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## **RESEARCH PAPERS**

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## THE STUDY OF SILICON MOULD'S THERMAL LOADING DURING SPIN CASTING OF ZINC ALLOYS

#### Matej BEZNÁK, Martin BAJČIČÁK, Roland ŠUBA

#### Abstract

The aim of this paper is to verify through experiment, the thermal loading of silicon moulds used for Tekcast spin casting technology. Heating of the moulds was studied from 1 through 50 casting cycles, as well as their cooling time after 5, 10 and 15 casting cycles. Subsequently, it has been determined that higher number of casting cycles and casting of thick-walled castings expose moulds to high thermal loading due to insufficient thermal conductivity of silicon rubber.

#### Key words

temperature, mould, silicon, casting, zinc

#### Introduction

Spin casting into silicon moulds is the process of the mould's cavities filling by increased forces. The material of the mould is Teksil – silicon rubber, which enables low cast melting point alloys like zinc and tin alloys, and even thin-walled castings from aluminum alloys. Teksil silicon material is soft during the mould's preparation and can be processed like plasticine. The final toughness and flexibility of mould is achieved by vulcanization (i.e. by pressure and heat application).

The process of mould making and casting is relatively short and simple. This technology has both advantages [1] and disadvantages. One of these disadvantages is the mould's lifetime, which is affected by thermal loading that causes them to crack. The next serious problem is the casting's quality (i.e. porosity, shrinkage cavities). These problems are caused by poor thermal conductivity of the mould. Although silicon moulds resist to temperatures up to 450°C during zinc alloys casting, they have low thermal conductivity, which causes the

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mould's overheating and delays the production process due to necessary cooling times. The cyclic heating of the mould during a larger number of casting cycles can cause defects on the mould's cavity surface and possible burnout of the mould's parts on the casting. Thus, it is necessary to find solutions for eliminating this disadvantage of silicon moulds during the casting process [2]. It is also very difficult to eliminate the non-uniform heat conduction in mould, which creates the risk of cracking in corners of complex shape castings with varying wall thickness.

#### **Teksil Silicon Material**

Teksil is material developed especially for Tekcast spin casting technology by TEKCAST Industries from the USA. It is used for production of silicon rubber moulds with high heat resistance for zinc, tin alloys, and even thin-walled aluminum parts casting. These very precise, chemically heat-resistant moulds are finished by vulcanization at 170°C with applied pressure, dependent on the mould's size. After vulcanization the mould is able to produce highly precise castings [3]. It also has high reproducibility of surface details and a relatively long lifespan (up to tens of thousands of castings from zinc and tin alloys). The advantages of this technology enable it to be used not only for decorative parts, but also for precise complex shape construction parts. One of its major disadvantages is low thermal conductivity. Tables 1 and 2 show basic properties of silicon compared with other materials. The typical thermal conductivity of rubber is  $\lambda = 0,2$  W/mK. This poor thermal conductivity leads to gradual heating of the mould during the casting process. Subsequent casting cycles cause increased thermal loading, which can lead to mould destruction and lower quality casting.

## THERMAL PROPERTIES: COMPARISON BETWEEN DIFFERENT METALS AND SILICONE [2]

Material	Silicone	Pure aluminum	Pure copper	Plain carbon steel
Specific heat [J/kg K]	~1250	903	385	434
Density [kg/m <sup>3</sup> ]	1535	2702	8933	7854
Thermal conductivity [W/m K]	0,71-1,0	237	401	60,5

#### THERMAL PROPERTIES OF DIFFERENT MATERIALS [2]

Table 2

Table 1

Material	Average specific Heat [J/kg. °C]	Latent heat [kJ/kg]	Average density [kg/m <sup>3</sup> ]	Melting point [°C]	Thermal conductivity [W/m.ºC]
Beeswax	*	174.6	2255.44	62.2	0.0744
Paraffin	905.4	146.7–200	2062.1	56.1	0.0713 (0.18)
Plain steel	434	N/A	7854	N/A	60.5
Silicone	1250	N/A	1535	N/A	0.71-1.0

x\*Value not available.

The small thermal conductivity of mould causes mould cracking for thick walls castings with more subsequent casting cycles, as well as influencing the casting's quality (Fig. 1).



Fig. 1. The crack in the mould's cavity caused by thermal loading

#### Experiment

For the mould's production, silicon material TEKSIL Silicone - GP-S, with a diameter of 305 mm, was used. The mould was vulcanized at 170 °C with 25 MPa. The patterns for mould making were polished by electrolytic – plasma technology [4]. Figure 2 shows the mould before casting with marked places of temperature measurements. Each measurement was made in the place of runner connection, due to the assumption that if molten metal solidifies here as last, the thermal loading of this part will be the greatest.



Fig. 2. The bottom part of the mould (temperature was measured in marked cavities)



Fig. 3. Tekcaster Series 100-D spin casting machine

The experiments were made on spin casting machine Tekcaster Series 100-D (Fig. 3). The casting cycle lasted 40 s and the interval between measurements was 60 s. Table 3 shows parameters of the casting process during experiments. The temperature was measured by CEM DT-8810 digital thermometer. Cast metal was zinc alloy Zamak 2 with a melting point of 420 °C. Its chemical composition is shown in Table 4.

THE PARAMETERS OF CASTING PROCESS DURING EXPERIMENTS Table 3

Parameter	Value
Mould's rotational speed	475 rpm
Casting cycle	40 s
Holding pressure	241,5 KPa

THE CHEMICAL COMPOSITION OF ZAMAK 2 ALLOY Table 4

Chemical element	Al	Cu	Mg	Fe	Pb +Cd	Zn
[wt.%]	4,0	2,8	0,04	0,075	0,004	balance

Figure 4 shows heating curves of the mould's cavities during the casting process up to 50 casting cycles. The difference between measured values in various mould's cavities is less than 2,5 %, thus the heating curve can be drawn from an average value (Fig. 5). Figure 6 shows details of the mould's cavities' heating curve from 5 to 50 casting cycles. Figure 7 shows the heating curve of the mould in central gate.



Fig. 4. The dependence of temperature of selected mould's cavities from the number of casting cycles

Fig. 5. The dependence of average temperature mould's cavities from the number of casting cycles



Fig. 6. Detail of curve from Fig. 5 in range from 5 and 20 casting cycles

Fig. 7. The mould's heating in central gate

Figure 8 shows cooling rates of mould's cavities measured after 5, 10 and 15 casting cycles. The cooling rates were monitored in period from 10 to 300 s.



Fig. 8. The cooling of mould's cavities

#### Discussion

From the heating curves in Figure 4, it is obvious that the heating is nearly similar for all three of the mould's cavities where the temperature was measured. The differences between temperatures in each mould's cavity are no greater than 2,5 %. This allows us to draw a curve of the mould's cavities' average temperature (Fig. 5). The rapid heating during the first casting cycle can be explained by the pouring of molten metal with a temperature of 420 °C into the mould with a temperature of 17 °C and low thermal conductivity of the mould. This rapid heating can be avoided by preheating of the mould. The small decreasing of the mould's temperature after the 2nd casting is caused by low thermal conductivity of the mould, which is great enough at this point because the mould is not cyclically heated by casting cycles every 60 s.

Figure 6 shows the temperature of the mould's cavities in intervals from 5 to 50 casting cycles. The heating of the mould is not as intensive as during the first 10 casting cycles, but the mould's temperature reaches more than 230 °C after 50 subsequent casting cycles. This has a negative effect on the mould's lifetime (Fig. 1). Figure 7 shows the heating curve of the mould in the central gate. The differences in temperature compared with the mould's cavities are caused by different amounts of metal poured into the mould, which leads to partial or complete filling of the central gate. This causes cyclic thermal loading of the central gate. In Figure 8 the cooling curves reveal that larger number of cycles leads to longer cooling of the mould, even if they start to cool at the same temperature.

#### Conclusions

The cyclic thermal loading of mould has significant influence on its lifetime [2]. The cyclic thermal loading can be eliminated by the heating of the mould before the first casting cycle and at minimum intervals of 120 s between two cycles. One casting cycle lasts about 40 s, depending on the mould's size. Therefore, it would be better to use more moulds, subsequently changing them in order to avoid the prolongation of the production cycle due to necessary cooling times. This can be accomplished by implementing a carousel mould changer. Such a solution can accelerate the production rate to meet mass production. It is also necessary to pour the same amount of molten metal into mould cavities to guarantee adequate filling of the central gate (maximum to half of the upper mould height).

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#### FORMABILITY OF CP-W 800 STEEL SHEETS

Jozef BÍLIK, Viktor TITTEL, Mariana DOBIŠOVÁ, Roland ŠUBA

#### Abstract

The paper is focused on the verification of CP-W 800 high strength steel mechanical properties and formability. This steel is used in automotive industry. There are results of tensile test and microhardness measurements and technological tests.

#### Key words

formability, uniaxial tensile test, Erichsen cup test, microhardness

#### Introduction

Very important role at sheet forming beside technological parameters and technological operations plays also the properties of formed materials. Recently automotive industry tries to improve safety and decrease mass of cars by using high strentgh materials. One of such materials is CP-W 800 steel. The aim of this paper is to analyze mechanical properties and formability of this steel used for production of chassis parts. [1, 2, 3]

#### Mechanical properties of CP-W 800 steel

CP-W 800 is high strength steel processed by controlled hot rolling. The material with 2 mm thickness is zinc plated. Its chemical composition is in Table 1 and required mechanical properties in Table 2.

CHEMICAL COMPOSITION OF CP-W 800 STEEL

Table 1

С	Si	Mn	Р	S	Nb	Ti	Al	Cr	Мо
≤0,18	$\leq$ 0,80	≤2,20	≤ 0,025	≤0,010	$\le$ 0,08	≤0,18	_	$\leq$ 0,60	≤ 0,40

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REQUIRED MECHANICAL PROPERTIES OF CP-W 800 STEEL

Table 2

Table 3

Yield strength R <sub>p0,2</sub> [MPa]	UTS R <sub>m</sub> [MPa]	Ductility A <sub>5</sub> [%]
Min. 680	800 - 980	min. 12

#### **Test results**

The tensile test was made after standard STN EN 10 002-1 (STN 42 0310) on sheet tensile test specimens (STN 42 0321). The shape and dimensions of sheet tensile test specimens can be seen on Fig. 1.



Fig. 1. Shape and dimensions of tensile test specimen

The measured and computed values from tensile tests are in Table 3. The Table 3 shows beside the ultimate tensile strength determined by the standard also effective ultimate tensile strength determined for change of the test specimen neck cross-section. Table also shows ductility up to neck creation beginning.

THE	E RESULTS O	F THE	STATIC	TENSIL	E STR	ENGTH	TEST
FOR	CP-W 800 M	ATER	IAL				

5			CP-W 800				
Specimen	Strenth characteristics		Effective ultimate tensile strength	Duc charac	tility teristics	Ductility up to neck creation beginning	
110.	R <sub>p0,2</sub>	Rm	R <sub>ms</sub>	A <sub>80</sub>	Z	A <sub>neck</sub>	
	[MPa]	[MPa]	[MPa]	[%]	[%]	[%]	
1.	799,90	860,04	1068,16	15,38	28,49	9,75	
2.	824,46	891,64	1046,59	13,81	40,36	9,19	
3.	830,63	899,85	1083,34	15,63	38,30	9,75	
Average value	818,33	883,84	1066,03	14,94	35,72	9,56	

From the measured and computed values of the tensile test is obvious that tested material fulfill required mechanical properties.

Erichsen cup test was made according to standard STN 42 0406. The test specimens were strips with dimensions 90 x 420 x 2 mm. The measured cup height at fracture are in Table 4.

THE RESULTS OF ERICHS	EN CUP TEST OF CP-W 800 MATERIAL	Table 4
	CP-W 800	
Specimen No.	The cup height at fracture h <sub>crit</sub> [mm]	
1.	12,00	
2.	11,70	
3.	11,80	
4.	11,65	
5.	11,70	
6.	11,50	
Average value	11,73	

The measured values from Erichsen cup test indicate that given material is suitable for deep drawing.

This material is tested by bend test and the cracking begins at angle 159° 30'.

It is also tested by 180° bend test (Fig. 2). There can be seen visible cracks on the external side of bend.



Fig. 2. The crack shape at 180° bend test (CP-W 800)

The microhardness was measured on specimens prepared for metallographic analysis with loading 0,05N during 10 seconds. For this measurement BUEHLER INDENTAMET 1105 test machine was used.

