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RESEARCH PAPERS

FACULTY OF MATERIALS SCIENCE AND TECHNOLOGY
SLOVAK UNIVERSITY OF TECHNOLOGY IN TRNAVA

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2011 Number 31

PARTICLE FILLED POLYETHYLENE COMPOSITES USED IN THE TECHNOLOGY OF ROTATIONAL MOULDING

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Martin RIDZOŇ[2], Jozef BÍLIK[2], Viktor TITTEL[2]

Abstract

The submitted article discusses rotational moulding technology and filled plastics. For testing, linear low density polyethylene filled with talc was used. The materials tested varied way of mixing the filler into the polymer. For the prepared samples were evaluated by tensile, elongation, melt flow index, density, Shore hardness and Vicat softening temperature. Experiments showed that, in principle, it is possible to produce rotational moulding technology filled thermoplastics.

Key words

rotational moulding, low-pressure, open-moulding, plastic-forming, particle composite, LLDPE, talc

Introduction

Development of basic types of plastics is virtually complete. New development of plastics is not expected mainly for economic reasons. Therefore, future development will be focused on improving the existing plastics' properties and processing technologies. One way to achieve this goal is the possibility of developing composites with inorganic fillers and increasing their share while maintaining reasonable mechanical and rheological properties. The aim of our research was to verify the rotational moulding technology and its use in the processing of thermoplastic composites. We tried to assess the impact of the dispersion of inorganic filler - talc in polyethylene on mechanical properties.

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Theoretical principles

Process description

Rotational moulding is a high-temperature, low-pressure, open-moulding plastic-forming process that uses heat and bi-axial rotation to produce hollow, one-piece parts (1). To rotationally mould a roll-out refuse container, a mould that defines the shape of the part to be produced is mounted on the arm of a moulding machine (Fig. 1). The machine is capable of bi-axially rotating and moving the mould through the four phases of the process. A predetermined amount of plastic material, in the form of a liquid or a powder, is then placed in the mould's cavity (Fig. 1a) The machine then simultaneously rotates the mould in two directions and moves the mould into the heating chamber or oven (Fig 1b). In the oven, the mould becomes hot and all the plastic material adheres to and sinters onto the inside surface of the cavity. While it continues to rotate, the machine moves the mould out of the heating chamber and into the cooling chamber, where the plastic is cooled so that the formed plastic part will retain its shape (Fig. 1c). The machine then moves the mould to the open station, and the mould stops rotating. The mould can then be opened and the moulded part removed (Fig. 1d).

The mould is then recharged with plastic material and the process can be repeated (1).

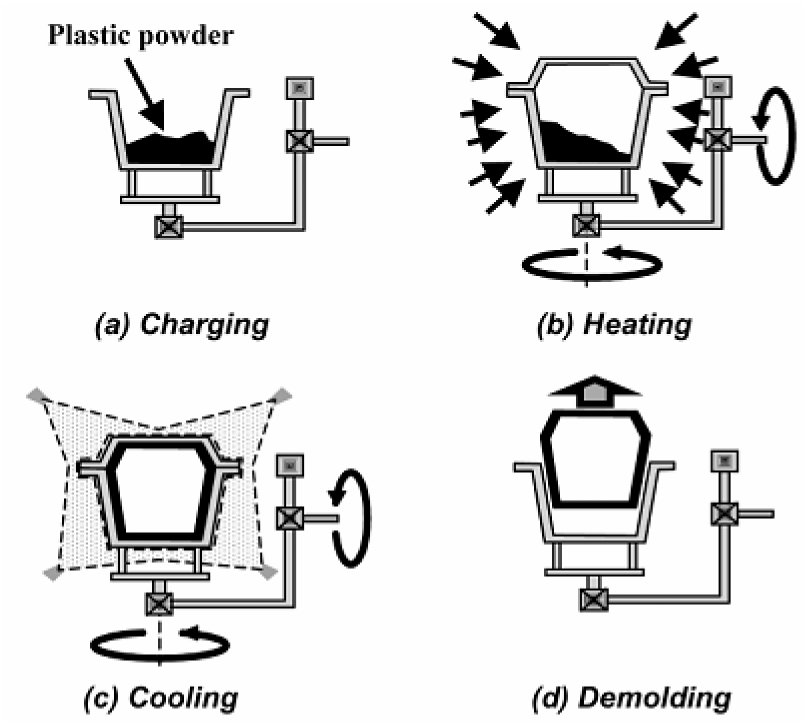

***Fig. 1** The four steps of rotational moulding process (2)*

Attributes of the process

Rotational moulding technology has always been regarded as ideal for producing large reservoirs (tanks). This process is, however, capable of producing many types of parts (Fig. 2), (1).

Fig. 2 *The typical array of RTM products (1)*

Like all other manufacturing processes, rotational moulding has advantages and disadvantages.

Advantages:

- low-pressure process,
- can produce complex shapes,
- light-duty moulds and machines,
- low post-mould warpage,
- walls can be extremely thin in relation to their overall size ability to produce two-color or two-material parts without multiple moulds or sophisticated machines,
- parts are free of weld-lines.

Disadvantages:

- can produce small quantities,
- no cores inside the hollow parts,
- the process requires the heating and cooling of not only the plastic material, but of the mould too.

Rotational molding materials

More than 80 % of all the materials used is from the polyethylene family: cross-linked polyethylene (PE), linear low density polyethylene (LLDPE), and high density polyethylene (HDPE). Other compounds are PVC plastisols, nylons, and polypropylene.

Order of materials most commonly used by industry:

- Polyethylene,
- Polypropylene,
- Polyvinyl Chloride,
- Nylon,
- Polycarbonate (1, 2).

Methods

Stage 1 was the preparation of samples. Stage 2 was measuring the mechanical and rheological properties. The samples were fitted from sewerage pipes.

Step 1: Preparation of samples consisted of seven steps:

1. We drew four samples of 2 kg.:
   - sample No. 1 content 100 % LLDPE ICORENE 4-3545;
   - sample No. 2 content 100 % LLDPE RESIN RX103 NATURAL;
   - sample No. 3 content 90 % LLDPE ICORENE 4-3545 + 10 % Talc;
   - sample No. 4 content 90 % LLDPE RESIN RX103 + 10 % Talc;
2. Preparation of samples:
   A) Samples No. 1 and Nr. 2 was mixed by small mixer for concrete
   B) Sample No. 3 was mixed by a small fluid mixer.
   C) Sample No. 4 was prepared mixing the talc into the melt polymer on double-screw homogenization equipment Bresdorff Φ 45mm.
3. We inserted the prepared samples to the two-part aluminium mould. Fitting the mould on three-arm carousel rotational moulding machine.
4. The mould was heated during rotation up to 285 °C for 23 minute.
5. Then the mould was cooled during rotation up to 23 °C for 20 minute.
6. After cooling, the product was selected from the mould.
7. Preparation of testing samples from the functional parts of the product.

Stage 2 was measuring the mechanical and rheological properties.

We measured the following properties: tensile property, melt flow index, density, Shore hardness and Vicat softening temperature (3).

Results

The knowledge gained showed that compared with the mixing of dry powder mixture to a fluid mixer, the intensive mixing of filler in the melt reaches better dispersion, which resulted in better mechanical properties of the final product. Measured values of properties are shown in Table 1.

MEASURED VALUES OF PARAMETERS (3)

Table 1

Sample No.	Yield stress (MPa)	Elongation (%)	Melt flow index (g/10 min)	Density (g /cm^3)	Shore hardness (°Sh)	Vicat softening temperature (°C)
1	18.86	172	3.4	0.923	53	114
2	20	132	3.8	0.939	59	123
3	10.7	0	3.2	0.972	50	114
4	15.6	10	3.7	0.993	57	121

Discussion

Evaluation of production technology

Sample No. 1 consists of 100 % LLDPE ICORENE 4-3545 has a smooth surface, the layers are compact and without undesirable colour degradation. The wall of the manufactured product is strong and solid.

Sample No. 1 consists of 100 % LLDPE RESIN RX 103 NATURAL has a smooth surface, the layers are compact and without undesirable colour degradation. The wall of the manufactured product is strong and solid.

Sample No. 3 consists of 90 % LLDPE ICORENE 4-3545 and 10 % talc has a rough, leathery finish. By the tool is smoother than the inside. Compact layer is formed. De-moulding took place without difficulty.

Sample No. 4 consists of 90 % LLDPE RESIN NATURAL RX 103 and 10% talc and an outer smooth surface as seen in Figure 3, layers are compact, rugged inner surface is as shown in Figure 4 Compact layer is formed. The product had the form of a charge for the use of power, while not necessarily undermining its unity as shown in Figure 5 De-moulding is difficult due to different shrinkage and the fulfillment of basic material.

Fig. 3 *Smooth outer surface of the product*

Fig. 4 *Rough inner surface of the product*

Fig. 5 *Deformed shape of the product after de-molding*

Evaluation of mechanical and rheological properties

Tensile strength and elongation

Tensile strength at yield is the sample No. 1 18.86 MPa at 172 % elongation. Sample No. 2 has 20 MPa at 132 % elongation. Sample No. 3 exhibits lower strength values than sample No. 1, composed of pure LLDPE ICORENE 4-3545. Tensile strength at yield is 10.7 MPa at 0 % elongation. In contrast, sample No. 4 shows the decrease of strength properties versus sample number 2 to 15.6 MPa at 10 % elongation.

Tensile strength at yield of Rezin NATURAL RX103 has a smaller decrease in value compared with the raw material, which is achieved through more complete dispersion of filler particles incorporated into the basic matrix intensive homogenization effect double-screw extruder. Decrease in ductility is due to better dispersing the filler in the polymer.

Density

The density of sample No. 1, composed of 100 % LLDPE ICORENE 4-3545 has a value of 0.923 g/cm^3 and sample No. 3 with 10 % addition of talc has a value of 0.972 g/cm^3. Sample No. 2, composed of 100 % LLDPE RESIN NATURAL RX 103 has a value of 0.939 g/cm^3 and sample No. 4 with 10 % addition of talc has a value of 0.993 g/cm^3. Higher density fillers are very influenced by the overall density of the product versus the product of pure LLDPE and is proportional to the concentration of filler.

Hardness Shore

The hardness value is dependent on the modulus, which depends on the relative weight of the material. The relatively low modulus of LLDPE and soft particles of talc, and also an imperfect connection matrix polymer filler, we reached the small differences of hardness of the samples. Hardness of sample No. 1 is 53 °Sh and sample 2 is 59 °Sh. For samples with 10 % talc is 50 °Sh in sample No. 3 and 4 57 °Sh.

Vicat softening temperature

Typically, the softening temperature using reinforced filler increases. The number of samples 1 and 3 reached the same value of 114 °C. For sample, in No. 4 we even noticed a decrease compared to sample No. 2 with primary LLDPE 2 °C to 121 °C, which is likely to be associated with different degrees of filler dispersion, which affects the thermal conductivity of the composite.

Melt flow index

Sample No. 1 has a value of 3.4 g/10 min and the sample No. 3 with the same LLDPE + 10 % talc has a lower value 3.2 g/10 min. Sample No. 2 has a value of 3.8 g/10 min and the sample No. 4 with the same LLDPE + 10 % talc has a lower value 3.7 g/10 min. A lower value for ITT samples with the addition of talc is caused by an increase in viscosity due to the addition of filler to polymer and the subsequent narrowing of the capillary flow (3).

Conclusion

Experiments showed that, in principle, it is possible to produce rotational moulding technology filled thermoplastics. However, it is necessary to choose optimal parameters of the polymer filler and the size of the particles, their dispersion and density. To increase the adhesion of the polymer matrix and filler and thus the increased compactness of the final product, we focused attention on improving the dispersion of filler in the polymer used double screw homogenization equipment used in the manufacturing of thermoplastic composites with conventional particulate filler.

The results obtained suggest that it will be filled with more efficient production of plastics: reduced price while maintaining the required mechanical properties.

Further experiments will focus on increasing the filler content. Mould modifications were due to different shrinkage of the base material and filler.

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ENGINEERING

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BUILDING A LABORATORY-SCALE BIOGAS PLANT AND VERIFYING ITS FUNCTIONALITY

Tomáš BOLEMAN, Jozef FIALA, Lenka BLINOVÁ, Kristína GERULOVÁ

Abstract

The paper deals with the process of building a laboratory-scale biogas plant and verifying its functionality. The laboratory-scale prototype was constructed in the Department of Safety and Environmental Engineering at the Faculty of Materials Science and Technology in Trnava, of the Slovak University of Technology. The Department has already built a solar laboratory to promote and utilise solar energy, and designed SETUR hydro engine. The laboratory is the next step in the Department's activities in the field of renewable energy sources and biomass. The Department is also involved in the European Union project, where the goal is to upgrade all existed renewable energy sources used in the Department.

Key words

biogas, laboratory-scale biogas plant

Introduction

Anaerobic digestion (AD) is the conversion of organic material directly to gas, termed biogas, a mixture of mainly methane (CH_4) and carbon dioxide (CO_2) with small quantities of other gases such as hydrogen sulphide (H_2S) (1), ammonia (NH_4), water vapour, hydrogen (H_2), nitrogen (N_2) etc.

AD is the process of decomposition of organic matter by a microbial consortium in an oxygen-free environment. It is a process found in many naturally occurring anoxic environments including watercourses, sediments, waterlogged soils and the mammalian gut (2).

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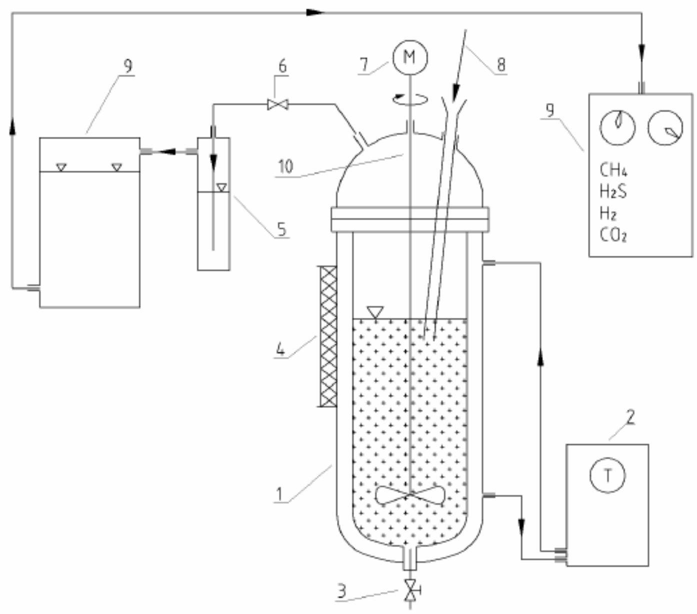
AD can also be applied to a wide range of feedstock including industrial and municipal waste waters, agricultural, municipal, food industry wastes, and plant residues. The production of biogas through anaerobic digestion offers significant advantages over other forms of waste treatment, including (2):

Materials and methodology

The Department of Safety and Environmental Engineering constructed a laboratory-scale biogas plant the scheme which can be seen in the following figures.



1-Bioreactor, 2-Thermostat, 3-Feedstock outlet, 4-Isolation, 5-Washer, 6- Permeable valve, 7-Engine, 8-Feeding, 9-Biogas analyzer, 10-Stirrer

Fig. 1 *Scheme of a biogas plant*

Fig. 2 *Picture of a real biogas plant*

Sewage sludge and kitchen wastes were used as feedstock. Sewage sludge did not have to be modified. Kitchen wastes were mixed.

Feeding and removing the material

The feeding of material to a bioreactor was performed by dosing syringe with the volume of 150 ml. Attached to the syringe was the hose with internal diameter of 7.75 mm. Feedstock was pumped to the hose and then dispensed through a plastic tube of internal diameter 18 mm and 450 mm length into the bioreactor. Plastic hose was installed through the rubber stopper which was inserted in one of the holes of glass cover (Fig. 3). The plastic tube was installed under the feedstock surface in the bioreactor to avoid bioreactor aeration.

Fig. 3 *Installed feeding tube*

Fig. 4 *Bioreactor outlet*

Removing the feedstock from the bioreactor was carried through the bioreactor outlet. The outlet was sealed with a rubber stopper into which a hole was drilled. A short glass tube with an attached short hose with tourniquet was inserted into the hole. (Fig. 4).

Bioreactor

The process of biogas production runs in bioreactor. The container had a volume of 3000 ml, with S40 as double outlet cover. The water circulated from the thermostat in double outlet cover. Constant temperature was maintained in the bioreactor. The volume of circulating water was 1.6 liters. Biogas process took place in the mesophilic phase at 37 ^{o}C. Bioreactor is shown in Fig. 5.

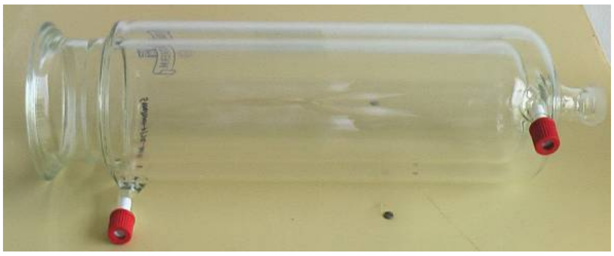


Fig. 5 *Bioreactor, volume 3000 ml*

A part of the bioreactor is the lid with two larger holes with a diameter of 29 mm and a height of 32 mm and two smaller holes with a diameter of 14 mm and a height of 23 mm. The holes are used for stirring, feeding and as a biogas outlet. The lid during the operation is shown in Figures 6 and 7.

