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PROPERTIES OF PARTICULATE MATTER EMITTED FROM MANUFACTURING OF CERAMIC PRODUCTS

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WŁAŚCIWOŚCI PYŁU EMITOWANEGO PODCZAS PRODUKCJI WYROBÓW CERAMICZNYCH

Poznanie właściwości fizyko-chemicznych pyłów emitowanych z instalacji przemysłowych jest warunkiem oceny stanu aktualnego i doboru metod zapobiegania degradacji jakości powietrza atmosferycznego, spowodowanej obecnością w nim pyłu zawieszonego. Wśród branż przemysłowych emitujących pył znajduje się szybko rozwijający się przemysł ceramiczny, produkujący płytki ceramiczne. Z istotnych węzłów technologicznych instalacji produkującej płytki ceramiczne w trzech przedsiębiorstwach pobrano próbki pyłów. Stosując metody instrumentalne zbadano ich skład ziarnowy, morfologię, skład fazowy i zawartość metali ciężkich.

Summary

Knowledge on the physicochemical properties of PM emitted from industrial installations is necessary for assessing current state of ambient air and selecting proper methods for preventing suspended PM from degrading the air quality. Similar to many other industries, fast developing ceramic tile industry releases some amounts of PM to the atmosphere. Samples of PM were taken from main technological operations of three tile manufacturing installations, located in three various plants. The collected PM was examined for granular composition, morphology, phase composition and heavy metal content by using instrumental methods.

INTRODUCTION

In Poland, particulate matter (PM) emitted from various sources, also from industrial installations, is one of the major causes of atmospheric air degradation [2]. Concentration of suspended PM in ambient air within Polish urbanized and industrialized areas is much higher than in comparable areas of Western Europe countries [6]. This phenomenon occurs despite of considerable improvements done in recent years. The Polish standard of 40 $\mu g/m^3$ for yearly mean concentration of suspended particulate matter (PM10) in ambient air is often exceeded.

Striving for compliance of Polish air quality management standards with the EU standards for PM10, PM2.5, and in the nearest future also PM1, gave priority to investigations of airborne PM for its basic properties: granulometric and chemical composition and its morphology. Major sources of airborne PM include local and industrial heat production utilizing hard or brown coal, iron and steel production, cement manufacturing, coal coking, industrial and commercial ceramics, glass making, oil refining, iron casting [1].

POLISH CERAMIC INDUSTRY

Polish ceramic tile industry develops very dynamically – Poland is a third producer of ceramic tiles in Europe. In 2003, about 90 million square meters of tiles were produced in Poland, while demands were slightly higher. The produced tiles are mainly wall tiles, but slowly they are giving way to universal glazed tiles, particularly to gres tiles. Since 2001, the annual domestic tile production exceeds the value of imported tiles. Export of tiles is not significant.

There are 18 ceramic tile manufacturing plants in Poland and this number has been stable for some period of time. The greatest tile manufacturers are Opoczno S.A., Ceramika Paradyż and Cersanit S.A.

TECHNOLOGY OF PRODUCTION, TECHNOLOGICAL SCHEME, RAW MATERIALS, PRODUCTS, SOURCES OF PARTICULATE MATTER EMISSION

Polish ceramic tile manufacturing utilizes modern and environment-friendly technologies. The tile body is made of high quality raw materials – natural or synthetic. They include hard and clayey ceramic materials, fluidizers, hardeners and plasticizers.

Coatings applied to ceramic tiles to improve their front surface and practical properties are made of angobe, glaze and color agents. The process of manufacturing of ceramic tiles, presented schematically in Figure 1, consists of:

- Raw materials storage and transportation,
- Weighing and milling of ingredients of tile body and glaze,
- Tile body drying (and granulation),
- Tile body pressing,
- Tile glazing,
- Tile firing in gas roller hearth kiln,
- Storage of complete products.

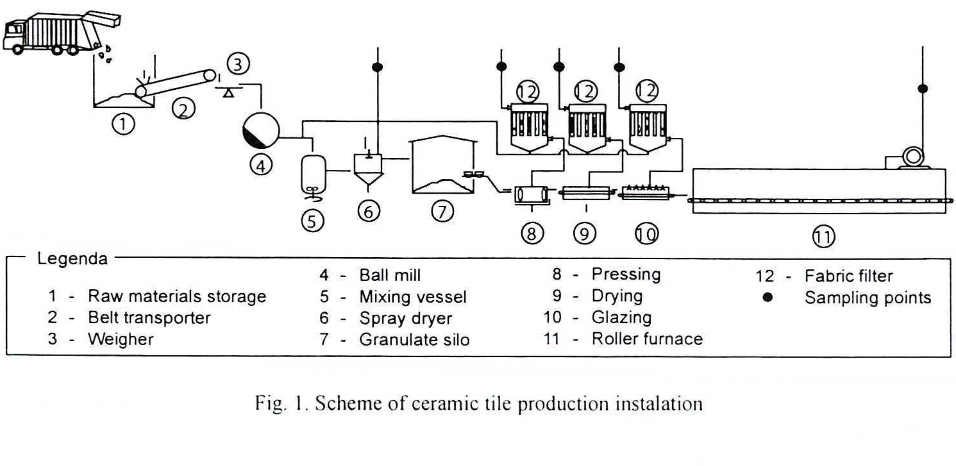


Fig. 1. Scheme of ceramic tile production instalation

GOAL AND SCOPE OF INVESTIGATIONS

The investigations were aimed at learning about properties of PM emitted from three installations producing ceramic tiles located in three different plants (A, B and C). The examined installations, equipped with mechanical and partially automated production lines, produce glazed wall and floor tiles, as well as gres tiles, by pressing the semi-dry granulated tile body and firing it in roller kilns.

The following technological operations of tile manufacturing were considered sources of PM emission characteristic of all investigated plants:

1 – spray dryer,
2 – tile transport and press line,
3 – tile glaze line,
4 – tile drying,
5 – roller hearth kiln.

PM was examined for its granulometric composition, density, morphology, phase composition, chemical composition and trace element content.

METHODS

PM samples from the five technological operations were examined for their granulometric composition by using a Fritsch „Analysette 22" measuring set, applying diffraction of He-Ne laser beam on particles in the size range of 0.16–1160 μm.

Absolute PM density was determined by using a liquid pycnometer according to the PN-74/Z-04002 norm.

Investigations of PM by using instrumental methods were done on the basis of earlier authors' experiences [3–5].

The particles' morphology was investigated by using two scanning electron microscopes (SEM): JSM35 (JEOL) and S4200 (HITACHI). The secondary electron image (SEI) microphotographs of the particles were received. The magnification coefficients were from 100 to 1000. The light microscope microphotographs of the particles were also done, the Nomarski contrast was applied.

The chemical composition of PM was analyzed by applying energy dispersive X-ray spectroscopy (EDS) with the use of two X-ray fluorescence spectrometers: LINK860 (Oxford Instruments, Si-Li detector, beryl exit window) and VOYAGER (NORAN, Si-Li detector, thin polymer exit window) in conjunction with the microscopes.

The qualitative phase analysis was done by applying X-ray diffraction on polycrystals. An X-ray diffractometer JDX-7S (JEOL) was applied.

The phase identification was done with the use of the PCSIWIN computer program basing on the JCPDS data library (International Centre for Diffraction Data 2000).

Selected trace elements were determined by using the Absorption Atomic Spectrophotometry (AAS) on a Perkin-Elmer spectrophotometer, Model 1100, using Merck's standards.

RESULTS

Kinds and amounts of PM emitted from particular technological operations is characteristic of the technology of production processes.