THE RESULTS OF CP-W 800 MATERIAL MICROHARDNESS TESTING	Table 5
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CP-W 800							
1.	2.	3.	4.	5.	Average value		
304,5	296,0	227,2	251,5	241,4	264,1		

#### Analysis of material's microstructure

The microstructure was analyzed by light microscope on cross-cuts of specimens prepared for metallographic analysis. The specimens were analyzed on NEOPHOT 30 light microscope. The preparations consists from cutting of specimens 15 mm long, grinding by abrasive coated paper with various abrasive grain size (abrasive coated paper codes in order of their use 220, 320, 400, 600, 800 a 1200), polishing with abrasive diamond paste (with grain size 3, 2 or 1  $\mu$ m), etching by 3 % Nital. [4, 5, 6].

Fig. 3 and 4 shows the microstructure of CP-W 800 steel in surface layer and in the centre. It contains ferite, bainite and martensite and residual austenite.



Fig. 3. The mikrostructure of CP-W 800 material's surface layer



Fig. 4. The mikrostructure of CP-W 800 material, centre

#### **Paper`s contribution**

The knowledges and data about higher and high strength automotive industry materials properties and formability are not widely obtainable from sources. The main paper's contribution are mechanical properties of CP-W 800 high strength steel, the results of its basic and technological tests. The sheet test specimen was to designed in compliance with standard to prevent the sliding of clamping jaws on the heads of test specimens.

#### Conclusions

The basic test and technological tests made for material CP-W 800 proved that the material is suitable for processing by forming technologies to make drawings and bended parts for automotive, electrotechnic and power generating industries. The measured ultimate tensile strengths  $R_m$  were in range from 860 to 900 MPa. The required ultimate tensile strength  $R_m$  have to be from 800 to 980 MPa and the values of tested material were from this range so the material fulfills this requirement. The measured values of ductility  $A_{80}$  were from 13,8 to 15,6 % and required ductility is minimum 12 % so the material fulfills also this requirement. The main parameter from Erichsen cup test cup height at fracture was  $h_{crit} = 11,73$  mm, which proves suitability of this material for streching".

The paper was realised with VEGA 1/0060/08 support.

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## COMPARISON OF CONVENTIONAL AND STRUCTURED ABRASIVES

Ľubica ELEKOVÁ, Zdenko LIPA

#### Abstract

This article describes two basic types of abrasive belts, which are most used in practice today. The first type is conventional abrasive, used for a long period and is currently applied because of its relatively low price. The second type described in the article is structured abrasives, which have found application mainly for their good properties (i.e. long life, constant cutting ability, and others).

#### Key words

grinding, conventional abrasive, structured abrasive, roughness

#### Introduction

Grinding is a machining method using a high number of cutting wedges. A grinding tool is characterized by irregular deployment of cutting wedges (abrasive grains), which have random orientation and hence, a randomly ordered geometry of cutting wedges.

In this article, I will focus on the description of a new method of grinding and its comparison to conventional abrasives. These abrasives are known in practice for many years. I describe a completely new method to grinding surfaces, referred to as structured abrasives.

#### **Description of Conventional and Structured Abrasives**

In practice abrasives include grinding wheels, grinding segments, abrasive belts and abrasive papers. Given the wide range of tools I will deal only with abrasive belts.

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Since the beginning, flexible grinding systems were produced in a conventional construction. These grinding tools are made of grain, resin, and the backing. Abrasives are applied chaotically on the surface and are characterized by gradual wear-cutting edges as shown in Figure 1.



Fig. 1. Wear of conventional abrasive belt [3]

Currently there are many non-conventional grinding systems on the market. One of them is a product from  $3M \ ^{TM}$  called Trizact - micro replication abrasives. The belt's surface consists of precise structures uniformly applied to the backing - providing a very even distribution of minerals. These abrasives are produced by creating small three-dimensional structures. The structures are applied on the surface. The synthetic resin puts together the abrasive structure [3].

Once the surface of a traditional abrasive belt is worn away, the belt needs changing. Using structured abrasives provides another new layer allowing the same quality grinding. Grinding power is increased because there is still a new layer opening the structure like a pyramid. This is ensured by the action of huge numbers of cutting wedges on the surface of the cut material (Fig. 2).



Fig. 2. Working life of structured abrasive belt [3]

The process continues until the material is no longer reaching the backing. That means the structured abrasive has a longer life than the conventional graded abrasive with a usefulness of over 95 %.

Figure 3 shows the macrostructure of these two abrasives:





Structured coatingRandom coatingFig. 3. Macrostructure look of structured and conventional abrasives [3]

Structured abrasives find application especially in these market segments:

- Manufacture of blades for turbines
- Production of aluminum, cast iron, and brass castings
- Manufacture of hand tools
- Production of medical implants

The structured abrasives are used especially for metals such as stainless steel, carbon steel, brass, titanium, cast iron, and chrome plating.

#### **Experiment 1 and Results**

To compare the course of time for wear of conventional and structured abrasives, an experiment was conducted. This experiment shows us the importance of the stability of abrasives. This is particularly important for the exchange of new abrasives. The roll steel section plate 17 441 (EN 10088-2) was ground. Initial arithmetical mean deviation (Ra) of the work piece was 1,24  $\mu$ m. Sample No. 1 was ground by the classic abrasive P150 (Main diameter in mm is 100 [4]). The surface was ground 5 times for 20 seconds each. The roughness after each surface grinding was measured at 4 different places. Surface roughness was measured by contact instrument TALYSURF Surtronic 3 + from manufacturer Taylor - Hobson. Graph 1 shows the average Ra results.

Sample No. 2 was ground by the structured abrasive 3M Trizact <sup>TM</sup> 237AA with the A45 grain size (Table 1). Number of grindings and measuring surface roughness was the same as for sample No.1. Graph 2 shows the results of this measurement.

The machine used for the experiment was PTX100 sander, which uses a belt size of  $100 \times 289$  mm.



Graph 1. Ability stabilization of conventional abrasive



Graph 2. Ability stabilization of structured abrasive

The graphs reveal that the cutting ability with conventional abrasives is highest at the beginning and stabilizes the abrasive as time runs. It can be assumed that the values of roughness Ra will be the same, which were measured after the fourth and fifth uses. We could say that the time abrasive has already stabilized. In structured abrasives we can see that from the beginning to the end it works about the same while cutting ability of the belt does not diminish and it is ultimately more constant.

#### TABLE OF 3M TRIZACT™ VS. FEPA GRADE COMPARISON Table 1

TRIZACT™ STRUCTURED ABRASIVES	FEPA P EQUIVALENT GRITS				
Δ3	P3500				
A5	P3000				
AG	P2000				
A16	P1200				
A20	P1000				
A30	P600				
A40	P500				
A45	P400				
A60	P320				
A65	P280				
A80	P240				
A90	P220				
A100	P220				
A110	P180				
A130	P150				
A160	P120				
A300	P80				
A400	P60				

#### **Experiment 2 and Results**

Structured abrasives 3M <sup>™</sup> Trizact are presented for customers as "a way to dramatically cut finishing costs". Experiment 2 was done to verify this claim.

The roll steel section plate 17 441 (EN 10088-2) was ground and initial arithmetical mean deviation (Ra) of the work piece was  $1,02 \mu m$ .

Sample No.1 was ground with classic abrasive belt size sorting: P150, P220 (Main diameter in mm is 68), P280 (Mean grain size  $d_{s50}$ -value in  $\mu$ m 52,2 ± 2), P320 (46,2 ± 1,5) and P400 (35,0 ± 1,5) [5]. The surface was ground in 20 seconds. The roughness after each surface grinding was measured at 7 different places. Surface roughness was measured as in Experiment 1 by contact instrument TALYSURF Surtronic 3+ manufactured by Taylor - Hobson. Graph 3 shows the average Ra.



Graph 3. Grinding with structured abrasives

Conventional abrasive P150 was used for sample No. 2 in the first step. 3M Trizact TM 237AA in grains A30, A16 were used for the following steps. Number of measuring surface roughness was the same as for sample No.1. The results of this measurement are shown in Graph 4.



Graph 4. Grinding with conventional abrasives

Graphs 3 and 4 show that with conventional abrasives it is necessary to use 5 kinds of abrasives to achieve roughness,  $Ra = 0.31 \mu m$ . While using a structured abrasive  $Ra = 0.23 \mu m$ , with only 3 kinds of abrasive belts being necessary.

#### **Results:**

*Conventional abrasives* Ra =  $0.31 \mu m \rightarrow 5$  kinds of abrasives  $\rightarrow 5$  stages

#### Structured abrasives

Ra = 0,23  $\mu$ m  $\rightarrow$  3 kinds of abrasives  $\rightarrow$  3 stages  $\rightarrow$  less time used for surface finishing  $\rightarrow$  cuts finishing costs

If we wanted to get through the classical abrasive roughness  $Ra = 0,23 \mu m$ , we would have still used abrasive P600.

#### **Own Contribution**

Own contribution to this article is to describe the structured abrasives and compare their performance with the conventional abrasives. The paper summarizes advantages of using structured abrasives. The primary advantages were confirmed by experiments.

#### Conclusion

Structured abrasives are increasingly used in practice. It is mainly due to its undeniable advantages. This abrasive saves and reduces working time and guarantees cutting costs. The consistency of the unique pyramid surface of Trizact structured abrasives, both in size and wear rate, delivers such a predictable, consistent level of abrasive performance, as confirmed by Experiment 1.

Results of Experiment 2 confirmed that structured abrasives reduce the finishing process – in fewer stages – in shorter sequence – with less operations.

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### THE APPLICATION OF MASTERY LEARNING IN THE TEACHING PROCESS

Helena HOLOŠOVÁ

#### Abstract

The teaching method of mastery learning is focused on the process of mastering small units – modules of the educational material to which prescribed material is divided. This paper deals with analysis and evaluation of the results obtained in the subject Physics I, teaching using the mastery learning approach in comparison with the results of the traditional teaching method. As this paper will demonstrate, teaching Physics I via mastery learning led to higher effectiveness because the students of the experimental group have been much more successful than the students of the control group with the traditional teaching method applied.

#### Key words

pedagogical research, mastery learning, modules of educational material, teaching process, mastery learning in Physics I, analysis and evaluation of didactic test

#### Introduction

Scientific and technical progress give way to the discovery of new information. Our students are expected to acquire a lot of new knowledge and skills. Although an engineering education places more emphasis on individual learning, working with literature, projects processing, laboratory exercises, and so on, it is still possible to improve the level and effectiveness of conventional lectures and exercises while applying new teaching methods. One such method is mastery learning. To proceed more efficiently it seems useful to work with small groups of students built up on the multiple intelligences theory [3].

This article deals with students' results achieved by tasks solved through didactic tests.

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#### **Mastery Learning and its Applications**

For the application of mastery learning in university courses we must take into account the different conditions of the educational process. The teaching process is usually divided into lectures, exercises, laboratory exercises, or practice. Educational material of one term is split from 1 to 4 modules according to the themes. The mastering of small units – modules of educational material allows students further individual study [2].

#### **Application of Mastery Learning in the Subject Physics 1**

The study of Physics for The Faculty of Materials Science and Technology in Trnava is divided into two parts. Lectures are given in the first and second year of study. Teaching Physics I, which is included in the summer term of the first year of studies, is carried out with the format: 2 hours of lectures and 2 hours of exercises. The exercises are used to improve understanding and mastering the prescribed teaching material. The general characteristic is that in the study of physics and other science subjects, students have many problems with the understanding of the prescribed material and it is therefore necessary to seek new, more effective ways of teaching [6]. One of the reasons that cause problems in the study of science (i.e. physics, mathematics, chemistry, as well as many technical subjects) is a low redundancy in the language of these subjects compared with the redundancy of natural language [1]. The core problem is that misunderstanding the importance of one or even several words in a sentence of natural language understanding, does not prohibit one from comprehending the sentence as a whole.

In physics, or other natural or technical subjects often incomprehension of one word of content results in the misunderstanding of the entire meaning of the context. Understanding the context of natural language in this respect is much easier. The aim of mastery learning in the subject Physics should be, first of all that students should thoroughly understand the fundamental concepts and technical terms and be able to utilize knowledge of Physics in the subsequent subjects.



Fig. 1. Structure of work modules in the subject Physics I

#### **Empirical Research**

**Hypothesis:** Through mastery learning, students of the experimental group achieve better results in the didactic test focused on understanding than traditional classroom students.

#### **Identification of the Sample of Respondents**

The basic sample consisted of the first year students MTF STU (study programs Applied Informatics and Automation in Industry, Quality of Production, Industrial Management). Two groups were chosen from this basic set at random. According to the results of the written work, the group of students had been divided into control and experimental groups as such:

Experimental group: 40 students.

Control group: 28 students.

