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Prospects for processing wastes into products used in agriculture*

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Abstract: The authors have proposed their own newly developed universal procedure for assessing waste and selecting methods of processing the waste for agricultural purposes. Increasingly more rigorous environmental legal regulations, especially pertaining to sustainability in agricultural and chemical production, were the most convincing motivation for such approach. The procedure is based on technological and environmental safety criteria. Special attention is devoted to the chemical processing of hazardous wastes into fertilizer products and the underlying reasons for such methodology. As opposed to physical and biochemical processes, in chemical processes the agents used completely change the chemical structure of the waste materials or at least that of some of their components. As a result, new phases are formed and the harmful properties of the initial material are eliminated. Prospects for the chemical processing of hazardous wastes are demonstrated using as an example the utilization of asbestos wastes. There are vast amounts of asbestos materials installed in industrial, communal, and service facilities. Landfill asbestos waste disposal is the common practice, but this does not solve properly the problem of environmental hazard. The proposed utilization concept consists in destroying asbestos with a phosphoric acid solution in a two-stage process. The obtained suspension is then filtered, and the solution of phosphates containing an excess of phosphoric acid is subsequently neutralized with lime and processed into phosphate fertilizers of TSP (triple superphosphate) or DCP (dicalcium phosphate) type. Experiments showed that the process yielded asbestos-free products which did not contain any respirable fibers. Comparative immunological tests showed that the products did not cause any degeneration of human lung cells exposed to them, as opposed to the original asbestos, which had a highly damaging effect on the cells.

Keywords: waste material; waste processing; sustainability; recycling.

INTRODUCTION

The utilization of wastes is one of the factors helping to put into effect the idea of sustainability in all areas of human economic activity. In agriculture, sustainability refers to the ability of a farm to produce food and other products indefinitely, without causing irreversible damage to the health of the ecosystem. In the case of small-scale production, this can be achieved by (among others)

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- recycling crop waste and livestock manure and
- growing legume crops and forages, such as peanuts or alfalfa that form symbiosis with nitrogen-fixing bacteria.

However, perfect sustainability in agriculture is rather impossible. At the present demographic development it would be very hard to produce sufficient amounts of food without using any additional sources of nitrogen, phosphorus, potassium, and other nutrients.

Since the basic micronutrients are taken up in large quantities by plants, large-scale mining of non-renewable resources (phosphate ores, potassium minerals, hydrogen derived from natural gas, etc.) and processing them into fertilizer products in various chemical forms are necessary. As regards phosphorous resources, their exploitation is often wasteful whereby many phosphorous deposits may be quickly depleted. Since the world resources of available phosphorous-bearing ores are estimated by the Food and Agriculture Organization of the United Nations (FAO) at 12 000 M Mg, and so at the current rate of extraction of about 145 M Mg/year they will last for only about 80 years [1].

A potential source of nutrients can be all kinds of waste produced as a result of different human activities. An analysis of the available data shows a great potential in this field. According to the European Environmental Statistics, each year about 1300 M Mg of wastes are produced in the EU countries. To this figure one should add 700 M Mg of agricultural wastes [2,3], which gives a total of about 2000 M Mg of various materials containing hundreds of thousands Mg of nitrogen, phosphorous, potassium, magnesium, calcium, and sulfur.

The great potential of waste utilization can be seen if one considers, for example, nitrogen whose uncontrolled emission in the European Union (EU) countries reaches millions of Mg per annum. It is estimated that in the European countries belonging to the Organization for Economic Cooperation and Development (OECD) it amounts to about 6.45 M Mg.

The utilization of wastes is consistent with the economic policy and the waste management strategy included in the legislative documents relating to environment protection. The Waste Framework Directive 75/442/EEC establishes a waste management hierarchy (Fig. 1) determining possible ways of waste handling. Waste reduction is most preferable, then waste re-use and energy recovery. The least desirable option is landfilling.

Fig. 1 Hierarchy of waste management established by Waste Framework Directive 75/442/EEC.