***Fig.** 6 Lid*

***Fig.** 7 Cover during the operation*

The perfect contact of the bioreactor with cover was fulfilled by lock, which is shown in Fig. 8.

***Fig. 8** Lock*

Thermostat

Another part of the biogas plant is a thermostat maintaining constant temperature in the bioreactor, which is one of the conditions for the optimal biogas production process. The principle of maintaining the temperature is based on a double-jacketed bioreactor, in which heated water circulates to maintain desired temperature of 37 °C. Circulatory thermostat HAAKE C10 was used (Fig. 10). There were no fluctuations in temperature in the operation of the bioreactor.

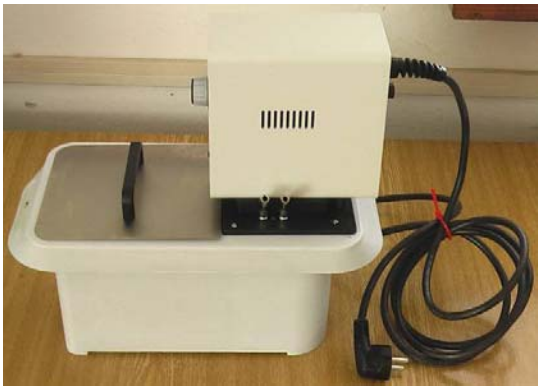


***Fig. 9** Thermostat HAAKE C10*

Stirring

To ensure optimal production of biogas during the process, it is necessary to mix the substrate. The stirrer is installed in the bioreactor through the rubber stopper which was inserted into the hole in the middle hole of the lid. Glass tube with a diameter of 4 mm and length 700 mm was inserted into the rubber stopper, where the hole was drilled. The stirrer was inserted into the tube (Fig. 11), which consists of a welding wire with a diameter of 3 mm and length 450 mm and the blades were welded to the wire and dual-layer coated to resist rust blade. Glass tube was installed under the surface of fermented substrate to prevent bioreactor aeration. The stirrer was powered by engine (Fig. 10). At the beginning, mixing was triggered manually, later on, a timer was purchased, which provide automatic mixing of the substrate by switching circuit according to the settings. The shortest interval of mixing can be adjusted for a period of 15 minutes.

Fig. 10 *Engine of stirring*

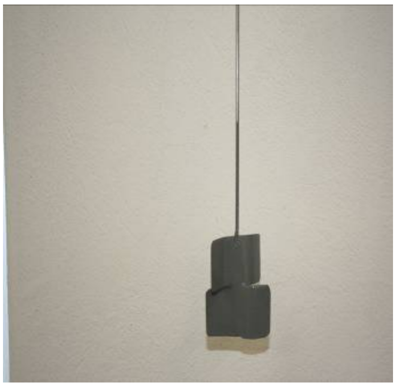


Fig. 11 *Stirrer*

Isolation

Bioreactor isolation was solved simply by using foam, which was wrapped with aluminum foil. The purpose of insulation is to create an environment free from light and heat insulated bioreactor due to heating and easier to maintain a constant temperature.

Biogas outlet

Biogas outlet is done to the washer, which indicates the production of gas with bubbling water. Biogas is then discharged into the room freely. When biogas is analyzed, it must be captured to a plastic bag with a patent.

Biogas analyzer MaMoS 400

Analysis of the biogas is only possible in sufficiently large quantities of biogas, and therefore it is necessary to capture the biogas and subsequently analyzed. The analyzer (Fig. 12) monitors the following four components:

- methane;
- carbon dioxide;
- hydrogen sulfide and
- oxygen.

Fig. 12 *Biogas analyzer MaMoS 400*

Results and discussion

The first operation of the biogas plant was conceived as a stress test. Observed was whether the thermostat can operate continuously and maintain the desired temperature in a reactor. The following chart shows the course of temperature in the bioreactor with temperature sensors that are installed in one of the lid holes.

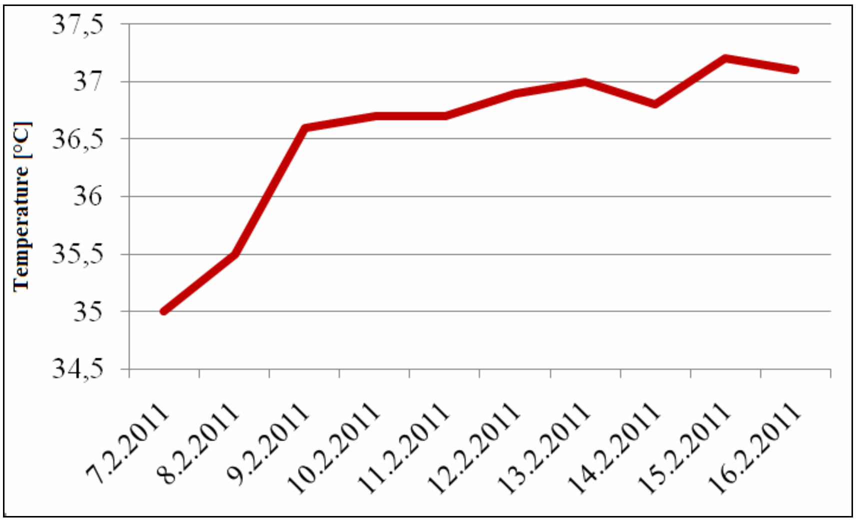


Fig. 13 *Course of temperature in the bioreactor*

Only the initial two days of operation, the temperature in the bioreactor was not adequate, which was resolved by simply raising the thermostat from 37 °C to 39 °C. Working temperature was set according to the literature and experiences from real biogas plants, where the temperature of 37 °C was the most common.

Mixing the substrate during the measurement was run manually, which was insufficient. A simple timer that could switch circuit at least every 15 minutes was purchased and set up to stir every 30 minutes, while mixing lasted 15 minutes. During the first operation, production of biogas was not indicated, which could also be due to the input material with low solids and imperfect mixing.

Sewage sludge with higher solids was used as a feedstock for the second operation, and thus the production of biogas was expected. In the second operation, temperature was monitored and the thermostat during the operation maintained a satisfactory temperature range. During this operation, feeding and removing the feedstock from the bioreactor was planned, since it was considered a longer operation. The process of feeding and removing began after 14 days. The process of feeding and removing was carried out without problems, so there was nothing to be corrected or optimized. After 14 days, biogas bubbling in the washer was indicated. Since a biogas analyzer was not yet available at that time, biogas was collected, withdrawn into the syringe and sprayed into the flame; the increased flame indicated methane content. During this measurement, there was an attempt to measure the volume of biogas produced by calibrated washer. This installation brought about bioreactor air pockets and stopped the production of biogas. The operation was canceled, when the substrate from the reactor through a hole, where is installed stirrer, spilled. This fact can be explained by incomplete mixing of material, and thus a shell was formed on the surface. The produced biogas under the shell pushed out the substrate. The first operation had not problems with mixing due dense substrate. The second operation was denser and the stirrer could not completely mix the substrate.

Before the third operation, it was necessary to resolve the imperfect mixing by installing a more powerful engine with speed control option. Kitchen waste was used as a feedstock. During the measurement, a biogas analyzer was installed, which needed a greater amount of biogas (several liters) for analysis. Hence, there was an effort to capture the biogas produced, because it is impossible to connect the analyzer to the reactor directly owing to the lower production of biogas. In this operation, no biogas was produced due to the low pH in the reactor.

In the fourth operation, sewage sludge from the Piestany wastewater treatment plant was used. Biogas production was recorded and the biogas was stored in a provisional storage of biogas. The provisional storage is a glass which is immersed underwater. The captured biogas displaces water from the cup. Since the glass is calibrated, it is possible to monitor the production of biogas. During operation, there was a problem with motor stirrer, which had to be replaced. The operation continues.

Conclusion

This contribution provides detailed information on the procedure for establishing a biogas plant. Provided is a detailed description of individual components as well as the problems encountered during the operation the purpose of which was to verify the operation of the device. Four operations were launched, during which, there were problems with the mixing and dispensing. In the future, it is certainly necessary to deal with the issue of trapping biogas produced in the subsequent analysis. There was an attempt to capture biogas into a plastic bag with a patent, but it was not successful due to the cessation of biogas production.

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BRIGHT COPPER PLATING USING PHOTOVOLTAIC AS AN ENERGY SOURCE

Jozef FIALA, Anna MICHALÍKOVÁ

Abstract

The paper deals with utilization possibilities of solar energy (photovoltaic systems) and with transformation of this energy to chemical energy as well as its utilization in the surface treatment of metals by electrochemical processes. Surface treatments significantly contribute to the resulting quality of technical equipment. Surface treatments affect lifetime, serviceability, usability, availability and maintenance of equipment. This technology can be widely applied in machine industry in the future due to cheap electrical energy generation. Next advantage of this electrical energy generation is the decrease of negative environmental impact. The whole system is now usable for bright copper plating, but owing to the low capacity, we can use it only for the objects of small areas, around 1.10 dm^2, 4.39 dm^2 in ideal conditions.

Key words

photovoltaic, electroplating, bright copper plating

Introduction

Solar energy is the main prerequisite of the life on the Earth. Solar radiation is a direct source for generating heat, cold and power. Indirectly, it is possible to use solar energy through hydropower, wind energy, energy of sea waves, heat energy of environs and energy of biomass (1, 4). Thanks to photoelectric effect in semiconductors, we can transform the solar energy in solar cells to power energy. Transformation of solar energy to power energy has wide utilization. Disadvantage of solar energy generation is its dependence on daylight, season and cloudiness in the area. Even though, it is a potential energy, which should not be ignored (1, 5). Photovoltaic effect which permits to construct photovoltaic (PV) cell, was discovered by A. Becquerel in 1839 (2, 4). Subsistence of the PV transformation from solar radiation to power energy is so-called inert photovoltaic effect.

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If solar radiation falls on the semiconductor material, the concentration of a charge carrier will rise when compared to the condition without luminance.

Incident photons transfer their energy making electrons and holes excite, what can be used for current conduction. It is necessary that the electric field is made in semiconductor, which will isolate electrons and holes from each other. This kind of field is acquired by PN junction (5). Equipment that can use this effect is called a photovoltaic (solar) cell. This equipment directly changes solar radiation to direct current (DC) (3, 4, 5). The solar photovoltaic cell is a semiconductor diode. PN junction is formed in the thin slices of silicon in a small depth below the surface whith metal contacts both sides. When solar radiation falls on the cell, electrons and free holes are generated. Electric field of PN junction separates them, and sends them to opposite sides; electrons to the N layer, which becomes a negative pole of the photovoltaic cell and holes to P layer, which becomes a positive pole. Electric voltage is generated on the contacts and electric current starts flowing to an appliance (2, 3, 6). Generally, solar photovoltaic systems fall into two main groups:

- systems are connected to the electricity grid - a "grid connected system" or just "on grid",
- systems without connection to the electricity grid - "off grid".

In some cases, a combination of both is used forming so-called hybrid or insular system that can supply electricity to the grid or operate completely independently (3). They are rarely found in the household because of the high investment costs. Regarding the changes in the economic sphere as well as dumping prices, these devices are expected to be widely used in the field of civil engineering (7).

Electroplating - Copper plating

Electroplating uses electric current and electrochemical reaction for making metal coatings. Coatings may be formed by copper, nickel, chromium, zinc, tin, cadmium, silver, gold and others. Electroplating is one of the most difficult surface adjustment technologies for pretreatment products. It is clear, because the transmission of metal ion from solution on the surface of cathode and its incorporation to the crystal grid require perfect contact of phases. Selection of technology depends on the type of electroplating products and bath, electroplating technique, condition of surface and technical equipment of electroplating plant (8, 9, 11). Technology of electroplating has been known for a long time, and it has been used for preparation of coating in models of complex form (galvanoplatics), and for thin coating on subjects for the purpose of protecting metals mostly from corrosion (galvanization). Electrochemical processes are of major importance for this branch.

Copper coats are most often used as an intermediate layer for protective or decorative electroplating in nickeling and silvering, either as a protective layer in cementation in galvanoplastics, or as a decorative coat. In last case, excluded coating must be protected from the corrosion effects of the outside atmosphere by a suitable coat. The most often used copper baths are cyanide solution and acid baths with brightener. Properties of excluded copper coatings depend on their structure, the type of bath and its composition. (11, 12).

Experiment

Technological procedure of bright copper plating

This experiment used thin sheets with approximately 50 x 50 mm with the weight of about 11g. Most of the plates' surface was hit by corrosion and grease. Pretreatment before electroplating is very important because the inclusion of metal ion from solution to the crystal lattice requires perfect contact phases.

Mechanical pretreatment - Abrasive paper was used for the removal of hard impurities and asperities caused by drilling. A part of the rust was removed by simple motions in various directions. **Rinse -** This operation was included among in between each treatment and also as a finish treatment. In the beginning, the rinse was done by sprinkling with distilled water, but this method left marks after drying. Therefore, rinse by immersion to hot water was selected.

Chemical pretreatment – The following chemical pretreatments were performed after mechanical pretreatment:

- **degreasing -** removal of all kinds of impurities from surface. Composition of a degreasing bath was determined according to the level of surface contamination and also according to the type of material,
- **bating -** removal of corrosion products from metal surfaces by chemical or electrochemical ways. It was carried out after surface degreasing,

Copper plating - The base of electrolytic excretion of metals is a sufficient performance source of direct current. For galvanotechnique, low voltage at intervals 2 - 12 V is used. Electric current is determined by the area to be electroplated. For copper plating, there are two types of surfaces - polished or opaque ones. Composition of polished bath is shown in Table 1. Electroplating bath was stirred with a magnetic stirrer.

COMPOSITION OF BATH FOR MAKING OPAQUE COPPER PLATING Table 1

Compound	Weight of compound for one litre of bath [g]	Temperature [°C]	Time [min]	Current density [A .dm^{-2}]
$CuSO_4.5H_2O$	160 - 230	20	20	1 - 8
97% H_2SO_4	60 - 78			
CH_4N_2S	0.2			

Experimental equipment for copper plating using PV panels

In the experiment, PV solar panels which were installed in the solar laboratory at SUT FMST Trnava were used as an electric power source. Basic parameters of PV solar systems:

- panel STR 36-50, optimal performance (peak) (+/−10 %): 50 W,
- panel AIT SG65, optimal performance (peak) (+/−10 %): 65 W,
- system SOLARTEC SG, optimal performance (peak) (+/−10 %): 645 W.

Figure 1 presents the scheme of experimental procedure, while Figure 2 shows experimental electrolyser.

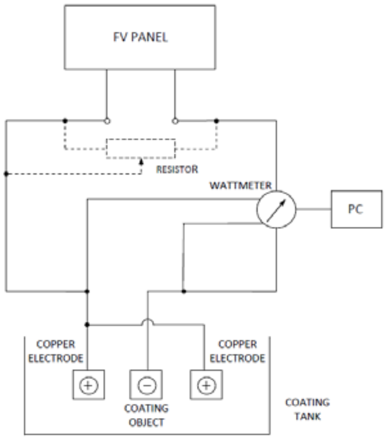

Fig. 1 *Scheme of experimental set with energy obtained from PV panel*

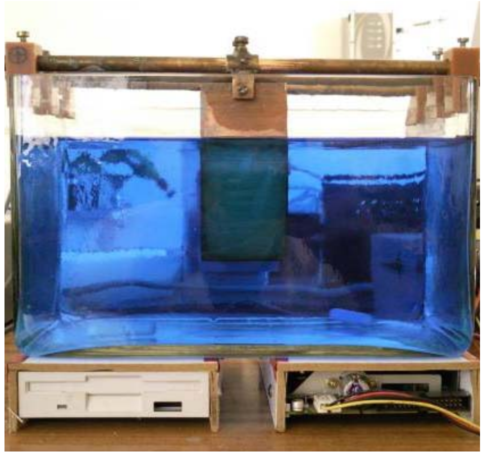

Fig. 2 *Experimental electrolyser*

To determine maximal coating area, it was necessary to find the average value of solar radiation during the experiment. Another needed value was the highest intensity of solar radiation during the whole operation of the solar laboratory. Supplying these values into Formula 1, it is possible to acquire maximal coating area.

$$\mathrm{I}_{\max} = \left(\frac{I_n}{N_n}\right) \cdot N_{\max}, \qquad [1]$$

where

I_{max} - the highest value of produced current at maximal recorded solar radiation intensity [A],

I_n - the highest measured value of electrical current during experiment [A],

N_n - solar radiation intensity during experiment [W. m^{-2}],

N_{max} - the highest recorded solar radiation intensity in the laboratory [W. m^{-2}].

This value can be then used in the final Formula 2 to determine the biggest possible coating area;

$$S_{\max} = \frac{I_{\max}}{I_S}, \qquad [2]$$

where

S_{max} - maximal coating area [dm^2],

I_S - current density (for copper plating 1 - 5 A.dm^{-2}) [A].

Excluding velocity of galvanic bath was determined by Formula 3;

$$v = \frac{m}{t}, \qquad [3]$$

where

v - excluding velocity [g.s^{-1}],

m - weight of excluded coating [g],

t - coating time [s].

Thickness of excluded coating can be determined in two ways, either calculation or measurement with micrometer. Formula 4 was used for calculation of coating thickness;

$$h = V \cdot \frac{10^3}{S}, \qquad [4]$$

where
h – Thickness of excluded coating [μm],
V – Volume of excluded coating [m^3],
S – Plate area [m^2].