#### **Research Methods**

Research methods used for statistical description and verification of the hypothesis was natural pedagogical experiment, didactic test, and Mathematics - Statistical methods (F-test and t-test)

#### **Realization of the Research**

Research was carried out in normal conditions for the MTF STU in the exercises of Physics I in two groups:

Control group: traditional teaching.

Experimental group: the teaching method of mastery learning.

#### **Statistical Description**

The students were given a didactic test, so-called NR test, at the end of the experimental research. The educational test was aimed at the understanding by Niemierko taxonomy of educational objectives, with a maximum of 26 points. Results of students in the experimental and control groups in the didactic test with a maximum of 26 points were the following:

#### STATISTICAL VALUES OF THE DIDACTIC TEST

Table 1

Group of students	Control	Control	Europinontal		
	+ Experimental	Control	Experimental		
Statistical characteristics					
Arithmetical average	57,9 %	43,5 %	72,3 %		
Variance	34,77	24,5	45,04		
Standard deviation	5,8	4,9	6,7		
Variational interval	71,15%	80,8 %	61,5 %		
Maximum	94,25 %	88,5 %	100 %		
Minimum	23,1 %	7,7 %	38,5 %		

Control group:  $\overline{x} = 43,5 \%$  (11,3 points).

Experimental group:  $\overline{x} = 72,3 \%$  (18,8 points).

The difference in the score: 28,8 %.

As a standard procedure for the data processing, providing the normality of the data distribution, we used F-test and t-test to compare the variances and the mean values, respectively [5], [7].

T-test confirmed, that at the 0.05 level of significance by means application of mastery learning in the exercises in the subject Physics I, students of the experimental group achieved better results than the control group students with traditional teaching.

#### Benefit

The application of mastery learning in physics represents one of the ways to enhance teaching effectiveness of this subject as to streamline and improve the quality of the educational process. This contribution highlights the appropriateness of the use of activation methods in the teaching process. The mastery learning method promotes a better understanding of students' ability to apply knowledge gained in Physics, thereby increasing the readiness of students to study technical subjects.

#### Conclusion

Due to their ability to master each module, students are highly expected to demonstrate superior knowledge and skills, gradually increasing their confidence in their own abilities (an achievement that occurs rarely where traditional teaching methods are practiced).

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### ANALYSIS OF DROP FORGING IN CLOSED DIE USING COMPUTER SIMULATION

#### Mária KAPUSTOVÁ

#### Abstract

This paper is focused on analysis of materials as they function in cavity filling during closed die forging. These analyses were completed using simulation software, SuperForge, during the production of forging with the shape of a toothed wheel determined for the gear box. The numerical simulation allowed for the optimal forging process, especially from the fold creation elimination perspective.

#### Key words

drop forging, forging without flash, closed die, numerical simulation

#### Introduction

The computer simulation of the forging process is very important for the forging of demanding die forging and for the application of progressive die forging methods. This simulation enables us to analyse principles of the forging process and to observe plastic flow of materials in the die cavity during its filling. Simulation software has a considerable advantage – they enable the verification of technological parameters and technical preparation of production before making forming tools and beginning the production [1,2,3].

#### Characteristics of used simulation software

The simulation software MSC.SuperForge was used in the simulation of forging in close computer simulation of 2D and 3D die forging processes with FEM or FVM methods. It is a modern simulation software with easy use that does not demand experience with FEM and enables the insertion of CAD tool geometry in STL format. The working environment of this software is similar to the Windows operating system environment and is clearly arranged for easy use. Simulation of warm forming processes utilizes elastic –

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plastic models of material behaviour. The advantage of this software is a large material database created according to strain hardness, temperature, and deformation velocity. Simulation software MSC.SuperForge enables us to observe the course of material plastic flow in tools and offers coloured depictions of deformation size and velocity, course of stress, temperature fields and contact pressures on tool surfaces during cavity filling. Numeric simulation of the die forging process consists of these phases:

- Preparatory phase of simulation creation of geometrical model of workpiece and tools (i.e. AutoCAD, Catia, etc.), choice of process kind, type of depiction 2D/3D, forming temperature, etc.
- Simulation beginning and course of forming process simulation.

The environment of this software comprises three working windows, two of them serve for entering of input data and creation of the "simulation tree". The third window is used for depiction of the simulation course and results.

#### Simulation of forging "Wheel" in closed die

Figure 1 depicts a simulated drop forging wheel. This forging when machined is used as a toothed wheel in gear boxes of agricultural and industrial machines. Output material is a rolled bar with circular section  $\emptyset$ 65 steel 16 220 (16NiCr4). This material is not heat treated, soft annealed, normalized, or hardened. It is proper for carburizing and is easily forged. It is used for over-stressed machine components with carburized surfaces (e.g. toothed wheel for gear boxes, spline



shafts, pins, etc.). Chemical composition of mentioned steel is shown in Table 1.

#### CHEMICAL COMPOSITION OF STEEL 16NiCr4

Table 1

Material	Content of	Chemical composition (%)									
	elements	С	Mn	Si	Р	S	Cr	Ni	Mo	Al	Ti
16NiCr4	min.	0,1	0,7	0,4	0,035	0,035	0,6	0,8	0,10	0,02	0,010
	max.	0,19	1,0				1,0	1,10		0,04	

The drop forging wheel is produced by HKS Forge, s.r.o. in Trnava, with the standard method of forging with flash, in common workmanship. For the purpose of reducing the waste of materials, a new technology of closed die forging was proposed. This technology represents very precise forging production according to STN EN 10243-1. Correct compensation of small material surplus is important for a flawless technological process of forging in closed die cavity. Compensation of surplus material into internal flash was also used for the aforementioned forging wheel. Forging in closed die requires precise preparation
of the workpiece, therefore, a high-powered belt saw was used for the separation of material. This saw guarantees a better quality cut surface. Round bars  $\emptyset$  65 will be cut into workpieces with batch weight 2,68 ± 0,03 kg. Length of workpiece – 105 mm is only informative. The technological process of forging in closed die consists of these operations:

- Induction heating of workpiece  $\emptyset$  65 x 105 on forging temperature 1150 °C;
- Upsetting of heated workpiece on height 40 mm;
- Blocking the shape in blocking die cavity;
- Finishing of drop forging shape in closed die cavity.

Drop forging will be produced by three strokes of crank forging press LZK 2500. The proposed process was verified by simulation software SuperForge. Computer simulation of the forging process relating to the drop forging "Wheel" requires choice of process and input data for simulation of upsetting, blocking, and finally, for the finishing process.

## **Defined Input Conditions for Simulation of Upsetting and Results**





Fig. 2. Simulation of workpiece upsetting process (on height 40mm)

## **Input Conditions for Simulation of Blocking and Results**

#### **Process 1 – process of blocking in closed die**

Press1 – Crank Press LZK 2500 Upper Die – model of Upper Die - material of tool: 19 552 Mat.No.(W. Nr.): 1.2343 - coefficient of friction : 0,25 - temperature of tool: 280 °C

Lower Die

- model of Lower Die
- material of tool:19 552 Mat.No.(W. Nr.): 1.2343
- coefficient of friction : 0,25
- temperature of tool: 280 °C

Compressed workpiece after upsetting process

- model of workpiece after upsetting
- material of workpiece: 16 220 Mat.No.(W. Nr.): 1.5714





Fig. 3. Simulation of material flow in die cavity and creation of a fold

Result of the blocking process simulation in Figure 3 confirmed incorrect plastic flow in the cavity of the blocking die. After locating a wad in the lower part of the forging, a visible

fold appeared. The reason for this is the incorrect flow of material. Therefore, a treatment in the shape of the blocking die cavity was made. The wad moved into the middle part of the forging and the radius of fillet increased from R3 to R4.

Numeric simulation allowed for the optimal shape of forging tool to be produced prior to the forging production. The simulation process shown in Figure 4 confirmed the forging cavity changing, as plastic flow of material was without folds [4, 5].



Fig. 4. Simulation of flow in arranged blocking cavity

## Input Conditions for Simulation of Finishing the Forging Shape and Results

## Process 2 – process of finishing in closed die

Press1 – Crank Press LZK 2500 Upper Die – model of Upper Die – material of tool: 19 552 Mat.No.(W. Nr.): 1.2343 – coefficient of friction: 0,25 – temperature of tool: 280 °C



Lower Die

- model of Lower Die
- material of tool: 19 552 Mat.No.(W. Nr.): 1.2343
- coefficient of friction: 0,25
- temperature of tool: 280 °C

Workpiece from blocking process

- model of blank
- material of workpiece:16 220 Mat.No.(W. Nr.): 1.5714

Results of simulation of finishing process in closed die are stated in Figures 5 and 6. Simulation confirms correct flow of material in closed die with complete cavity filling.



*Fig. 5.* The material flow in finishing tool cavity – a small surplus of material is extruded into internal flash



Fig. 6. Course of deformation and stress in finished forging

## Self-scientific addition

Forging of "Wheel" drop forging in closed die is interesting especially for its cost savings, requiring less materials and machining. Comparison of the common production method using forging with flash and production using forging in closed die is presented in Figure 7. This comparison enables us to see considerable savings of input material. Moreover, production of forging in closed die brings a reduction of forging weight [6]. The batch weight and the weight of scrap is reduced, resulting in lower material costs and overall production costs. Particular material savings are visible in Figure 7 and represent, in this case, a savings of 0,42 kg per one par to the batch weight.



Fig. 7. Comparison of present and proposed production of forging Wheel

## Conclusion

The aim of this paper was to point out the importance of simulation software for development of die forging technology and for application of new forging methods into production practice, on a particular forging wheel. Computer simulation confirmed the possibility to change the production of this forging from forging in open die to forging in closed die - without flash. New technology assumes reduction of overall production costs [7]. In this case the saving of materials is most significant because of their relatively high costs.

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## PERFORMANCE EVALUATION PROCESSES FROM THE PERSPECTIVE OF CURRENT TRENDS

## Renata NOVÁKOVÁ, Ondrej KUSÝ

## Abstract

This contribution is focused on the summary of knowledge on the measurement of business processes and current trends in business practice. Part of this contribution is an overview of the most common practices, but also discusses some lesser known methods. Overall, closer attention is given to the Balance Scorecard (BSC) method as it is one of the most utilized in measuring the economic performance of business processes.

## Key words

performance process, performance measurement, balance scorecard, performance management

#### Introduction

In the case of performance measurement, no two organizations are identical, whether it be size, focus, or number of employees, there are no clearly standardized methods for suitable monitoring of their performance. If we want to talk about trends, we primarily focus on monitoring and evaluation of business processes. Procedural understanding is declared as such by the standards of ISO 9000:2000, which assumes base orientation on performance measurement processes. There is a direct dependency between performances of business processes are the basic assessment of business performance.

Under the performance measurement process, it is vital to understand certain activities in order to provide objective and accurate information about the individual processes. This ensures that these processes could be the owner of the process continuously, meaning operatively controlled in order to meet all the requirements imposed on processes [1].

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# Methods for measuring performance of processes from the perspective of modern management

Before we begin in more detail to address this topic, we should consider it necessary to specify that there are conflicting literary sources interpreted differently by various authors, including the concept of performance itself.

If we evaluate an enterprise based on performance, it is necessary to define what performance means to us. In the literature there is no single definition to define the concept of performance. Sometimes the performance is usually understood as rate utilization of resources, but overlaps with the concept of productivity, which is defined as the ratio of output to input. In the EFQM model, performance is defined as rate achievement by individuals, groups, organizations, and processes.

Modern management emphasises different performance measurements. In practice, these measurements do not have the necessary degree of objectivity and accuracy. The performance evaluation process is intended to give owners the right information to process a real-behavior process. Measuring performance quality management systems then provide information to senior management of organizations on how this system performs its basic functions.

The management organization is essential to measure (as it is possible to control what can be measured). There are several types of measurements in the organization - the measurement of stakeholder satisfaction, measuring the effectiveness of a quality management system, organization and performance measurement processes, measuring performance of suppliers, the effectiveness of training, the cost of quality, and so on. A key measurement in an organization is designed to measure the performance of the organization. These measurements determine the degree of obtained results. [2.]

In performance measurement processes the top managers act as the guarantors or assurance part of the process, while middle managers are process owners, and employees are responsible for collecting and processing information. The results of performance measurement processes directly affect the motivation of all employees, carrying out the processes and activities. If a company were to link performance measurement processes with payroll, we can say that employees are directly involved in the performance process, which creates good preconditions for process improvement either through corrective and preventive actions or performance improvement projects organization. The experience of performance measurement processes shows that dealing with such difficult operations can only be done when doing simple things together, methodically, and with the support of software tools.