The waste utilization situation differs considerably between different countries in the world (Fig. 2). In agriculture, the most wastes are utilized in South Korea and in the old EU countries, whereas in other (particularly African) countries much of the wastes end up in uncontrolled landfills [4].

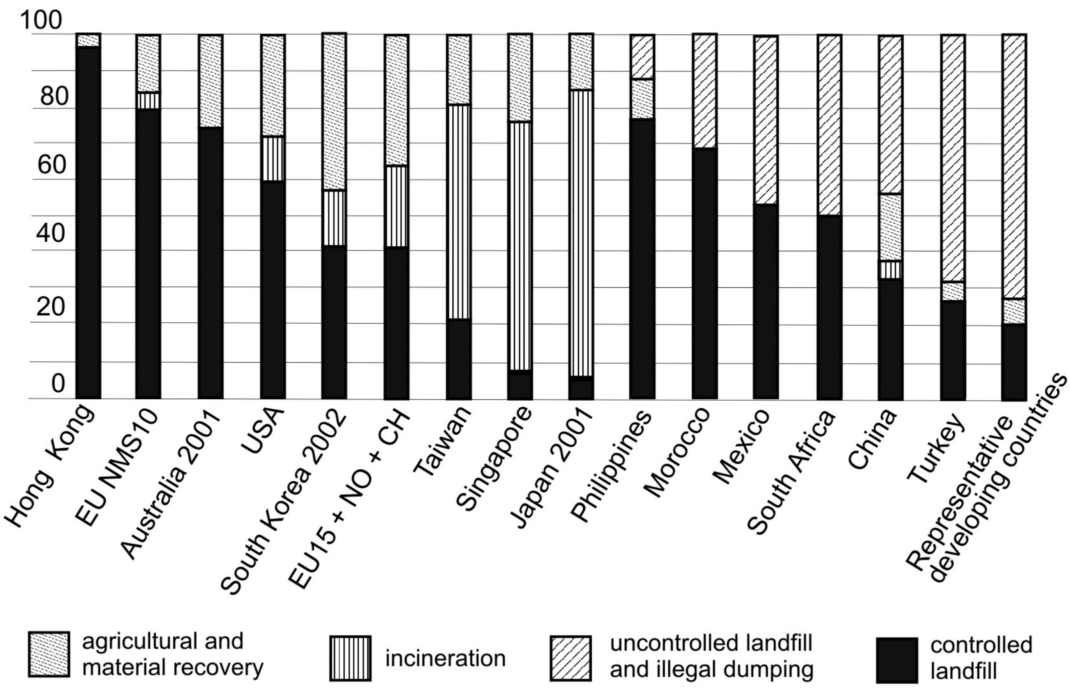

Fig. 2 Municipal waste treatment breakdown in selected number of countries (in %).

PROCEDURE FOR ASSESSING MATERIALS FOR AGRICULTURAL PURPOSES

The suitability of wastes for processing into products used in agriculture is assessed according to several criteria allowing one to choose a proper procedure for processing the wastes. So far, no clear-cut method of assessing wastes with regard to their use as a source of nutrients has been developed. Because of that, a lot of nutrient-containing waste that could potentially be utilized as raw materials for fertilizer manufacture is still being landfilled.

The aim of the work was development of an innovative, universal procedure for assessing any materials, including low-grade raw materials, with regard to their potential agricultural utilization. The procedure has been tested in laboratory and pilot studies for selected representative wastes varying widely in their origin and physical, chemical, and toxicological properties. Among others, the procedure was evaluated using asbestos wastes as an example. A flow chart of the procedure is shown in Fig. 3.

The procedure is a multistage process in which the necessary conditions and the possible processes stemming from them, leading to the production of safe products according to the set criteria, are checked step by step.