The data on granulometric composition of the PM is presented in Tabs 1–3 as cumulated mass contributions of granular fractions for assumed upper cut limits, and in charts (Figs. 2–6). The granulometric composition of emitted PM was considerably differentiated depending on technological operations. The highest PM2.5 share (about 31%) was in PM released to ambient air from roller kilns. The highest PM10 content was in flue gases emitted from the roller kilns (about 50%) and spray dryers (about 52%). The later result evidences low efficiency of a wet dedusting device installed behind the drying room.

Table 1. Cumulated mass share of granulometric fractions in PM emitted from technological operations of ceramic tile manufacturing, plant A

No.	Technological operation	Upper cut limit [μm]					
		< 2.5	< 5	< 10	< 30	< 50	< 100
		Cumulated mass share [%]					
1	Spray dryer	22.45	36.57	58.01	89.36	95.54	99.97
2	Tile transportation and pressing	33.72	48.21	69.00	93.89	98.47	100.00
3	Tile glazing	7.87	18.17	37.44	81.55	93.02	99.16
4	Tile dryer	9.57	18.34	38.01	82.28	93.21	99.22
5	Tunnel kiln	13.06	27.69	43.56	83.60	93.95	98.31

Table 2. Cumulated mass share of granulometric fractions in PM emitted from technological operations of ceramic tile manufacturing, plant B

No.	Technological operation	Upper cut limit [μm]					
		< 2.5	< 5	< 10	< 30	< 50	< 100
		Cumulated mass share [%]					
1	Spray dryer	10.28	22.33	49.33	91.10	97.47	99.95
2	Tile transportation and pressing	28.18	43.16	67.67	96.52	99.18	100.00
3	Tile glazing	8.53	17.08	36.76	84.05	94.13	99.36
4	Tile dryer	9.70	18.70	43.25	91.21	96.50	99.68
5	Tunnel kiln	12.78	25.33	48.62	89.55	96.58	99.67

Table 3. Cumulated mass share of granulometric fractions in PM emitted from technological operations of ceramic tile manufacturing, plant C

No.	Technological operation	Upper cut limit [μm]					
		< 2.5	< 5	< 10	< 30	< 50	< 100
		Cumulated mass share [%]					
1	Spray dryer	11.77	25.34	48.48	81.94	90.97	99.68
2	Tile transportation and pressing	3.29	6.58	13.16	26.00	40.02	82.54
3	Tile glazing	7.26	14.65	31.21	62.66	75.46	93.55
4	Tile dryer	8.06	14.37	33.00	76.39	85.68	97.64
5	Tunnel kiln	26.40	42.53	68.02	95.76	98.42	99.79

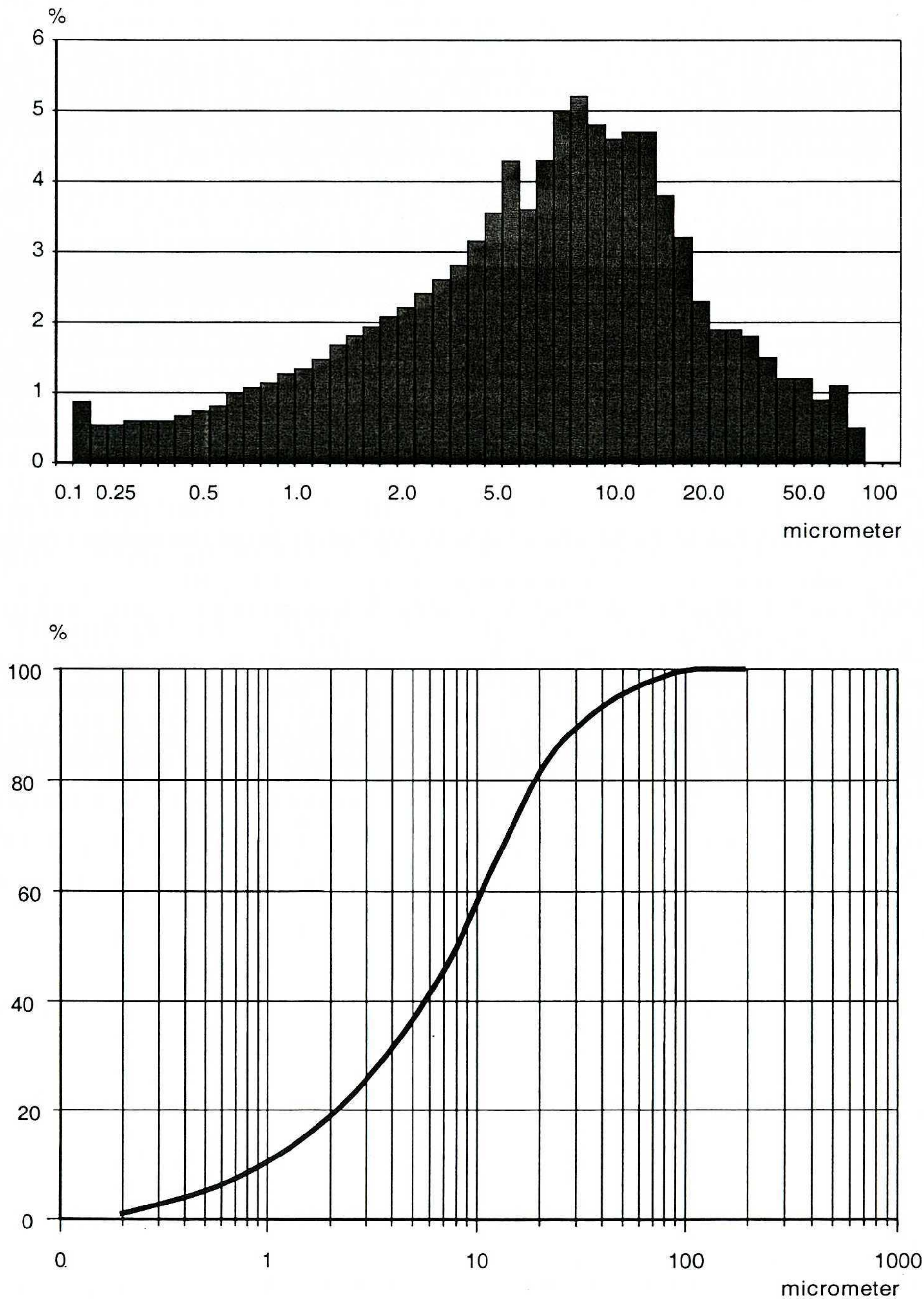
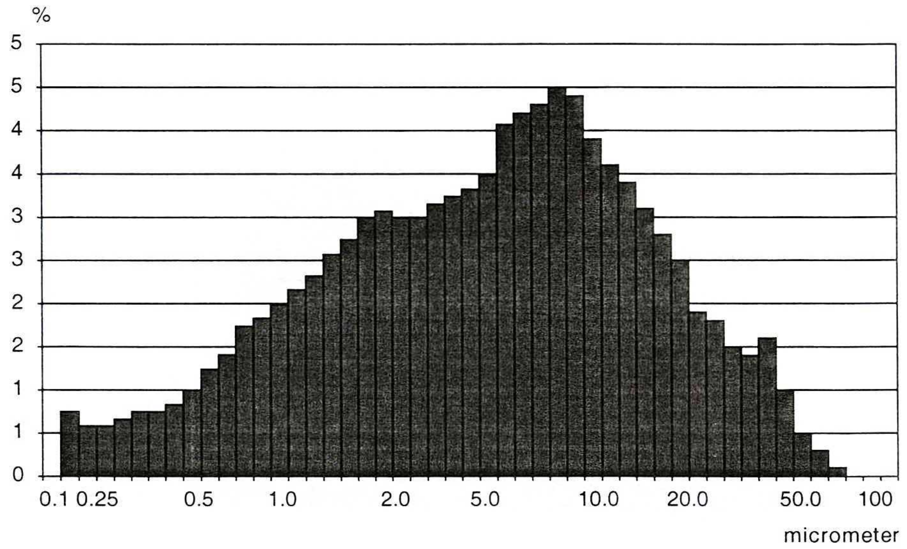


