the solid. Chromium, Cd and Pb are leached within the error of analysis, whereas the amount of SO_4^{2-} (as SO_3) rinsed out created only 1/3 of that of [57]. The authors of [61] regard As, Cd, Cr, F (and seldom occurring Se, Tl, Hg and Ni) of fly ashes (FA), and, Al and Ba of bottom ashes (BASH) – as important toxic elements. The magnetic separation of FA seems to be ineffective, e.g. due to intimate intergrowths of diverse minerals, cf. [17,62]. Thus, this method was abandoned. The magnetic separation can be applied upon the production of zeolites [37]. The highest melting temperatures of the fly ashes do generally correlate with the highest amounts of silica + alumina, however, the high melting temperature of the KL-sample is surely based on CaO content (after calcite). Against this background, authors of [18] have incorrectly reckoned CaO and MgO among the non-refractory oxides, unless there is a potential on eutectics. An admixture of biomass to basic fuel can also increase the melting temperature (the Sb-sample). However, the deflagration of biomass is not necessarily safe due to verdure-enrichment in toxic elements, cf. e.g. [63−65]. The cenospheres originate only from 'common' (hybrid) fly ashes, close to the F-type (Sze, Dos, O2, O3, Oh, P8 and P4), alumina of which is higher than 24%, and CaO below 9%. The main minerals of these ashes being mullite, quartz, Fe-oxides, anhydrite or sillimanite. A calcium chlorine and calcium hydroxide mixture is quite conceivable as established by chemical technology (the Liebig method of $KClO_3$ production). Likewise, known or conceivable minerals in the mineralogy of ashes are the following: brownmillerite, stilpnomelane, epidote, xonotlite, rokuhnite, hydromolysite, carpatite, hydromagnesite, Fe-Ni alloy, hartite or hoelite.

The chemical (XRF) analyses convey information concerning trace elements, besides those on the main ones. Trace or minor elements (after recasting from oxides), amount thousandths or hundredths of ppm (Ni, Pb, Cr, Cu, As, Zn, Sr). It should be added that dry/wet

