GOSPODARKA SUROWCAMI MINERALNYMI

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Characteristics of mineral fibres waste as source of ecological threats

Key words

Mineral fibres, glaze devitrification, fibres respirability, fibrous waste, waste utilisation

Abstract

The article presents full mineralogical and chemical characteristics as well as physical and mechanical properties of mineral fibre (basalt, glass and ceramic) waste formed in the process of insulating materials' dismantling. On the basis of chemical investigations (using an electrone microprobe), X-ray and DTA analyses, changes in microstructure, chemical and phase compositions were determined after insulating materials had been used. The examined fibres have been ranked in the following order with respect to the increasing degree of changes: basalt, glass and ceramic. In basalt and glass fibres, changes occur only in chemical composition of individual fibres. Use of ceramic fibres leads to formation of new phases: mullite and cristobalite. Comparison of physical, mechanical and chemical properties of mineral fibre waste with those of asbestos (completely different) must result in different technological characteristics, including respirability, which in the case of mineral fibre is less aggressive in terms of biological effect on a human organism. It cannot be excluded, however, that the increased respirability (signalled in the literature) of certain types of ceramic fibres partially results from a supporting role played by chemically different secondary fibres formed in devitrification process. In the case of ceramic fibres examined by the author these are new phase fibres, easily separable from each other at higher temperatures.

Introduction

In the process of dismantling, insulating materials containing artificial mineral fibres emit into the environment microscopic fibres which for a long time remain in the air in the form of permanent aerial-fibrous aerosols. Depending on the doses of fibre emitted, fibrous aerosols may stay in the air within 5 km from the source of emission.

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When breathed in, they may cause injuries leading to irreversible pathogenic effects including cancer changes. As shown by the measurements of fibrous aerosol concentration in the Province of Silesia (Pastuszka 1995), in some regions, increased or even high levels of asbestos fibre concentration have been noted and consequently, higher risk of lung cancer has been involved. Biological effect of mineral fibre suspended in the air has been relatively well examined for asbestos fibre (Zurer 1985; Asgharian, Yu 1988; Myojo 1990; Lis, Pastuszka 1995; Lutz, Krajewska 1995; Pastuszka 1997). The research was aimed at explaining a mechanism of asbestos fibre toxic effect on human respiratory system. It was revealed that the increased biological aggressiveness (respirability) of the fibre was dependent on the mineralogical type of asbestos which falls into two categories: serpentine (mineralogically chrysotile) or amphibole (mineralogically amosite, termolite or crocidolite). These fibres are characterised by microscopic divisibility, leading to formation of fibres whose diameter is below 0,1 microns. They affect lungs, resulting in chronic, frequently carcinogenic lung dust disease combined with a circulatory-respiratory failure.

Biological effect of artificial mineral fibre (basalt, glass and ceramic), in world literature referred to as MMMF (Man Mad Mineral Fibres), is far less known compared to asbestos fibres. On the whole, the research indicates their lower respirability in comparison with asbestos (Singh, Coffman 1991). Moreover, only fine fibres of diameters below 3 microns and length/diameter ratio higher than 3 : 1 may be biologically aggressive. Over a longer period of time they bring about skin irritation, medically defined as “maculate erythema”. Single cases of oral cavity cancer have also been reported. The authors emphasise the increased biological aggressiveness of certain types of ceramic fibres. The problems of respirability of ceramic fibres produced in Poland were the subject of investigations conducted by the scientists in the Institute of Work Medicine (Wojtczak, Lao, Krajnow 1996; Krajnov, Lao, Stetkiewicz 1997; Kabała-Dzik, Pastuszka 1998). The undertaken investigations, including experimental tests on animals to evaluate the risk of lung cancer in people exposed to the effect of ceramic fibres bring us to the conclusion that certain types of ceramic fibres are characterised by similar carcinogeny to that of crocidolite or chrysolite asbestos. The European Union Health Committee has included artificial mineral fibres along with asbestos into a group of increased health harmfulness, their disposal being subject to legal consequences. However, an unequivocal assessment of artificial mineral fibres’ respirability is difficult. Discrepancy in evaluations presented by different laboratories results from different conditions of dismantling, industrial safety, concentration of fibrous aerosols and finally, health and biological immunity of the examined employees.