Results and discussion

RESULTS OF BRIGHT COPPER PLATING Table 2

PV system	Current density	Solar radiation	Weight before plating	Weight after plating	Weight of excluded coating	Thickness of coating	Excluding velocity
	J [$A.dm^{-2}$]	N_n [$W.m^{-2}$]	m_1 [g]	m_2 [g]	Δm [g]	h [μm]	v [$g.s^{-1}$]
STR 36-50	4	697	10.5923	11.4582	0.8659	19.3931	0.0007
AIT SG65	4	747	10.6782	11.5915	0.9133	20.4546	0.0008
SG	4	721	10.6357	11.5568	0.9211	20.6293	0.0008

Table 2 shows results of bright copper plating. The difference of weight coatings using all the solar panel is minimal, ranged from a tenth of a gram. Also, excluded coating thickness and excluding velocity were approximately the same. It follows that the bath had a good ability of exclusion.

Determination of maximum coating area

RESULTS OF DETERMINATING THE MAXIMUM COATING AREA Table 3

PV system	Current density	Highest value of current	Solar radiation	Maximal coating area
	J [$A.dm^{-2}$]	I_n [A]	N_n [$W.m^{-2}$]	S_{max} [dm^2]
STR 36-50	4	2.83	726	1.10
AIT SG 65	4	3.43	773	1.25

For example (PV system 36-50): maximum recorded value of solar radiation intensity in solar laboratory is $N_{max} = 1125$ W.m^{-2}. This experiment ran over 5. 5. 2011 at 12:30 -14:50, and the value of solar radiation intensity was 726 W.m^{-2} (Table 3). The values of produced electric current at this intensity were around 2.83 A. At the intensity of 1125 W.m^{-2}, according to Formula 1, it is possible to achieve around 4.39 A.

Assuming the recommended current density in the range 1 - 8 A.dm^{-2}, we can coat objects with area up to **4.39 dm^2** according to the formula No. 2. **1.10 dm^2** in compliance with the current density 4 A.dm^{-2}.

Visual evaluation

Figure 3 shows the correct excluded bright coat: light rough, homogenous and coat total adhesives to the tin surface. Figure 4 illustrates microscopic image of the correct bright copper coated tin in ten times magnification. Coat perfectly adheres to the metal surface without signs of delamination or other defects.

Fig. 3 *Appearance of correct bright copper coated tin with bright coat using PV panels*

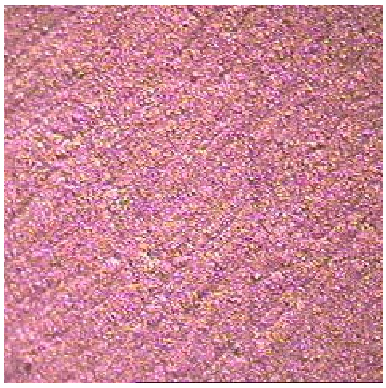

Fig. 4 *Microscopic image of correct bright copper coated tin in ten times magnification*

Conclusion

The main task of the paper was to verify the photovoltaic system of solar laboratory and find the utilization possibilities of this system for electrochemical processes – copper plating.

The whole system is now used for bright copper plating, however, due to the low capacity we can use the system only for subjects with small areas, around 1.10 dm^2, 4.39 dm^2 in ideal conditions. The result of visual assessment of the coated sheets is that on sunny days, and with good intensity of solar radiation, photovoltaic process can be easily competed with the usual sources of electricity. Used photovoltaic panels have sufficient capacity for the coating technology.

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2011 Number 31

OZONE PRETREATMENT OF WHEAT STRAW AND ITS EFFECT ON REDUCING SUGARS IN HYDROLYZATE

Kristína GERULOVÁ, Lenka BLINOVÁ

Abstract

The aim of this contribution is to measure the effect of the pretreatment of lignocellulosic phytomass utilization for bioethanol production. The first step of bioethanol production from lignocellulosic phytomass is pretreatment of raw material. The next step is hydrolysis, and then the fermentation of sugars follows. The physical (grinding, breaking) and chemical (ozonization) processes were used as pretreatment. Ozone was applied to the aqueous suspension of lignocellulosic phytomass before and during the hydrolysis. Ozone pretreatment did not perform as effectively as expected. The results of study, which are focused on evaluation of reducing sugars are included in this contribution.

Key words

lignocellulosic phytomass, pretreatment, particle size, ozone, reducing sugars

Introduction

The increased concern for the security of the oil supply and the negative impact of fossil fuels on the environment, particularly greenhouse gas emissions, has put pressure on society to find renewable fuel alternatives. The most common renewable fuel today is ethanol produced from sugar or grain (starch); however, this raw material base will not be sufficient. Consequently, future large-scale use of ethanol will most certainly have to be based on production from lignocellulosic materials (1).

Bioethanol production

Bioethanol can be produced by fermenting sugary crops (sugar cane, sugar beet), starch-containing materials (corn, potatoes, wheat) (2, 3) and lignocellulosic biomass (wood, agricultural and forest residues – corn stover, cereal straws, bagasse) (4, 5). Bioethanol

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production depends on the used entry materials, because conversions of sugar, starch and lignocelluloses to ethanol are different.

Lignocellulosic biomass, including forestry residue, agricultural residue, yard waste, wood products, animal and human wastes, etc., is a renewable resource that stores energy from sunlight in its chemical bonds. It has great potential for the production of affordable fuel bioethanol, since it is less expensive than starch (e.g. corn) and sucrose (e.g. sugarcane) producing crops and available in large quantities (6). Lignocellulose composed of cellulose (40 – 50 %), hemicelluloses (25 – 35 %) and lignin (15 – 20 %) is extremely resistant to enzymatic digestion (7).

Production of bioethanol from lignocellulosic biomass contains three major processes, including pretreatment, hydrolysis and fermentation (6, 8).

The prerequisite in the utilization of lignocellulose for bioethanol production is to efficiently yield a fermentable hydrolyzate rich in glucose from the cellulose content present in the feedstock. The purpose of pretreatment is to break down the shield formed by lignin and hemicellulose, disrupt the crystalline structure and reduce the degree of polymerization of cellulose. Pretreatment has been viewed as one of the most expensive processing steps within the conversion of biomass to fermentable sugar. With the advancement of pretreatment technologies, the pretreatment is also believed to have great potential for the improvement of efficiency and reduction of cost (6). Pretreatment is required to alter the biomass macroscopic and microscopic size and structure as well as its submicroscopic structural and chemical composition to facilitate rapid and efficient hydrolysis of carbohydrates to fermentable sugars.

Hydrolysis refers to the processes that convert the polysaccharides into monomeric sugars (6).

The hydrolysis of lignocellulose is limited by several factors. Several researchers conclude that crystallinity of celulose is just one of the factors. Other factors are degree of polymerization, moisture content, available surface area and lignin content (9). The fermentable sugars obtained from hydrolysis process could be fermented into ethanol by ethanol producing microorganisms, which can be either naturally occurred or genetically modified (6).

Pretreatment processes

Physical (e.g. mechanical comminution, hydrothermal pretretment), physico-chemical (e.g. steam or CO_2 explosion, ammonia fiber explosion), chemical (e.g. ozonolysis, acid or alkaline hydrolysis) and biological processes (with microorganisms such as fungi) can be used for pretreatment of lignocellulosic materials. Each pretreatment has its own effect(s) on the cellulose, hemicellulose and lignin; the three main components of lignocellulosic biomass (9). The goal of pretreatment is to remove lignin and hemicellulose, reduce cellulose crystallinity, and increase the porosity of the material. Successful pretreatment can significantly increase the quantity of reducing sugars and improve the hydrolysis (10).

Lignocellulosic phytomass can be comminuted by a combination of chipping, grinding and milling to reduce cellulose crystallinity. This reduction facilitates the access of cellulases to the biomass surface increasing the cellulose conversion. The energy requirements of mechanical comminution of lignocellulosic materials depend on the final particle size and biomass characteristics. Although mechanical pretreatment methods increase celulose reactivity towards enzymatic hydrolysis, they are unattractive due to their high energy and capital costs (11).

The effect of ozone pretreatment has been found to be essentially limited to lignin degradation. Hemicellulose is slightly attacked, while cellulose is hardly affected. Ozonation has been widely used to reduce the lignin content of both agricultural and forestry wastes (12).

Experiment

Pretreatment is the first and the most important step in the experiment. Hydrolysis is the next step. The physical (grinding, breaking) and chemical (ozonization) processes were used as pretreatment. Impact of pretreatment on sugars (defined as reducing sugars) occurring in the hydrolyzate was studied. Hydrolyzate was accrued after hydrolysis from raw materials as the main product for bioethanol production. Scheme of the experiment is shown in Figure 1. For the comparative study of different pretreatment methods, the best pretreatment conditions of each method was first selected on the basis of quantity of total reducing sugars of the pretreated sample.

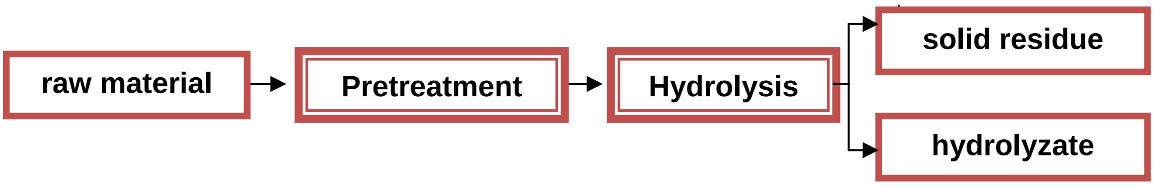


Fig. 1 *Scheme of experiment*

Raw material

Lignocellulosic phytomass – wheat straw, variety Bardotka, was used as a raw material. The straw was grown, harvested and stored in hay after a drought period in Slovakia during the summer 2010. The straw was cut into 40–100 mm pieces and stored in plastic bags at room temperature until pretreatment. The chemical composition of the untreated wheat straw can be seen in Table 1.

CHEMICAL COMPOSITION OF UNTREATED WHEAT STRAW USED IN THE EXPERIMENT

Table 1

Total solids		96.16 %
Cellulose		44.38 %
Lignin	**insoluble (Klason)**	22.07 %
	soluble	2.56 %
Ash		5.1 %

Pretreatment

The first type of the straw pretreatment was breaking and grinding. The straw was pretreatment into 1–30 mm pieces. Pretreated straw was divided according to the sieve analysis (size: ≤ 1 mm, 1–12 mm, 15–30 mm). After pretreatment, the straw was hydrolyzed with acid.

The second type of straw pretreatment was pretreatment by ozone. Ozonizator DEZOSTER, machine of company HIVUS, Žilina was used for pretreatment. Ozone was produced from air, which was sucks into equipment by pneumatically by means of pump. Ozone was applied to the aqueous suspension of lignocellulosic phytomass before and during the hydrolysis.

Ozonization before hydrolysis
The straw with particle size ≤ 1 mm, 1–12 mm, 15–30 mm was used for experiment. Suspension was prepared in the ratio of 1 part straw and 8 parts distilled water in a boiling flask. This suspension was pretreated with ozone for 5, 10, 15, 30, 45, 60 minutes at a room temperature and ozone flow rate 3.61 mg minutes^{-1}. After pretreatment, the suspension was hydrolyzed with acid.

Ozonization during hydrolysis
The straw with particle size ≤ 1 mm, 1–12 mm, 15–30 mm was used for experiment. Suspension was prepared in a boiling flask under the conditions of acid hydrolysis. This suspension was pretreated with ozone for 5, 10, 15, 30, 45, 60 minutes with the ozone flow rate of 3.61 mg minutes^{-1}. At the same time, this suspension was hydrolyzed with acid.

Hydrolysis

The hydrolysis was carried out with sulphuric acid. Acid hydrolysis was conducted under the following conditions: hydrolysis duration - 60 minutes, 10 % (w/w) straw, sulfuric acid 20 % v/v aqueous solution in an amount of 30 % for landfills phytomass.

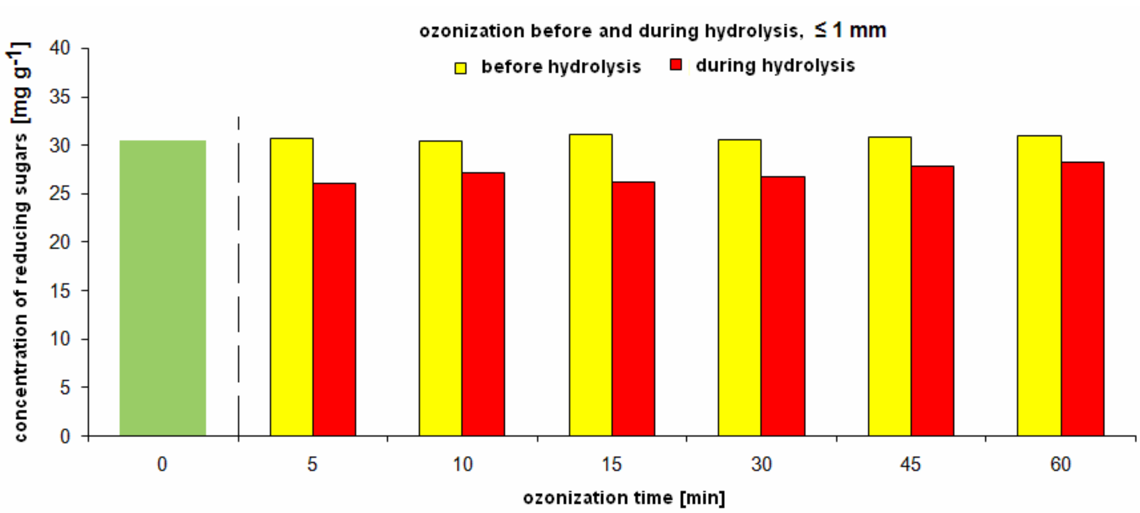
Analytical methods

The total solids content in the solid fraction was determined by drying app. 1 g of the sample overnight at 105 °C. The ash content of the solid fraction was determined by incineration of app. 1 g of dried sample at 575 °C for 7 hour. The cellulose content of the solid fraction was determined by oxidative hydrolysis. Acid insoluble lignin and acid soluble lignin in the raw material were estimated following NREL laboratory analytical procedures. The reducing sugars in the hydrolyzate was determined by Miller (1959) with 3.5-Dinitrosalicylic acid.

Results and discussion

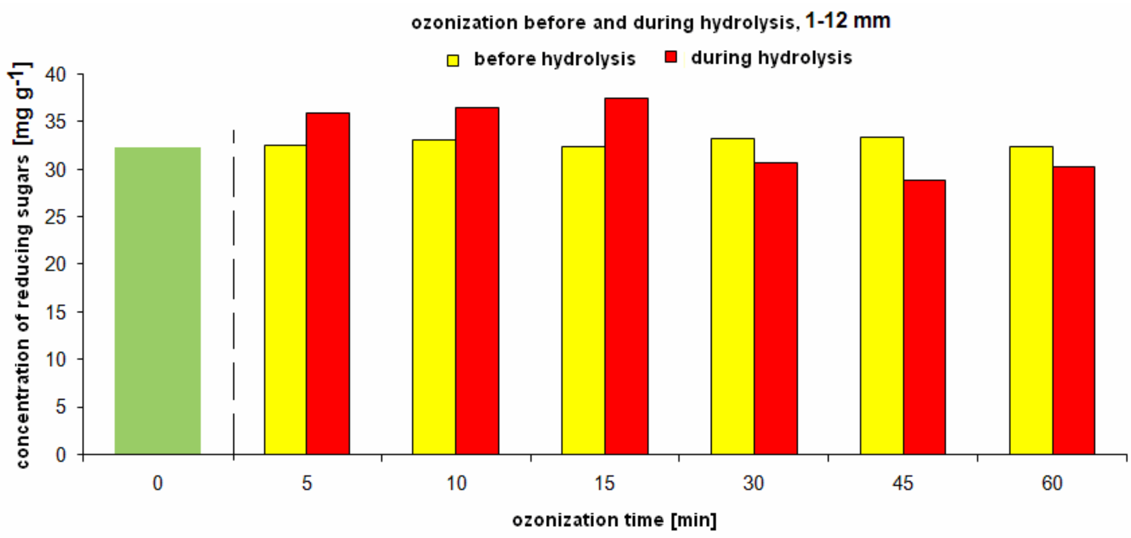
The effect of pretreatment on sugars (defined as reducing sugars) occurring in the hydrolyzate was analyzed. In the next graphs, the concentration of reducing sugars in hydrolyzate can be seen. The concentration of reducing sugars evidently depends on the conditions of pretreatment (ozonization before or during hydrolysis).

As seen in Graph 1, ozonization of straw (particle size ≤ 1 mm) during hydrolysis is a preferable method of pretreatment compared with ozonization before hydrolysis. Both kinds of pretreatment, ozonization before and during hydrolysis, are not appropriate for pretreatment, as the concentration of reducing sugars in pretreated straw are similar or lower than the concentration of reducing sugars in the straw which was not pretreated.