One of the principal criteria which must be fulfilled in order for a material to be admitted to agricultural use is the nutrient content. From the environmental engineering point of view, however, the safety criterion is the most important one. Waste treatment processes eliminating the properties posing a risk to the environment should be selected. The content of all harmful components, both toxic and undesirable for sanitary or human and animal safety reasons (explosiveness, aggressiveness, inflammabil-

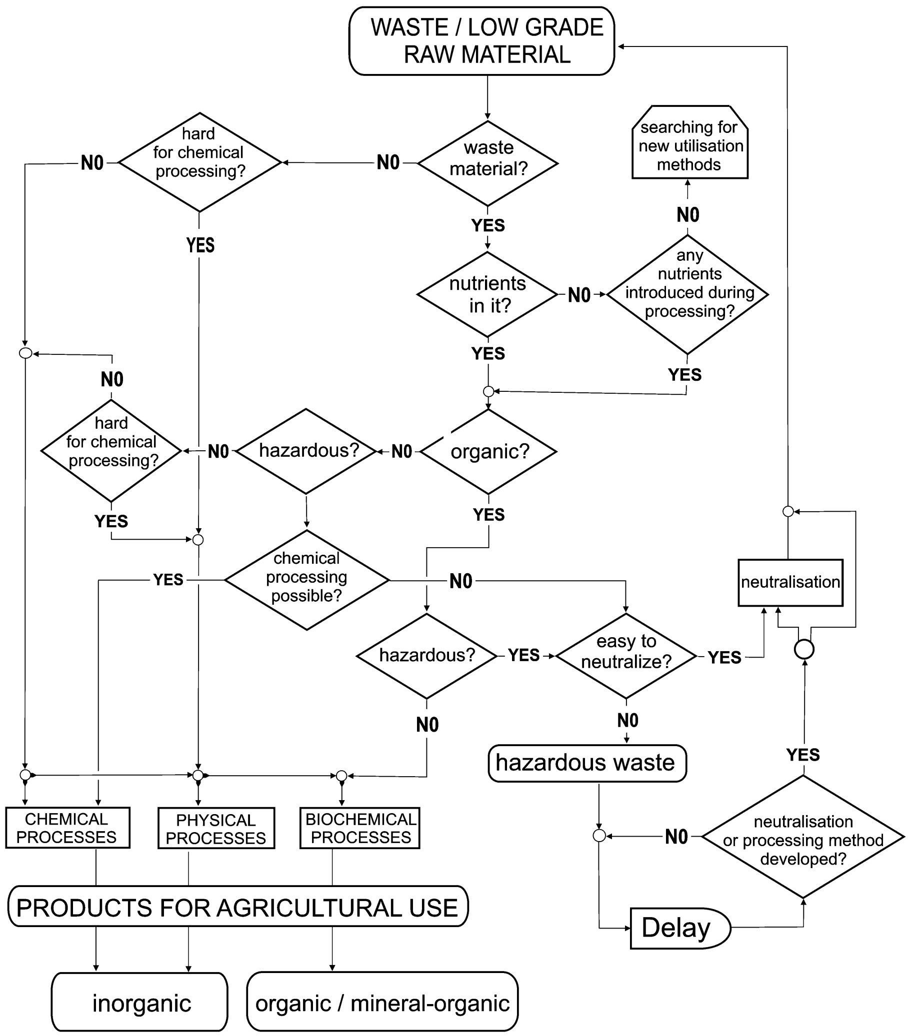

Fig. 3 Flow chart of procedure for assessing suitability of wastes and low-grade raw materials for processing into fertilizer products.

ity, etc.), should be taken into account. Thus, the processes should yield products containing nutrients and eliminate harmful factors.

According to the authors' proposal, the technological potential of recycling and processing depends on the physicochemical properties of materials, mainly on their content of components which make processing difficult, their chemical form, reactivity, etc. This criterion determines the choice of a transformation process capable of yielding products with desirable manurial properties at relatively low costs.

During the drafting process of the procedure, five pairs of materials (A, B, C, D, and E) with opposing properties were specified in order to facilitate the decision-making process, as follows:

A) • wastes
- low-grade raw materials

B) • wastes containing nutrients
- wastes containing no nutrients

C)
- inorganic wastes
- organic wastes

D)
- materials difficult to process chemically
- materials easy to process chemically

E)
- hazardous wastes
- neutral wastes

According to the flow chart, wastes and low-grade raw materials (A) are distinguished in the first steps. Then the procedure eliminates wastes that do not contain nutrients from the pair of materials B.