The article presents an assessment of toxicity of domestic mineral fibre (basalt, glass and ceramic), released in the process of dismantling of different insulating linings. The analysis was based on determined (selected as significant for evaluation of respirability) physical and chemical properties as well as mechanical strength of mineral fibres and its results were compared to the properties of asbestos fibres, functioning as a model of toxic effect on a human organism. The effect of soluble fibre components accumulating on the surface and permeating into soil on contamination of soil and ground waters was also evaluated.

1. Properties of the examined mineral fibres waste

Due to the manner of artificial mineral fibre production — molten material defibring, in most cases mineral fibres adopt a fully amorphous structure. When in use, they may undergo partial devitrification. The evaluation of changes in fibres was based on X-ray, DTA and chemical analysis.

In the case of basalt and glass fibres, diffraction patterns (Fig. 1) confirm their amorphous state in a characteristic shape of X-ray photograph background and lack of X-ray reflections.

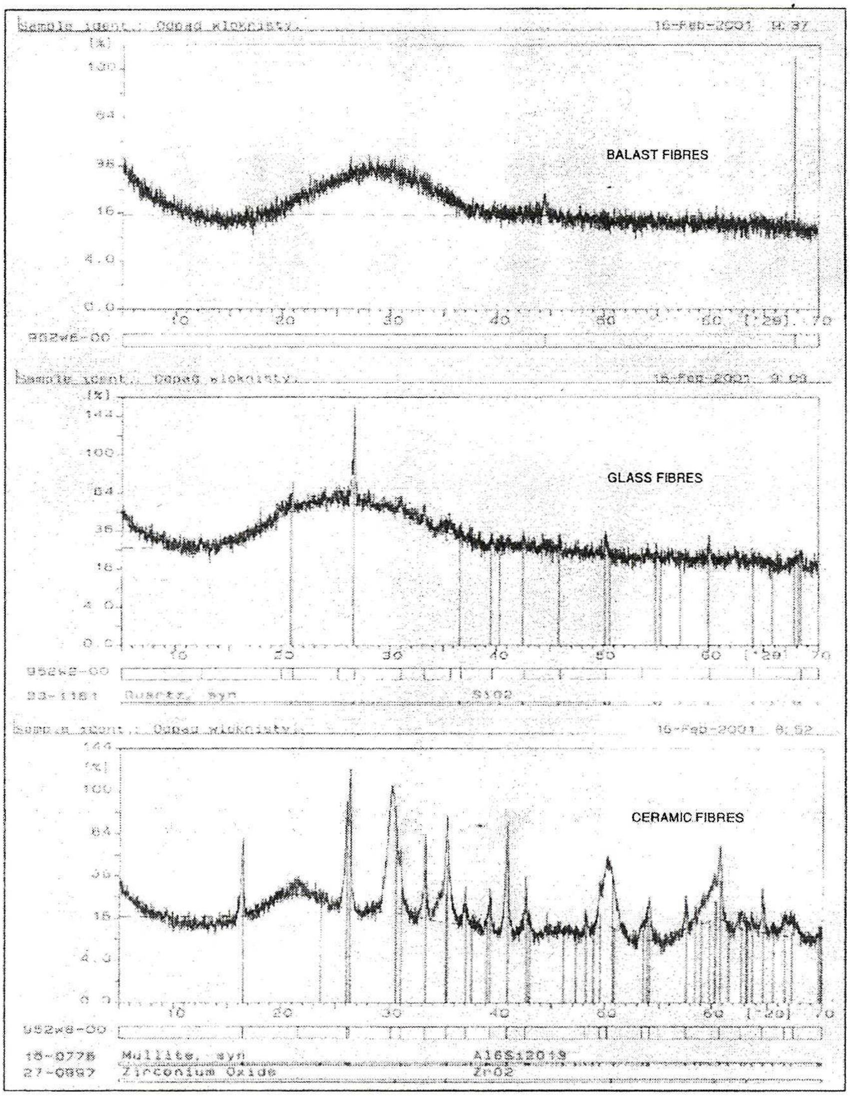

Fig. 1. Diffraction patterns of the examined mineral fibres waste

Rys. 1. Dyfraktogramy badanych odpadów włókien mineralnych

The state of ceramic fibres is clearly devitrified and a group of X-ray reflections characteristic of mullite and cristobalite occurrence may be observed. DTA patterns illustrating chemical and phase changes in the process of fibres' heating have been shown in Fig. 2. *Basalt fibres* undergo recrystallization at 840—880°C, and crystalline phase is composed of pyroxenes. These minerals grow in a magnetite phase which appears early at 300—500°C. However, as the temperature of basalt fibres' use generally does not exceed 300°C (lower than the earliest temperature of devitrification), most fibres remain amorphous. *Glass fibres* are also amorphous. When they are being used, however, partial