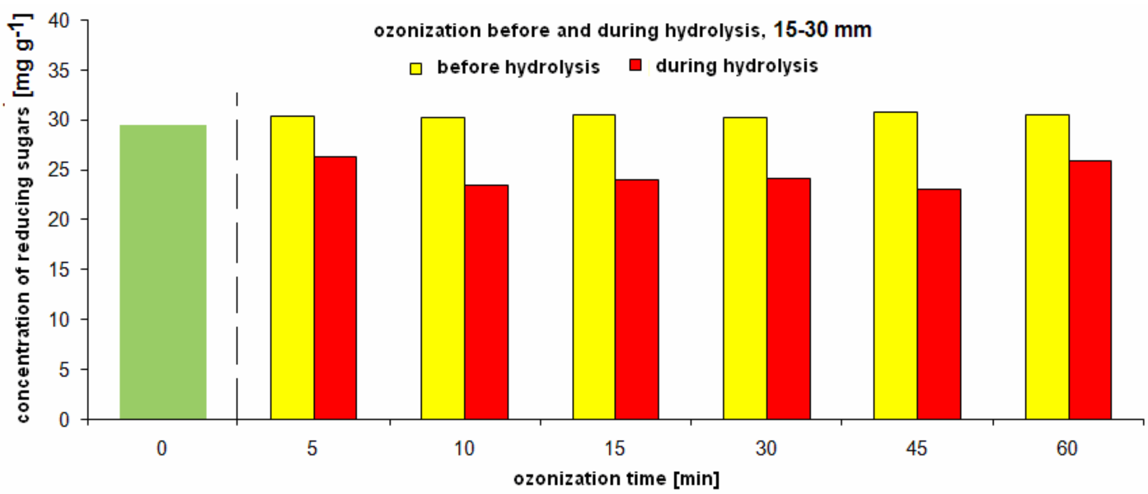
Graph 1 *Concentration of reducing sugars – ozonization before and during hydrolysis, particle size ≤ 1 mm*

In the next graph, the concentration of reducing sugars in hydrolyzates which was obtained from pretreated straw with size 1 – 12 mm can be seen. The most appropriate method of pretreatment is ozonization during hydrolysis for 5, 10, 15 minutes. Here, we obtained the highest concentration of reducing sugars and this type pretreatment was used for pretreatment. The concentration of reducing sugars is lower for ozone pretreatment during hydrolysis for 30, 45 a 60 minutes. The concentration of reducing sugars is similar for ozone pretreatment before hydrolysis for all periods. Therefore, this method of pretreatment cannot be considered appropriate.



Graph 2 *Concentration of reducing sugars – ozonization before and during hydrolysis, particle size 1 – 12 mm*

In the next graph, the concentration of reducing sugars in hydrolyzates which was obtained from pretreated straw with size 15 – 30 mm can be seen. The concentration of reducing sugars as for ozone pretreatment before hydrolysis for all treatment time, as well as that without ozone pretreatment is similar. The concentration of reducing sugars is lower for ozone pretreatment during hydrolysis than that of reducing sugars without ozone pretreatment. The concentration of reducing sugars after pretreatment of straw is similar to or lower than the concentration of reducing sugars in hydrolyzate for not pretreated straw. Therefore, this method of pretreatment with this straw size is not appropriate.



Graph 3 *Concentration of reducing sugars – ozonization before and during hydrolysis, particle size 15 – 30 mm*

A cotton stalks were pretreatment by ozone for 30, 60, 90 minutes. Ozone did not cause any significant changes in lignin, xylan, or glucan contents over time by Silverstein (12).

Conclusion

The aim of ozonization pretreatment was to break the complex structure of lignocellulosic materials. We can state that this method of pretreatment is appropriate only for specific conditions. In certain circumstances, the best method of pretreatment is ozonization during acid hydrolysis for 5, 10 a 15 minutes for particle size of straw 1 – 12 mm. The concentration of reducing sugars was increased by 3,59 – 5,22 mg g^{-1} dry compared with that of reducing sugars in not pretreated straw. Ozone pretreatment for other treatment time is not appropriate. Ozone pretreatment for particle size of straw $\leq$ 1 mm and 15 – 30 mm is not appropriate, as the concentration of reducing sugars is lower than or similar to the concentration obtained from not pretreated straw. When assessing the effectiveness of pretreatment methods, we should considered, whether minimum increase the concentration of reducing sugars is favorable due to the energy consumption.

Ozone pretreatment did not perform as effectively as expected. Possible explanations include unsuitable pretreatment conditions (low ozone concentration, uneven distribution of ozone throughout the sample) and hydrolysis conditions.

This contribution was written with the support of the Operational Programme Research and Development for project: "*Hybrid power source for technical and consulting laboratory use and promotion of renewable energy sources*" (ITMS 26220220056), financed from the resources of the European Regional Development Fund.

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ECOTOXICITY AND BIODEGRADABILITY ASSESSMENT OF METALWORKING FLUIDS BY ACTIVATED SLUDGE BACTERIA

Kristína GERULOVÁ, Adriána MIHÁLKOVÁ, Magdaléna ŠERGOVIČOVÁ, Alexander GUOTH, Zuzana NÁDAŠSKÁ

Abstract

The main aim of this study was to evaluate toxicity of metalworking fluids to bacterial consortium of activated sludge according to OECD 209 (STN EN ISO 8192) and a potential of the same sludge to degrade a part of the fluids according to OECD 302B.

Toxic impact can affect different responses, particularly the inhibition of respiration measured from the oxygen consumption in a closed bottle. The degradation rate was calculated from COD according to the authors such as van der Gast and Ian Thompson (1, 2) who tested the degradability of some MWFs in bioreactors by measuring the COD. The lowest toxic MWF´s were Cimstar 597 and Emulzin H (the highest tested concentration was below EC_{50}), then Zubora TXS (EC_{50} - 11 349 mg l^{-1}), Aquamet LAK-E (EC_{50} - 5 228 mg l^{-1}), Adrana D 407 (EC_{50} - 4 351 mg l^{-1}) followed, and finally, Hocut 3380 (EC_{50} - 2 339 mg l^{-1}) was assessed as the most toxic.

Important in this test (OECD 302B) is that the starting concentration of the tested substance must not decrease below 20% after 3 hours of cultivating. After that, it is impossible to distinguish biological degradation of organic matter from abiotic elimination from the suspension through adsorption. Tested were 8 MWFs of similar concentration and different addition of activated sludge – 0.25 g l^{-1}, 0.50 g l^{-1} and 1.00 g l^{-1}. The test showed that, after the first 3 hours of cultivating, adsorption grew with the increasing amount of inoculums, except of Akvol B (the decrease of the starting concentration after the first 3 hours of cultivating was the lowest of all and below 20%). It can be stated that, according to the test basic conditions, all the tested MWFs have a potential to ultimate degradation.

Key words

biodegradability, ecotoxicity, metalworking fluids

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Introduction

Future lubricants or coolants, which are used in cutting process, have to be more environmentally adapted, have a higher level of performance, and lower total life cycle cost (LCC) than presently used lubricants (3). The most interesting group for formulation of environmentally adapted lubricants is base fluids such as vegetable oils, synthetic fluids (polyglycols, polyalpha olefins (PAO), synthetic ester) (3-7). Properties related to environmental fate of metalworking fluids are toxicity (non toxic to human beings, fishes, bacteria etc.) (8), degree of biodegradability, bioaccumulability and biomagnification, and relative content of renewable raw material.

Biodegradablity of MWFs

Biodegradation represents a major route for removal of oil from soil and water compartments. Although the biodegradability of organic substances can be evaluated using a wide variety of testing procedures, the greatest significance is put to the standard tests specified in the OECD. Guidelines for the testing of chemicals and in the ISO standardized methods. The biodegradation process can be analyzed under aerobic or anaerobic conditions, in fresh water or seawater, or in soil (9).

Primary biodegradation is the alteration in the chemical structure of a substance, brought by biological action, resulting in the loss of a specific property of that substance. ***Ultimate biodegradation*** (aerobic) is the level of degradation achieved when the test compound is totally utilized by microorganisms resulting in the production of CO_2, H_2O, mineral salts and new microbial cellular constituents (biomass). ***Readily biodegradable*** is an arbitrary classification of chemicals which have passed certain specified screening tests for ultimate biodegradability; these tests are so stringent that such compounds are assumed to biodegrade rapidly and completely in aquatic environments under aerobic conditions. ***Inherently biodegradable*** is classification of chemicals for which there is unequivocal evidence of biodegradation (primary or ultimate) in any test of biodegradability (10-13). ***Inherent biodegradability*** demonstrates the potential degradability of a compound. Unlike in ready biodegradability tests, the conditions for biodegradation are optimum. Also, these methods have a screening function in the sense that "hard" chemicals are selected - a negative result indicates that a chemical is too persistent and that, tentatively, no further research on biodegradation has to be performed (14).

The choice of an appropriate test is an essential prerequisite for the determination of the biodegradability of lubricants. The CEC L-33-A-93 test, for example, enables the evaluation of primary biodegradability while the OECD test permits the ultimate biodegradability to be assessed. The OECD tests for ready biodegradability (OECD 301 series and OECD 310) play an important role in the environmental classification of chemicals. A substance is considered as readily biodegradable if it has reached a sufficient level of degradation in one of these tests, 70% in the case of DOC removal or 60% for CO_2 or BOD. The pass-levels have to be reached within the 28-day test period by the end of a 10-day window, which begins when biodegradation reaches 10%. When the substance fails to meet the ready biodegradable criterion, it can be made subject to inherent biodegradability tests, which are used to assess whether a substance has any potential for biodegradation. Biodegradation rates above 20% (measured as $ThCO_2$, ThOD, DOC or COD) may be regarded as evidence of inherent, primary biodegradability, whereas biodegradation rates above 60% $ThCO_2$, ThOD or 70% DOC or COD may be regarded as evidence of inherent, ultimate biodegradability (9).

Toxicity of metalworking fluids

Toxicity to aquatic organisms is generally used to reveal potentially adverse environmental effects of a compound or product (15).

According to OECD 302B test, there is a presumption with appropriate methods that no inhibition of sludge occurs at the chosen concentration of the test substance if this is not already known. If an inhibitory effect is found, it is needed to reduce the concentration of the test substance to a level which is unlikely to be inhibitory. The test of activated sludge inhibition of respiration is recommended also when OECD 301A-F for primary biodegradation is realized. Compounds with an EC_{50} value greater than 300 mg l^{-1} are not likely to have toxic effects in ready biodegradability testing.

MATERIALS AND METHODS

Fresh activated sludge from sewage treatment of the Jaslovské Bohunice plant was used as inoculums for the both tests (toxicity and degradability by activated sludge) the same day as the experiment started. In each of degradability tests, used were 0.25, 0.50 and 1.00 g of dry matter per liter in the final volume and 0.10 g of dry matter per liter in the final volume for toxicity evaluation. The degradability of MWFs was evaluated by OECD 302 B, while the toxic effect caused by inhibition of respiration was evaluated by OECD 209.

Adrana D407 – Shell Adrana D 407 is used for general and medium severe machining on materials as steel, aluminum and cast iron. Shell Adrana D 407 is specially recommended for all kinds of grinding operations in the bearing industry are good stability when tramp oil is present, it has very good stability in water with high hardness, good anti-foam characteristics in soft water, extremely good anti-corrosion protection, even with higher chloride content and high detergency properties, due to balance of boron, amine and biocide (17). Per oral acute toxicity LD50 > 2000 mg kg^{-1} (rat), dermal toxicity – information are out-of-reach, eye irritation – information are out-of-reach, dermal irritation – information are out-of-reach. The producer of the fluid wrote in the MSDS that ecotoxicity was not especially assessed. No information on degradability was found in the sheet. Water class dangerous (German class WGK) is by the MSDS No. 2 (18, 19).

Aquamet LAK-E – There is no information regarding acute or chronic toxicity, mutagenity, carcinogenity or teratogenity in MSDS. Also, there is no information on ecotoxity or biodegradability. Water Class Dangerous (German class WGK) was established as No. 2 (20).

Hocut 3380 – Hocut 3380 is a low foaming milky emulsion which gives superior surface finish and tooling performance. It is ideal for machining automotive aluminum, titanium, inconel and alloy steels due to its non-staining characteristics. It is particularly designed for high-pressure coolant systems associated with modern CNC machine tools with ultra-long life and freedom from biocide additions, making it suitable for both centralized systems and single-sump machines (21). The information on toxicity and ecological information are not available according to the material safety data sheet supplies by producer. By the MSDS, the main components defined as hazardous ingredients are Amine (Cas No. 101-83-7) 1-5%, Ethoxylated Alcohol (Cas No. 68213-23-0) 1-10%, Mineral Oil (Cas No. 64742-52-5) 30-60%, and Monoisopropanolamine (Cas No. 78-96-6) 1-5% (22).

***Cimstar 597* –**MSDS was not available due to the poor communication with the producer.

***Akvol B* –** By the MSDS, the main components defined as hazardous ingredients are 1, 3, 5-hexahydrotriazine (Cas No. 4719-04-4) 1-3%. Toxicological and ecological information is not defined in MSDS (23).

Ecocool MK3 – **Fuchs Ecocool MK 3** is specially compounded emulsifying cutting oil composed of petroleum oil and special emulsifiers. The information on toxicity and ecological information is not available according to material safety data sheet supplied by producer. By MSDS, Water Class Dangerous (German class WGK) was established as No. 1 (24).

***Emulzin H* –** exotoxicity test was carried out according to fishes LC50, 96 hours exp.: 30.1 mg/l, and daphnia EC50, 48 hours: 9.8 mg/l. Ecological information states that the product has unfavorable effect on environment. According to CEC L-33-A-93, products and water form biodegradable emulsion and the level of biodegradation were evaluated to 67%. By MSDS, the main components defined as hazardous ingredients are sulfonated acids (Cas No. 271-871-5) > 6%, ethoxylated alcohol C13 (Cas No. 500-027-2) 2.4%, alkylalcohol (Cas No. 248-469-2) < 0.9%, ethoxylated alcohol C12-C15 (Cas No. 500-195-7) 0.8%. (25).

Zubora TXS – By MSDS, the main components defined as hazardous ingredients are oxazolidine derivate (Cas No. 66204-44-2) 1-3% and fatty alcohol polyglycolether 3-5%. There is no information on biodegradability of the product in MSDS (26).

***Quakercool 7030* –** Information on ecotoxicity is not available. MSDS listed dangerous components such as polyol polyether in addition 1-5%, Alky alcohol in addition 1-5% and Poly(oxy-1,2-ethanediyl), a-tridecyl-w-hydroxy-, branched (Cas No. 69011-36-5) in addition 1-5% (27).

RESULTS AND DISCUSSION 1

Biodegradability testing

The test is considered valid if the procedural control shows the removal of the reference compound by at least 70 % within 14 days. If the rate of biodegratation reaches a constant level (more than 80%) before the 28th test day, the test is considered completed. If the degradation starts at the end just before the 28th day, the test has to be prolonged until the biodegradation is finished. The displayed data of biodegradation curve suggest that: ***Lag phase*** t_1 – is defined as the time from inoculation until the biodegradations rate increases up to 10 % from the initial COD (or DOC) value. Lag phase is variable and the repeatability is low. It is measured in days. ***Ultimate biodegradation degree*** – it is the degree of biodegradation, over which no other biodegradation occurs. ***Biodegradation time*** t_2 – is defined as the degradation time from the end of the *Lag phase* until it reaches 90 % of biodegradation's rate.

Figures 1-8 show the degradation/elimination curves from testing eight selected metalworking fluids: Adrana D407, Hocut 3380, Aquamet LAK-E, Quakercool 7030, Cimstar 597, Akvol B, Ecocool MK3 and Emulzin H, which are commonly procurable in the Slovak market. If more than 20% of adsorption occurs after the first 3 hours of cultivating, the curve can be considered an elimination one, since it is impossible to distinguish between biotic and abiotic elimination of substance from the solution. Figure 9 shows the adsorption rates after the first 3 hours of cultivating in different additions of activated sludge – 0.25 g l^{-1}, 0.50 g l^{-1}, and 1.00 g l^{-1}.