Fig. 2. Frequency and integration frequency distribution, spray dryer, plant A



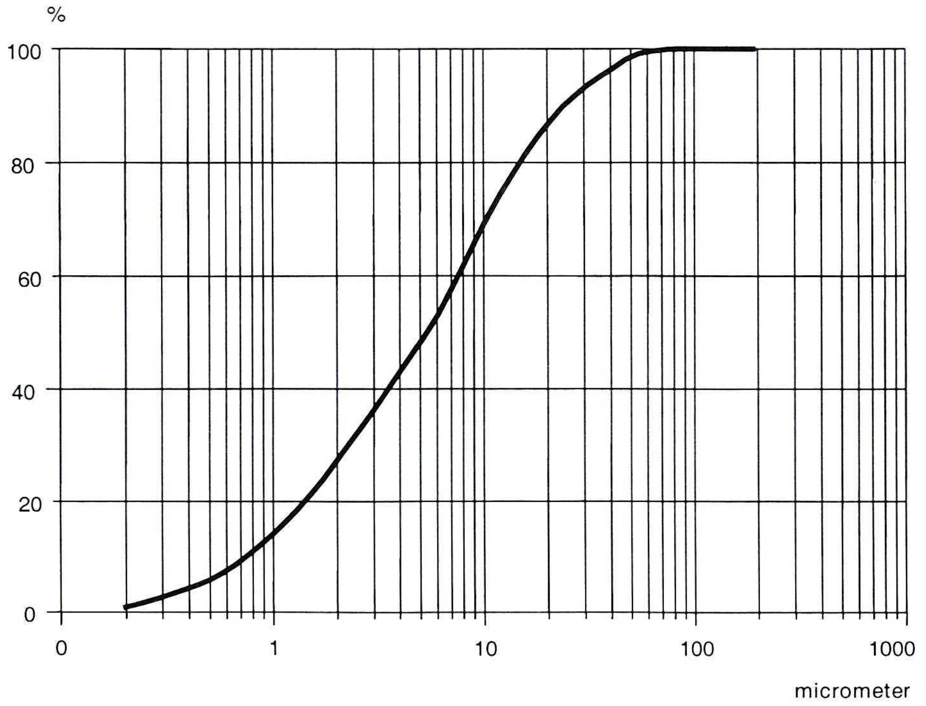


Fig. 3. Frequency and integration frequency distribution, transport and pressing line, plant A

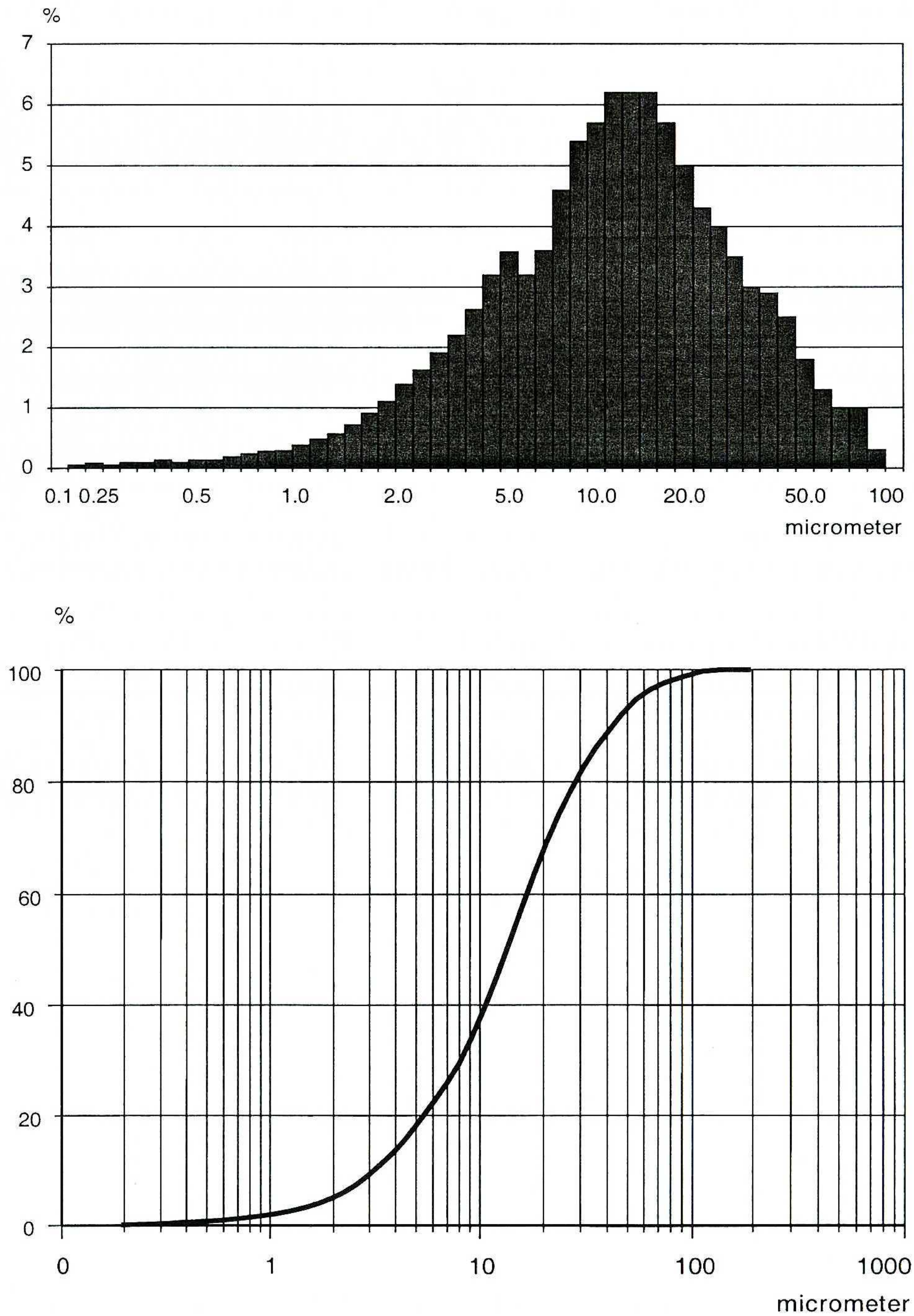
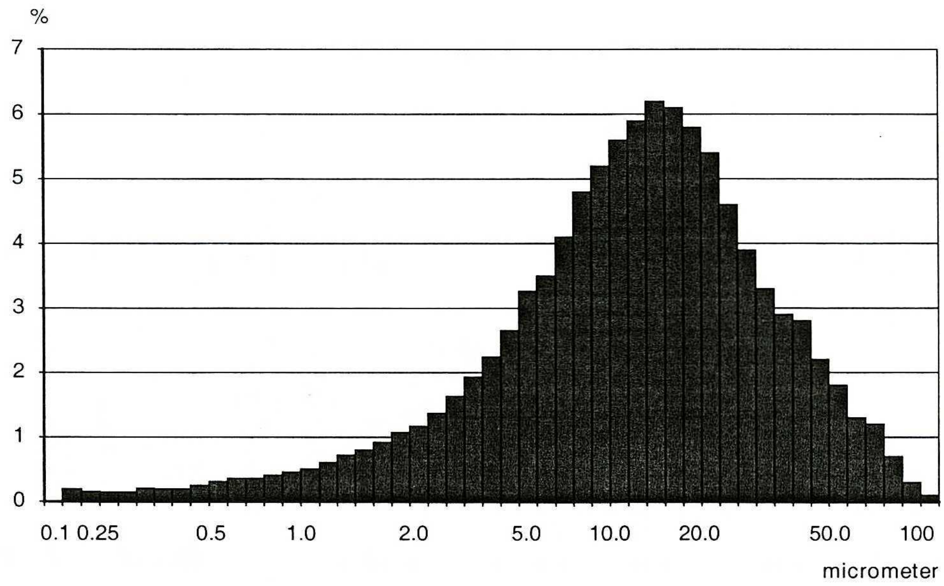