Organic and inorganic materials and materials difficult and easy to process chemically are distinguished as, respectively, pairs C and D. The last pair includes hazardous and neutral wastes.

Depending on the kind of material, the procedure allows one to choose a path leading to a proper transformation process. At the end of decision-making, there are three groups of transformation processes: physical, chemical, and biochemical processes.

The most common physical processes are: washing, heat treatment, blending, comminution, extraction, microwave treatment, and other processes and operations known from chemical engineering. Mechanical activation, consisting of intensive treatment of materials in grinders, opens up new possibilities.

Chemical processes require reagents to change the chemical composition of materials or some of their components. The most common reactions in such processing are neutralization, reduction, oxidation, and decomposition. Thanks to the deep changes of substrates, as a result of which completely new phases are formed, chemical processes allow one to eliminate harmful properties.

Biochemical processes involve microorganisms that are mostly used to process organic wastes by composting. This method is constantly modified in order to improve the useful properties, reduce the environmental nuisance, reduce the production cycle, and so on.

CASE OF ASBESTOS

The huge quantities of asbestos wastes generated in the few decades of the use of asbestos-containing products have become one of the most serious environmental challenges in the world and in Europe. The introduction of Directive 89/106/EEC in the EU countries started a search for effective ways of disposing asbestos-containing materials used by then in construction, public utilities, transport, personal protection, industry, and so on.

The use of asbestos has also been banned in non-European countries. In South Africa total asbestos usage declined by about 40 % between 2000 and 2002. A National Economic Development and Labour Council study estimated that by banning asbestos, South Africa could save nearly R27-million every year in disease compensation and health costs [5].

In the world, especially in the United States, methods of rendering asbestos and the asbestos products harmless gained a lot of popularity. The methods consist of protecting the asbestos materials installed in the buildings without taking them down by covering them with special substances that increase their mechanical strength and resistance against erosion. Most often the following materials are used to obtain the desired result: urethane, latex, the substances containing powdered metal, etc. [6–8].

Most literature reports concerning both the basic research as well as the utilitarian one, concern the chemical treatment of the waste, where the compounds from the serpentine and amphiboles asbestos group are decomposed, utilizing strong bases and inorganic as well as the organic acids.

One of the patents [9] presents processing asbestos with a concentrated solution of NaOH in a reactor-autoclave at the temperature of 175–200 °C and under the pressure of 0.3–1.0 MPa. The waste obtained after the decomposition may be utilized for the production of cement.

Many literature reports concern the destruction of pure asbestos and the asbestos contained in various products using strong inorganic acids, very often in the presence of aggressive fluorine ions [10–12]. Significant faults of all these methods are

- the limited life of the insulating materials that preserve the asbestos against erosion and releasing its fibers to the environment,
- the necessity of treating secondary liquid and solid wastes originating in the chemical methods of asbestos neutralization, and
- highly corrosive conditions of such processes due to the use of aggressive chemicals and high temperatures and preassure applied.

The authors consider the asbestos wastes (containing magnesium and calcium) as potential raw materials for manufacturing products to be used in agriculture. Based on this approach, the new method of asbestos waste processing has been developed. Since they belong to hazardous inorganic materials, they require processing methods that ensure total elimination of danger of damage to the environment.

Figure 4 shows the authors' procedure for dealing with hazardous wastes for the case of asbestos.