devitrification and internal structural order may take place. Thermal changes of *ceramic fibres* are chiefly connected with initial crystallisation of mullite at 945°C, whose gradual growth and formation of cristobalite is the main reason for fibre destruction. Since the temperature of ceramic fibres' use (1200—1400°C) is much higher than devitrification temperature — used fibres are always, to a lesser or greater extent, recrystallized.

Results of chemical analyses of mineral fibre waste have been given in Table 1. Chemical composition shows the composition of raw materials prepared to be melted as well as changes

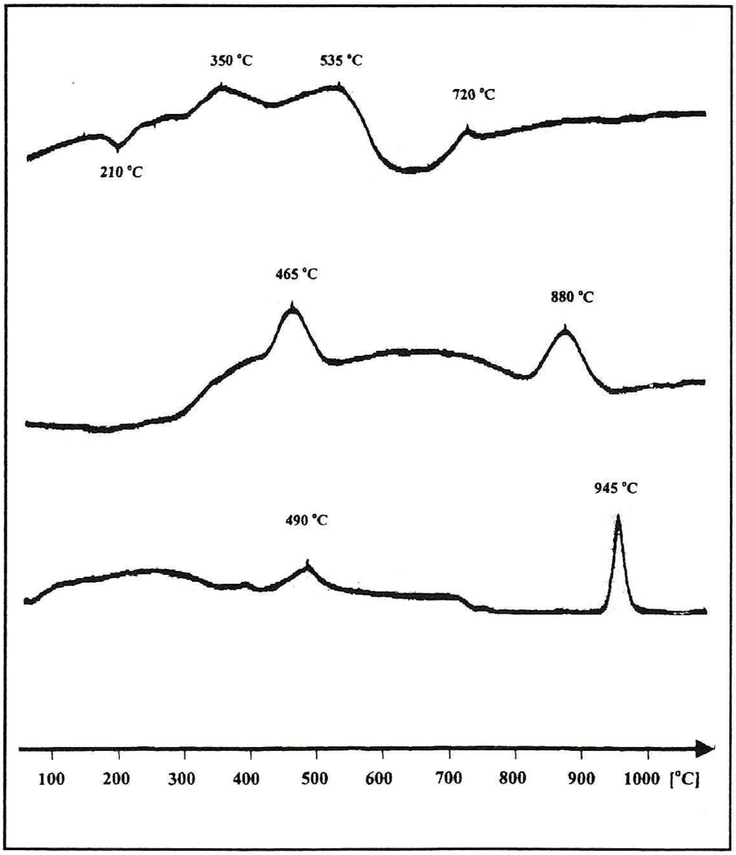

Fig. 2. DTA patterns of the examined mineral fibres waste (Witek, Łukwiński, Wasielewski 2002)

Rys. 2. Derywatogramy badanych odpadów włókien mineralnych (Witek, Łukwiński, Wasielewski 2002)

TABLE 1

Chemical composition and basic properties of mineral fibres waste (Witek, Łukwiński, Wasielewski 2002)

TABELA 1

Skład chemiczny i podstawowe własności odpadów włókien mineralnych (Witek, Łukwiński, Wasielewski 2002)

Type of fibres	Chemical composition [%]							Phase composition	Refractoriness [sP]	Fibre diameter min-max / mean [μm]	Average length of fibre [mm]
	SiO_2	Al_2O_3	ZrO_2	CaO	MgO	Fe_2O_3	K_2O+ Na_2O				
Basalt	47.3	13.8	—	16.2	12.9	5.7	3.7	amorphous	114	0.8—51.23 7.05	100—130
Glass	67.9	2.7	—	7.8	3.8	0.2	17.7	amorphous, small amounts of SiO_2	100	0.8—24.51 4.52	150—200
Ceramic	48.1	34.1	14.3	0.1	0.5	0.05	0.6	devitrified, mullite + ZrO_2	171	0.8—45.23 6.69	50—70

occurring when fibres are in use. To give a better insight into these changes, the analyses have been supplemented with research using an X-ray microanalyser (microprobe). On the basis of local analyses performed by penetrating into microareas of several fibres, ranges of changes in their chemical composition have been determined. The results are given in Table 2. By way of example, Fig. 3 presents concentrations of basalt fibres in the image of electron microscope,