coal cleaning can change the element relationship in coal [25], and hence, in ash. However, the differences may be meagre, cf. [16]. Some of those elements are not especially hazardous for the environment or can be deemed so (Zn, Sr). The (bio)geochemistry of lead is different from common notion [66,67]. This notwithstanding the amounts of Pb in the Polish FAs, with the exception of the highest ones (Rp, KL), are enriched in relation to the common clarke of soils and sediments. Based on the geochemical-prospecting experience of one of the authors, one can assume for the purpose of this paper the following clarke values of elements in ppm: Pb(20), Cu(10), Cr(40), Ni(10) and Zn(60). Such the clarke values should be assumed for soils and stream sediments of many terrains in Central and Eastern Europe, i.e. those not or slightly contaminated by the anthropogenic factor. If so, then disregarding the maximum amounts, the following enrichments may be obtained: Pb (<4.6−18.6 times), Cu (16−63.9), Cr (<1.7−15.4), Ni (<7.8−78.4) and Zn (2.7−12.1 times). Such the enrichments are generally not comparable with those of [17], where the enrichments in FAs in relation to bituminous coals are given, i.e. Pb (2−4), Cr (7−14) and Ni (3−6). Cadmium was only found in the biomass-originating sample (KL), whereas the Rp-sample indicates the presence of almost all the analysed elements. Niobium (especially in the KWR, BASH) and the erratic content of Ce might (hypothetically) prove the existence of basic, alkaline rocks being primarily in contact with the charge coal, albeit [68] relates Nb to the heavy fraction of clays and to columbite. The Y content of the FAs is comparable with those of ashes described by [17,23,19]. Nickel, Cr, Cu and As may be dangerous for environment (health), especially As, cf. [5]. Commonly As is linked to pyrite from coal, however [5] have bounded the amount of As to the amorphous phase and non-deflagrated coal, whereupon CaO quenches the volatility of As [ibidem]. Except for the Rp-sample, the content of As in the FAs is less than or equal to 76 ppm, being comparable with definite values of [17] but two times higher than the averages of [23,24], and there is no relationship to pyrite, sulphates or Fe oxides in our ashes (not in coals!). *Owing to the diverse provenance of the feed coals used by the power plants we cannot (precisely) indicate the enrichments of the elements in relation to the coals*. The analysed ashes display more Cr, Ni and Cu than the ashes of [17,23,24], whereas Zn and Pb amounts are either higher or lower than the values given in [ibidem]. In the FAs of brown coal, As, Cr, Cu, Pb, Ti and Zn are enriched ten times in relation to the average in FAs of [25] (vis. ibidem), but we have not detected Br, Cd, Co and Sb. As compared with the *world-wide average for ashes from brown coals*, vis. [8], the samples B3z and Bs show P, Ti and Nb amounts below that average. Arsenic, Mn, Y and Cl are either not detected in these samples or somewhat comparable with that average. The remaining elements are enriched in relation to the values given in [8]. Based on the *world-wide averaged (and range) values for ashes from bituminous coal* [69], one can say that Polish ashes display the highest possible amounts of Ti, Ni, Mn, Co, Cl and SO_4^{2-}. The erratic occurrence of Br, Ce, Ge, Nb, Se, Sn, Sb, Tl, Cd and F is detected but they are also enriched 10−100 times as compared with the aforementioned average. Likewise, all the other elements are *heavily enriched as compared to the world-wide average for the ashes*, cf. [69]. Unfortunately, we have no analyses concerning Hg, but the amount below 1 ppm of [17] is not cheering since the shipment of Polish coal to the Netherland shows the highest possible value [26]. Large amounts of Cl (up to 3.17%) or F (up to 0.28%), on average, emphasize not only the high level of them in bituminous coal (Sz, Skp), but also the large scale contamination of the environment (KL). The KL fly ash originates namely from biomass. The moderate amounts of TiO_2 should be noted; it can be beneficial for ceramics but not for community health (dusts, allergy). The addition of biomass to basic fuel involves enrichment of K_2O, SiO_2, Al_2O_3 and (generally) depletion in CaO and SO_3. The high level of K_2O in almost all the samples can bear the witness of low quality of bituminous coal deflagrated. K_2O is namely not unique for majority of the coals, but rather Na_2O is. Refraining from discussion concerning the volatility of elements, one may find that U is somewhat volatile, i.e. based on its easy-changing chemical character. Though Ra^{226} is a measure of U^{238}, U may be volatile and emitted to the atmosphere [70]. Nonetheless, the increase of the 'safe' radioactivity index in course of time (the year of publication) appears astonishing, i.e. for f_1 and f_2 from 1 and 185 Bq/kg (1996,1999) to 1.2 and 240 Bq/kg (2013), respectively, cf. [70,31,19]. By taking into account the low energy of K^{40} radiation, and without conducting a chemical analysis for U, one may find that the IAEA-K-Th-Ra formula is nonsensical. Moreover, such and the higher values are not comparable with those admitted by EU, i.e. 120 and 150 Bq/kg for building materials [71]; a half of the latter value, ≈6 ppm U, would be admitted as safe in Slovakia [ibidem]. Anyhow, the investigated ashes are generally safe except for the O_2 and O_3 sample (we have used $f_1 = 1$ and $f_1 = 200$). Several samples of [31] are also above this level. Finally, we can skip the misprint in the IAEA formula of [19] and say that the ashes originating from contemporarily-mined coals (Poland) are generally, relatively safe. Furthermore, the authors of [69] have found that Polish FAs are U-enriched. The mineral assemblage of the investigated FAs and BASH generally matches the assemblages of, e.g. [1−5] but there are much more minerals (phases) than described by [17−18,20,31]. One could scarcely classify the investigated fly ashes into the C class (KL, Sz, Skp, Bs, B3z and Bi1) and into the F class (all the other ones), but they do not strictly meet the respective criteria, cf. [28,31] for such classes, nor is it possible to