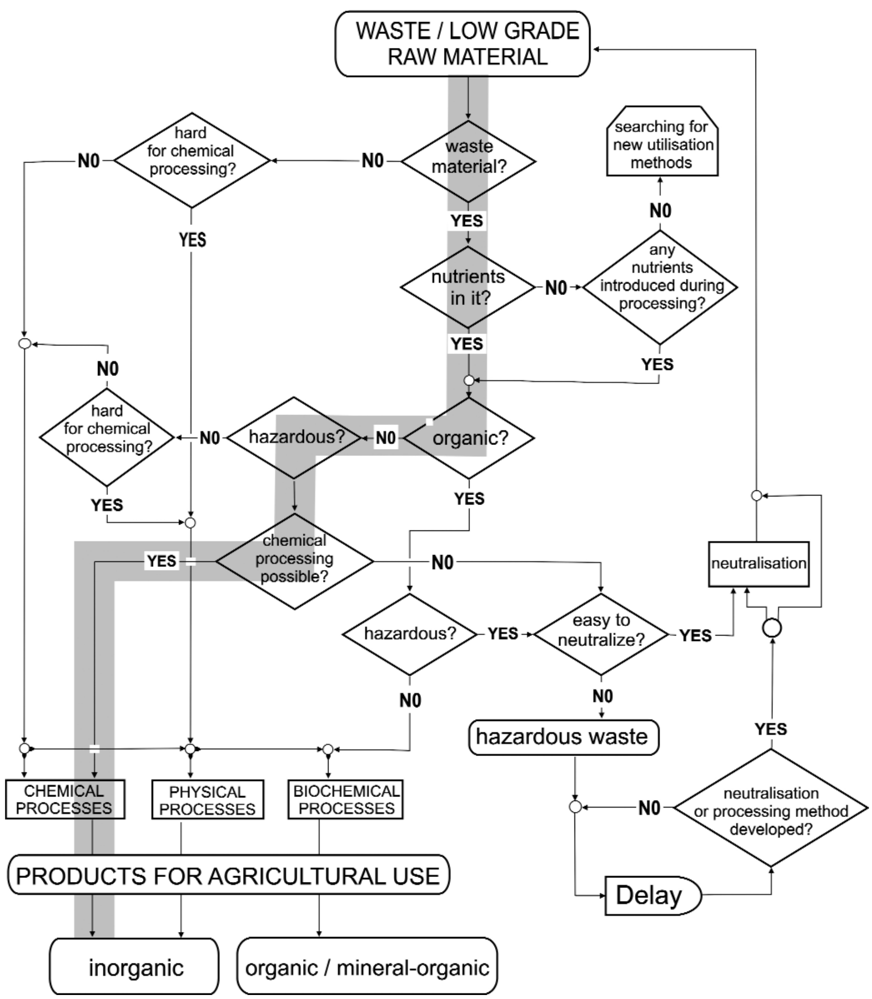

Fig. 4 Flow chart of procedure for evaluating wastes and low-grade raw materials, with marked procedural path for dealing with asbestos wastes.

According to the procedure proposed in Fig. 3, only chemical methods ensure that asbestos will be processed into harmless products. Laboratory studies of such methods carried out by the authors have resulted in the development of an idea of a suitable process. The latter consists of digesting asbestos wastes using chemicals that are not as strongly aggressive as in other known processes. A solution of phosphoric acid at a temperature of 80 °C in a specially designed two-stage technological system is used in the method proposed by the authors (Fig. 5). The process is conducted at a stoichiometric excess of phosphoric acid of up to 10 %. The suspension obtained after decomposition is separated into filtrate and a solid by-product (silica) by means of a filter. The acid filtrate containing phosphorous, calcium, and magnesium ions is neutralized with calcium hydroxide or calcium carbonate and processed into phosphatic fertilizers [13]. The method allows one to break up the fibrous structure of natural magnesium silicates whereby the harmful respirable fibers are destroyed.