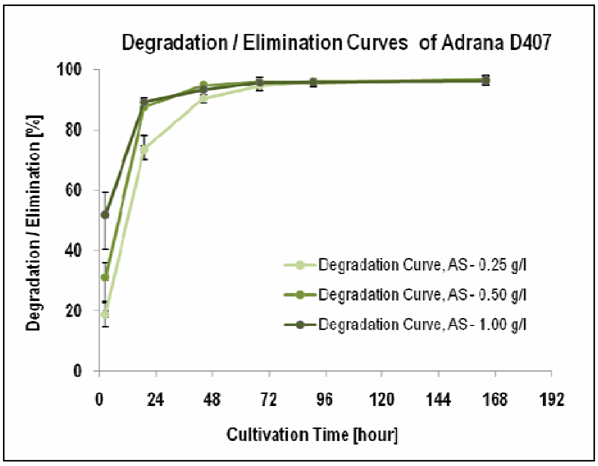

Fig. 1 Degradation/Elimination curves of Adrana D 407

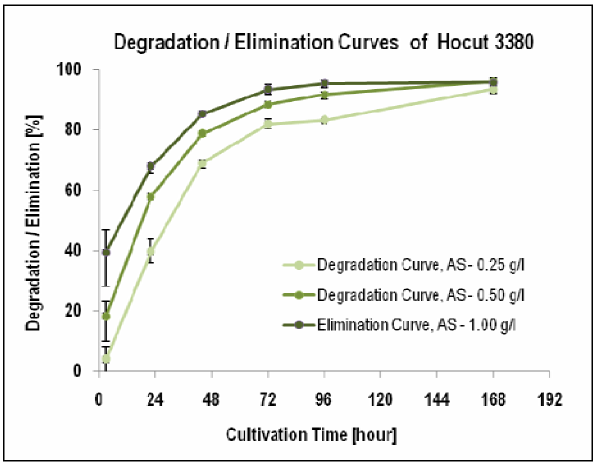

Fig. 2 Degradation/Elimination curves of Hocut 3380

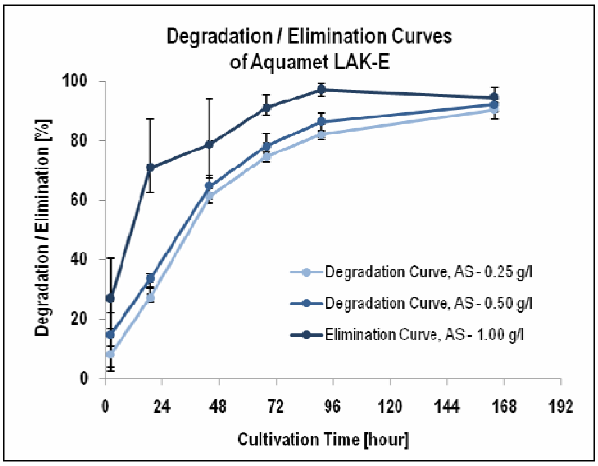

Fig. 3 Degradation/Elimination curves of Aquamet LAK-E

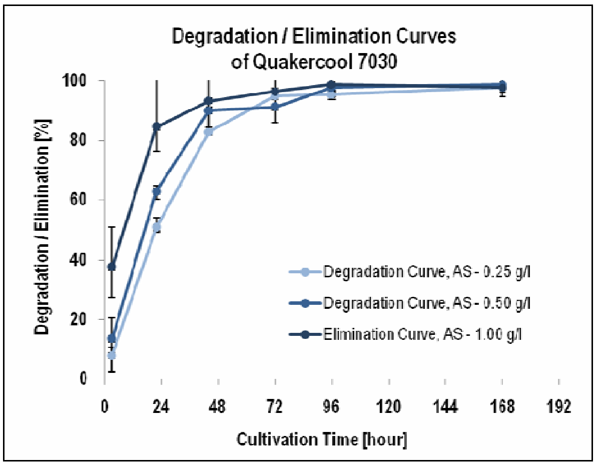

Fig. 4 Degradation/Elimination curves of Quakercool 7030

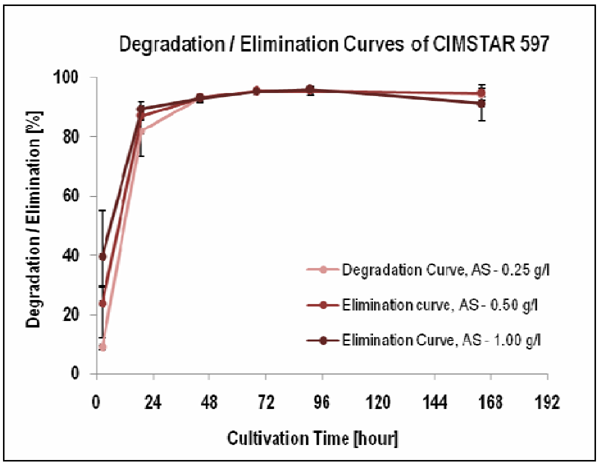

Fig. 5 *Degradation/Elimination curves of CIMSTAR 597*

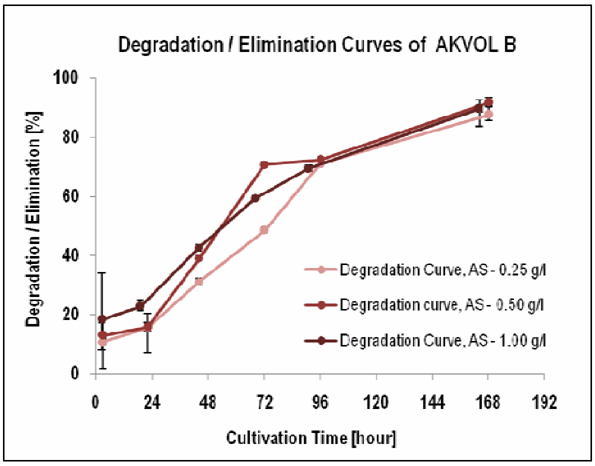

Fig. 6 *Degradation/Elimination curves of Akvol B*

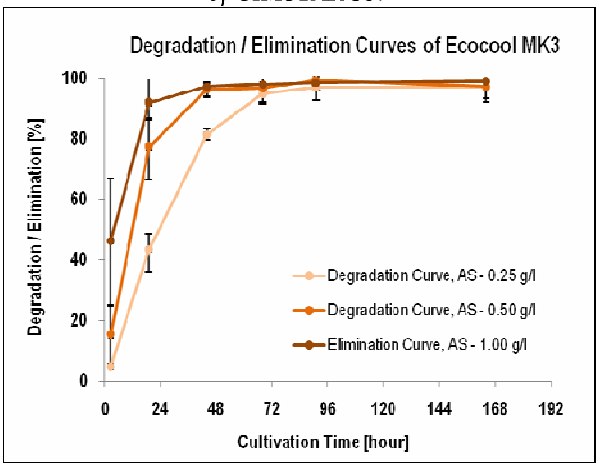

Fig. 7 *Degradation/Elimination curves of Ecocool MK3*

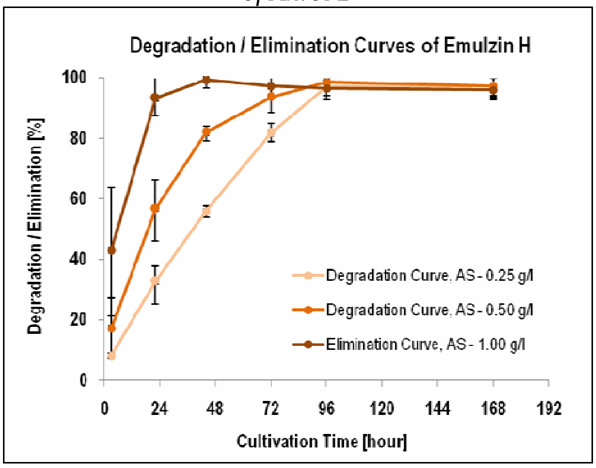

Fig. 8 *Degradation/Elimination curves of Emulzin H*

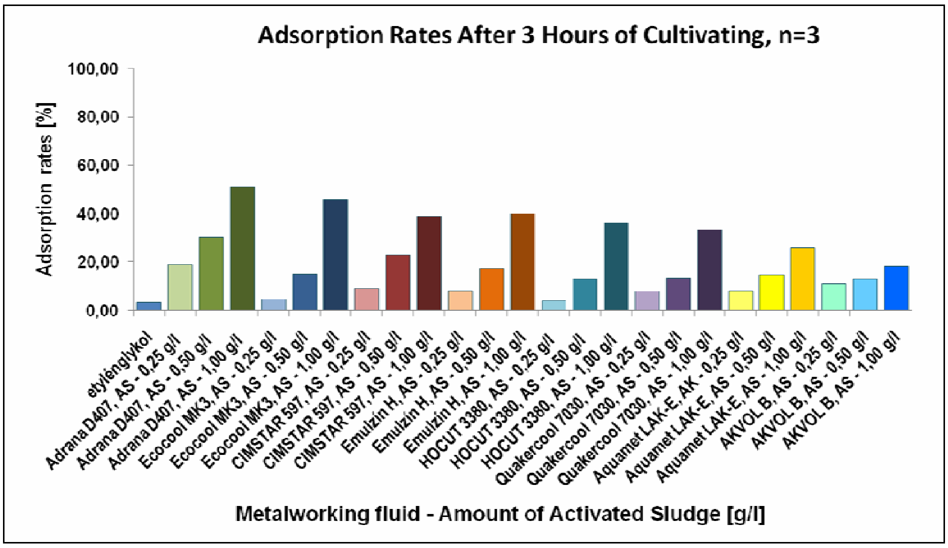

Fig. 9 *Adsorption rate of tested substances after the first 3 hours of cultivating AS – addition of activated sludge*

As all graphs in the Figs. 1-9 show that, with the increasing addition of activated sludge (AS) inoculums, the adsorption rate also increases after the first 3 hours of cultivating. The abovementioned suggests that adsorption on the floccules of AS plays an important role in elimination of the organic matter from the substance. To distinguish the main route of elimination (adsorption or degradation), it is recommended to use other analytical methods, such as the absorbance of Methyl (C-H) bond stretch in 2926 cm^{-1} and Methylene ($C\text{-}H_2$) bond stretch in 2956 cm^{-1} by FTIR analyses according to the CEC L-33-A-93 test which was released mainly to measure degradability of automotive lubricants. The lowest adsorption rates were recorded for Akvol B and Aquamet LAK-E. None of the tested metalworking fluids passed 20% of adsorption after the first 3 hours of cultivating with addition of activated sludge 0.25 g l^{-1}. In the case of Akvol B, the *Lag*-phase was also registered, which means probably the adaptation of the bacteria to the source of organic carbon in the solution. Results of the degradability testing are summarized in Table 1.

SUMMARIZED RESULTS FROM ZAHN-WELLENS TEST Table 1

	Average value n=3 AS addition	**Starting concentration of COD [mg l^{-1}]**	**lag phase t_l [day]**	**adsorption [%]**	**total decrease $D_t´$ (if >20 % of adsorption)**	**ultimate degradation degree D_t [%]**	**Biodegradation time t_2 [day]**	**ultimate biodegradability (pass 80 %)**
Adrana D407	0.25 g l^{-1}	915	no	19	-	96	2	yes (2 days)
	0.50 g l^{-1}	871	no	30	96	-	-	yes (2 days)
	1.00 g l^{-1}	746	no	51	96	-	-	yes (2 days)
Aquamet LAK - E	0.25 g l^{-1}	957	no	8	-	90	6	yes (7 days)
	0.50 g l^{-1}	880	no	15	-	92	11	yes (7 days)
	1.00 g l^{-1}	818	no	26	97	-	-	yes (4 days)
CIMSTAR 597	0.25 g l^{-1}	852	no	9	-	95	2	yes (2 days)
	0.50 g l^{-1}	848	no	23	95	-	-	yes (2 days)
	1.00 g l^{-1}	782	no	39	96	-	-	yes (2 days)
Ecocool MK3	0.25 g l^{-1}	1038	no	4	-	98	3	yes (3 days)
	0.50 g l^{-1}	1012	no	15	-	99	2	yes (2 days)
	1.00 g l^{-1}	867	no	45	99	-	-	yes (2 days)
Hocut 3380	0.25 g l-1	1153	no	4	-	93	7	yes (4 days)
	0.50 g l-1	981	no	13	-	95	-	yes (3 days)
	1.00 g l-1	1046	no	36	96	-	-	yes (2 days)

Quakercool 7030	0.25 g l-1	1019	no	8	-	98	4	yes (2 days)
	0.50 g l-1	1066	no	13	-	99	3	yes (2 days)
	1.00 g l-1	937	no	33	98	-	-	yes (1 day)
Akvol B	0.25 g l-1	879	yes (1 day)	11	-	87	-	yes (6 days)
	0.50 g l-1	808	yes (1 day)	13	-	92	7	yes (6 days)
	1.00 g l-1	790	yes (1 day)	18	-	90	7	yes (6 days)
Emulzin H	0.25 g l-1	1128	no	8	-	98	5	yes (3 days)
	0.50 g l-1	1109	no	17	-	98	4	yes (2 days)
	1.00 g l-1	987	no	40	96	-	-	yes (1 day)

Ecotoxicity testing on bacteria of activated sludge – inhibition of the respiration according to OECD 209 (STN EN ISO 8192)

Preliminary study of six selected MWFs' ecotoxicity with bacterial consortium is shown in Figures 13-18. The purpose of the method is to provide the quick screening test to identify substances that have unfavourable influence on sewage treatment plant and identify noninhibition concentration of tested substances applicable in biodegradability test according OECD 301 A-D. Respiration rate is calculated from the oxygen decrease curves for all of tested concentrations of substances approximately between 6.5–2.5 mg l^{-1} O_2. A part of the respiration curve above which the respiration rate is calculated has to be linear.

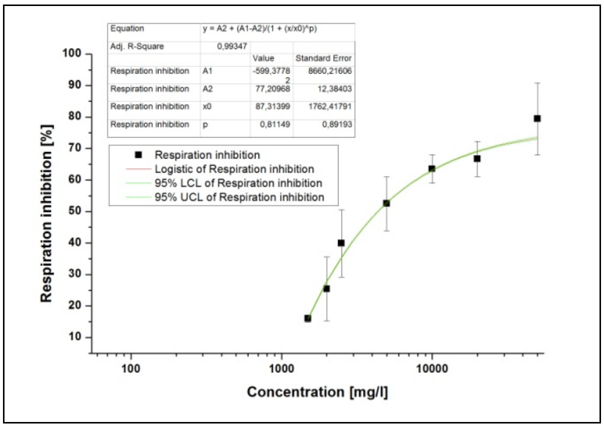

Fig. 13 *EC_{50} evaluation of Adrana D407 (Origin Pro8)*

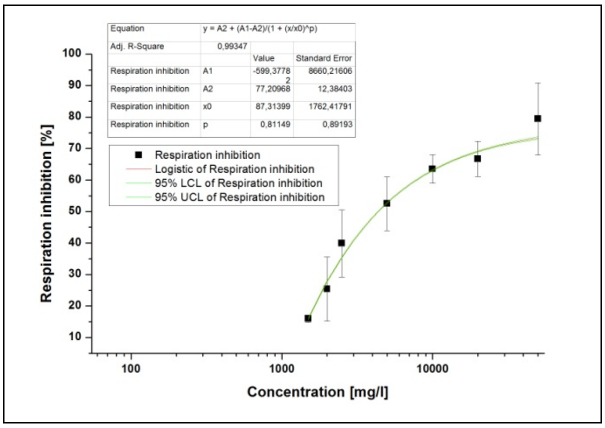

Fig. 14 *EC_{50} evaluation of Aquamet Lak-E (Origin Pro8)*

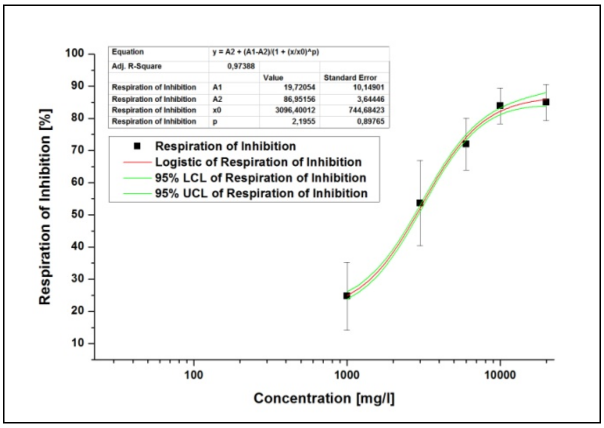

Fig. 15 *EC_{50} evaluation of Hocut 3380 (Origin Pro8)*

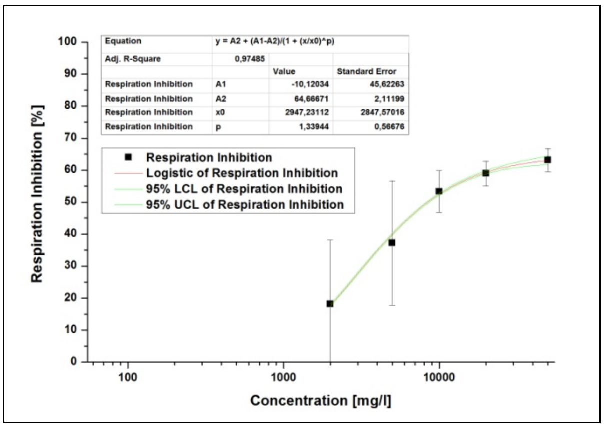

Fig. 16 *EC_{50} evaluation of Zubora TXS (Origin Pro8)*

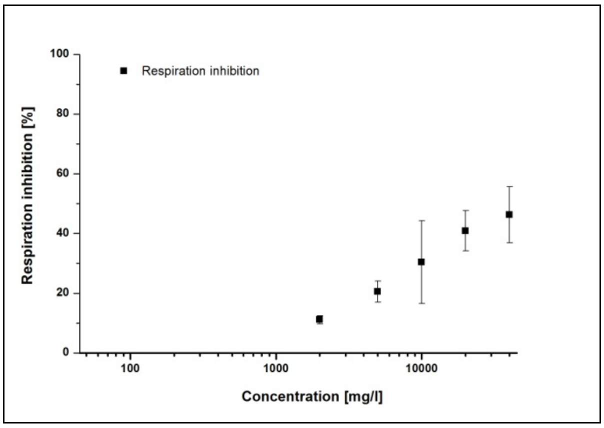

Fig. 17 *EC_{50} evaluation of Cimstar 597 (Origin Pro8)*

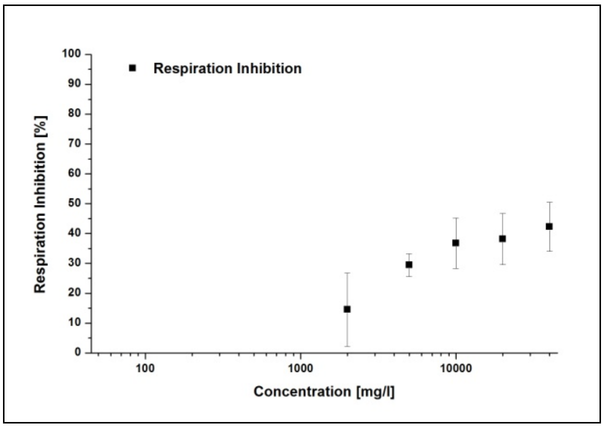

Fig. 18 *EC_{50} evaluation of Emulzin H (Origin Pro8)*

Table 2 are summarised results of testing. Shown are the calculated values for EC_{20}, EC_{50}, EC_{80} for the MWFs such as Cimstar 597, Emulzin H and Hocut 3380. Adrana D407, Aquamet LAK-E and Zubora TXS by the two methods – polynomial function of Excel application and Logistic function by OriginPro8. Just selected data (those which were in replicates, with the error bars) was used for the OriginPro8 program which allows calculating also 95% confidence interval to calculate the inhibition of the respiration.