ditions. The preheating of the amphibole-containing samples has led to their decomposition and to pyroxene formation. *If cordierite were present there, it (or a considerable part of it) should have emerged (survived) in the XRD pattern of the preheated samples, but it did not.* Hence, there was no cordierite (indialite and/or the other varieties) in the raw samples. The transformation of amphiboles (from the raw to the preheated sample) can be abstracted as (1,2), cf. [79]:

$$2\text{hastingsite} + 1.5\text{O}_2 = \text{pyroxene} + \text{plagioclase (labradorite)} + 4\text{haematite} + 2\text{H}_2\text{O or,} \qquad (1)$$

$$\text{richterite} + 0.5\text{O}_2 = \text{aegirine-augite} + \text{haematite} + \text{cristoballite.} \qquad (2)$$
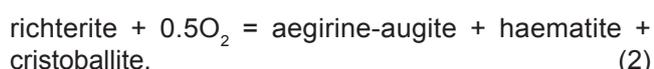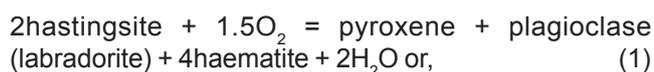
Another problem is the formation of *leucite* in these samples. It has a very low crystallization force in spite of being framework silicate. There must be catalysts, and reversing the inhibition of crystallization of leucite seems to be necessary, e.g. by limiting the crystallization of mullite – vis. [80]. One may also suppose that a high temperature and/or local quench takes place, i.e. from the melt of incongruently melted K-feldspar. Let us consider the provenance of several other compounds in only a few samples. Phosphates are commonly regarded as primary (*apatite*) but hydrated phosphates can be attached to the glass spheres – in that sense – secondary [2]. With regard to the FAs from the dumps (DASH), the Bi3s and Dos appear to be freshly deposited. However, metahalloyisite and illite (Dos) may be either due to contamination from soil or 'primary-secondary' relics from coal, cf. [2]. The occurrence of the hydrated Mn-Fe-phosphates (*hureaulite, gatehouseite*) in the KL sample does not seem out of place, and appears likely. That sample displays a high enough content of Mn and P, and not all of the Mn can be required for Fe-Zn-rhodochrosite. Bearing in mind that the aforementioned minerals display diagnostic peaks in the powder pattern, and, that the KL-sample is from the dump – nothing more can be said at this stage of the investigation. While observing the latest results concerning sillimanite [81], one should reckon *sillimanite* of the Dos and Wy1 – among the primary (relic) minerals. *Hydromagnesite* (Poe) may be the result of the storage of FAs, cf. [2], whereas stilpnomelane (O3, Sze) may be of primary origin (relic) or – by analogy to vermiculite [2] – formed by the alteration of biotite or chlorite. Taking into account the paper of [82], it is likely that *xonotlite* (Rp) has been formed by low-temperature-hydrothermal synthesis without high pressure. The authors of the paper synthesised gyrolite and truscottite, using only lime, corundum (gibbsite) and silica. In these circumstances, such a synthesis of xonotlite is, at least, likely. Moreover, xonotlite can easily be synthesised using lime and quartz [83]. The co-occurrence of *calcite* and *lime* in Bi1 involves primary origin of calcite which could partially