TABLE 2

Ranges of changes in chemical composition of mineral fibres waste as determined on the basis of local analyses in X-ray microanalyser

TABELA 2

Zakresy zmian składu chemicznego odpadów włókien mineralnych, wyznaczonych na podstawie analiz punktowych w mikroanalizatorze rentgenowskim

Components	Ceramic fibres	Glass fibres	Basalt fibres
SiO_2	48.15—50.32	68.56—63.03	42.16—47.07
Al_2O_3	34.11—34.32	2.59—2.60	12.22—13.97
MgO	0.69—0.70	3.83—3.86	9.93—12.74
CaO	0.09—0.10	7.68—8.27	16.50—23.82
Fe_2O_3	0.03—0.04	0.18—0.26	5.67—9.68
K_2O	0.13—0.20	0.39—0.60	0.20—0.43
Na_2O	0.11—0.20	16.15—17.02	1.78—3.52
ZrO_2	14.32—15.23	—	—

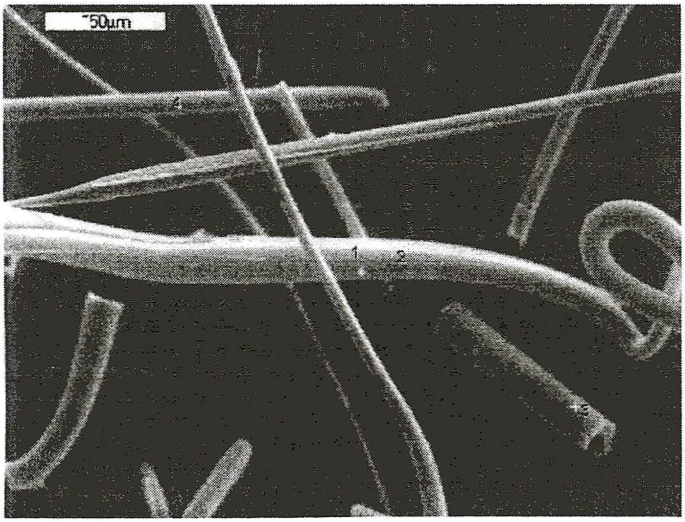

Fig. 3. Basalt fibres aggregates as shown in electron microscope image (400×)
1, 2, 3, 4 — local analyses points

Rys. 3. Skupienia włókien bazaltowych w obrazie mikroskopu elektronowego, pow. 400×
1, 2, 3, 4 — miejsca wykonanych analiz punktowych

where the conducted local analyses, given in Table 3, have been marked. The analyses and established scope of research indicate that ceramic and glass fibres are characterised by a very low variability in chemical composition of particular fibres. In basalt fibres (Table 3) differentiation in CaO and Fe_2O_3 contents may be observed, which is connected with incomplete homogenisation of main alloy components (basalt and limestone) as well as formation of nuclei of iron oxides' (magnetite) crystallisation. As indicated by investigations into microareas, the amorphous structure shown in X-ray photograph does contain initial devitrification elements in the form of crystallising nuclei and diversified chemism of particular fibres. They may lower mechanical properties and increase brittleness.

TABLE 3

Results of research on chemical composition of basalt fibres waste in X-ray microanalyser

TABELA 3

Wyniki badań składu chemicznego odpadów włókien bazaltowych w mikroanalizatorze rentgenowskim

Components	Analysis locations			
	1	2	3	4
SiO_2	47.07	43.68	42.16	46.84
Al_2O_3	13.67	13.54	12.22	13.97
MgO	12.73	10.58	9.93	12.74
CaO	16.80	20.84	23.82	16.50
Fe_2O_3	5.67	7.42	9.68	6.43
K_2O	0.20	0.43	0.39	0.31
Na_2O	3.52	3.11	1.78	3.15

To determine strength of individual fibres, the author applied his own indirect method of determination. A water suspension of a strictly determined amount of fibres was formed and then subjected to intensive mixing at due time. Following the whole operation, the suspension underwent 1-minute sedimentation, next its top part (100 ml) was decanted and after filtering, mass of fibres contained in the suspension was determined. Comparing this amount to the initial one, we obtain a percentage indicator of brittleness (strength) of the examined fibres. To ensure full reliability, each result was calculated as an arithmetic mean of 5 determination values. Determination results (average values) have been shown in Fig. 4.