CALCULATED VALUES OF EC_{20}, EC_{50} AND EC_{80} FOR THE MWFs Table 2

Type of Metalworking Fluid Emulsion	**Statistical Function**	**EC_{20} [mg l^{-1}] 95 % confidence interval**	**EC_{50} [mg l^{-1}] 95 % confidence interval**	**EC_{80} [mg l^{-1}] 95 % confidence interval**
1. CIMSTAR 597	Polynomial	4 943	-	-
	Logistic	4 808 4 726 – 4 890	- -	- -
2. EMULZÍN H	Polynomial	2 425	-	-
	Logistic	2 625 2 539 – 2 719	- -	- -
3. ZUBORA TXS	Polynomial	2 264	11 349	-
	Logistic	2 196 2 166 – 2 228	8 449 8 309 – 8 587	- -
4. Aquamet LAK-E	Polynomial	1 010	5 228	-
	Logistic	- -	5 600 5 567 – 5 658	- -
5. Adrana D 407	Polynomial	1 688	4 351	62 252
	Logistic	1 643 1 643 – 1 654	4 354 4 354 – 4 405	- -
6. HOCUT 3380	Polynomial	894	2 339	9 931
	Logistic	- -	2 827 2 740 – 2 911	8 282 7 758 – 9 060

Two of the six metalworking fluids – Cimstar 597 and Emulzin H were evaluated as the less toxic. In these two emulsions, the highest used concentration caused around 50%response, so that it was impossible to calculate the EC_{50} value with required accuracy. Than the list continues with Zubora TXS (EC_{50} - 11 349 mg l^{-1}), Aquamet LAK-E (EC_{50} - 5 228 mg l^{-1}), Adrana D 407 (EC_{50} at 4 351 mg l^{-1}) and finally Hocut 3380 which proves to be the most toxic of all the tested substances (EC_{50} - 2 339 mg l^{-1}). Unfortunately, all tested emulsions passed 100 mg l^{-1}. According to [16], it is satisfactory to arrange the tested substances into 4 classes < 1 mg l^{-1}, 1-10 mg l^{-1}, 10-100 mg l^{-1}, > 100 mg l^{-1}. We suppose that the tested metalworking fluid will not cause inhibitory problems in degradability test when lower concentrations are used, as listed in Tab. 2.

Conclusion

The study of degradability of 8 MWFs selected according to OECD 302B shows the increasing adsorption after the first 3 hours of cultivating with increasing the addition of activated sludge. This may play an important role in elimination of the organic matter from the solution. To distinguish biotic and abiotic eliminations, it is recommended to use other appropriate analytical methods.

The study of ecotoxicity of 6 selected MWFs according to OECD 209 shows very high effective concentration which can mean that the tested MWFs are low in toxicity to the inoculums. As the less toxic substance were evaluated two from six metalworking fluids – Cimstar 597 and Emulzin H. In these two emulsions, the highest used concentration caused the response around 50%, so that it was impossible to calculate the EC_{50} value with required accuracy. The following on the list are Zubora TXS with EC_{50} at 11 349 mg l^{-1}, Aquamet LAK-E with EC_{50} at 5 228 mg l^{-1}, Adrana D 407 with EC_{50} at 4 351 mg l^{-1} and finally Hocut 3380, which proved to be the most toxic of the tested substances.

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FORMATION OF ACID MINE DRAINAGE WATER AT Sb (Au) DEPOSIT PEZINOK

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Štefan ASCHENBRENNER [4], Jozef KRNÁČ [4], Ján DUBIEL[4]

Abstract

The article presents the results of leaching experiments regarding the comparison of chemical and biological-chemical leaching of ores from the Sb-(Au-) base metal deposit Pezinok (Malé Karpaty., the Western Carpathians) under the same conditions in solution. Discussed are the differences between chemical and biological-chemical leaching activity. The extent and the kinetics of the biological-chemical leaching of the technogenous sediments from the setting-pits are significantly higher than those without bacteria.

Key words

AMD, biological-chemical oxidation, Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans

Introduction

More than 100 years of mining at the Pezinok deposit has caused some changes of the land relief. The ore material was displaced from the original environment of the mountain massive, in which it was in the relatively equilibrium state, to the environment exposed to the combined action of atmosphere and water saturated with atmospheric gases and to the biological effects. The fine grinding of ores and application of chemical reagents in the technological process of sulphide concentrates production have increased the reactive surface of the relict sulphides in the deposited waste.

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Sludge lagoons and setting-pits contain a lot of waste sulphide minerals which represent the main substrates necessary for the metabolic activity of autochthonous, acidophilous and thionic bacteria *Acidithiobacillus ferrooxidans* (*ATF*), *Acidithiobacillus thiooxidans* (*ATT*) and *Leptospirillum ferrooxidans* (*LF*) catalysing the sulphide minerals oxidation processes. The high residual concentrations of metals Sb, Fe and As in the deposited solid wastes and contaminated soils are currently being the permanent source of in-situ pollution and, due to the activity of autochthonous microflora, the source of acid mine drainage (AMD) generation. Surface and underground waters are also polluted with the elements from the floatation agents used in the ore processing. The released metals and other chemical agents may enter the food chain of animals and humans through plants and water.

Characteristics of the Pezinok deposit

The Pezinok – Kolársky-vrch (Fig. 1) deposit is situated in a 1200 m long tectonic fault of NW-SE direction. The mineralized structure is 25-70 m thick at the surface and about 430 m long (Chovan et al., 1992).

At the Pezinok deposit, two types of ore mineralization were described: 1 – metamorphosed, primarily exhalation-sedimentary pyrite mineralization genetically related to the Devonian basic volcano-sedimentary cycle which was subsequently metamorphosed and 2 – hydrothermal Sb-Au-As mineralization of epigenetic character which is most frequently localized in beds of tectonically deformed black schists (Chovan et al., 1992).

About 20 000 tons of antimony was exploited from this deposit. The reported content of Sb ranges from 1% to 4%, of As from 0.5% to 1.5% and the average content of Au is 3.60 ppm (Uher et al. 2000). The exploitation of Sb-Au ores at the Pezinok deposit was terminated in 1991. The mine was closed in 1992.

Characterisation of the deposited waste

The mining-waste is deposited in several tailing impoundments and two sludge lagoons containing 380 000 m^3 of material (Trtíková, 1999). During the ore dressing process, As- and Fe- minerals (predominantly arsenopyrite and pyrite) were suppressed and moved to the waste. The content of these minerals in the sludge lagoons is considerably higher than that of Sb-minerals. The most frequent sulphide minerals in the sludge lagoons are arsenopyrite and pyrite. Gudmundite and stibnite occurs rarely, pyrhotine sporadically. In some samples, determined were Sb- and Fe- oxides, tetrahedrite, löllingite and chalcopyrite (Chovan et al., 1994).

The gangue minerals are represented mainly by carbonates and quartz. The schist fragments occur only rarely. The dominant clay mineral is illite. Chlorite is abundant but kaolinite is very rare (Chovan et al., 1994). Also Fe-oxyhydroxides and Sb-oxides are formed in the oxidation zone of the sludge lagoons (Trtíková, 1999; Trtíková et al., 1999).

Biological – chemical oxidation

The principle of biogenic catalysis of sulphide oxidation consists in the activity of acidophilous, thionic, sulphur and iron oxidising bacteria having a transporting function in the oxidation process, i.e. in the transfer of released electrons from donor - sulphide to acceptor – oxygen (Mustin et al. 1992). Such activity of specific species of acidophilous bacteria results in the 2.10^5 multiple acceleration of Fe^{2+} oxidation (Bennett and Tributsch 1978; Martyčák et al. 1994; Dopson and Borje 1999).

As for sulphide minerals, the autochthonous, acidophilous, chemolithotrophic bacteria of *Pseudomonales* family and *Thiobacillus* genus represent one of the basic components of the biogenic catalysis. A large number of species of these bacteria was discovered and at least 14 species fall into the *Acidithiobacillus* genus. Mesophilic *ATF* species are of the highest value, sometimes *ATT*, but also the *Spirillaceae* tribe *LF* bacteria oxidising Fe^{2+} in ultra acidic environment. *Acidithiobacillus ferrooxidans* species are gram-negative nonsporeforming rods, 0.5 – 0.8 μm in diameter and 0.9 – 1.5 μm in length with one spiral flagellum (Spirito et al. 1982). Bacteria obtain the energy by oxidising of Fe^{2+}-sulphides. All bacteria of *Acidithiobacillus* genus also oxidise the elementary sulphur formed during the sulphides decomposition.

Sulphide minerals can be oxidised by indirect biological-chemical process (metabolic catalysis), i. e. by products of *ATF* bacteria metabolism formed in the presence of sulphides. In most cases, both processes occur simultaneously. In addition to the oxidation of sulphides, reactions with CO_2 are observed in the system.

Activity of *ATF* is usually associated with the aerobic environment. In the anaerobic conditions, *ATF* bacteria oxidise sulphur indirectly by the biological-chemical oxidised Fe^{3+} cations (Pronk et al., 1994).

The direct effect of biological-chemical oxidation processes is the marked alternation of surface morphology and consequently the structure uniformity of oxidised minerals. The changes are of individual character and related to the energetic state of individual parts and the complete crystalline structure of attacked sulphide mineral (Kušnierová and Štyriaková, 1994; Gueremont et al. 1998).

Morion et al. (1991) reported that there is a galvanic interaction between sulphide minerals resulting in the transport of electrons from the sulphide mineral forming anode to the electrochemically less electro-active mineral. According to Crundwell (1989) and Silva (2003), it is possible to interpret this effect as a modification of the semiconductive properties of sulphide minerals accompanied by the tiny changes in the structure and physical properties such as reflection, microhardness, conductivity, etc.

Materials and methods

The AMD waters (samples P-1, P-2, P-3 and P-4; fig. 1) were analysed by atomic absorption analysis for Fe, Mn, As, Cu, Ni, Pb, Sb and Zn. Two types of leaching experiments were carried out to study the mobility of previously mentioned metals from the tailing impoundment sediments:

1. During the first experiment, the samples of tailing impoundment sediment were introduced to the solution containing *ATF* bacteria isolated from the mine waters from the Pezinok deposit (biological-chemical process) at pH 1.57.

Biogenic catalysis of the selected sulphides oxidation was studied using the leaching nutrient medium 9K, part A according to Silverman and Lundgren (1959) with the content of nutrients for *ATF* cells growth.

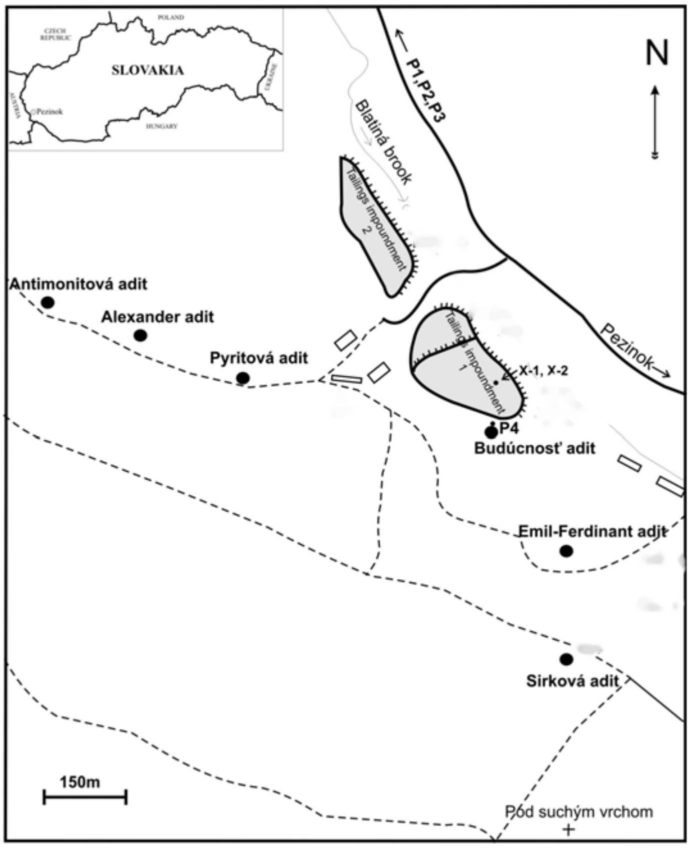

Fig. 1 *Sketch of the studied area of the setting pits at the Pezinok deposit with localisation of the samples of water (P1 - P4)) and sediments (X-1, X-2)*

2. The second experiment was the abiotic control carried out with the chemically identical leaching agent without bacteria *ATF* (chemical process).

The selected sample of the sediment X-1, the ochre sample X-2 (fig. 1) from the tailings impoundments and the AMD of various pH and origin were analysed by atom absorption analyse.

Results

The selected sample of the sediment X-1, the ochre sample X-2 from the tailings impoundments and the natural drainage waters of various pH and origin were analysed by atom absorption analyse. The research proved that both the sediments of the tailing impoundments and the secondary ochres are very rich in content of selected metal elements: As, Cd, Cu, Co, Fe, Ni, Sb and Zn.

Sulphide minerals (mainly arsenopyrite, pyrite, less Sb-minerals) in the tailings impoundments are oxidized and the toxic elements (As, Sb, Cd etc.) are loosed to water solutions. The chemical composition of groundwater and surface water is influenced by mine water and by sludge water. They leak to the streams without any clearing and dressing. The metal content in the drainage waters depend preferrentially on their origin and not on their pH. This part of our present research proved the data published by Kušnierová et al. (1994), Trtíková et al. (1998), Trtíková (1999), Andráš et al. (1994, 2004) and others. The acid drainage waters with pH <5 are rich in bacteria *Acidithiobacillus ferrooxidnas* (*ATF*) and *Acidithiobacillus thioooxidnas* (*ATT*) species. The activity of the bacteria in drainage waters of pH 4.5 to 7 is very low.

For the first experiment, drainage mine water P 1 from Pezinok with autochtonous microorganisms – sulphur and iron oxidizing bacteria *Acidithiobacillus ferrooxidnas* (*ATF*) and *Acidithiobacillus thioooxidnas* (*ATT*) was used. Presence of other species was not verified. The pH of the water was 4.5. The second sample of mine water used for the experiments was a mine drainage water from Pezinok P 3 without bacteria (pH = 6.45). During the study of catalytic influences, parallel experiments with rainwater were carried out for comparison. The results show no important differences of leaching activity between the bacteria species containing liquid phase and those without bacteria, but there was a great difference between the two natural drainage waters and the rainwater. We assume that as the pH of the bacteria containing drainage water was above 4, the activity of the bacteria was very low (the highest activity of bacteria is in media with pH <3), causing the comparable results with the drainage water without bacteria.

The second experiment was conducted using nutrient medium sensu Silverman and Lundgren (1959) 9K with bacteria and without bacteria (abiotic control). To study of the biogenic catalysis influence in oxidation processes of weathering at the tailings impoundments, pure culture of autochtonous bacteria *Acidithiobacillus ferrooxidnas* (*ATF*) isolated from mine drainage water P 4 from the Pernek deposit was used. Bacteria were dispersed in the nutrient medium. The pH was 1.5 at the following conditions: P:K=1:3, temperature 30° C, aeration by mixing in laboratory whisk device during 4 weeks. The leaching of the X-1 sediment sample and of the heavy fraction of this sample by bacteria containing media was compared with the results of the X-1 sample leaching by nutrient medium without media. The leaching continuance was studied by monitoring the selected elements (As, Cu, Co, Fe, Ni and Sb), and the experiment was interrupted after 4 weeks to segregate the product of precipitated secondary salts and Fe ochres created by biological-chemical transformation. Together with the liquid phase, the products were analysed using X-Ray diffraction analysis which proved the origination of the secondary minerals jarosite, hydrojarosite and gypsum, as well as the presence of quartz, muscovite, phlogopite, chlorite and clinochlore.

The investigated sample of the sediment from tailing impoundmentsX-1 used for the folowing experiments was analyzed by the atom absorption analysis (Tab. 1).

AAS ANALYSIS OF THE CHEMICAL COMPOSITION OF SEDIMENT SAMPLE FROM TAILING IMPOUNDMENTS

Table 1

Sample	pH	ppm							
		Fe	Mn	As	Cu	Ni	Pb	Sb	Zn
X-1	1.67	1 071	3.45	0.104	0.69	1.34	0.05	220.7	0.76
X-2	1.67	1 014	2.57	0.090	0.48	0.02	0.05	196.1	0.52

The X-1 sediment sample from the tailing impoundments was employed in experimental work for the investigation of the leaching process by using both types of drainage waters: acidic and neutral.

The acidic as well as the neutral drainage waters contain relatively high contents of Sb, As, Fe, Cu, Cd, Ni, Zn and other metals. The set of the drainage waters from Pezinok was completed with a sample of water from the wider mining ore field (P 1) (Tab. 2).