survive high temperature (or has been synthesized), and not all of the full amount was converted into lime. *Portlandite* should be, at least, secondary. *Calcite, arcanite or Fe-Zn-rhodochrosite (FZR)* of the KL-sample are deemed a primary product of deflagration of biomass, whereas *ettringite* should be deemed a tertiary product. Besides, ettringite may be of diverse origin, e.g. it occurs by adding to the ash the following: smectite [29], cement kiln dust, Portland cement or lime [59]. Authors of [84] surmised ettringite formation by reaction of Ca-aluminates and sulphates from water – thence it is secondary in character. Following the contemporary terminology, it should be tertiary due to its origin from dumps. Diverse hydrated sulphates, carbonates or phosphates should be deemed secondary (with regard to the reaction), though there are prospects that water 'survives' quite high temperature in unburned particles. Finally, with regard to the organic compounds (hartite or carpathite), the presence of which should be corroborated by extraction, they are quite likely to be present since diverse organic compounds are known from burning dumps, cf., e.g. [85]. Nothing more can be said concerning the uncertain compounds/minerals – they can be, in part, the contamination of the raw ('pristine') ashes. In the literature, there are given examples of diverse (glass)-spheres (aggregates), e.g. [17,31]. These spheres are dominated either by a single element (Si, Al, Ca, C or Fe) or by two elements (Si-Ca, Si-Al). They can also be decorated by sulphates or goethite [17,31,20]. Finally, the Fe-oxide-aluminosilicate spheres intimately intergrown with monazite-composition substance were found [19]. Diverse magnesiaspheres and phosphospheres [13] seem to be a novelty. Cenospheres and microgranules also differ in composition [31]. Glass spheres need not be the main component of the FAs, they also can amount to (only) 1.6−35.8% of FA, depending on the technology and the kind of the feed coal [31].

4.3. Re-heating of the FAs

The transformation Skp → Skt upon heating is better described by reaction No. 2 than No. 1. It is conceivable that sulphates of the sample may make a contribution to the formation of plagioclase, whereas haematite and richterite may play a part in the formation of haematite, maghaematite and spinel; especially when there is an augmented content of actinolite [79]. Quartz, mullite and leucite survived this transformation but these minerals especially can create glasses. One of the products of the reaction (2) should be cristoballite but from the XRD pattern, one can detect (read off) the presence of tridymite. Transition to tridymite is easily understood in the context (milieu) of alkalis, F⁻ and plagioclase, cf. [79]. Moreover, tridymite is an ubiquitous mineral, and well-known from diverse slags, glasses, ceramics and rocks; its provenance and ontogeny may be absolutely diverse, in general [79]. The transformation

Sz → M7 is better described by reaction No.1, and the transformation amphibole → pyroxene is obvious. Åkermanite and (uncertain) fluororichterite and fluorophlogopite are the remaining products of heating. Again, sulphates, silicates and oxides (magnetite, haematite) have made a contribution to form plagioclases, glasses, åkermanite and surely brownmillerite in the M7 sample. Fluororichterite is certainly formed with the assistance of fluorite, whereas the presence of fluoro-phlogopite (if any, uncertain) cannot be explained at this stage of the investigation. Further heating of the Sz-sample to 1460°C (Sz → FLYASH) produced mainly glass with traces of the surviving minerals (anorthite, åkermanite, diopside and spinel), the presence of which is not quite certain. However, oligoclase should originate from the labradorite.