Fig. 4. Frequency and integration frequency distribution, line glazing, plant A



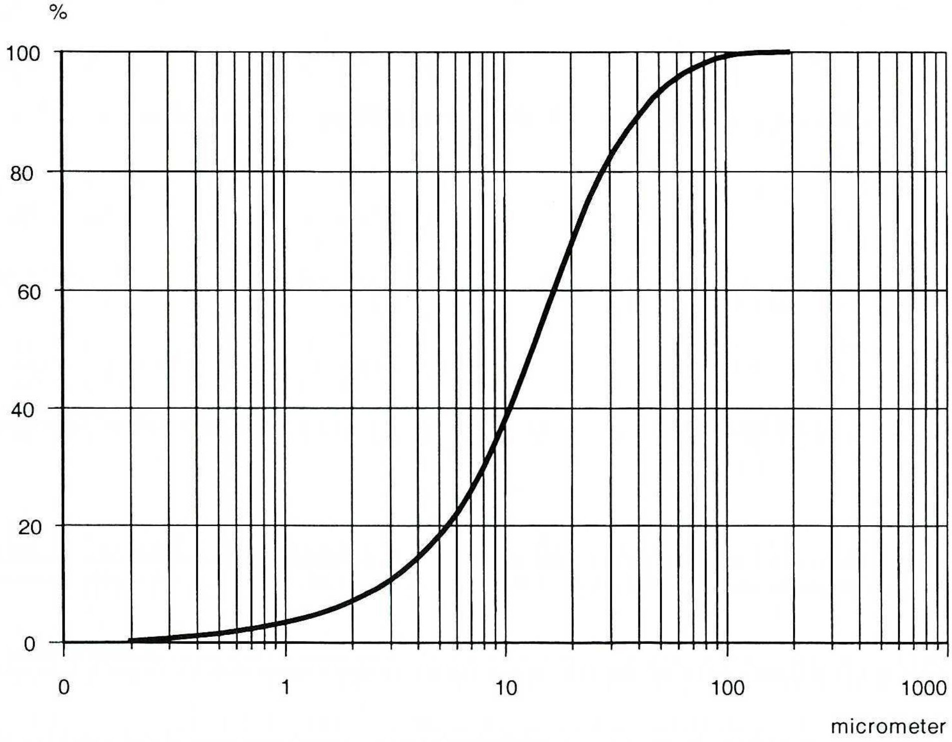
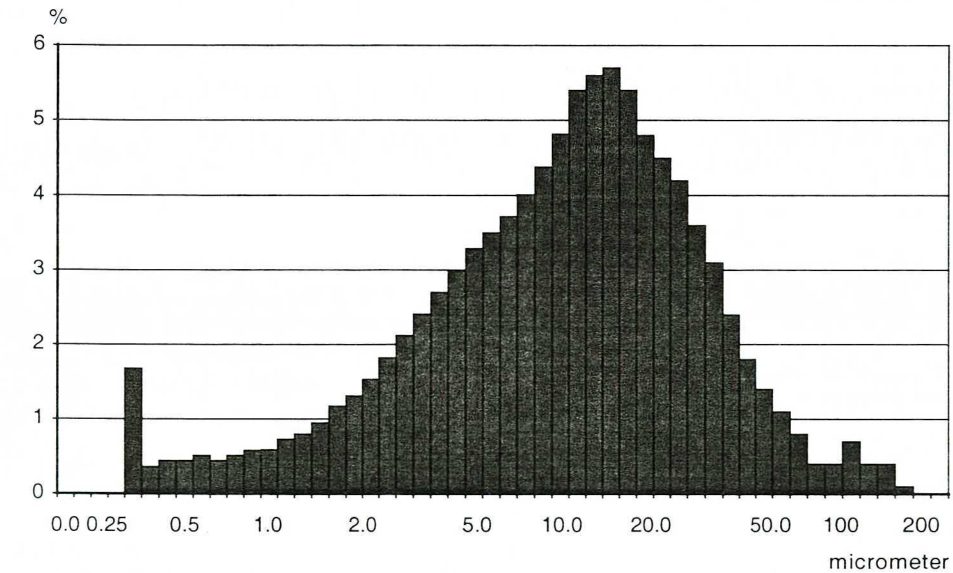


Fig. 5. Frequency and integration frequency distribution, tile drying, plant A



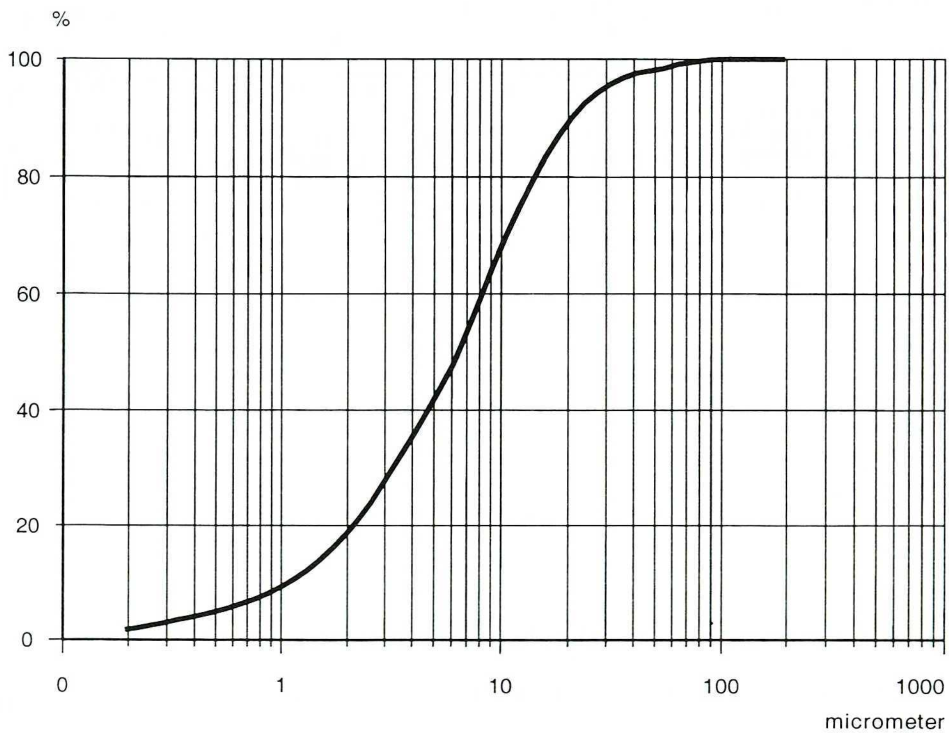


Fig. 6. Frequency and integration frequency distribution, tunnel furnace, plant A

The values of absolute density of the PM are presented in Tabs 4–6. The absolute densities of PM from particular operations and plants are close and vary between 2.31 and 3.03 g/cm^3. These results are characteristic of the investigated materials.