CHARACTERISTIC OF ACID MINE WATERS FROM PEZINOK MINING AREA. INCLUDING pH, CONTENT OF INVESTIGATED ELEMENTS AND PRESENCE OF ACIDOPHILOUS BACTERIA. EXPLANATORY NOTES:
P 1 – drainage water from the Pernek, P 2 – drainage water from measuring-point 8,
P 3 – drainage water from the creek near adit Michal, P 4 – Pezinok, drainage water from adit Budúcnosť, *ATF – Acidithiobacillus ferrooxidans, ATT – A. thiooxidans*

Table 2

Sample		g/l						mg/l		Bacteria	
	pH	As	Cu	Fe	Pb	Sb	Zn	Ag	Au	ATF	ATT
P 1	5.54	<5	<0.02	24.50	<2	<2	0.16	1.3	<2	+	+
P 2	4.50	<5	0.03	0.12	3.1	<2	0.11	0.9	<2	+	+
P 3	6.63	<5	<0.02	8.36	<2	3.4	0.12	0.8	<2	-	+
P 4	6.64	5.1	<0.02	31.20	<2	6.6	0.12	0.9	<2	-	-

The leaching activity in dependence on the leaching medium is presented in Tab. 3. For this experiment, drainage water P 2 from Pezinok with autochtonous bacteria *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* was used. Presence of other species was not verified. The pH of the water was 4.5. The second sample of drainage water used for experiments was drainage water from Pezinok P 4 without bacteria (pH = 6.45). During the study of catalytic influences, parallel experiments with rainwater were carried out for comparison.

AAS ANALYSIS OF VARIOUS LIQUID MEDIA OF DIFFERENT pH AND RAINWATER USED FOR LEACHING OF THE SEDIMENTS FROM THE TAILING IMPOUNDMENTS.

ATF - Acidithiobacillus ferrooxidans, ATT - Acidithiobacillus. thiooxidans

Table 3

Medium	Time of leaching (weeks)	mg/l					
		As	Co	Cu	Fe	Ni	Sb
Drainage water P 2 *ATF+ATT* pH = 4.5	I	17.8	<0.06	0	213.7	2.7	8.0
	II	16.5	<0.06	0	253.4	5.3	8.8
	III	<2.0	0	6.3	195.7	5.2	<0.4
	IV	<2.0	0	5.2	126.5	4.4	<0.4
Drainage water P 4 pH = 6.45 no bacteria	I	16.8	<0.06	0	225.2	3.0	9.4
	II	12.1	<0.06	0	157.0	3.9	7.0
	III	<2.0	0	5.9	156.0	5.4	<0.04
	IV	<2.0	0	5.2	84.2	4.4	<0.04
Rainwater pH = 5.6 no bacteria	I	13.3	<0.06	0	188.9	2.9	8.8
	II	9.6	<0.06	0	142.1	3.5	7.4
	III	<2.0	0	4.1	115.3	3.2	<0.4
	IV	<2.0	0	5.1	95.6	4.1	<0.4

The results show negligible differences of leaching activity between the medium containing bacteria species and those without bacteria but there was a great difference between two natural drainage waters and rainwater. We suppose that when pH of drainage water containing bacteria was >4, the activity of bacteria was very low (the highest activity of bacteria is in medium with pH <3), causing the comparable results with the results of drainage water without bacteria.

The next experiment was conducted using nutrient medium 9KA according to Silverman and Lundgren (1959) with bacteria and without bacteria (abiotic control). For the study of the biogenic catalytic influence in oxidation processes of weathering at the tailings impoundments, pure culture of autochthonous bacteria *A. ferrooxidans* and *A. thiooxidans* isolated from the drainage water P 1 at the Pernek deposit was used. Bacteria were dispersed into nutrient medium WHH pH 1.57 at following conditions: P : K=1 : 3, temperature 30° C, agitation at laboratory shaker during 4 weeks (Tab. 4).

LEACHING OF THE SEDIMENT SAMPLE (A) AND OF ITS HEAVY FRACTION (B) FROM THE TAILING IMPOUNDMENTS BY *ACIDITHIOBACILLUS FERROOXIDANS* (*ATF*). A) nutrient medium (pH = 1.57); B) abiotic control without bacteria (pH = 1.57)

Table 4

Medium	Time of leaching (weeks)	mg/l					
		As	Co	Cu	Fe	Ni	Sb
(A) 9K-A *ATF* pH = 1.57	I	23.9	<0.06	0	4259.0	<0.1	9.0
	II	123.2	<0.06	0	2100.0	1.2	12.3
	III	72.0	0	3.3	167.4	1.5	7.5
	IV	58.6	0	3.6	135.6	1.7	9.2
(B) 9K-A *ATF* pH = 1.57	I	72.1	<0.06	0	4576.0	0	12.6
	II	317.3	<0.06	0	3183.0	0	21.6
	III	288.0	0	8.0	280.2	7.2	19.7
	IV	208.1	0	7.5	249.4	6.5	13.0
(A) 9K-A no bacteria pH = 1.57	I	32.6	<0.06	0	167.0	1.2	1.2
	II	36.8	<0.06	0	578.4	4.5	10.1
	III	22.6	0	8.8	378.0	7.1	<0.04
	IV	<2.0	0	7.4	271.1	5.9	<0.04

The leaching of the X-1 sediment sample and heavy fraction of this sample by nutrient medium containing bacteria was compared with the results of X-1 sample leaching by nutrient medium without bacteria. The leaching continuance was studied by monitoring of selected elements (As, Cu, Co, Fe, Ni and Sb) and the experiment was interrupted after 4 weeks to segregate the product of precipitation: secondary salts and Fe ochres created by biological-chemical transformation.

The results presented in the Tab. 4 show, that in strongly acidic medium (pH=1.57) *bacteria A. ferrooxidans* are active, vigorously assisting the oxidation of sulphides. Extraction rate of Fe, As and Sb is the highest in the first week of leaching. As it could be expected, concentration of metal cations in the leaching product is the highest in the run, where the heavy fraction of the sediment sample was employed.

In the second period of leaching, we can observe the gradual decrease of Fe concentration in liquid phase in consequence of precipitation of Fe-oxyhydroxides. After leaching, the solid fraction was examined by means of XRD. Besides the detritic minerals (quartz, muscovite, phlogopite, chlorite and clinochlore), the secondary minerals, such as jarosite, hydrojarosite and gypsum were detected.

Discussion

Research studies of Trtíková et al. (1999), Trtíková (1999) and Andráš et al. (2004) demonstrated that there are two types of acid mine drainage in the area of the Pezinok deposit:

- the first type → extremely acid (pH < 3) mine waters associated with synsedimentary massive pyrite-pyrhotine ores,
- the second type → neutral mine waters (pH 5.5 – 7) associated with Sb-carbonate mineralisation.

The activity of *ATT* and *ATF* bacteria in the first type of the acid mine drainage is much higher. It is the neutral waters that percolate through the sludge lagoons of Sb-ores in the Kolársky hill area and that is why the leaching intensity is much lower than in the area of pyrite-mineralised parts (Augustín adit and the like). A considerable amount of Fe precipitates in form of ochres during the neutralisation of solutions. Ochres form the geochemical barrier and their surface serve as a sorbent of a considerable amount of metals. It is impossible to exclude that during torrential rains and under other influences the ochres may overcome the barriers of the tailing dams and reach the water flows. According to Luptáková (2001) concentration of heavy metals in the waters of sludge lagoons may be influenced also by anaerobic sulphate reducing bacteria producing hydrogen sulphide reacting with ions of heavy metals producing the secondary minerals. Luptáková conducted the isolation of those bacteria from the solid samples of the reducing zone of the sludge lagoon. The undercritical content of metals in waters, if flowing through the country for a long time, intoxicates river-sediments and gradually increases the metal concentrations as well.

Conclusion

The control of acidity is of utmost importance in leaching, since the acidic environment must be maintained in order to keep ferric iron and other metals in solution. Acidity is controlled by the oxidation of iron, sulphur and sulphides, by the dissolution of carbonate ions and by the decomposition of ferric iron through reaction with water.

The process of studied ore minerals degradation during biological-chemical oxidation in the presence of autochthonous, acidophilous, sulphur and iron oxidising *ATF* and *ATT* bacteria and during chemical oxidation is principally similar, but the kinetics of both processes is different. Higher kinetics of biological-chemical oxidation processes of studied minerals confirms the bio-catalytic influence of autochthonous bacteria.

The comparison of biological-chemical oxidation with chemical oxidation enabled to find the differences in the leaching mechanism. The activity of *ATF* bacteria considerable accelerated predominantly the extraction process of Fe, As and Sb both from the sample of the sediment (X-1) as well as from the sample of the heavy fraction.

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ENVIRONMENTAL REPORTING OF ORGANISATIONS

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Abstract

Top managers are aware of the necessity of open and honest informing about their environmental activities, which is preconditioned by the development, maintenance and subsequent improvement of the system of environmental informing in the enterprise. Environmental reporting is a tool for providing information about organisation´s activities and their impact on environment.

Key words

environment, management, reporting

Introduction

The issue of environmental protection of society becomes topical in the large, medium-sized and small enterprises. This is due to legal tools and pressure of non-governmental environmental associations as well as the management who have started to realise that environment issues directly concern every subject mainly that involved in production activity.

Industrial enterprises are often major environment polluters and their activity poses a potential threat to the quality of environment, safety and health of population. Their environmental accountability is expressed in various active measures oriented to the

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environment protection. Implementing the systems of environmental management, they build up their positive image to impress environmental associations, state administration and their contemporary or potential business partners.

Introducing the environmental managerial systems and other pro-environmentally oriented tools, e.g. publishing environmental reports, the organisation promotes itself to the professional and lay public.

Voluntary reporting on environment protection

The accession of the Slovak Republic to the European Union has raised the need of guaranteed information in the framework of environmental reporting.

Potential benefits of voluntary reporting on environment protection are as follows:

- it raises of the confidence of shareholders, warrantors and investors,
- it simplifies the accession to capital and investment markets,
- it raises the confidence of bank supervision,
- it improves the competitiveness,
- it raises motivation and satisfaction of employees,
- it improves communication with stakeholders (4), (7).

In practise, environmental report can be apprehended as a tool for improving both societal and business relations, for determination of details and elaborated verification of business´ environmental goals, procedures, strategies and future steering of the enterprise in the sphere of environment protection.

Communication with surroundings in the framework of EMS

Good communication is a basis for the right functioning of the environmental management system. The environmental management system (EMS) contains the reasons why to give information to the stakeholders inside and outside the organisation, such as financial institutions or neighbouring communities that may require the publication of the document on the organisation activities in the field of environment protection. The purpose of such activity is to increase the public appreciation of the organisation (15).

The goals of the communication on environment protection are:

- to satisfy the demands of banks and financial groups, related to the reporting on implementation of environment protection,
- to inform the partnering organisations,
- to develop a system for facilitating the communication with public an for reporting on environment protection implementation,
- to reduce the number of complaints,
- to raise the trust between the enterprise and its warrantors (11).

Environmental reporting

Environmental reporting is a tool that gives information on the organisation's activities and their influence on environment. The target groups are mainly business partners (also potential ones), employees, offices and environmental governmental and non-governmental organisations.

Nowadays, the enterprises are due to keep the records on their share of environment pollution, water and waste management, dangerous chemicals charging etc. on the basis of legal regulations in the sphere of environment. These records are regularly provided to state environment administration. In the framework of these reports, many enterprises started to public their first environmental reports (17).

The environmental reporting was initiated by industrial enterprises as well as the state institutions engaged in environmental protection and their response to the industrial accidents that raised the public concern for possible negative consequences. In 198, CCPA established the fundamentals for the Programme of Responsible Care. The enterprises that adopted the Programme of Responsible Care have to inform public on their environmental activities. Responsible Care is a reaction of chemical industry to this interest.

Implementation of EMS/EMAS helped to broaden the environmental reporting, when the enterprise is due to inform on its environmental policy.

The advantages of environmental reporting comprise:

- better feelings of employees – they do something for themselves and for their surroundings,
- initiation of good relationships between the enterprise and environmental associations,
- contributing to the improvement of the enterprise image on the market and broad public,

Environmental reports contain mostly these items:

- introduction by the director of organisation,
- history of organisation,
- environmental policy of the organisation,
- global status of the organisation with respect to the environment,
- development towards the fulfilment of specific tasks defined in previous report,
- specifying new tasks or activities for improving environmental behaviour of the organisation in future (18).

Environmental reports

The environment protection is now a key interest of broad expert and lay public. It is globally reflected in the business sphere. For this reason, the enterprises are forced to consider their attitude to environment. i. e. they have to take full responsibility for the impacts of their products, services and activities on the environment. Top managements and owners of enterprises are aware of the inevitability of open and true informing on their environmental activities. This supposes developing, keeping and continuously improving the system of environmental information in the organisation.

Main reasons for publishing the environmental reports are:

- demands of stakeholders,
- legal demands of individual countries.

The environmental reports can be presented at various levels:

- global (e.g. the Report "Our Common Future" (14), (1), The Reports of Roma Club (13), (12), (22) and suchlike),
- national (e.g. Report on the environment of the Slovak Republic regularly published by the Ministry of environment of SR every year, report Rio+10 (10)),
- regional, municipal... reports,
- reports of enterprises.

The Reports on the environment of the SR

The Reports on the environment of the Slovak Republic share the common fact that they are based on statistic data and information coming from the Ministry of environment of the SR (MoE SR), Statistic Office of the SR, expert organisations of the MoE SR branch and their experts. The Reports on environment belong to the duties required by the Aarhus convention of 1998 (5). Such reports belong to the national environment reporting. The Directive of the European Parliament and Council No. 2003/35/ES of 26 May 2003 issued to assure the compliance of community legislation with the 2nd pillar of the Aarhus convention. It is implemented in the Slovak legal system by:

- Act of NC SR No. 24/2006 Coll. On environmental impact assessment,
- Amended Act NC SR No. 245/2003 Coll. On integrated prevention and pollution control.

Selected kinds of reports dealing with national reporting are as follows:

- reports on environment status according to the D-P-S-I-R structure,
- reports on the economy branches influences on the environment of the SR (sector reports) – process of environmental impact of selected sectors of economic activities assessment,
- regional reports on environment status,
- information leaflets on the environment of the SR (21).

Assets of environment reports issuing

Nature of the environment reporting is a process of collecting, processing, analysing, evaluating and verification and finally reporting the selected important and useful information on the impacts of the enterprise activities, products and services on environment in relation to the stakeholders and users. The enterprise management can then adopt the measures to meet the global environmental goals of the enterprise, i.e. to contribute to the process of sustainable development and improvement.

Benefit of environment reporting varies in every enterprise, but generally involves the following issues:

- providing documents for permanent EMS of enterprise improvement,
- raising employees motivation,
- utilising positive "green" image to persuade the creditors and investors on the enterprise interests in environment,

- functioning environmental reporting and well prepared environmental audits can show the options of improving the communication with stakeholders,
- emphasizing the environmental profile of enterprise an thus getting the advantage in business negotiations,
- introducing the environmental aspects as a company priority.

Standardization of environment reports

The standards of ISO 14000 are the most important common standards. STN EN ISO 14063:2010 *Environmental management. Environmental communication. Instructions and examples* (ISO 14063: 2006) is directed to the communication issues.

World Business Council of Sustainable Development (WBCSD) presents publications and reports on its website (23). WBCSD has not published any directive on environment reports. These projects are more contemplation on sustainable development than any instruction regarding how to write a report.

The Global Reporting Initiative (GRI) started issuing some Sector Supplements that are supplements of GRI Directive (20). The report plan and the selection of indicators are prescribed.

The International Network for Environmental Management initiative (INEM (9)) advocates the report structure and indicators types for every sphere, but it gives much more freedom to the report author than the GRI Initiative (2). This tool gives advice on how to elaborate a good report on sustainable development. It is aimed at the economic interests of enterprise presentation as well as at reliable and persuasive communication, informing of stakeholders and their interests. It features the development of sustainability report principles and elements and gives a sum of good examples for enterprise presentation. Besides, it draws attention to the reliability of the sustainable development report. This handbook is based on INEM sustainability reporting and general GRI principles (8).

The Responsible Care is a world-wide initiative of continual improvement of all aspects of health, safety and environment protection in chemical industry, challenging the open communication on its activities achieved results (16).

Types of enterprise environmental reports

The enterprises can provide environmental information via:

- Voluntary reports - enterprises issue environmental information on commitments, sustainable development or as separated reports (enterprises decide alone how to give the most transparent information to the stakeholders´ groups),
- Obligatory reports – enterprises often present environmental issue as parts of annual reports.

The types of voluntary environment reports are as follows:

- Environment report (TYPE I) – enterprise care for environment;
- Environment report – HSE (TYPE II) - enterprise care for health, safety and environment;

- Environment report – UR (TYPE III) - sustainable development of the enterprise – economic, environmental, social;
- The Report on responsible enterprise (CSR) – ethical behaviour of enterprise towards the society in the financial, environmental and social spheres.

Survey on environmental reporting of the SR enterprises with implemented EMS/EMAS

Management of industrial enterprises realizes, in accordance with the implemented EMS or EMAS, the need to manage the enterprise activities and publish environmental reporting. The implemented environment management requires a system of communication on the environmental profile of enterprise with stakeholders (6). The EMA programme prescribes a written form of providing the environmental information and its releasing procedure.

In 2010, we carried out a survey aimed at the environmental information provided by the enterprises in the SR having EMS (3), or EMAS, resp. implemented via the Internet (19). Involved in this survey were 375 enterprises (3).