4.4. Factors of enrichments of the selected minor and trace elements

In spite of possessing a vast block of data concerning Polish coals, we *cannot* consider precisely the problems of enrichments of elements in the FAs in the relation to the feed coals, since we have no data on definite feed-coal shipments related to the definite FAs. *The Polish power plants are in the habit of blending diverse feed coals.* The problems of the possible enrichments were partially covered above. However, one may observe the highest amounts of Zn, Mn, Cd, moderate amounts of Pb and quite high amounts of Cl in the KL sample. Zinc and Mn have a moderate biogeochemical mobility, whereas Cd and Pb are generally (!) not especially mobile [63]. The KL-ash originates from the deflagration of biomass. Hence, the aforementioned high contents are the result of anthropogenic contamination. Enrichment in Pb, Cr and Ni, in relation to the feed coals may be based on the low mobility of these elements, vis. [17]. In Poland, one may suppose local enrichments in feed coals and, consequently, in FAs, e.g. enrichments in Cd, Ni, Pb and Zn are confined to the Pb-Zn deposits. The alike situation occurs with regard to Sr and Ba (barite veins). Copper, Cr, Pb and Zn are related to high ash contents, whereas the enrichments in As, Be and V to the low ash amount [24]. It is also known that Co, Cr, Cu, Ni and V are enriched in inertine [24]. 'Arsenic, Cd, Ga, Ge, Pb, Sn, Sb, Te, Tl and Zn are generally volatile, become oxidised and accumulate on particles of the FAs' [25]. Thus, they can be enriched there, especially in the form of anions. We can trace the low volatility of Ni, Co and Mn in BASH (KWR), cf. [27] – and hence enrichment in the KWR. The problem of As was touched upon in part, earlier in this paper [5]. Refraining from a discussion concerning the role of CaO in FAs [5,25], we may suppose the following (*conjecture, in part*), Pb, Sr, Ba, Ge and Tl can easily enter the structure of feldspars, and their melts. A less likely scenario are replacements of Zn (filatovite) and B (reedmergnerite). Especially B, Pb and partially As (geochemistry) can easily enter diverse glasses and aggregates (originations). Such a supposition is based on the possible disordered structure of the compounds (minerals) and the short heating time. Hence, as is well-known from geochemistry, such the structures display a huge isomorphic capacity. Likewise melilites should scavenge Zn (hardystonite). Thus, FAs enrichment should occur in minor and trace elements and can probably be 'performed' in this 'FAs-intrinsic' way. There are various possibilities of the enrichments, i.e. based on crystal-chemistry.

4.5. Utilization

It should be stressed that usages or technologies mentioned in this section are already mastered (performed) or elaborated upon. Thus, in essence, these technologies are no more than potential-prospective in their character. The usages and the technologies are based on the FAs described in this paper. Firstly, it should be stressed that the large amounts of BaO and ZnO (SrO) in FAs can be of benefit in the manufacture of ceramics (whiteness, sinterability, synthesis of feldspars). Also, chromia – for the crystallisation of, e.g. pyroxenes. According to traditional practice, Polish FAs are used to build up composites with Mg- and Al-alloys for the motor industry, e.g. pistons. Apart from that, several other potential usages are possible. These include the production of ceramics or glass-ceramics from FAs. Cenosphere preforms were a starting material to intimately penetrated composites (IPC), whereupon Al or the Al-7075 alloy was used [86]. Following the use of long-lasting preheating or the floatage of the preforms (or ceramics) in the metal bath, composites were made, containing mainly oxides and silicon [86]. 'A liquid preform' (this is the established name of the technology!) – but what does it stand for? One can simply obtain an armoured metal, i. e. armoured by FA-glass; the process of mimicking window-panel technology – by pouring the melted FA on already melted metal and *vice versa* [86]. In spite of joining, no intimate intergrowths of the FA-phases and the metal were found. The HA fly ashes appear to be the most common ones. Diverse ceramics can be produced from them by adding, e. g. oxides. The IM ashes are especially well suited to glass-ceramics production, even without catalysts, whereas the CRI ones are mainly a source of CaO. According to one of the authors [80,87] seven technological methods of the fly-ashes utilization have been launched. By way of example, the anorthite-containing ashes may be used for the construction of glass-ceramics. Several ashes from the HA-group show chemical analyses close to those of particular clays – hence, they can be used to produce brick-like materials (blanks). *Glasses were also produced.* Moreover, the synthesis of cordierite from fly ashes with moderate amounts of CaO and SO_3, may occur in 3 diverse ways, according to [87] this should
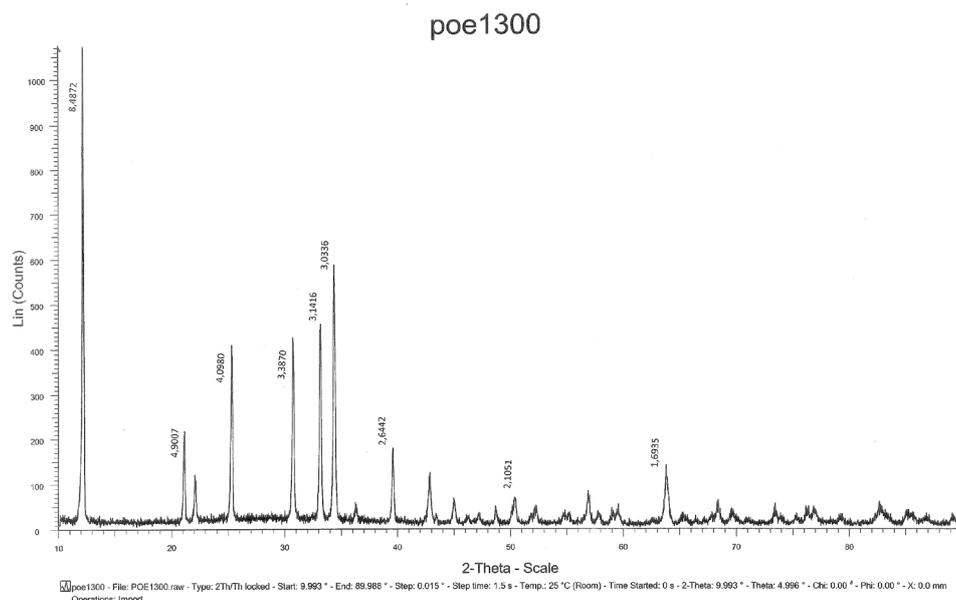
Fig. 13. The XRD powder pattern of indialite (with minute amount of hercynite) synthesized at 1300°C: indialite 8.4872, 4.9007, 4.0980, 3.3870, 3.1416, 3.0336, 2.6442, 2.1051, 1.6935; a part of the remaining ones – hercynite