The analysis of the above results leads to the following general conclusions:

— Basalt fibres (Fig. 4) are characterised by the highest brittleness (the lowest strength). This probably results from diversified chemical compositions of individual fibres, as observed in electron microprobe examination, and formation of iron oxides crystallisation nuclei when fibres are in use (fibres crack in those places). Ceramic and glass fibres feature much lower brittleness (higher strength).

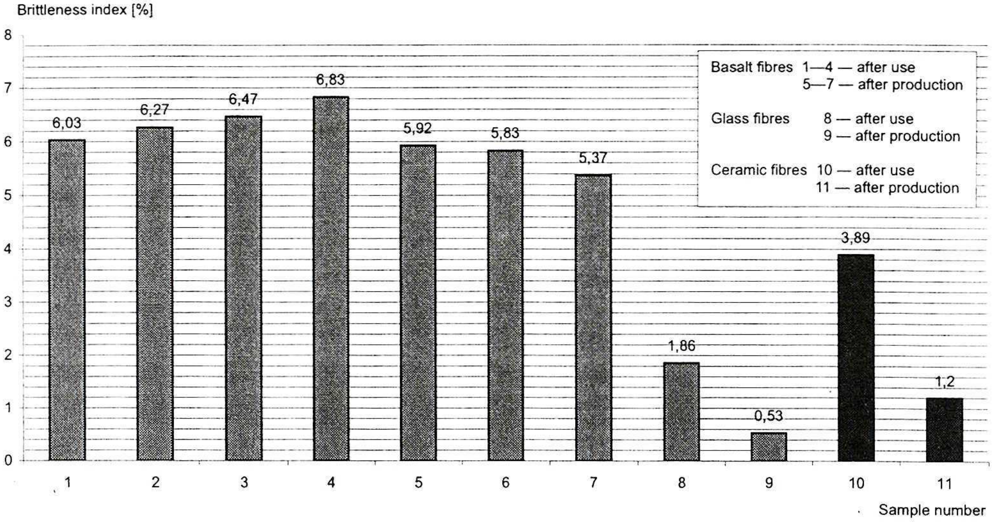

Fig. 4. Brittleness of the examined mineral fibres waste (Witek, Łukwiński, Wasielewski 2002)

Rys. 4. Kruchość badanych odpadów włókien mineralnych (Witek, Łukwiński, Wasielewski 2002)

— The process of devitrification of initial, amorphous fibrous material, taking place when ceramic and glass fibres are in use, favours higher brittleness (lower mechanical strength) of fibres. Over a longer period of time this process leads to deterioration in the quality of insulating material and during dismantling works, favours release of fibres which have unfavourable properties from the point of view of ecological threats.

2. Comparison of asbestos and artificial mineral fibres' properties

A qualitative evaluation of toxic effect of mineral fibre waste has been based on a comparison of their physical and chemical properties as well as strength with those of strongly toxic asbestos fibres. Asbestos fibres, assumed as reference for evaluation, occur in nature as a component of chrysotile serpentinites represented by chrysolite or amphiboles (amphibole asbestos), which are formed with the participation of hydrothermal solutions from magnesium-rich silicates (usually from olivine); they may also be a component of amphiboles (tremolite, amosite, crocidolite) formed at conditions of partial water loss. Following the colloidal phase, biologically aggressive chrysotile, precipitated in a hydrothermal process, separates anew in rock cracks to form uniform, subtle needle-type fibres, perpendicular to crack surface. Fibres have a tubular structure; "cleavage" is fibrous, parallel to elongation. Fibres are flexible and easily separable. The latter accounts for possible formation of biologically aggressive fibres of respirable asbestos dust.