Simplicity lies in defining realistic and measurable goals within reason as well as mutual relations. It is especially useful if the performance measurement process is carried out by a responsible owner of a process and the collection of information by a responsible employee.

Teamwork should be based on the interests of an owner's process of objectivity of information, creative working atmosphere, and mutual trust. Among the known methods of performance measurement processes are: the discrepancy concerning the recording method, method of performance measurement derived from the process capability index, measuring the performance of processes using Six Sigma methods, and competence of the Balanced Scorecard. Each of these methods includes a sequence of steps for measuring performance of processes [3].

Currently implementing new approaches to monitoring the performance of firms, although traditional, can be complemented by additional aspects. The modern method of performance evaluation is based on the premise that the firm is efficient if it is able to achieve predefined strategic objectives.

In practice, two basic approaches are applied:

- 1. The first is based on the definition and evaluation of strategic objectives for the four main areas (financial, customer, internal processes of learning, and growth), which has taken the English name of Balanced Scorecard, a system of balanced indicators.
- 2. The second approach is based on measuring the performance of organizations through performance measurement processes, the so-called Performance Management.

The common denominator of both approaches is to move away from evaluation of business performance only on financial indicators and instead concentrate more on the extensive use of other types of indicators (e.g. qualitative and time). The performance of the organization can monitor and also use modern methods to manage. Indirect methods can evaluate the performance of a specific person, and use process analysis to identify useful and useless work outputs of individual people and teams.

Based on the classic arguments of critical performance measurement systems since the early 90s, the formulation of requirements for a performance measurement system was established to satisfy the following criteria:

- Companies should establish such systems of performance measurement to support their strategy;
- Performance measurement systems should include non-financial indicators, which indeed complement the financial indicators, particularly with regard to customer perception and performance of internal processes;
- The general system of performance measurement should be decomposed into sub-meters to allow companies to transfer targets better managed by subs [4].

#### **Comparison of methods for performance evaluation**

If we further specify the methods most commonly used to assess, the processes need to be divided into two basic groups. The first group will consist of methods that were developed in research and consultancy practice. The second group will be formed by methods which have arisen on the ground.

The methods are classified in Table 1, which contains 10 methods developed in a manner of expert advisory practice and 4 that are developed by practice. These methods are much more entailed, but among them there are only very small differences because we have focused only on the comparison of the following methods.

Table 1 provides a brief overview of some of the practices' essential methods of performance measurement processes:

Table 1

Development	<b>Development Duties</b>	Methods
Science and /	Developed based on research	- Data Envelopment Analysis
or consulting	work in universities or	- Performance Measurement in service
experience	institutions.	Businesses
	Most large-scale tested in	- Balanced Scorecard
	practice or improved application	- Tableau de Bord
	in practice.	- Productivity Measurement and
		Enhancement System(PROMES)
		- Performance Measurement Model
		- Performance Pyramid
		- Quantum Performance Measurement
		- Concept Ernst and Young
		- Business Management Window
Corporate	Development of performance	- Concept J.I. Case
Practice	measurement concepts well suited to their needs addressing	- Concept Caterpillar
	issues of performance	- Concept Honeywell Micro Switch
	management and measurement specific to particular firms	- Hewlett-Packard concept of the internal market

These 14 methods for measuring performance are compared using the relevant criteria. Each of these benchmarks describes the important aspects necessary to the function of performance measurement methods:

- 1. Continuity of the concept of vision and strategy (link to strategic planning), and rules for the stated aim of the plan.
- 2. Use differentiation to stakeholder goals.
- 3. Addressing multiple levels of performance.
- 4. Description of rules for management indicators (creating and maintaining variables).
- 5. The modalities of measurement (measuring cycles, the measurement points).
- 6. Procedure for consideration and performance analysis of derogations.
- 7. Addressing aspects of incentives and remuneration.
- 8. Integrating the concept of reporting.
- 9. Institutional framework (process and participants in PM).
- 10. Application tools in the PM.
- 11. Link to performance management and integration aspects of continuous improvement [4].

Criterion	Continuity	Differenti-	Addressing	Manage-	The	Assessme-	Addressing	Concept	Institutio-	Applica-	Integration
Concept	of vision	ation of	multiple	ment	modalities	nt and	motivatio-	Reporting	nal	tion tools	Preforman-
	and strategy	stakehol-	levels of	indicators	of	analysis of	nal aspects		framework	in the PM	ce Manage-
		der-oriented	performan-		measurem-	performan-					ment
		goals	ce		ent	ce deviations					
Data Envel.						deviations					
Analysis								1			
PM in Service											
Business											
Balanced											
Scorecard											
Tableau											
de bord											
ProMES											
PM – model											
Performance											
Pyramid											
Quantum PM											
Concept											
Ernst&You											
Business Mgt.											
Window											
Concept											
J.I. Case								1			
Concept		l						l			
Caterpinar				1						_	
Honeywell				J			-			J	
C Hewlett											
Packard								1			
i ackaiu											

## TABLE COMPARISON CONCEPTS OF PERFORMANCE MANAGEMENT [5]Table 2

Black	Conceptually extensively reflected
Gray 75%	Conceptually reflected
Gray 50%	Conceptually, hardly reflected / only conditionally
Gray 25%	Conceptually NOT TAKEN
White	Not assessed for missing information

## Advantages and disadvantages of the methodsof Balance Scorecard

The concept of Balanced Scorecard (BSC) has recently came to the forefront as an interest to senior managers. It allows them to introduce a performance management system, focusing on the organizational and personnel departments, and what the company expects from them. It also regularly and systemically evaluates whether the company is successful in meeting its objectives.

Balanced Scorecard is a strategic performance measurement system that arose in the early 90s thanks to the American experts Robert Kaplan and David Norton. Major changes that have been brought on by BSC were the extension and connection of measuring business performance from purely financial indicators rather than indicators from other perspectives of the enterprise's activities.

Objectives and indicators are based on the vision and business strategy. Its founders have proposed four BSC perspectives: Values (financial), customer, internal business process perspective, and learning and growth. [6.]

BSC Development is a systematic business process. It enables the creation of consensus and clarifies how to implement the mission and strategy of each SPJ. The teamwork of senior management plays an important role as the BSC-making process consists of the following steps [7]:

- 1. Establishment of strategic objectives
- 2. Link strategic objectives' chain of cause and effect
- 3. Choice and design parameters
- 4. Setting targets
- 5. Approval of strategic actions

The processing of these steps forms the core of the implementation of BSC.

The problem is that this method, as the authors themselves point out, is not applicable to the desired result always and everywhere. It is said that this method was shown to fail when an organization did not produce the desired effects. Many critics also argue that they are practiced in the organization of certain forms of measurement and evaluation is not always desirable to make radical and extreme change. In any case, however, the BSC method is considered a method that could bring a system into monitoring with evaluation indicators, which are part of different perspectives.

## Own contribution to the subject

The authors pointed to the contribution of different options and methods of performance measurement processes recorded in literary sources, but not always economic practices used. An important benefit is also a demonstration of the various links and functionality for comparing methods from those who have practiced them.

#### Conclusion

This article discusses measuring the performance of business processes in practice. According to the findings of this measurement, the most used method is Balanced Scorecard, but Slovak managers, being among a few exceptions, found this method did not work. Many businesses where this method is known do not use it because of newer methods of performance evaluation, which suits them better. This system does not have long to satisfy the requirements for measuring performance, but there is no effort to change the past and its traditional approaches to corporate governance.

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## **RESEARCH PAPERS** FACULTY OF MATERIALS SCIENCE AND TECHNOLOGY IN TRNAVA SLOVAK UNIVERSITY OF TECHNOLOGY IN BRATISLAVA

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## **RE-ENGINEERING TUBE PRODUCTION THREE-DRAW SINGLE-RUN TECHNOLOGY**

# Martin RIDZOŇ, Andrej MALÍK, Jozef BÍLIK

## Abstract

This contribution discusses the re-enginnering production of precision seamless steel tubes, cold drawn three-draw single-run technology. The aim of the experiment is to verify the possibility of hauling rolled tubes (material E355) of size  $\emptyset$  70 x 6,3 mm without intermediate re-crystallising annealing to obtain the final size  $\emptyset$  44 x 3 mm, in terms of mechanical properties for tensile testing of the base and in terms of internal pipe surface roughness.

## Key words

three-draw single-run technology, mandrel drawing of tubes, reduction, material E355, surface roughness

## Introduction

It's known as drawing tubes with cold-forming means, whereby the starting material (pipe) ductile beams in such a way that reduces the cross-section, resulting in thinner or thick wall tubes, and increases its length. Forming takes place in a number of routes, depending on the source and ultimate size of the pipes. An important role performs a proportional reduction in choice for the individual sections because the uneven distribution has resulted in reduction of tension and the deformation or cracks by drawing, which are then reflected on the surface roughness of tubes.

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#### **Experiments**

The experimental material is non-alloy structural steel grade E355 (see Table 1), which were subsequently produced with a hot rolled pipe diameter  $\emptyset$  70 x 6.3 mm.

С	0,1800	Mn	1,1800	Si	0,2300	Р	0,0150	S	0,0140	Cr	0,0500
Ni	0,0800	Мо	0,0200	Ti	0,0020	V	0,0030	Nb	0,0010	Ν	0,0090
Al	0,0230	Zr	0,0020	Са	0,0022	As	0,0060	W	0,0100	Zn	0,0040
Cu	0,2000	Sn	0,0160	Pb	0,0010	0	0,0032	Sb	0,0040	Ce	0,0010

CHEMICAL COMPOSITION OF EXPERIMENTAL MATERIAL E355 Table 1

The experiment was conducted on pipes with a rolling temperature at 830 ° C according to the following procedure: Deburring - chemical treatment - drawing tube at a fixed mandrel roller, and other operations. Technological parameters of the drawing tube size  $\emptyset$  70 x 6.3 mm in size  $\emptyset$  44 x 3 mm are listed in Table 2. Detailed view of the internal pipe surface is shown in Figure 1.

## TECHNOLOGICAL PARAMETERS OF DRAWING TUBES (THREE-DRAW SINGLE-RUN TECHNOLOGY)

Table 2

O.D.	W.T.	Dĺžka	L hrotu	hrotu	O.D.	W.T.	r	I.D.1	I.D.2	r W.T.	r O.D.	predĺž	L po ťahu
70,00	6,30	4300	300	40	57,00	5,00	35,21	57,4	47	20,63	18,57	1,54	6174
57,00	5,00	6174			50,00	3,75	33,29	47	42,5	25,00	12,28	1,50	9255
50,00	3,75	9255			44,00	3,00	29,08	42,5	38	20,00	12,00	1,41	13050
							69.35						

O.D. – outer diameter tube [mm], W.T. – wall thickness tube [mm], L mandrel – mandrel length [mm], r – reduction, length – length tube, I.D.1 – internal diameter before drawing, I.D.2 – internal diameter after drawing



*Fig. 1.* Detail of internal tube surface, material E355 a) Ø57x5, 1. - draft, b) Ø50x3,75, 2. - draft, c) Ø44x3,3. - draft

#### **Evaluation experiment**

Sequence sampling for mechanical testing of tubes:

- 1.) After first draft from size  $\emptyset$  70 x 6,3 mm in size  $\emptyset$  57 x 5 mm
- 2.) After second draft from size  $\emptyset$  57 x 5 mm in size  $\emptyset$  50 x 3,75 mm
- 3.) After third draft from size  $\emptyset$  50 x 3,75 mm in size  $\emptyset$  40 x 3 mm

Measured values of mechanical properties of pipes to individual drafts are shown in Graph 1 and values of the internal pipe surface roughness after different drafts are shown in Graph 2. Graph 2 shows the mean values of measured surface roughness. Surface roughness measurements were performed on the device Taylor Hobson Surtronic 3 +.



Graph 1. The resulting measured values of mechanical tube

0 - rolled tube (intermediate input), 1s - first draft, 2s - second draft, 3s - third draft



**Graph 2.** The resulting measured values of surface roughness tube Ra (Arithmetical deviation of the assessed profile) [µm]

The required mechanical properties according to EN 10305-1, thus forming and heattreated steel E355 +C (+C = no heat treatment after the last cold forming) are: Rm min 640 MPa, A5 min 4%, and the resulting roughness Ra 4  $\mu$ m. Roughness measurement was carried out in accordance with EN ISO 4287th.

## Conclusion

A comparison of mechanical values imposed by EN 10305-1, where Rm = min 640 MPa and A5 = min 4 %, and the resulting roughness Ra 4  $\mu$ m measured mechanical values obtained by static tensile test where Rm = 928 MPa, A5 = 5,9 % and measurement of internal surface roughness tubes Ra 0,442  $\mu$ m. This shows that the material meets the requirements in standard EN 10305-1 and is suitable for further forming operations.