be noted. The product is almost pure indialite with minor amounts of hercynite or spinel. Through its use, several ceramics have been produced, and composites (of MMC- and CMC type) with that cordierite were made. The XRD powder pattern of almost pure cordierite (indialite) is presented above (Fig. 13). A Mg-alloy with the addition of the aforementioned cordierite is two times stronger [88], whereas the addition of cordierite to another Mg alloy produced mechanical resistivity against impact (shock resistance) of 300 000 cycles, instead of 15 000 (demanded), and the experiment was ceased [89]. Several alike (similar) results will be published elsewhere.

5. Conclusion

In this paper 24 (25) ashes from Polish power plants were described and their utilization mentioned. Their mineralogy, chemistry, and radioactivity – from the industrial point of view – were recognised. More and more 'new' minerals are 'conveyed' to the mineralogy of fly ashes, e.g. vaterite ($CaCO_3$, hexagonal), mackinawite ($FeS_{0.96}$) [15] or new REE oxides [19]. Against this background, leucite, amphiboles (as the main mineral) or Fe-Mn phosphates (hureaulite, gatehouseeite) are no longer an oddity, they are, however, a novelty. It is important to recognize that the XRD powder pattern of a FA has to be made *by using a minute 2Θ step while observing diverse data-bases, and/or corroborating the results by other technique*, e.g. IR spectroscopy. It turns out that absolutely diverse materials can be produced from the fly ashes or using them. To date, apart from

the manufacture of ash-Al-alloy pistons and the recognition of definite processes, the IPC composites, 'liquid preform', cordierite, novel CMC and MMC composites and cordierite-strengthened alloys were all produced by our Institute. Hence, this paper demonstrates a much broader mineral assemblage of (Polish) fly ashes than was hitherto assumed. Moreover, the usage of fly ashes, being different from the contemporarily one known world-wide, was indicated. Incidentally, particular glass-ceramics can be more leachable (toxic) than the glass itself [90]. One of the future tasks would be preparation, separation and cleaning/rinsing of particular fly ashes for particular technology. To cope with those tasks, the deep-going mineralogical and crystal-chemical knowledge of the fly ashes is required. A constancy of composition is also a prerequisite for production of materials from FA. At present, there are only a few papers which recognise the nano- or micro-mineralogy and chemistry of fly ashes, e.g. [91,5,12,13].

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