Table 4. Absolute density of PM emitted from technological operations of ceramic tile manufacturing, plant A

No.	Technological operation	Absolute PM density [g/cm^3]
1	Spray dryer	3.03
2	Dedusting of tile transportation and press line	2.56
3	Dedusting of tile glaze line	2.81
4	Tile dryer	2.57
5	Tunnel kiln	2.84

Table 5. Absolute density of PM emitted from technological operations of ceramic tile manufacturing, plant B

No.	Technological operation	Absolute PM density [kg/dm^3]
1	Spray dryer	2.80
2	Dedusting of tile transportation and press line	2.57
3	Dedusting of tile glaze line	2.76
4	Tile dryer	2.62
5	Tunnel kiln	2.31

Table 6. Absolute density of PM emitted from technological operations of ceramic tile manufacturing, plant C

No.	Technological operation	Absolute PM density [kg/dm^3]
1	Spray dryer	2.84
2	Dedusting of tile transportation and press line	2.70
3	Dedusting of tile glaze line	2.71
4	Tile dryer	2.53
5	Tunnel kiln	2.66

The light microscope microphotographs of particles sampled at a spray dryer granulate and press lines, glaze line, and vertical dryers are presented in Figs from 7 to 10. The granular structure is visible, shapes of the particles are very differentiated and their sizes fall into wide interval. The images of particles are similar for the dryers – spray and vertical – and glaze line. Considerably greater particles may be observed in PM from the granulate and press lines. The sizes of the particles may be evaluated by comparing with the micrometric scale in the microphotographs. Only some of the particles are of definite shapes. Evidently, particles of quartz have sharp edges, and particles of amorphous potassic and ferric alumosilicates, occurring in majority of samples, are spherical.

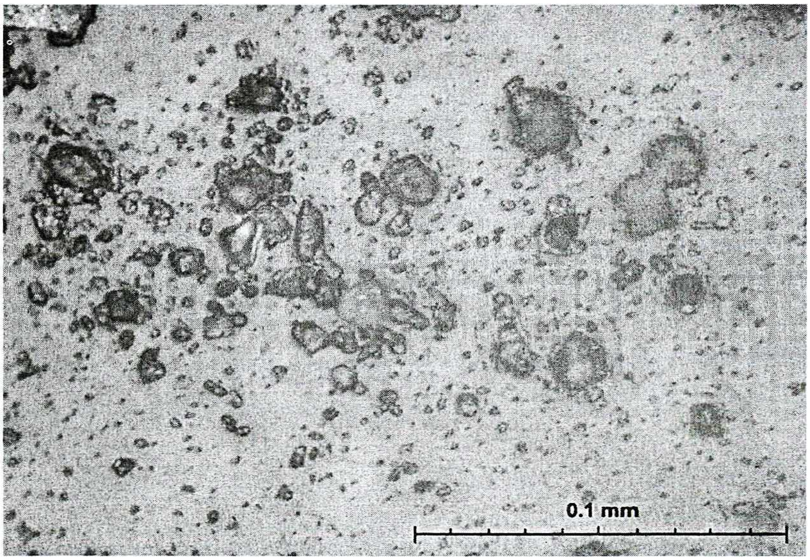


Fig. 7. Microphotograph of PM from spray dryer

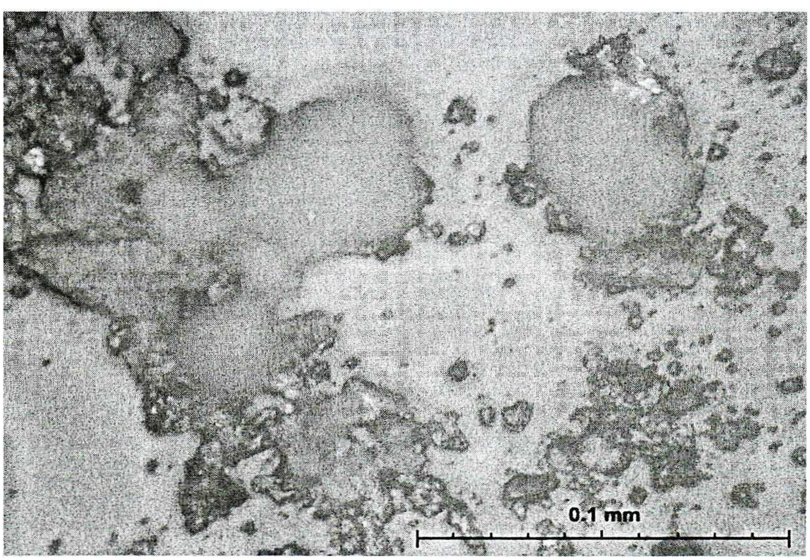


Fig. 8. Microphotograph of PM from granulate line and tile pressing

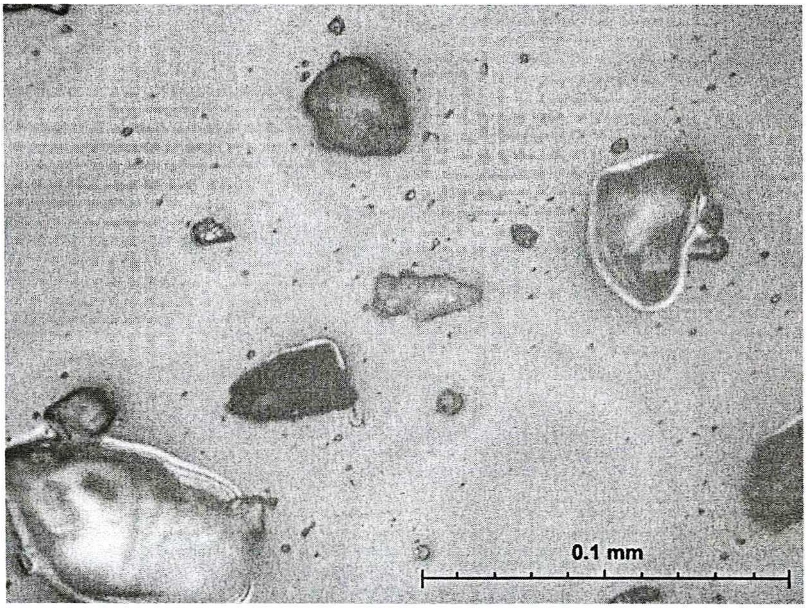


Fig. 9. Microphotograph of PM from tile glaze line

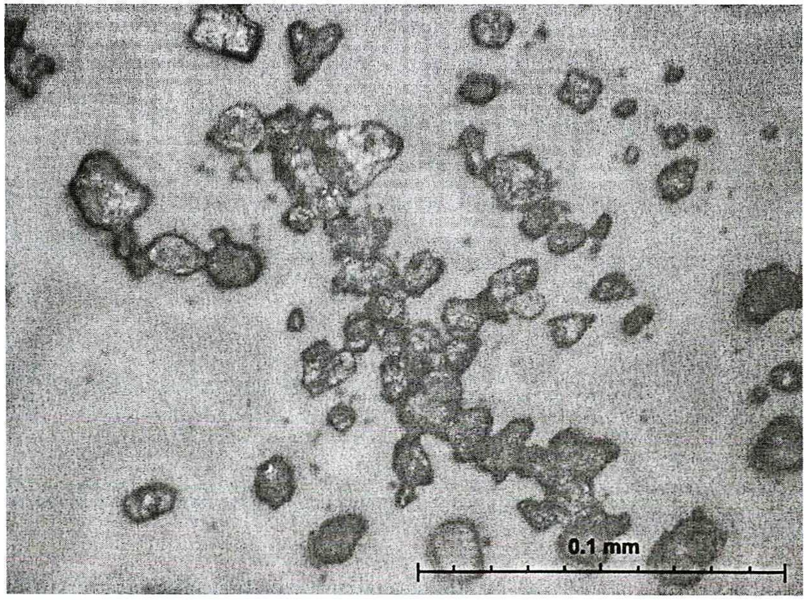


Fig. 10. Microphotograph of PM from vertical dryer

Confronting results received by means of the scanning electron microscopy (SEM), X-ray microanalysis of elemental composition (electron probe X-ray microanalysis – energy dispersive spectroscopy, EPMA-EDS) and measurements of X-ray diffraction (XRD, to determine chemical compounds), allowed identification of the phases in the investigated PM. The chemical and phase compositions of PM emitted from the technological operations of production of ceramic tiles are shown in Tables 7, 8, and 9. The samples of PM comprised elements that occur in raw materials utilized in tile manufacturing (quartz, cristobalite, kaolinite, feldspars), in glass opacifiers (TiO_2) and in coloring agents ($K_2Cr_2O_7$ – potassium dichromate, $ZnO \cdot Al_2O_3$ – zinc spinel, $FeO \cdot Cr_2O_3$ – chromite). In the process of production, the raw materials and admixtures are subjected to high temperatures. Some are decomposed or enter chemical reactions. Some elements they comprise react to create volatile compounds.