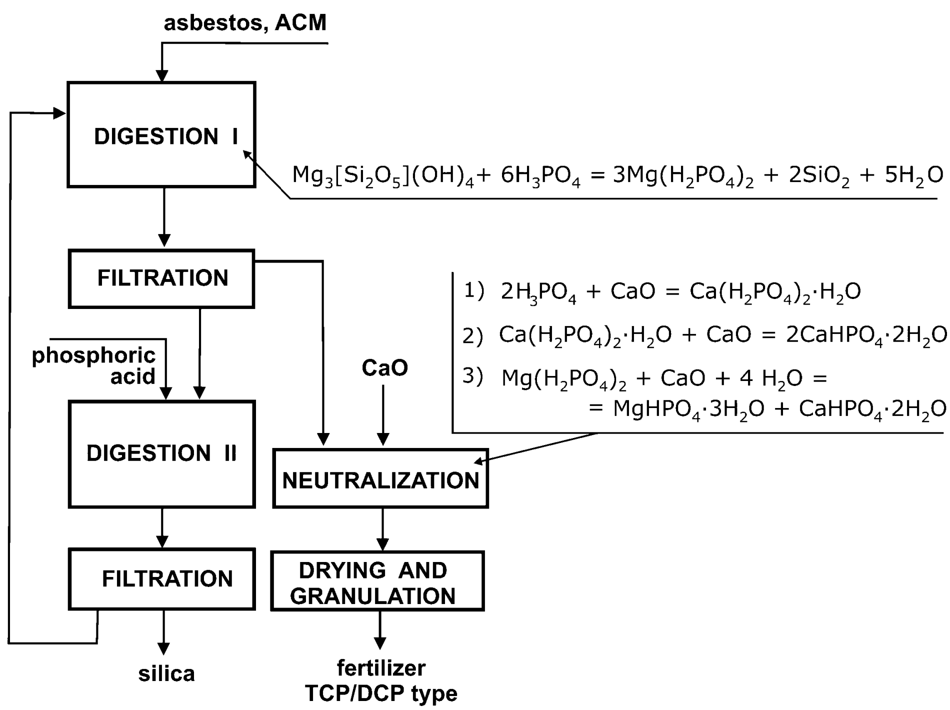

Fig. 5 Flow chart of technological system for processing asbestos wastes into mineral fertilizers and equations of chemical reactions taking place at particular stages of process.

The decomposition of asbestos belonging to the serpentine group and the amphibole group by phosphoric acid proceeds according to this simplified equation

$$Mg_3[Si_2O_5](OH)_4 + 6H_3PO_4 + H_2O = 3Mg(H_2PO_4)_2 \cdot 2H_2O + 2SiO_2 \quad (1)$$

The more detailed equation is

$$(OH,F) \cdot (Ca,Na)_3 \cdot (Mg,Al,Fe) \cdot [(Si,Al)_8]O_{22} + nH_3PO_4 = Ca(H_2PO_4)_2 + Mg(H_2PO_4)_2 + NaH_2PO_4 + AlPO_4 + FePO_4 + CaSiF_6 + SiO_2 + H_2O + (n - x)H_3PO_4 \quad (2)$$

In order to determine whether the respirable fibers undergo complete destruction and if the obtained products are harmless, extensive studies (including microscopic examinations, chemical tests, and immunological tests) of the products were carried out.

Microscopic examinations

First, a semi-quantitative microscopic analysis of the products of decomposition of asbestos and eternite (asbestos-cement roofing material), obtained at different decomposition temperatures and phosphoric acid concentrations, was made.

The microscopic examinations show that depending on the decomposition conditions, products considerably differing in their fibrous structure are obtained. Fibrous structures remain in products obtained in mild digestion conditions, mainly when the decomposition is conducted at lower temperatures at a fixed stoichiometric ratio of the substrates. As the process temperature and the hydrogen ion concentration increase, the fibrous structures quickly disappear. The best results were obtained at a 10 % excess of phosphoric acid at a temperature of 80 °C.

Chemical tests

In order to verify whether the silicate structures actually had undergone decomposition with release of magnesium ions into the liquid phase, chemical analyses of both the sediment obtained after the separation of the postreaction suspension and the filtrate were carried out. Sediment obtained from the decomposition of asbestos and eternite at a temperature of 80 °C at a 10 % excess of phosphoric acid was selected for the tests. The sediment was treated with aqua regia in order to decompose the magnesium silicate minerals forming the asbestos fibers in case they were present in the postreaction residue. The presence of magnesium in the sediment would indicate incomplete decomposition of the fibers and so the latter might remain in the product.

In Table 1, results of analyses of filtrates and sediments obtained after decomposition of asbestos and eternit with phosphoric acid in a periodic process, after rinsing the sediments with water are presented.