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## **RESEARCH PAPERS** FACULTY OF MATERIALS SCIENCE AND TECHNOLOGY IN TRNAVA SLOVAK UNIVERSITY OF TECHNOLOGY IN BRATISLAVA

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## METHODS AND TOOLS FOR SUSTAINABITILY MEASUREMENT

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#### Abstract

The complexities involved in measuring changes in social, environmental and economical capital are enormous and there is no unique standardized method for measuring sustainability. Various measurement methods have been proposed. However, it is possible to detect some common features, which all have their origin in the UN conference on Environment and Development which took place in Rio de Janeiro in 1992. In the present article the authors outline methods and tools used for measuring sustainability.

## Key words

sustainability, measurement methods, measuring tools

## Introduction

Perspectives of sustainability differ in regard to the relationship between human development and nature. To measure sustainability, it is necessary to integrate spheres that have traditionally been measured separately. The main objective of measuring sustainability is frequently to monitor the evolution of indicators over time. Indicators help us to choose targets for the future and to determine how far we are from where we want to arrive.

#### **Sustainable indicators**

**Indicators** represent a specific phenomenon that cannot be measured directly. They are obtained by the combination of different variables (e.g. energy intensity as energy consumption per capita, etc.). They should generally give enough information for a subjective

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evaluation of the problem. This evaluation is usually made by comparing the value of the indicator to a threshold value.

Sustainability indicators are tools that communicate information of a complex phenomenon such as gross domestic product (GDP), emissions of carbon dioxide per person, etc. They can be calculated per period and/or per area and allow one to evaluate the progress of a region/city/country towards a specific goal.

To allow policy assessments, it must be clear which value of the indicator is more or less desirable. This requires a gradient that can have different forms:

- **Nominal scales** consist of only two values such as yes and no. Nominal scales provide little meaningful information, but are easy to agree on in case of controversial themes. For example, whereas the effectiveness of a national sustainability council may be questionable, their existence is easy to report.
- **Ordinal scales** are based on a hierarchy of qualitative states, e.g. the quality of training of personnel, the transparency of decision-making processes or the possibilities for public participation in them. To apply these scales properly, the hierarchy has to be made explicit and the relative distances between the different classes defined. However, these distances are often based on value judgments and not easily agreed on.
- **Cardinal scales** give quantitative information. If sustainable development goals are linked to a quantitative target, the distance towards this goal can be measured. Such indicators are called "performance indicators". To derive the scales, quantified targets have to be agreed on.

Cardinal performance indicators are preferred, with ordinal indicators providing an alternative. In general, indicators have to be:

- General, i.e. not dependent on a specific situation, culture or economic organization,
- Indicative, i.e. truly representative of the phenomenon intended to be characterized,
- Sensitive, i.e. they have to respond early and clearly to changes in what they are monitoring,
- **Robust**, i.e. with no significant changes in the case of minor changes in the methodology or improvements in the database.

Sustainable development indicators need a benchmark that gives them an objective. The assessment process can then begin, in which sustainable and unsustainable tendencies are measured.

The main framework models for the integration, design and presentation of indicators are:

- PSR model
- DPSIR model
- Framework of themes and sub-themes.

## **PSR MODEL**

The Pressure-State-Response (PSR) framework model is used by international institutions – especially the OECD. The indicators are structured according to three basic categories (Fig. 1).

- **Pressure** refers to human activity that creates some type of pressure on natural systems such as emissions of greenhouse gasses, production of waste, etc.
- **State** refers to the changes in the quality and in the quantity of natural resources, and the measure of these changes evaluated in a certain period of time. This gives us the "state" of

the natural system. Examples of state indicators include global mean temperature, threatened species and concentrations of substances.

• **Response** refers to the answer in terms of policies or specific actions that were taken as a response to changes detected in the natural system such as recycling rates, international commitments, etc.



Fig. 1. PSR model

## **DPSIR MODEL**

An enlarged version of this model is called DPSIR (Driving forces – Pressure – State – Impact - Response). It widens the PSR framework by adding the Driving forces of Pressure and Impacts of state on society (see Figure 2).



Fig. 2. DPSIR model

## **CSD FRAMEWORK**

This framework, which was drawn up by the UN World Commission on Sustainable Development (CSD), recognizes four key dimensions of high priority:

- Environmental
- Social
- Economic
- Institutional.

Each of these dimensions is divided into themes and sub-themes that reflect the main priorities established in the chapters of Agenda 21. Finally, each sub-theme leads to one or more indicators. The set of indicators obtained presents the four dimensions, 15 themes and 38 sub-themes.

Table 1

SOCIAL D	IMENSION	Environment	TAL DIMENSION
Themes	Sub-themes	Themes	Sub-themes
Justice	Poverty	Atmosphere	Climate change
	Equity		Ozone layer
Health	Nutritional state		Air quality
	Mortality	Land	Agriculture
	Sanitation		Forests
	Drinking water		Desertification
	Health benefits		Urbanization
Education	Educational level	Oceans and coasts	Coastal areas
	Illiteracy		Fisheries
Housing	Living conditions	Freshwater	Water quantity
Security	Crime		Water quality
Population	Population dynamics	Biodiversity	Ecosystems
			Species
Industriai	L DIMENSION	Economic	DIMENSION
Themes	Sub-themes	Themes	Sub-themes
Industrial framework	Strategies for sustainable development	Economic structures	Economic development
	International cooperation		Trade
Institutional capacity	Access to information		Finance
	Communications	Patterns of consumption and	Energy use
	infrastructure	production	
	Science and technology		Production and management
			of waste
	Preparation for and aid		Transport
	capacity in natural disasters		

## CSD THEMES AND SUB-THEMES

#### **Measurement tools**

In the following passage we are introducing some of the best known tools used for measuring aspects of sustainable development.

## Life cycle assessment - LCA

LCA is a tool that allows the total environmental impact of a design or a product to be analysed. It can be used during different phases of the design process. It can also be used to optimize the environmental performance of a design. LCA quantifies the environmental impact of a certain product or system. The LCA of an existing product or system can set the bottom line for a new design. The product system encompasses all phases of the product life, such as:

- Raw materials acquisition and refining
- Processing and production of product and product equipment
- Distribution and transport
- Use, re-use and maintenance
- End-of-life: landing, incineration, litter and recycling.

In all these phases, the contribution of the product to different forms of pollution (e.g. the greenhouse effect, ozone layer depletion, acidification etc.) is calculated.

## Ecological footprint

One of the best known sustainable development indicators is the ecological footprint. This method produces an index that gives a quantitative reference of the way of life of individuals, a certain group of persons, a region or a country. This index is not measured in monetary units, but in surface area. The ecological footprint is the quantity of land that a person needs, directly or indirectly, to:

- Consume products and services
- Produce resources and assimilate waste.

This in turn means the land needed to produce the food and the materials for housing, buildings, reads, infrastructure and the trees that regenerate the  $CO_2$  produced by burning fossil fuels.

The name *ecological footprint* therefore refers to the land area that people, a country, a region or a city would use if they were sustainable.

The size of the ecological footprint depends on a number of factors, including:

- The development and lifestyle of the subject
- The quality of utilized resources
- The utilized technology
- Social and economic organization.

## Conclusion

Measuring sustainability can be crucial for decision-making in a variety of ways. It can translate physical and social science knowledge into manageable units of information that can facilitate the decision-making process. It can help to measure and calibrate the process towards sustainable development goals.

Sustainable Development is a framework for a long-term vision of sustainability in which economic growth, social cohesion and environmental protection go hand in hand and are mutually supporting. In this point of view we can consider sustainable development as one of the measures for the solution of actual economical crises, due to equal consideration of social-economical and environmental development of society.

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## THE ROLE OF NATURAL SORBENTS AT THE L'UBIETOVÁ REINER AND PODLIPA DUMP-FIELDS

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## Abstract

This article presents the results of an environmental study at the Lubietová Podlipa dump-field. The distribution of the selected elements and heavy metals is unequal and depends on the geochemical behaviour of the elements (mainly on their migration ability). The present natural sorbents are predominantly clay minerals (illite, muscovite, caolinite, smectite) and hydrogoethite. The clay minerals are good sorbents of K, Na, Li, Al, Rb, Sr, Hf, V, Cr, Ti, W, Zr, Nb, Ta and Th, and for the hydrogoethite of Cu, Zn, Mo, Mn, Mg, P ( $\pm$  Fe, Cd, Co, Ca). In the case of the Fe, As, Sb, Ag, Pb, Zn, Mn, Mo, Bi, U proved also free sorption capacity.

## Key words

dump-field, heavy metals, sediments, clay minerals, sorption

#### Introduction

The Ľubietová – Podlipa deposit is among important deposits in the suroundings of Banská Bystrica. It is situated in the northeast part of the Slovenské Stredohorie Mountains which also include the north part of the Pol'ana neovolcanic massive and the north part of the Vepor Mountains. According to archeological findings, copper from the surface cementation zone in the surroundings of Ľubietová was exploited already in the time of the Bronze Age (Koděra et al., 1990).

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Ore bodies, formed mainly by ankerite –  $Ca(Fe,Mn,Mg)(CO_3)_2$  and siderite –  $FeCO_3$ , are localised predominantly in acid crystalline rocks and in series of the Permian age. The main ore minerals are chalcopyrite –  $CuFeS_2$ , tetrahedrite –  $Cu_{12}Sb_4S_{13}$  (often Ag-bearing) and pyrite –  $FeS_2$ . A substantial part of the territory is built by Permian rocks and, as is typical for Permian terraines, increased radioactivity of the rocks was described. In the locality it is possible to also find numerous rare secondary minerals [libethenite –  $Cu_2(PO_4)(OH)$ , brochantite –  $Cu_4(SO_4)(OH)_6$ , langite –  $Cu_4(OH)_6(SO_4).2H_2O$ , malachite –  $Cu_2(CO_3)(OH)_2$ , azurite –  $Cu_3(CO_3)_2(OH)_2$ , etc.].

Weathering of the reactive minerals first under acid conditions mobilises the heavy metals and numerous additional elements. This process causes contamination of the landscape components. A pH decrease in the technogenous sediments of the Cu-deposit at Ľubietová affects a heavy metals release (Cu, Fe, Cd, As, Sb, Pb, Zn, Mn, Ni, Co) from the solid phase, where are they present in the form of less soluble minerals or in a sorption complex to groundwater or to surface water. Resistance of the landscape components against heavy metal contamination is significantly conditioned by various natural sorbents (e.g. clay minerals and hydrogoethite). They form a natural geochemical barrier, on which the precipitation of the metals to stable bondings is realised. Utilisation of the present natural sorbents could be a very good method of remediation.

As very good sorbents for remediation, it is possible to utilise clay minerals (and zeolites). These predominantly crystalline alumosilicates with foliated texture, usually have negative surface charges (Kozáč, 1969) and therefore they are able to fixate Ca(II), Mg(II), K(I), Na(I), Al(III), Mn(II) cations and heavy metal cations on their surface. These cations could be substituted by other cations (Čurlík, 2003).

Hydrogoethite - FeOOH.H<sub>2</sub>O ("limonite") can also be a very good sorbent. It is formed under weathering conditions by oxidation of Fe containing ores and of some mafic rockforming minerals. Fe-hydroxide, which originates during the hydrolysis of FeSO<sub>4</sub>, forms a well coagulating hydrosalt. The precipitated gel is partly dehydrated and results in Femonohydrate. As hydrogoethite has negative surface charge and enormous reaction surface, it is predetermined to be an excellent natural heavy metal sorbent.

#### Experiment

## Sampling

The sampling was done during the summer months in 2007. Twenty-three samples of technogenous sediment (samples marked by indexes HD and A), and one sample of mud from the bottom of the terrain depression underneath the dump of the Andreas adit (sample JP-1) were collected. Each of them represent a 30 cm deep horizon and an area of 50 x 50 m (fig. 1). The grain size of the samples was below 1 cm and their weight about 30 - 35 kg. The set was supplemented by 2 samples of hydrogoethite rich rocks: A-17 and VZ-A. Sample A-17 represents several homogenised samples from sampling localities A-2, A-3 and A-5, and sample VZ-A was obtained at the sampling locality A-15.



Fig. 1. Location of samples

## Elaboration and analysis of the samples

The monomineral fractions of clay minerals were prepared according to Šucha et. al. (1991). This procedure consists of displacement of organic mater, of carbonates, of chlorides as well as of iron and manganese from the sample.