Contrary to asbestos fibres, artificial mineral fibres obtained by liquid alloy defibring adopt an amorphous structure, which by nature does not have any privileged directions of divisibility (cleavage). Fibre disintegration is accidental and leads to diversified fibre habits, usually of increased diameters and lengths. Therefore no longitudinal shred (division) of fibres accompanied by formation of biologically active, asbestos-like respirable dust is observed, as in the case of asbestos. Scale of morphological diversification of mineral fibres released from insulating materials in comparison with asbestos fibres has been reflected in a list of diameters of different kinds of fibres, quoted in the study of Łącki (1974) and given in Table 4. As may be seen in the list, the diameters of artificial fibres are several times bigger than those of asbestos, which results in a completely different biological effect of both kinds of fibres. Similar relations may be observed when mechanical bending strength is compared. If the author's method of breaking fibres by means of whirling water is used, the best way to compare mineral fibres with asbestos ones is a standardised method of torsional strength. By way of example, torsional strength of chrysolite asbestos from Quebec (Canada) as determined by the number of broken asbestos fibres reaches 35%. For mineral fibres examined by the author this number is higher and ranges from 30 to 70%, despite less strict conditions of fibre brittleness determination. Another issue connected with artificial mineral fibres is their effect on environmental contamination. The problem concerns storage of fibrous waste on dumping grounds as well as the degree and type of subsoil waters contamination. Bigger-size fibres which are suspended in the air and fall on the ground may also accumulate and permeate into the soil, leading to particular changes in circulatory waters. To determine the effect of accumulated mineral fibres on the changes in soil chemism, mineral fibre waste was leached with water and analyses of the obtained water extracts were carried out. The results have been given in Table 5. Apart from slight exceeding of admissible pH and COD (chemical oxygen demand) values in some samples, values of the remaining parameters are much lower than the standard ones for sewage carried off to waters and grounds.

TABLE 4

Diameters of some types of fibres

TABELA 4

Średnice niektórych rodzajów włókien

Type of fibre	Fibre diameter [µm]
Bast fibre (flax, jute)	12—80
Cotton	10
Wool	20—30
Human hair	38
Nylon	6—9
Glass fibre	1—7
Basalt fibre	3—9
Chrysolite asbestos	0.015—0.042
Amphibole asbestos	0.12—0.25

TABLE 5

Chemical analyses of water extracts from the examined mineral fibres waste

TABELA 5

Analizy chemiczne ekstraktów wodnych z badanych odpadów włókien mineralnych

Type of determination	Unit.	Basalt fibres		Glass fibres		Ceramic fibres		Admissible concentration
		after production	after use	after production	after use	after production	after use	
Reaction	pH	8.6—9.1	7.2—9.4	6.1	10.6	9.9	7.9—8.5	6.5—9.0
Electric conduction	μs/cm	62—65	79—713	609	396	25	91—93	—
COD (chemical oxygen demand)	mg/l	10—261	27—87	225	105	10	10.0	150.0
Chlorides	mg/l	1.0—1.4	2.6—3.2	4.7	7.6	1.2	1.5—3.6	1 000.0
Ammonium nitrogen	mg/l	0.23—1.29	—	0.13	—	1.0	—	—
Sulphates	mg/l	10—16	12—245	1 35.0	8.7	10	18.0	500.0
Fenols	mg/l	0.05—6.1	0.05	0.1	0.1	—	—	0.5
Formaldehyde	mg/l	0.05—1.93	0.05	0.078	0.05	—	—	2.0
Total chromium	mg/l	0.01—0.02	0.01—0.02	0.36	0.01	0.01	0.01	—
Zinc-Zn	mg/l	0.05—0.06	0.12—0.25	0.05	0.05	0.05	0.05	2.0
Cadmium-Cd	mg/l	0.01	0.01	0.01	0.01	0.01	0.01	0.1
Manganese-Mn	mg/l	0.01—0.02	0.02—0.15	0.02	0.01	0.01	0.01	—
Copper-Cu	mg/l	0.05	0.05	0.05	0.05	0.05	0.05	0.5
Nickel-Ni	mg/l	0.01	0.01	0.01	0.01	0.01	0.01	2.0
Lead-Pb	mg/l	0.05—0.09	0.05—0.07	0.05	0.05	0.05	0.05	0.5
Iron-Fe	mg/l	0.01—1.05	0.05—0.23	0.08	0.01	0.01	0.02	10.0

Summary

The presented mineralogical and chemical analysis as well as the determined physical and chemical properties of mineral fibre waste (basalt, glass and ceramic) released during insulating materials' dismantling made it possible to evaluate the fibres under examination as sources of ecological threat:

1. Basalt fibres analysed after service life of insulating materials had finished retained their primary amorphous state. However, chemical composition of particular fibres underwent changes and crystallisation nuclei of iron oxide formed in glaze matrix. They caused a considerable drop in fibres' mechanical strength (increased brittleness) and in consequence, decreased biological respirability of fibrous aerosols in the air and led to soil contamination through accumulation of fibres on their surface.