Table 1 Results of analyses of solutions and sediments obtained after decomposition of asbestos and eternit with phosphoric acid (% by weight).

Component	Decomposition of asbestos		Decomposition of eternit	
	Filtrate	Sediment	Filtrate	Sediment
P_2O_5	42.3	0.012	38.9	0.009
MgO	6.92	0.011	1.61	0.006
CaO	0.12	0.120	12.3	0.263
Fe_2O_3	0.73	0.013	0.67	0.011
Al_2O_3	0.34	0.010	0.49	0.034

The analytical data show that magnesium in almost its entirety passes (in a soluble form) into the filtrate, which is evidence that the asbestos has been decomposed and practically is absent in the sediment. The latter after aqueous washing (at a ratio of 4:1) is high-purity silica with considerably extended specific surface.

Acid, post-decomposition solution contains first of all phosphate anions, magnesium, and calcium cations and other ions characteristic for natural minerals belonging to serpentine group. The solution, after neutralization with calcium hydroxide or carbonate, can be processed into fodder phosphates monocalcium phosphate (MCP) or dicalcium phosphate (DCP) type as well as triple superphosphate (TSP) or DCP for fertilization purposes.

Immunologic tests

It was necessary to carry out cytotoxicity tests in order to ultimately prove the thesis about the absence of respirable asbestos fibers in the decomposition products and so no harmful effect on living organisms. The cytotoxicity tests were carried out in the Laboratory of the Polish Academy of Sciences Ludwik Hirszfeld Institute of Immunology and Experimental Therapy in Wroclaw.

Continuous human epithelioid series A549 cells (isolated from a pulmonary neoplasm) were selected for the tests [12]. Table 2 shows the cytotoxic effect of asbestos and eternite samples and products obtained from their decomposition on human lung cells in in vitro tests. According to the table, the exposure of the cells to the action of preparation A1 (asbestos) and E1 (eternite) causes their degeneration even at a low concentration (78 and 9.7 µg/cm^3, respectively) while the preparations subjected to chemical neutralization with phosphoric acid after the exposure of the cells for 48 h show, respectively, 16 and 515 times weaker cytotoxic effect. The results presented in Table 1 have been corroborated by microscopic examinations of the lung cells.

Table 2 Cytotoxic concentrations of tested samples.

Material	Concentration of investigated material (µg/cm^3)	
	Exposure time: 24 h	Exposure time: 48 h
Asbestos (A1)	78	78
Asbestos after decomposition (A2)	1250	1250
Eternite (E1)	9.7	9.7
Eternite after decomposition (E2)	10 000	5000

The presented results of chemical tests, microscopic examinations, and cytotoxicity tests indicate that the solid products of decomposition of asbestos by phosphoric acid are composed of active silica which shows no harmful effect on human lung cells even at high concentrations in vitro.

The proposed process worked out by the authors, along with useful products of agricultural use, also generates a by-product, but as opposed to other known methods presented in the literature, the latter constitutes a material of a real market value.

The method of evaluating and handling wastes shown in Fig. 4 allows one to choose the most proper way of hazardous waste management. The case of asbestos demonstrates that it is possible to obtain useful products not only from neutral wastes (posing no hazard to human or animal health) but also from wastes which, as it is commonly accepted, can be rendered harmless only by depositing them on specially secured sites. This goal can be achieved only through the chemical transformation of wastes, as a result of which the chemical composition of a hazardous substance is totally changed.

CONCLUSIONS

The proposed procedure for assessing and handling inorganic wastes and low-grade raw materials and the physical, chemical, and biochemical processes being its end elements can be helpful in the implementation of the strategy of waste management for agriculture. It can contribute to a reduction in the amount of deposited organic and inorganic wastes, including hazardous wastes. Another benefit is that the extraction of non-renewable resource deposits, particularly the ones which are of high technological value, can be reduced. The procedure is an example of a proper approach to the problem of the excessive amount of wastes, consistent with the current EU regulations and world-wide conventions. It is one of the best possible solutions leading to the implementation of the principles of sustainable development.

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