To remove carbonates from the sample pulverised to <0,16 mm grain size, 100 cm<sup>3</sup> of natrium acetate (SOTR) buffer is added to 10 g of the sample. The reacted solution is, after 2 days, segregated from the solid phase and the solid phase is dispersed by SOTR addition in an ultrasound device for 2 - 3 minutes. The sample is heated three times up to 90 °C, with 100 cm<sup>3</sup> SOTR addition, and then the suspension is decanted.

Organic matter was removed by reaction with 10 cm<sup>3</sup> of concentrated hydrogen peroxide and 100 cm<sup>3</sup> of SOTR. The mixture was heated at 70°C for 15 minutes. This procedure was repeated two times and the reacted solution was removed.

The free Fe and Mn oxides are removed by addition of 90 cm<sup>3</sup> citrate solution and by heating up to 75 - 85 °C. After 5 minutes, double additions of 2 g of natrium hydrosulphite was realised and the solution was decanted. The rest of the sample was irrigated by distilled water.

After completion of these procedures, it is possible to realize the true separation of individual clay minerals (<2  $\mu$ m fraction). The coloidal rest of the sample in 2 dm<sup>3</sup> of distilled water is, after 41 hours and 8 minutes (the time is calculated according to Stokes rule for gravitation sedimentation), decanted to beakers and saturated solution of NaCl is added. After treating, the is solution fleeced. The remaining solid is transposed to calciferous form using 1 mol.dm<sup>-3</sup> CaCl<sub>2</sub> solution. This procedure regulates the replacable cations in clay minerals.

Dialysis is used for chloride removal and the presence of chlorides is verified by addition of AgNO<sub>3</sub> solution. After removal of chlorides, the rest of the sample is drained at 30  $^{\circ}$ C.

To 0,14 g of the sample  $3,5 \text{ cm}^3$  of distilled water was added and using ultrasound the sample was dispergated. Suspension was applied using a syringe on mount glass and the sample was drained at laboratory temperature to get an oriented mount. These oriented mounts were saturated by ethylenglycol gasses in an exicator for 8 hours on a ceramic skid at 60 °C to optimise the conditions of the rtg-diffraction analysis.

Rtg-diffraction analysis of clay fraction was done in laboratories of the Geological Institute of Slovak Academy of Sciences in Bratislava using a Philips rtg-difraktograph.

The pH of the sediments was measured in  $H_2O$  and in 1M KCl lixivium, according to the method described by Lintnerová and Majerčík (2005). To 10 g of sample was added 25 ml of distilled water or 1M KCl and, after two hours mixing in the laboratory mixer, the pH and Eh were measured by pH-meter.

In samples of the technogenous sediments (HD-1 to HD-15), sediment from terraine depression beneath the Mária-Empfängnis adit (JP-1), fractions of the clay minerals (A-1c to A-8c) as well as in the samples of hydrogoethite (A-17, VZ-A), a set of 22 elements was analysed by ICP-MS analysis. The efficiency of the sorption was studied in the clay minerals and in the hydrogoethite. The samples for the sorption efficiency of clay mineral fraction (mixture of clay minerals) study were prepared by separation of the clay fraction based on dispersion of the sediment sample using distilled H<sub>2</sub>O in a volumetric cylinder (of 2 dm<sup>3</sup> volume). After 41 hours and 8 minutes sedimentation (calculated according to Stokes rule), the clay minerals containing suspension (< 2  $\mu$ m fraction) were decanted. The clay fraction was drained at laboratory temperature.

The existence of clay mineral free sorption capacity was studied using heavy metals containing drainage water from a terraine depression beneath the dump of the Maria-Empfängnis adit. To 20 g of clay sample (A-1c to A7c and A-17), 50 cm<sup>3</sup> of 5-times concentrated drainage water was added. Analyses were completed from 1 g of sample (A-1c\* to A7c\* and A-17\*) after 14 days maceration in drainage water.

The samples for Ca, Na, K, Mg, Ti, Al, P, S, Cd, Bi, Co, Ni, As, Sb, Mn, Mo, Rb, Sr, Hf, V, Ba, Li, La, Cr, W, Zr, Ce, Sn, Y, Nb, Ta, Be, Sc, U and Th determination were melted using addition of Li-metraborate and Li-tetraborate mixture and solved in diluted nitric acid. The Au, Ag, Fe, Pb, Zn and Cu was determined from 0,5 g weight of sample after leaching by hot aqua regia. The samples were analysed using ICP – MS in ACME Analytical Laboratories Vancouver Ltd. Canada.

#### Results

#### Heavy metal distribution in technogenous sediment components

Heavy metal distribution in technogenous sediments and ores of the Lubietová – Podlipa dump-field is variable (tab. 1 - 3). The distribution of individual elements reflects the primary concentration in separate parts of the dump-field as well as their geochemical relations (fig. 2 - 4), and their migration ability.

The pH of the sediments determined in water-lixivium range from 4.21 to 7.93. The pH interval of the sediments measured in 1M KCl lixivium range from 4.0 to 7.34.

## ICP-MS ANALYSES OF TECHNOGENOUS SEDIMENTS

Element	Unit									Sample								
		HD-1	HD-2	HD-3	HD-4	HD-5	HD-6	HD-7	HD-8	HD-9	HD-10	HD-11	HD-12	HD-13	HD-14	HD-15	JP-1	VZ-A
Ca		0.08	0.19	0.04	0.19	0.47	0.13	0.04	0.14	0.25	0.14	0.27	0.11	0.17	0.12	0.07	1.35	8.93
Na		0.305	0.039	0.082	0.311	0.081	0.067	0.066	0.036	0.062	0.195	0.765	0.189	0.299	0.184	0.067	0.363	0.269
K		2.49	4.27	3.96	4.29	4.29	4.14	3.48	3.47	4.23	2.44	2.43	3.24	2.91	2.79	2.66	0.62	0.28
Fe		1.33	1.64	3.59	2.67	2.26	2.14	2.58	2.37	1.84	1.12	1.38	2.25	1.61	1.66	1.01	1.19	33.22
Mg	%	0.49	0.64	0.63	0.61	1.07	1.41	0.52	0.61	0.85	0.34	0.53	0.61	0.52	0.46	0.48	1.98	0.32
Ti	, •	0.092	0.124	0.096	0.134	0.116	0.099	0.112	0.097	0.111	0.108	0.176	0.115	0.122	0.111	0.116	0.075	1.166
Al		4.44	6.45	7.12	7.97	7.11	8.03	6.65	5.68	6.89	4.27	4.99	5.63	5.15	4.91	4.45	9.31	4.18
Р		0.041	0.049	0.098	0.081	0.076	0.081	0.112	0.055	0.079	0.039	0.032	0.075	0.058	0.066	0.034	0.009	0.419
S		0.1	0.2	0.3	0.1	0.5	0.1	0.1	0.2	0.3	<1	<1	0.2	0.1	0.1	0.1	0.1	0.1
Cu		4044	2956	2243	331	7486	1977	541	>10 000	5466	390	25	6766	1388	2402	29	5	>10 000
Pb		10.4	15.8	27.9	30.3	15.6	7.9	24.1	13.5	17.8	53.6	16.1	17.7	16.2	20.1	29.8	9.1	114.6
Zn		14	211	13	19	21	23	20	15	24	36	39	19	29	21	25	44	188
Cd		<1.0	0.9	0.1	0.1	<1.0	0.1	0.1	0.1	0.1	0.3	0.2	<1.0	0.3	0.1	0.2	0.1	1.3
Bi		3.5	3.1	102.7	0.4	3.8	2.2	9.2	2.6	8.1	1.7	0.2	7.1	3.8	5.1	0.5	0.5	38.8
Со		59.3	69.9	43.2	15.5	82.5	36.2	53.6	84.5	96.3	7.1	5.1	34.9	15.1	15.5	2.1	0.5	50.1
Ni	ppm	14.2	35.6	35.5	11.5	48.7	17.1	31.6	62.1	51.9	7.8	8.5	25.8	16.6	23.2	5.5	1.5	188.6
As		60	77	397	58	138	34	294	206	130	32	7	153	85	105	11	12	1144
Sb		15.5	25.6	98.2	12.1	5.2	15.6	39.2	36.3	27.7	17.5	10.4	26.4	17.7	18.3	13.4	14.2	62.6
Mn		657	500	598	2755	486	377	517	1258	391	486	559	372	416	231	47	392	821
Мо		0.2	0.1	0.4	0.4	0.2	0.1	0.6	0.7	0.2	0.3	0.3	0.3	0.2	0.2	0.3	0.2	4.8
Au		<1	<1	<1	<1	0.1	<1	0.1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0.2
Ag		0.4	0.3	3.4	0.1	0.9	0.3	1.6	0.3	0.6	0.3	0.1	0.7	0.6	0.8	0.1	<1	4.3

Table 1

ICP-MS ANALYSES OF TECHNOGENOUS SEDIMENTS

	Table	1 (	continuation
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Element	Unit								1	Sample								
		HD-1	HD-2	HD-3	HD-4	HD-5	HD-6	HD-7	HD-8	HD-9	HD-10	HD-11	HD-12	HD-13	HD-14	HD-15	JP-1	VZ-A
Rb		93.9	149.3	148.6	166.2	147.3	134.2	131.8	119.2	151.4	103.3	88.4	123.9	108.5	103.2	119.4	12.5	12.5
Sr		23	44	57	32	33	18	35	16	23	37	40	25	33	27	21	137	218
Hf		0.5	0.8	0.8	0.7	0.7	0.9	0.9	0.6	0.7	0.6	1.4	0.9	0.9	0.7	0.7	3.2	11
V		22	33	46	26	32	43	51	29	32	22	31	36	31	30	19	5	400
Ва		349	390	350	531	315	216	410	343	269	346	391	375	370	314	377	608	74
Li		24.1	30.9	37.6	47.8	43.8	53.2	29.5	28.8	38.7	19.7	26.9	31.3	26.6	24.3	27.7	227.3	52.1
La	ppm	19.8	21.4	31.2	28.3	20.6	15.1	33.9	23.8	27.5	19.8	24.7	25.8	23.9	26.1	17.2	5.7	105.8
Cr		8.6	8.8	17.9	9.1	8.8	11.7	19.3	9.4	11.8	12.5	18.9	14.3	13.2	11.6	13.6	0.6	348.6
W		0.9	1.3	1.4	0.6	1.2	1.4	1.6	1.1	1.1	0.9	1.2	1.3	1.1	1.1	0.9	0.1	3.4
Zr		13.3	23.2	21.9	16	18.2	23.3	22.5	14.2	19.2	18.7	36.7	22.2	20.9	22.5	19.1	72.1	363.5
Ce		38	43	62	5	41	31	67	47	51	38	48	51	47	51	34	69	201
Sn		4.4	4.5	17.6	2.2	11.4	7.1	19.6	9.1	12.1	4.1	1.7	8.8	7.4	8.7	1.9	3.7	70.8
Y		4.4	5.6	6.2	9.1	4.8	4.4	7.1	5.1	5.6	3.4	6.6	6.5	5.2	5.1	3.1	16.2	74.2
Nb		2.5	2.5	2.1	2.6	2.4	1.9	2.6	1.9	2.2	2.9	4.1	2.9	2.9	2.5	3.1	45.5	38.7
Та		0.3	0.3	0.2	0.2	0.3	0.2	0.2	2	0.2	0.3	0.4	0.3	0.3	0.3	0.3	5.2	2.9
Be		2	3	3	3	4	3	3	3	2	1	3	2	2	1	5	4	3
Sc		3	4	7	4	4	4	7	4	4	3	4	5	4	4	3	2	39
U		1.4	2.6	2.5	2.5	1.7	1.3	3.1	1.5	2.1	1.1	2.2	1.7	1.5	1.6	0.9	3.4	10.7
Th		7.2	6.9	10.9	8.4	7.3	5.7	10.1	7.1	8.8	6.4	7.7	8.3	7.5	7.4	5.9	35.9	30,9

# ICP-MS ANALYSES OF TECHNOGENOUS SEDIMENTS AND OF CLAY FRACTION AND CLAY FRACTIONS AFTER 14 DAYS MACERATION IN DRAINAGE WATER CONTAINING HEAVY METALS