2. After use, glass fibres, chiefly ceramic ones, were characterised by high devitrification of primary glaze matrix, reflected in the formation of microareas of ordered internal structure (in glass fibres) or crystallisation of new phases — mullite or crystaballite (in ceramic fibres). Generally, the strength of these fibres is higher and brittleness lower compared to basalt type. Over a longer period of time, however, the revealed tendency to devitrification may enhance fibres' biological respirability and increase a negative effect on soil contamination.

3. Analysis of the properties of the examined fibres and asbestos ones, accepted as a respirability model, show that they are practically incomparable, both from the point of view of different structure and fibre morphology and due to higher crushing strength of asbestos fibres.

4. Although numerous investigations and experiments revealed aggressiveness of ceramic fibres having similar pathogenic effect to that of asbestos, it was not unequivocally established in the conducted research in terms of the effect on human respiratory system. Since the properties of artificial mineral fibres and asbestos ones turned out to be completely different, it is hard to expect any similarities in this respect. Attention should be drawn, however, to the above-mentioned high degree of ceramic fibre devitrification in the process of insulating material use. It cannot be excluded that, depending on production technology, there may appear secondary, chemically different, respirable fibres. In the case of fibres under examination they could be e.g. subtle, mechanically resistant, needle-type mullite formations released in the process of dismantling which easily separate from glaze mass at higher temperature. Another characteristic thing is occurrence of ZrO_2 (baddeleyite) — phase of high mechanical strength, in the examined fibrous material. We cannot exclude its supporting role in increasing aggressiveness of certain types of ceramic fibres. The question of ceramic fibres' higher respirability requires further scientific investigations.

5. The possibility of leaching harmful substances (heavy metals: Pb, Cd, Cu and others as well as phenols and formaldehydes) from mineral fibre waste is lower that admissible values for the sewage carried off to waters and grounds, which enables their safe storage without posing a threat of soil and water contamination.

This article was elaborated basing the investigations realized within research project PCZ-010-19 entitled: "Technique and system utilization of inorganic, synthetic fibres waste".

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CHARAKTERYSTYKA ODPADÓW WŁÓKIEN MINERALNYCH JAKO ŹRÓDŁA ZAGROŻEŃ EKOLOGICZNYCH

Słowa kluczowe

Włókna mineralne, dewitryfikacja szkliwa, respirabilność włókien, odpady włókniste, utylizacja odpadów

Streszczenie

W artykule przedstawiono pełną charakterystykę mineralogiczno-chemiczną i własności fizykomechaniczne, powstających w czasie demontażu wyłożeń izolacyjnych, odpadów włókien mineralnych: bazaltowych, szklanych i ceramicznych. Na podstawie badań chemicznych (w tym z wykorzystaniem mikrosondy elektronowej) oraz rentgenograficznych i derywatograficznych prześledzono zmiany w mikrostrukturze, składzie chemicznym i fazowym włókien po eksploatacji materiału izolacyjnego. Według wzrastającego stopnia zaawansowania zmian uszeregować można badane włókna w kolejności: włókna bazaltowe, szklane i ceramiczne. We włóknach bazaltowych i szklanych ograniczają się one do zmian w mikrostrukturze włókna i zróżnicowanym (w przypadku włókien bazaltowych) składzie chemicznym poszczególnych włókien. We włóknach ceramicznych eksploatacja prowadzi do pojawienia się nowych faz: mullitu i krystobalitu. Z porównania własności fizykomechanicznych i chemicznych opadów włókien mineralnych z własnościami azbestu (diametralnie różnych) wynikać muszą odmienne cechy technologiczne, w tym również respirabilne, w przypadku włókien mineralnych mniej agresywne przy biologicznym oddziaływaniu na organizm człowieka. Nie można wykluczyć, że w sygnalizowanej w literaturze światowej podwyższonej respirabilności niektórych odmian włókien ceramicznych wspomagającą rolę odgrywać mogą powstałe w procesie dewitryfikacji odmienne chemicznie wtórne włókna — w przypadku badanych przez autora włókien ceramicznych reprezentowane przez włókna nowych faz, łatwo oddzielających się od siebie w wyższych temperaturach.