Environmental information of the enterprises (with implemented EMS or EMAS) that were issued on their websites can be categorized as follows (fig.1):

- A - the information on EMS implementation,
- B - the information on EMAS implementation,
- C - environmental report,
- D - environmental policy,
- E - air quality protection,
- F - water quality protection,
- G - waste management,
- H - vegetation care,
- I - safety and industrial hygiene reports,
- J - another activities.

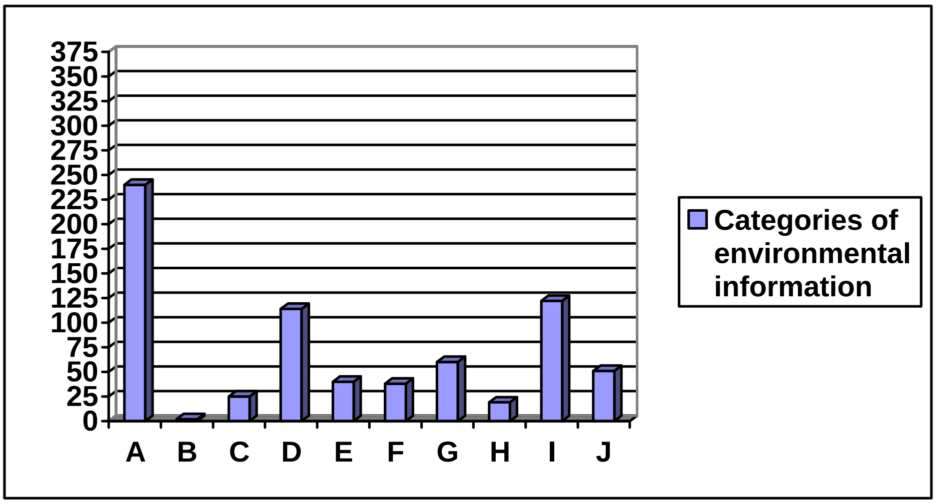

***Fig. 1** Environmental information of the enterprises (with implemented EMS or EMAS), that were issued on websites*

The heading “other” comprises some activities of various character, like:

- envirnonmentally appropriate product certificate,
- contributions to environmental programmes,
- Responsible Care,
- old environmental burdens,
- cooperation with NGOs in the environmental policy implementation (e.g. SKANSKA Technologies Ltd., that, in cooperation with Ekopolis Fundation, has developed the “People for Trees” Programme),
- and various other activities regarding the environmental issues.

Results

The most effective form of presentation of environmental reports is their publication on websites where they are available for each interested party. It is important for an enterprise to establish a scale of values that will become a part of the enterprise profile presented to the public. Environmental report, as any other information, has to be objective and true in relation to receivers (stakeholders). It has to be a part of an integrated information system of the enterprise, too.

The environmental reporting is being implemented mainly by large and profitable enterprises. Small and medium-sized enterprises include it into their annual reports.

We can see a positive importance of environmental reporting in the informing not only of fulfilment environment protection regulations but on pro-environmental approach of the enterprise as such. The environmental reporting enables the communication with stakeholders. The main goal of environmental information is therefore a presentation of the enterprise attitude to the environment.

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SOLUTION TO THE PROBLEMS OF THE SUSTAINABLE DEVELOPMENT MANAGEMENT

Miroslav RUSKO [1], Dana PROCHÁZKOVÁ [2]

Abstract

The paper shows that environment is one of the basic public assets of a human system, and it must be therefore specially protected. According to our present knowledge, the sustainability is necessary for all human systems and it is necessary to invoke the sustainable development principles in all human system assets. Sustainable development is understood as a development that does not erode ecological, social or politic systems on which it depends, but it explicitly approves ecological limitation under the economic activity frame and it has full comprehension for support of human needs. The paper summarises the conditions for sustainable development, tools, methods and techniques to solve the environmental problems and the tasks of executive governance in the environmental segment.

Key words

Environment. Human System. Sustainability. Sustainability Management. Methods and Tools

Introduction

The paper summarizes the results of the systematic study of environment in the recent 30 years. It starts from cognition of the studied subject on the present level and summarizes the conditions and limits of sustainable development, as well as the tools, methods and techniques used to solve the environment problems and tasks of executive governance in the environmental segment.

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The environment itself is a system of systems that, from the viewpoint of human existence and development, is a part of the superior system of systems, the human system (1). From the given fact that it is evidently impossible to elevate the environment existence and return to original state under the interests connected with human existence and development, but, simultaneously, it is impossible to damage the environment irresponsibly, because it creates the medium necessary for human existence itself. Therefore, we have to introduce the compromises that respect human needs and environment into the practice, based on our knowledge and experience. Their impact and benefits are monitored in the way that allows carrying out the corrective measures if they seem to be necessary.

Based on recent cognition, sustainability (sustainable development), is not only related to the environment, but also to the entire human system and it basic assets (i.e. public assets) on which the human lives are dependent. Basic human system assets are human lives, health and security; environment; property and public welfare; infrastructures and technologies, in particular those that belong to the critical ones (2). The sustainability assessment in general sense is the formalised process for identification, prediction and assessment of potential impact of arbitrary inputs including the variants for society sustainable development (e.g. legal rules, ordinances, regulations, political intent, plan, program, and project). From the viewpoint of present cognition of human system and its assets, the mentioned assessment might be performed always at good governance of territory (2).

Conditions for sustainable development

From the system viewpoint, the sustainable system has attributes as productivity, resilience, adaptability and vulnerability, and therefore, sometimes it is not easy to find a suitable reference state or conditions:

- The reference point of sustainability is a demanded future state (scenarios, techniques and foresight).
- The reference points are, on the one hand, inputs and, on the other hand, outputs of system processes (ecological trace, product life times etc.).

We can thus assume the context given in Figure 1. Since these attributes are mutually tied up, in the relation to the existence of system, the sustainability is on the peak. The decision-making on system adaptive capacity is defined by the relation given in the decision matrix in table 1 (3).

Sustainability is often misinterpreted as the goal that we all strive for. In fact, sustainability is not an achievable final state, since it is rather the basic characteristics of a dynamically developed system. Thus, ***sustainability is permanent adaptation to changing conditions***. This adaptive property is natural to all ecosystems. It is only a question of education to introduce the adaptive procedures to the public administration decision-making on human, i.e. socio-ecologic-technical system (3). For the implementation in practice it holds several pieces of knowledge:

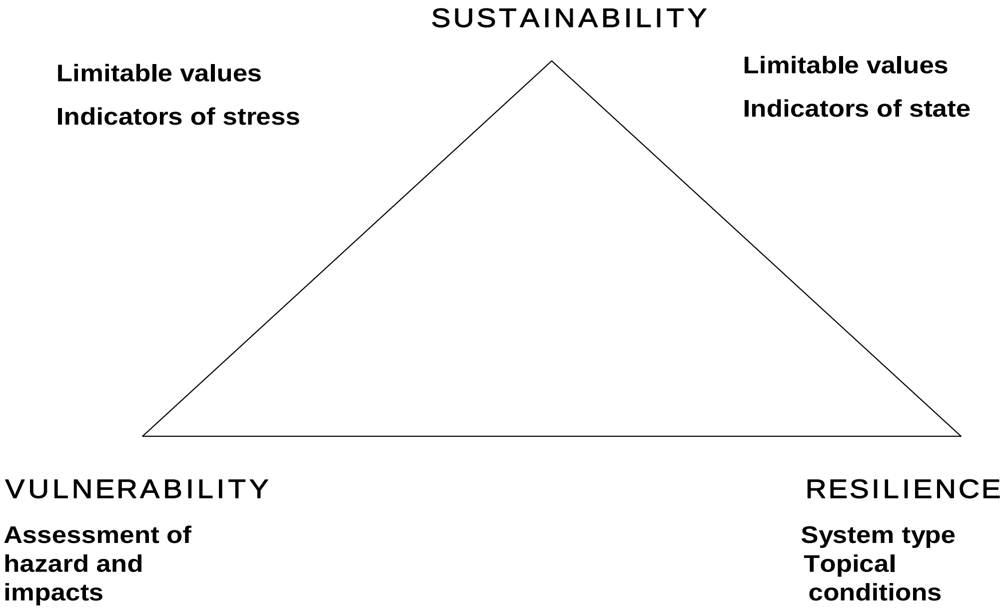

Fig. 1 *Relation among sustainability, vulnerability and resilience*

SYSTEM ADAPTIVE CAPACITY Table 1

Impacts	**Adaptive capacity**	
	Low	*High*
High	*Vulnerability*	Chance of development
Low	Rest risks	*Sustainability*

1. Criticality is directed to failures and hazards, while sustainability deals with the existence. Therefore, more and more important are the approaches and procedures that deal with the sustainable infrastructure, namely both, the grey one and the green one. The procedure for searching the sustainable elements is the following:
   - list of activities,
   - key impacts induced by human activities,
   - identification of receptors,
   - identification of ways of impacts spread,
   - identification of the secondary and further order impacts on main and other receptors.

   This approach can be used only for grey (i.e. by human created) infrastructure, whereas the green infrastructure cannot be investigated in the way that its parts are separately analysed, since landscape and ecosystems create a complex super system, i.e. system of systems (1).
2. The landscape sustainability is also connected with its sensitivity; the assessment is done by scoring, i.e. decision matrix in Table 2.

3. The human needs, however, depend mostly on functions of ecosystems, and therefore, it is necessary to understand the ecosystem functions, because:
   - the ecosystem functions vary and thus influence the human health,
   - responses of ecosystems to human activity (intended or non-intended) are not always immediate, they can cumulate, affect vicariously or retrospectively, and through the retrogressive links to create emergency up to critical situations.

   Therefore, the procedure in which we define firstly the grey/engineering infrastructure for human settlements and, after that, the proposal is transformed into the landscape is incorrect as it completely ignores possible cumulative, long term and delayed impacts on environment sources and ecosystems services. Therefore, it is necessary to search for the solution suitable for local conditions; i.e. it is site specifications.
4. The orientation to the interface of grey and green infrastructures relays on technologies that might solve present and future problems. New technologies, however, bring in uncertainty and vagueness into green infrastructure, because the technology impacts on environment are hard to forecast. Therefore, it is necessary to use and process the methodology of foresight not only on technological level, but also on societal level, i.e. societal foresight aimed at the trends of behaviour of grey infrastructure (i.e. theory of normal accident, highly reliable organisation, industrial ecology) and green infrastructure (adaptive environmental management, industrial ecology etc.) (3).

DECISION MATRIX ON LANDSCAPE SUSTAINABILITY Table 2

Land-scape type	Sensitivity of land-scape features	Sensitivity of partial elements of landscape	Sensitivity of aesthetic viewpoints of landscape	Visual sensitivity of landscape	Total sensitivity of landscape	Value of landscape	Acceptable landscape Capacity
Type 1	High	Medium	Medium	High			
Type 2	Low	Medium	Low	Low			
etc.							

Tools, methods and techniques for solutions to environmental problems

The humans did not come in the environment with intent to subvert the nature. The problems started at the time when humans tried to separate themselves from the nature, and they placed technology / engineering between themselves and the nature. Initially, it was not evident, the biosphere has kept its reserves and it contrived to equilibrate with a range of activities. However, the human activity has been progressively taking on the intensity and in some directions the biosphere has been globally affected (4, 5).

The present worldwide problems are of a global character. Apart from the environment contamination, other major global problems involve the questions of peace and war, the differences between developed and developing countries, providing the food for future population, energy demand, lack of water, soil, sources, as well as the questions of health care, culture and education. THEREFORE, it is necessary to introduce STRATEGIC, SYSTEM AND PROACTIVE MANAGEMENT (6, 7), based on a realistic, systematic and proactive view of human system and its problems. The given view is necessary from the following reasons:

- Humans have been getting to a certain life standard that they do not repudiate; this standard is conditioned by interventions to nature.
- The environment is an adaptable system. During their development, the humans have accumulated much knowledge and experience, and therefore, they are supposed to know the ways to limit the interventions to a system, so that to ensure the system development in the direction supporting the mankind's development.
- For many humans, the environment today represents a stylish stalking horse which makes them take up the actions that have nothing in common with real environment (e.g. the reality that the soil is left unexploited does not prosper to environment).

For decision-making, a model of environment that is restricted to human medium has been used, because the aim of human strive is to ensure the human society development, i.e. by recent words said the such development trajectory of whole environment system that onward enables humankind development.

Based on the present knowledge (6, 7), each quality management, including environmental management, must carry out the decision-making process with respect to the following goals:

- to prevent emergency situations and to localize emergency situations (the accidents can origin in the frame of both, individual components or even in the frame of the whole environment system),
- to ensure the healthy development of human society,
- to implement ecological programmes in the socio-economic sphere.

The management must monitor (4-7):

- impacts of anthropogenic activities into the environment that can be divided into:
  - pollution of environment component (may be either of the material character, manifested by concentrations of agents or of physical origin manifested by noise, heat, electromagnetic oscillation etc.,
  - biologic diversity, i.e. reduction of number of species, change of species composition etc.,
  - deterioration of health state of human population,
- pressure of antropogenic sphere on environment that is divided to:
  - emissions of agents (or better wastes of human activities) into natural medium,
  - consumption of renewable sources.

Administration management and its tasks on environment sector

Since its origin, the basic function of state has been to ensure the protection and development of a given human society which is impossible without ensuring the safe space in that the human society has been living. The management of state includes generally the concepts of government, control and office hearing of the public affairs. It represents the conscious activity that is directed to the determination and control of course of topical processes for achievement of appointed goals. It puts individual activities in harmony and it fulfils general functions of the whole, i.e. the state / territory / object / organisation etc. The governance is the form of activity of authorities, particularly executive ones that consists in organizing and practical implementation of tasks given by managing team / state management / territory / object / organisation in harmony with laws and the other legal rules.

According to (6, 7), the basic tools of state for management directed to sustainability are:

- management (strategic, tactical, operational) based on qualified data, knowledge, professional assessments, qualified decision-making methods, land-use planning, correct sitting, designing, building, operation, maintenance, reparation and renovation of buildings, technologies and infrastructures,
- citizen’s education, schooling and training,
- specific education of technical and management workers,
- technical, health, ecological, cyber and other standards, norms and rules including the best practice procedures, i.e. tools for control/regulation of processes that may or might lead to disaster occurrence or to the increase of its impact,
- inspections and audits,
- executive security forces for qualified response to emergency and critical situations,
- systems for critical situations defeating,
- security (land-use and spatial), emergency, continuity, crisis and contingency planning,
- specific system for defeating the critical situations - safety, emergency, continuity and crisis management.

The analysis of the development of environment and the development of political, social and economic situation worldwide shows that it is necessary to solve the cases and actions that by their intensity induce the critical situations leading to relevant crises of the type denoted as a humanitarian catastrophe or social crisis.

Therefore, from the viewpoint of human security, human system development, conservation of quality environment, existence, stability and development of state must comprise a safety concept connected with the concepts of development codified and implemented by safety management (2). O the basic (usual) level of management, the target is security and sustainable development, thus connecting emergency and crisis management.

The goal of human society management is to ensure the protection of: human lives, health and security; property, welfare; environment; infrastructures and technologies, which are inevitable for human survival, i.e. the mobilisation and co-ordination of utilization of national sources (energy, labour force, production capability, food and agriculture, resources, telecommunications etc.), the co-ordination of such activities as they are notification system, rescue system and medical services that reduce impacts of natural or other disasters and ensures the continuity of activity of public administration, the adherence of legislation and also generate the conditions for start of development (4-8).

The land and regional development is manifested by the construction of industrial regions coming closer and closer to the residential zones. Possibility of harm thus increases, and society (community) is not willing to accept all risks. This is the reason for the necessity of risk management and consecutively risk engineering that includes risk assessment, risk reduction and harm explanation. In short, the risk engineering is connected with technical systems (only in advanced forms, the human factor influence on complex process safety is considered) and in the broader sense, it is possible to generalize it to renewal of landscape with utilization of engineering approaches. Therefore, the risk engineering plays such an important role. Its target, on the one hand, is the optimum protection of humans, property and environment, and, on the other hand, the optimum renewal of damaged landscape with utilization of engineering procedures and findings (9). Both concepts require structured a system approach and qualified utilization of planning the scenarios for decision-making support.

The territory management understood as strategic and proactive territory safety management differs from normal environment management in the following items:

- It is directed to the long-term sustainability.
- The aim is the system integrity (including the so called ecological integrity) because ecosystem services/utilities (i.e. utilities that environment offers to humans) promotes live supporting functions.
- It considers the human as an element of system and it integrates human activity with environment protection.
- It sentient reacts to human needs in the system contexts.

It includes quality environment management (10-12).

Conclusion

From the viewpoint of society needs, it is necessary to ensure the further development of economy on the one hand, and, on the other hand, to reduce the environment contamination and to ensure the environment protection.

The artistic creation is the high degree of proficiency. The complex problems of the human/nature relation are based on certain philosophical foundations in each historical era. The present period can be characterized as the era in which the humans incessantly start turning the higher merry-go-round of substances and energies in order to satisfy their needs, with reality that the bulk of these substances is growing much faster than the human needs. On one side it displays deficiencies of resources and energy (resource stocks have been stretched) and on the other side it wastes with resources and with energy.

Sustainability considers the nature and human from the viewpoint of optimum development of the whole biosphere. The ecological behaviour should not be reduced to the riotous discussions around the nuclear power plants and water structures or industrial complexes. We must plan and build big structures. At the same time, we must consider the impacts of these constructions on the environment and human health.

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