Table 7. Chemical and phase composition of PM emitted from technological operations of ceramic tile manufacturing, plant A

No.	Technological operation	Elements detected (EDS)	Crystalline phases identified (XRD)	Other probably occurring phases
1	Spray dryer	Al, Si, S, Pb, Cl, K, Ca, Ti, Cr, Mn, Fe, Cu, Zr	$(NH_4)(Mn,Fe^{3+}{}_3)(OH_6)(SO_4)_2$; NH_4CuSO_3 $Ca_2Pb_2O_5(OH)_2$ $Pb_6Al_{12}Si_{12}O_{48}$; SiO_2	$(NH_4)_2SO_4$ $AlSiKTiFeO_x$ (amorphous) $ZrSiO_4$
2	Dedusting of tile transportation and press line	Na, Al, Si, K, Ca, Ti, Fe, Zr	Al_2SiO_5; SiO_2 (quartz, cristobalite); $Al_2Si_2O_5 \times (OH)_4$ $CaCO_3$	$AlSiKTiFeO_x$ (amorphous) $ZrSiO_4$
3	Dedusting of tile glaze line	Al, Si, K, Ca, Ti, Fe	SiO_2 (quartz, cristobalite); Al_2SiO_5; $Al_2Si_2O_5 \times (OH)_4$; TiO_2; $CaCO_3$	$AlSiKTiFeO_x$ (amorphous)
4	Tile dryer	Na, Al, Si, K, Ca, Ti, Fe, Zn	SiO_2 (quartz); Al_2SiO_5; Al_2O_3; $CaCO_3$	$AlSiKTiFeO_x$ (amorphous) ZnO
5	Tunnel kiln	Al, Si, S, Cl, K, Ti, Cr, Fe, Ni, Zn, Se	FeS_2; ZnS; $(NH_4)_2(Fe,Cr,Ni)(SO_4)_2 \times 6H_2O$; NH_4-Fe-Cl; $K_2Al_2Si_3O_{10} \times 2H_2O$; $(NH_4)_2SO_4$	SiO_2 $AlSiKTiFeO_x$ (amorphous) $ZnCl_2$

Table 8. Chemical and phase composition of PM emitted from technological operations of ceramic tile manufacturing, plant B

No.	Technological operation	Elements detected (EDS)	Crystalline phases identified (XRD)	Other probably occurring phases
1	Spray dryer			
2	Dedusting of tile transportation and press line	Mg, Al, Si, K, Ca, Ti, Fe, Zr	SiO_2 (quartz, cristobalite); Al_2SiO_5; $Al_2Si_2O_5{\times}(OH)_4$; TiO_2	$AlSiKTiFeO_x$ (amorphous) $ZrSiO_4$
3	Dedusting of tile glaze line			
4	Tile dryer			
5	Tunnel kiln	Mg, Al, Si, S, K, Ca, Ti, Mn, Fe, Zn	SiO_2; $(NH_4)_2SO_4$; $(NH_4)_2$ $(Fe,Mn)(SO_4)_2{\times}6H_2O$ $NH_4Al(SO_4)_2{\times}12H_2O$; ZnS	$K_2S_3O_{10}$ $AlSiKTiFeO_x$ (amorphous) $CaSO_4$; $ZnCl_2$

Table 9. Chemical and phase composition of PM emitted from technological operations of ceramic tile manufacturing, plant C

No.	Technological operation	Elements detected (EDS)	Crystalline phases identified (XRD)	Other probably occurring phases
1	Spray dryer			
2	Dedusting of tile transportation and press line	Al, Si, K, Ca, Ti, Fe	SiO_2 (quartz, cristobalite); Al_2SiO_5; $Al_2Si_2O_5{\times}(OH)_4$; TiO_2; $CaCO_3$	$AlSiKTiFeO_x$ (amorphous)
3	Dedusting of tile glaze line			
4	Tile dryer			
5	Tunnel kiln	Mg, Al, Si, S, Cl, K, Ca, Ti, Fe, Zr	SiO_2 (quartz); $NH_4Al(SO_4)_2{\times}12H_2O$; $NH_4Fe(SO_4)_2{\times}12H_2O$; $CaSO_4$; $(NH_4)_2\,Ca_2\,(SO_4)_3$; $(NH_4)_3Fe(SO_4)_3$	$ZrSiO_4$; $K_2S_3O_{10}$ $AlSiKTiFeO_x$ (amorphous)

Results of investigations are illustrated with characteristic X-ray spectra and diffraction patterns where concrete chemical compounds are attributed to particular spectral lines. Examples of microphotographs of particle surfaces and respective characteristic X-ray spectra are presented in Figs 11–14. Exemplary diffraction patterns are presented in Figs 15–18. Shapes of all diagrams in their small-angle regions indicate presence of amorphous phases. Apart from the identified phases, small amounts of crystalline compounds, not detected due to limitations of the X-ray phase analysis, may occur. Some of them are marked as probable in Tabs 7–9 because the microanalysis revealed presence of particles having characteristic chemical composition.

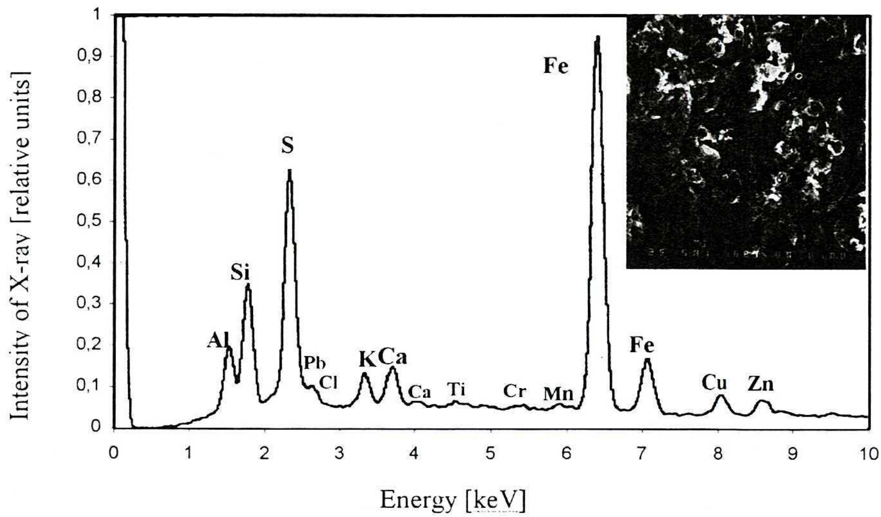


Fig. 11. Microphotographs of surface of particles from spray drier (SEM, magnification 500×) and respective characteristic X-ray spectra