Table 2

	IInit								Sample							
Element	Unit	A-1	A-1c	A-1c*	A-2	A-2c	A-2c*	A-3	A-3c	A-3c*	A-4	A-4c	A-4c*	A-5	A-5c	A-5c*
Ca		0,05	0,09	0,18	0,20	0,26	0.20	0.09	0.13	0.17	0.15	0.11	0.14	0.25	0.19	0.20
Na		0.053	0.042	0.403	0.217	0.171	0.462	0.147	0.171	0.654	0.054	0.070	0.365	0.150	0.087	0.373
K		2.86	3.42	4.80	2.40	3.59	4.36	2.22	3.66	4.33	2.06	3.60	4.74	2.25	3.58	4.82
Fe		1.31	1.45	2.98	1.42	1.46	2.17	1.94	2.14	2.90	2.64	2.47	3.65	1.71	1.66	1.83
Mg	%	0.51	0.47	0.99	1.01	0.93	1.50	0.81	0.77	1.16	0.70	0.67	1.26	0.71	0.73	1.35
Ti		0.090	0.075	0.148	0.127	0.107	0.174	0.127	0.138	0.200	0.117	0.092	0.159	0.102	0.089	0.169
Al		5.99	4.98	9.26	6.76	6.05	8.75	7.33	6.64	8.77	6.88	6.35	10.22	5.87	5.42	9.49
Р		0.048	0.074	0.144	0.047	0.048	0.030	0.065	0.065	0.056	0.080	0.080	0.079	0.053	0.047	0.020
S		0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	<0.1	< 0.1	0.02	< 0.1	0.2	< 0.1	< 0.1	< 0.1
Cu		2829	1693	2345	199	574	472	828	624	857	4471	3324	3112	3150	3001	2078
Pb		28.1	63.8	229.1	130	22.4	27.9	16.0	23.1	37.4	9.6	14.9	37.8	16.9	14.8	21.9
Zn		14	18	95	21	36	62	20	25	47	23	16	27	19	18	45
Cd		< 0.1	< 0.1	0.2	0.1	0.2	0.1	< 0.1	< 0.1	< 0.1	0.3	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Bi		2.8	4.5	14.6	0.2	1.4	1.5	8.5	7.2	12.1	23.7	39.2	90.9	1.7	2.1	3.2
Co		10.4	11.3	18.3	5.9	10.3	6.4	14.0	17.0	11.0	50.0	58.3	32.1	24.4	30.4	29.6
Ni	ppm	36.8	36.0	71.8	9.8	12.2	17.0	32.1	28.3	30.4	55.0	42.4	64.4	34.0	34.1	55.4
As		162	258	628	10	19	15	71	110	105	169	237	300	60	64	105
Sb		61.6	60.1	153.2	7.1	9.2	12.6	22.4	24.0	28.0	59.5	79.3	129.8	17.2	16.3	30.3
Mn		34	64	87	212	348	133	252	334	207	420	446	216	570	631	512
Мо		0.5	1.2	2.1	< 0.1	0.2	0.2	< 0.1	0.4	0.4	0.1	0.3	0.4	0.1	0.2	0.2
Au		< 0.1	< 0.1	< 0.1	< 0.1	<0.1	<0.1	< 0.1	<0.1	< 0.1	< 0.1	<0.1	<0.1	< 0.1	<0.1	<0.1
Ag		0.7	0.8	1.7	< 0.1	0.1	0.2	0.4	0.6	0.9	1.4	2.1	4.1	0.1	0.1	0.2

*Explanations to the tabs. 2 and 3: A-1to A-8 technogenous sediments; A-1c to A8c clay fractions\* clay fractions after 14 days maceration in drainage water; A-17 hydrogoethite* 

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	Unit								Sample							
Element	Onit	A-1	A-1c	A-1c*	A-2	A-2c	A-2c*	A-3	A-3c	A-3c*	A-4	A-4c	A-4c*	A-5	A-5c	A-5c*
Rb		116.2	129.7	173.2	93.9	143.5	144.8	91.7	156.7	172.7	85.6	142.1	160.8	90.0	132.4	156.9
Sr		27	24	49	26	25	27	16	22	41	24	28	63	16	13	21
Hf		0.5	0.5	0.9	0.6	0.7	0.9	0.7	0.9	1.2	0.6	0.6	1.0	0.4	0.5	0.8
V		29	22	49	39	33	46	57	50	77	52	39	70	38	30	50
Ba		397	381	548	343	351	481	246	267	385	349	320	498	251	261	432
Li		29.4	25.0	54.3	50.0	34.4	67.5	43.4	36.0	68.8	35.6	25.3	64.1	34.1	28.7	60.9
La		20.6	18.2	15.4	22.9	18.6	2.9	30.2	28.2	9.8	27.5	26.0	5.9	20.8	19.8	5.3
Cr		38	9	24	36	17	26	34	21	37	38	15	30	30	10	22
W		0.9	1.0	1.9	1.5	1.0	1.5	1.2	1.3	1.8	1.2	1.1	1.8	0.9	0.9	2.0
Zr	ppm	14.7	15.1	30.9	21.8	23.5	30.4	19.9	32.8	41.8	19.2	19.9	31.8	12.6	15.6	28.4
Ce		38	39	35	43	38	7	56	61	22	52	54	14	38	42	12
Sn		10.9	11.1	29.4	3.5	2.7	4.4	9.8	7.2	9.5	17.3	12.8	22.7	4.9	3.3	8.1
Y		3.5	3.7	5.3	5.4	4.7	2.6	5.5	6.1	4.6	5.1	5.1	3.6	4.6	4.8	2.8
Nb		1.9	2.3	3.8	3.2	3.3	4.4	2.9	4.0	5.7	2.2	2.6	3.6	2.0	2.4	3.8
Та		0.2	0.2	0.2	0.2	0.2	0.3	0.2	0.2	0.3	0.1	0.1	0.2	0.2	0.2	0.2
Be		3	3	6	2	2	3	2	3	4	3	3	5	2	2	4
Sc		2	3	5	3	4	5	5	6	8	5	5	7	3	3	5
U		1.3	1.4	3.3	1.4	1.1	1.1	1.7	1.8	1.9	1.6	1.7	2.2	1.0	1.2	1.4
Th		5.8	6.0	9.5	7.6	5.9	2.2	9.1	9.2	5.2	8.3	7.8	5.0	5.9	5.8	4.0

# ICP-MS ANALYSES OF TECHNOGENOUS SEDIMENTS AND OF CLAY FRACTION AND CLAY FRACTIONS AFTER 14 DAYS MACERATION IN DRAINAGE WATER CONTAINING HEAVY METALS

Table 2 (continuation)

ICP-MS ANALYSES OF TECHNOGENOUS SEDIMENTS AND OF CLAY FRACTION AND CLAY FRACTIONS AFTER 14 DAYS MACERATION IN DRAINAGE WATER CONTAINING HEAVY METALS Table 3

Element	Unit						S	Sample					
Element	Unit	A-6	A-6c	A-6c*	A-7	A-7c	A-7c*	A-8	A-8c	A-8c*	A-17	A-17c	A-17c*
Ca		0.17	0.09	0.12	4.74	1.99	1.35	0.08	0.71	0.11	0.02	>100	< 0.10
Na		0.076	0.061	0.302	0.819	0.606	0.911	0.034	0.111	0.109	0.110	< 0.10	>100
K		2.16	3.92	4.69	2.01	1.99	4.49	2.22	4.70	3.18	0.022	0.040	1.020
Fe		2.06	2.09	3.36	1.32	1.43	2.81	0.91	1.29	0.79	1.72	1.50	13.10
Mg	%	0.80	0.71	1.25	3.15	1.61	1.75	0.47	0.91	0.46	12.92	11.80	0.20
Ti		0.128	0.102	0.171	0.111	0.114	0.198	0.112	0.190	0.086	0.01	< 0.10	0.02
Al		7.60	6.70	10.02	4.91	4.51	8.79	6.37	10.43	5.66	0.36	0.37	1.90
Р		0.067	0.070	0.081	0.041	0.041	0.069	0.054	0.056	0.051	0.90	1.00	0.40
S		0.2	< 0.1	0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Cu		4797	2503	2918	756	855	2026	716	836	837	>10 000	20 360	23 060
Pb		15.6	24.6	72.3	16.8	20.2	73.7	6.5	6.3	4.2	8.4	49.0	60.0
Zn		13	14	65	26	33	176	7	14	4	59	80	50
Cd		0.2	< 0.1	0.3	< 0.1	0.2	0.7	< 0.1	< 0.1	< 0.1	0.2	0.2	0.2
Bi		25.4	24.4	51.7	0.9	1.2	3.6	0.5	0.7	0.8	7.2	6.0	5.0
Со		41.8	40.9	32.0	10.2	12.0	15.5	89.9	69.7	104.5	73.4	70.0	83.0
Ni	ppm	51.6	45.1	61.7	10.4	10.1	26.0	58.0	66.5	62.5	51.7	43.0	58.0
As		134	224	305	16	17	33	61	52	46	289	260	280
Sb		49.8	56.2	92.3	11.5	7.1	17.4	17.9	20.2	18.9	43.2	40.0	34.0
Mn		198	254	147	372	547	931	1190	905	1458	1074	960	1010
Мо		< 0.1	0.3	0.4	0.2	0.3	0.6	< 0.1	0.3	0.3	2.2	2.0	30.0
Au		< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Ag		1.0	1.6	3.0	0.2	0.2	0.4	< 0.1	<0.1	0.1	0.8	1.0	1.0

## ICP-MS ANALYSES OF TECHNOGENOUS SEDIMENTS AND OF CLAY FRACTION AND CLAY FRACTIONS AFTER 14 DAYS MACERATION IN DRAINAGE WATER CONTAINING HEAVY METALS Table 3 (continuation)

Element	Unit	Sample											
		A-6	A-6c	A-6c*	A-7	A-7c	A-7c*	A-8	A-8c	A-8c*	A-17	A-17c	A-17c*
Rb		87.5	155.1	167.6	77.3	80.1	168.9	91.9	138.3	132.9	47.4	45.0	46.0
Sr		23	24	51	67	49	90	19	48	31	6	6	6
Hf		0.7	0.8	1.2	0.6	0.7	1.5	0.5	1.3	0.6	0.2	0.2	2.0
V		44	34	57	40	39	67	35	69	22	15	16	15
Ba		303	307	405	342	340	680	248	470	229	286	250	270
Li		40.5	32.0	73.4	20.7	14.4	67.0	35.8	65.3	31.9	5.6	6.0	11.0
La		24.9	20.9	4.4	17.3	17.6	21.3	40.6	15.0	34.2	24.8	21.0	23.0
Cr		31	11	23	28	11	35	23	21	7	7	8	8
W		1.2	1.4	2.0	1.5	0.7	1.5	1.4	2.2	1.5	0.4	0.4	0.5
Zr	ppm	20.2	23.5	37.1	18.3	22.1	48.9	14.7	43.9	23.1	7.7	9.0	9.0
Ce		46	47	10	31	35	43	77	41	68	49	40	50
Sn		14.9	12.9	19.6	4.0	2.6	6.8	3.9	7.1	3.0	8.8	4.0	9.0
Y		4.6	5.0	2.9	4.9	6.2	10.4	6.7	6.7	8.0	9.8	9.0	9.0
Nb		2.5	2.8	4.1	2.6	3.5	6.3	2.2	5.0	2.6	0.5	0.5	0.5
Та		0.2	0.2	0.2	0.2	0.2	0.4	0.1	0.4	0.2	< 0.1	< 0.1	0.1
Be		3	4	5	1	1	4	3	5	2	2	2	3
Sc		4	4	6	3	4	7	4	6	3	4	5	5
U		1.4	1.6	2.2	1.1	1.1	2.3	2.6	2.5	2.1	2.3	2.0	1.0
Th		6.9	6.1	4.1	4.8	5.3	11.8	6.8	5.7	6.7	2.5	2.0	2.0



Fig. 2 Distribution of Fe, Sn, Cu, Pb, Zn and Ag at dump-field Lubietová - Podlipa

EXPLANATIONS TO Fig. 2 (Fe, Sn, Cu, Pb, Zn and Ag content)

Table 4

Fe	Sn	Cu	Pb	Zn	Ag	
%	ppm					
< 1	< 5	< 1000	< 5	< 15	< 1	
1 – 2	5-15	1000 -4000	5-15	15-35	1-2	
2 – 3	15-25	4000-7000	15-25	35-50	2-3	
> 3	> 25	> 7000	> 25	> 50	> 3	



Fig. 3. Distribution of Ni, Co, As, Sb, Th and U at dump-field Lubietová - Podlipa

Ni	Co	As	Sb	Th	U		
ppm							
< 15	< 10	< 50	< 20	< 5	< 1,5		
 15 – 35	10-50	50-150	20-40	5-8	1,5-2,5		
35 – 50	50-80	150-350	40-60	8-10	2,5-3		
> 50	> 80	> 350	> 60	> 10	> 3		

EXPLANATIONS TO Fig. 3 (Ni, Co, As, Sb, Th and U content) Table 5


Fig. 4. Distribution of Cd, V, Bi and Cr at dump-field Lubietová - Podlipa

			Table 6
Cd	V	Bi	Cr
	рр	m	
< 0,1	< 30	< 10	< 10
0,2	30-40	10-30	10-25
0,3	40-50	30-100	25-35
0,9	> 50	> 100	> 35

EXPLANATIONS TO Fig. 2 (Cd, V, Bi and Cr content)

The presented results show that the distribution of selected elements at the dump-field is non-uniform. The maximal concentration of theoretically extractable elements in the dump-field material ranges from 30 000 ppm (Fe) to 0,9 ppm (Cd). Also, important concentrations of Cu (7000 ppm) and As (350 ppm) were described. Noticeable are also high concentrations of Pb and Zn (Cd) at the reference area. We have no explanation for this evidence. (Both within the territory of the reference area and of the whole deposit, there are no occurrences of sphalerite or other minerals which could explain the high Zn and Cd contents.) The source of the increased U and Th contents at the reference area is in the Permian rocks (rauwackes). In

the dump range oriented in E - NE vs. W - NW direction (samples HD-6, A-2, A-3, A-5 and A-11) only low contents of Ag, Bi and Cd were described.