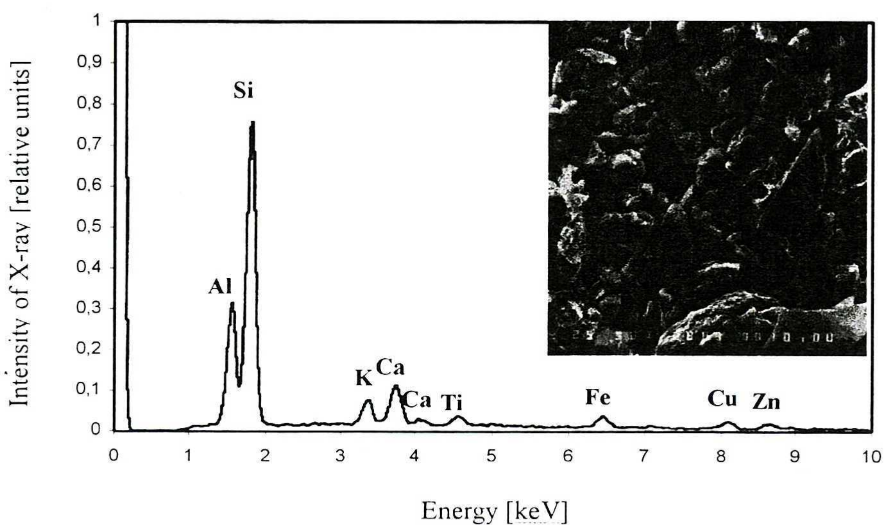


Fig. 12. Microphotographs of surface of particles from granulate line and tile pressing (SEM, magnification 500×) and respective characteristic X-ray spectra

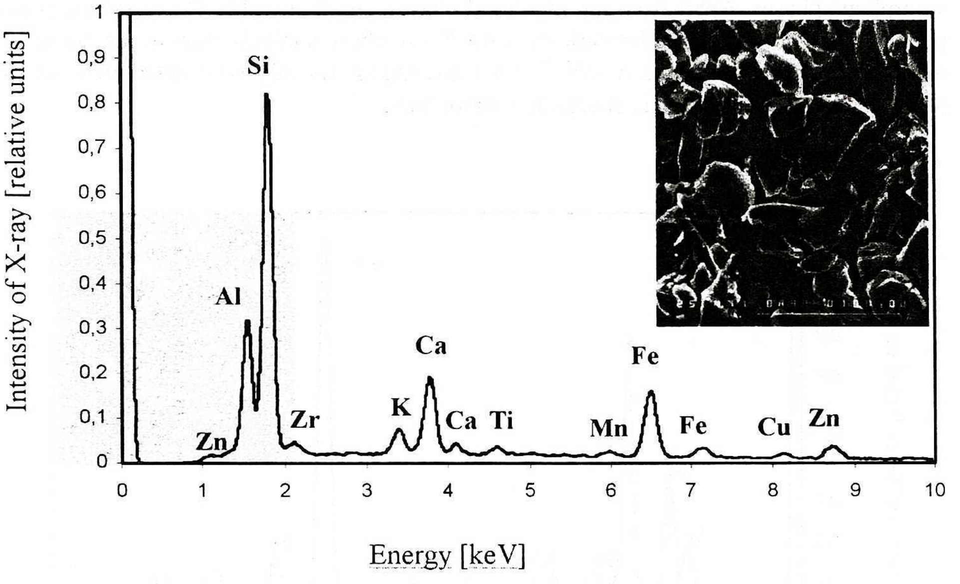


Fig. 13. Microphotographs of surface of particles from tile glaze line (SEM, magnification 470×) and respective characteristic X-ray spectra

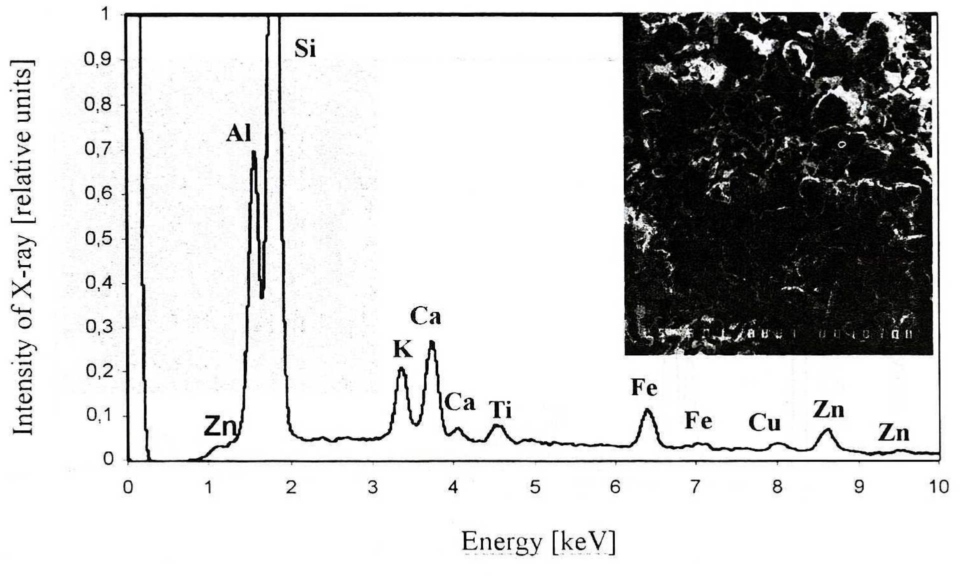


Fig. 14. Microphotographs of surface of particles from vertical drier (SEM, magnification 500×) and respective characteristic X-ray spectra

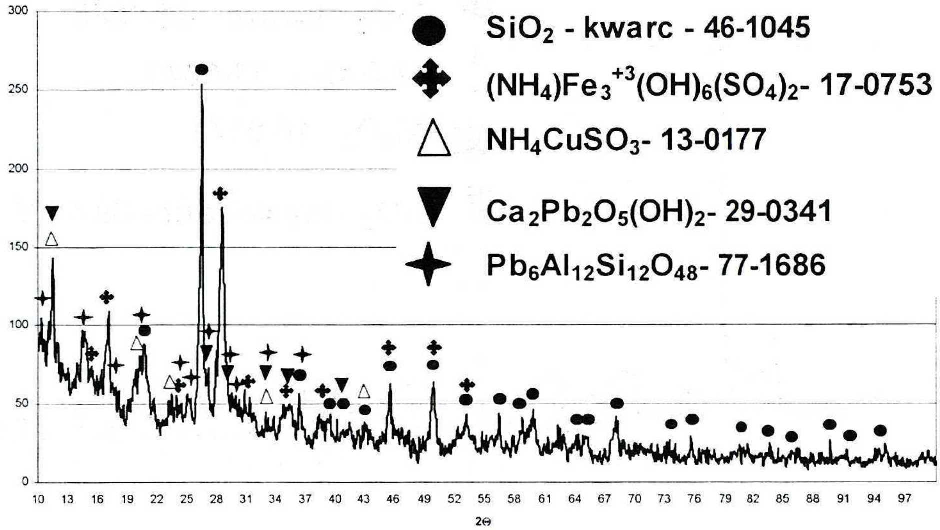


Fig. 15. Diffraction pattern of PM from spray dryer

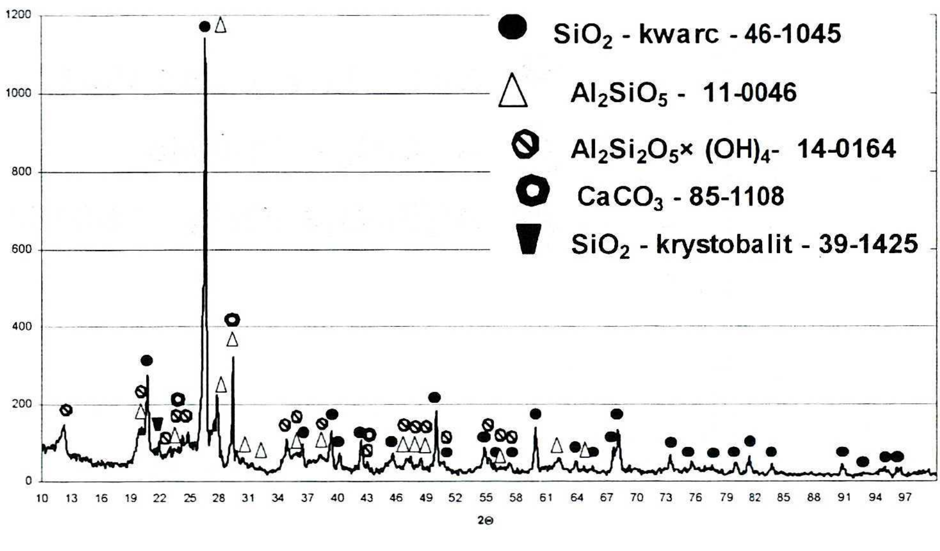


Fig. 16. Diffraction pattern of PM from granulate line and tile pressing

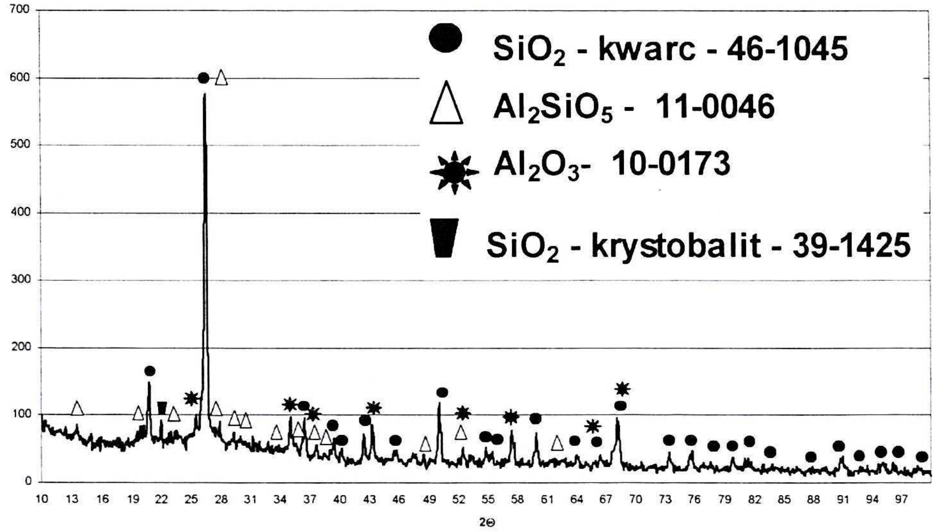


Fig. 17. Diffraction pattern of PM from tile glaze line

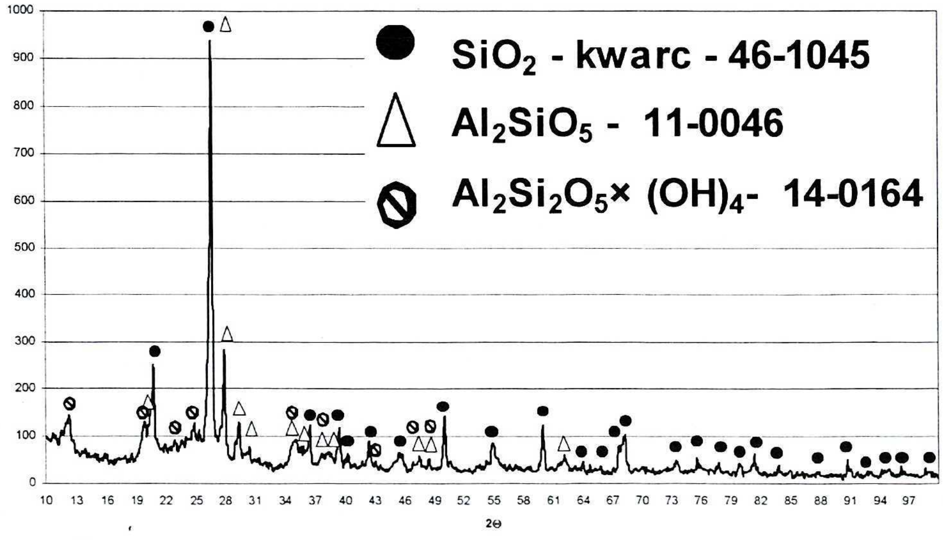


Fig. 18. Diffraction pattern of PM from vertical dryer

Content of trace elements in emitted PM depends on composition of raw materials used in a production process. Concentration of heavy metals in PM was very differentiated. Due to preliminary character of the investigations and tentativeness of the results, Table 10 present results averaged over all three installations.

Table 10. Mean concentrations of selected trace elements in PM emitted from technological operations of ceramic tile manufacturing, plants

No.	Technological operation	Trace element								
		Cr	Zn	Cd	Ba	Co	Mn	Cu	Ni	Pb
		Concentration [ppm]								
1	Spray dryer	244.9	5401.0	15.2	n.o.	46.1	265.2	1085.3	87.1	658.9
2	Tile transportation and press line	336.9	7456.6	2.6	n.o.	58.6	213.6	2480.3	89.8	163.9
3.1	Sanitary product glazing	n.o.	8245.1	n.o.	55.6	n.d.	n.d.	n.o.	n.o.	n.o.
3.2	Tile glazing	216.7	15040.0	11.9	249.9	27.8	331.3	5294.0	143.4	212.1
4	Tile dryer	517.9	109.4	4.0	n.o.	89.0	564.6	42.0	319.3	80.4
5	Tunnel kiln	361.3	312.1	13.2	n.o.	68.9	393.8	36.6	176.1	135.8

n.d. - not determined

In PM taken from investigated operations, the dominating elements were iron (2.23–20.34 mg/g) and zinc (0.11–15.0 mg/g). Copper content exceeded 5 mg/g, lead – 0.6 mg/g, chromium and manganese – 0.5 mg/g. The lowest content in the PM was that of cadmium (reaching 15 ppm) and of cobalt (89 ppm). Concentrations of chromium, cobalt and manganese were independent of sampling points. High differences were observed between content of zinc, copper and cadmium in PM at various sampling points. The lowest concentration of the determined metals occurred in PM emitted from tile dryers and roller kilns, the highest – in PM from spray dryer and tile glaze line.

CONCLUSIONS

1. The granulometric composition of emitted particulate matter (PM) was quite differentiated and depended on a technological operation PM was emitted from.
2. PM emitted from the tunnel kilns had the greatest share of PM5 – it was about 31%.
3. The highest share of PM10 was in flue gases emitted from the tunnel kilns (about 53%) and spray driers (about 52%).
4. In the microphotographs, granular structure of collected PM may be seen; shapes of the particles are differentiated and their sizes fall into wide interval. PM from the spray dryer, the vertical dryer and the tile glaze line has similar morphology. Significantly greater grains occur in PM from the granulation and press lines.
5. The observations and measurements allowed identification of phases of investigated PM.

6. Content of trace elements in emitted PM depends on composition of raw materials used in a process of production. Concentration of heavy metals in emitted PM was very differentiated.
7. Due to great PM10 share in emitted PM, more efficient dedusting devices should be applied.

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