#### Natural sorbents

Rtg.-diffraction analysis proved that the most important potential natural sorbents in the studied area are the clay minerals and hydrogoethite –  $FeO(OH) \cdot nH_2O$ , which are formed during the weathering process of rock-material. The research confirmed that the clay minerals are represented by illite –  $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$  and muscovite –  $KAl_2(AlSi_3O_{10})(F,OH)_2$ , caolinite –  $Al_2Si_2O_5(OH)_4$ , as well as smectite and chlorite mixture. Illite and muscovite are dominant in all samples. The next important mineral is smectite.

#### Heavy metals sorption in clay minerals and hydrogoethite

The heavy metal sorption study of clay minerals and hydrogoethite from technogenous dump sediments, and the study of the free sorption capacity of these natural sorbents in individual samples, is a relatively complex problem and the interpretation of these data is very confusing. Better reproducibility enables the complex interpretation of the results if the concentrations of the individual elements in technogenous sediment, in clay mineral mixture, and in clay fraction after maceration in drainage water, are presented in the form of total values for each element (tab. 2 and 3). Such total data enable better understanding of the studied processes and trends.

Preferential sorption of K, Na, Li, Al, Rb, Sr, Hf, V, Cr, Ti, W, Zr, Nb, Ta and Th on surface of clay minerals in comparison with hydroghoethite was found. On the hydrogoethite surface, Cu, Zn, Mo, Mn, Mg, P ( $\pm$  Fe, Cd, Co, Ca) are preferentially fixed. The following elements: Sb, Bi, Ba, La, Ce, Sn, Y, Be, Sc, S, Pb, Ag, Ni, As and U show no legible trends of preferred sorption both on clay minerals and on hydrogoethite rich rock (tab. 2 and 3).



Fig. 5. Total content of Fe, As, Sb, Pb, Cu and Th in technogenous sediments (A), in clay fraction (Ac), in clay fraction after 14 days maceration in heavy metals containing drainage water (Ac\*)

The following heavy metals: Fe, As, Sb, Ag, Pb, Zn, Mn, Mo, Bi and U show not only good sorption efficiency on clay minerals but also free sorption capacity of the clay fraction. The opposite trend – lower heavy metal content in the clay component in comparison with the sediment and metal elements washing during maceration – was proved in the case of Th and Cu (fig. 5). Co shows a moderate increase of content in clay minerals but no free sorption capacity was proved. The Cd, Ni, Co, V and Cr behaviour is very complex (fig. 6).



**Fig. 6.** Total content of Cd and Ni in technogenous sediments (A), in clay fraction (Ac), in clay fraction after 14 days maceration in heavy metals containing drainage water (Ac\*)

Cd, Ni and V are preferentially fixed in the sediments; lower Cd, Ni and V contents are in the clay fraction but the clay mineral mixture proved to have a good ability to fix the mentioned heavy metals (Cd, Ni and V) on their surface (Fig. 6). The probable reason of this behaviour is the fact that the Cd, Ni and V majority is bound in the solid phase and only with difficulty create soluble forms, so in consequence of this behaviour in the weathering process the autochthonous clay minerals are insufficiently saturated by V. The same trend was described for Cd, Ni, V and Co in the case of hydrogoethite. The Cr behaviour is very similar, only with the difference that while V concentrations in macerated clay are higher than in the original sediment, the Cr concentrations are the highest in the original sediment. The most complex relations were recognized in the case of Co.

The highest Th content was described in sediments and in soil. The Th contents in clay minerals are lower than in the sediment, and after maceration Th washed out from the clays. This trend is noticeable because in general U considered to be more mobile than Th. The better mobility of U was described also at the Lubietová deposit (Andráš et al. 2008), where the content of Th in soil is several times higher than the content of U, while in plants the contents both of U and Th are in consequence of better U mobility approximately identical. The Th/U rate is about 1 : 1.

### Discussion

The mobility of most heavy metals in nature is determined mostly by their solubility and sorption ability on natural sorbents, among which the most important are clay minerals (Missanaet et al., 2008). According to sorption mechanics, it is possible to distinguish several of the following types: a) mechanic sorption, b) physical adsorption conditioned by surface tension at the phase interface, c) physical-chemical replaceable sorption, which is realised by ion replacement, d) chemical adsorption, which makes possible the anion fixation in form of coagulums, e) bioacumulation – e.g. intake of biogenic elements by root systems of plants and by bacteria (Chmielewska and Lesný, 1995; Lischke and Frank, 1988). In the case of clay minerals, the dominant process is represented by ionic replacement between solution and solid pase but partially also the physical process of adsorption (Kozáč, 1969).

Caolinite is in general a very good sorbent of the majority of heavy metals (Wahba and Zaghloul, 2007). Cu, Pb, Zn and Cd are fixed preferentially on smectite, but Pb also on illite (Rybicka et al., 1995). Illite and smectite are very good sorbents of Pb and Cu. The sorption of Zn, Ni and Cd on illite and smectite is not so efficient. The sorption of Mg, Fe and Al on clay minerals is substantially more efficient at higher pH. It is caused by the lack of free H<sup>+</sup> ions and by the increase of negative charge on the surface of clay minerals (Kishk and Hassan, 1973). The pH<sub>(H2O)</sub> of technogenous sediments from the dump-field Podlipa (tab.7) range from 4.21 to 7.93 (pH<sub>(KCl)</sub> 4.00 – 7.34), so it is possible to observe that the sorption conditions of Cu, Pb, Zn and Cd on clay minerals are not the best but, on the other hand, they are not wholly ineffective.

From the viewpoint of environmental risk, according to Andráš et al. (2008), at the studied locality the most important metals are Cu, As and Sb.

The main sources of Cu at the dump-field are tetrahedrite, chalcopyrite and Cu-secondary minerals (libethenite, brochantite, langite, malachite, azurite and pseudomalachite). Cu released to the solutions during the weathering process contaminate the whole local water-table. Andráš et al. (2007) described at the locality a cementation process which enables Cu precipitation on Fe oxides (hydrogoethite) and on the iron surface. In natural water are present the following forms of Cu: hydrated Cu(II) ion, complexes  $[CuCO_3(aq)]^0$ ,  $[Cu(CO3)_2]^{2-}$  and hydrocomplexes [CuOH],  $[Cu(OH)_2(aq)]^0$ ,  $[Cu(OH)_1^{3-}$  and  $[Cu(OH)_4]^{2-}$  (Pitter 1990).

Cu sorption on clay mineral surfaces depends on pH. In the case of a lack of carbonate (as it is at Ľubietová-Podlipa), during the sorption process are formed complex compounds  $\equiv$ SOCu<sup>+</sup>,  $\equiv$ SOCuOH and  $\equiv$ SOCu<sub>2</sub>(OH)<sub>2</sub><sup>+</sup>, less often also  $\equiv$ Cu(OH)<sub>2</sub> and  $\equiv$ SOCu<sub>2</sub>(OH)<sub>3</sub> precipitates (Quinga et al. 1996).

	H <sub>2</sub> (	)	1M 1	KC1
Sample	pН	Eh	pН	Eh
A-1	5.14	77	4.61	109
A-2	5.89	34	5.40	63
A-3	4.87	94	4.21	131
A-4	5.46	59	5.33	66
A-5	5.77	42	5.37	64
A-6	5.17	74	5.06	83
A-7	7.93	-84	7.34	-58
A-8	5.42	36	5.22	42
A-9	5.03	83	5.01	85
A-10	5.25	71	5.14	78
A-11	6.11	22	5.95	30
A-12	4.21	133	3.47	173
A-13	5.20	75	5.11	85
A-14	4.91	97	4.32	125
A-15	4.47	111	4.00	165
			No	te <sup>.</sup> Fh (mV)

## pH OF TECHNOGENOUS SEDIMENTS AND THEIR EH MEASURED IN H<sub>2</sub>0 AND 1M KCI LIXIVIUM Table 7

The most important As source at the Ľubietová is tetrahedrite. The weathering of the Asminerals (their oxidation) causes modification of native As and As(III) to As(V) containing compounds of arsenic acid (Lin and Puls 2000). The arsenic acid is water soluble, but only rarely migrates greater distances, because it quickly reacts with heavy metals and As is fixed in the form of various arsenates. As is in the water solutions, it is most often present in the following forms:  $H_2AsO_4^-$ ,  $HAsO_4^{2-}$  and  $HAsO_2^{0}$  (Greenwood and Earnshaw 1990). As(III) is in the weathering zone much more mobile than As(V) (Manning and Goldberg, 1997).

In oxidation (weathering) conditions of the Ľubietová-Podlipa dump-field As(V) markedly prevails (Andráš et al. 2008). The sorption capacity of clay minerals, of hydrogoethite, and Fe-oxyhydroxides related to As is very high (up to 76 mg As.g<sup>-1</sup> in Fe oxyhydroxides at pH 5). As sorption depend on pH, time, As concentration in solution, and on temperature (Mohapatra et al., 2007). The most efficient sorption was described at pH 4 (García-Sancher et al. 2002; Lombi et al., 2000). According to Mohapatra et al. (2007), caolinite is the best As(V) sorbent from the natural sorbents described at Ľubietová dump-field. The sorption of the less toxic As(V) in comparison to As(III) on clay minerals is much more efficient and more quantitative. As(III) is during this process oxidized to As(V). The reductive process during the sorption of As was not confirmed (Lin and Puls, 2000).

The most important part of Sb descends from tetrahedrite. Both Sb(III) and Sb(V) exist in environmental conditions in the following soluble compounds: Sb(V) in the form of Sb(OH)<sub>6</sub><sup>-</sup> and Sb(III) in the form of Sb(OH)<sub>3</sub> (Filella et al., 2002). Hydrogoethite and Fehydroxides are the most important Sb sorbents. Sb(III) as well as Sb(V) form complex compounds on the hydrogoethite and Fe-hydroxides surfaces. The best Sb(III) sorption conditions are at pH 3 – 12, and the maximal Sb(V) sorption was described at pH <7. The Sb(III) on the hydrogoethite and Fe-hydroxides surface can be, within a pH range from 3 to 5.9, oxidised during several days. At pH ~ 9 its mobilisation and dissolution start, while at pH <7 it is fixed on the Fe-oxides surface (Leuz et al., 2006).

The main soluble lead-compounds in nature are mainly Pb(II) and  $[PbCO_3(aq)]^0$ . The latter one may be in a wide pH range the dominant form of occurrence. In alkaline conditions substantial concentrations of  $[Pb(CO_3)_2]^{2-}$ ,  $[Pb(OH)_2(aq)]^0$  and  $[PbOH]^+$  complexes are also formed (Pitter 1990). Lead is, in solid matter, present usually in the form of PbCO<sub>3</sub> and PbSO<sub>4</sub>, and the ulmous substances affect its immobilisation (Beneš and Pabianová 1987). Pb shows affinity to formation of complexes with insoluble ulmous matters and in consequence of the mentioned trend it is fixed in the upper part of the soil level (in the mould). Copper and Pb are usually, in comparison with Zn, fixed on clay mineral surface much more strongly (Sipos et al., 2008). The increasing pH causes increasing Cd sorption on clay minerals (Hayashi and Liu 2008).

Soluble Cd is present in water in the form of the simple hydrated ion Cd(II), in the form of inorganic complexes  $[CdOH]^+$ ,  $[Cd(OH)_2(aq)]^0$ ,  $[Cd(OH)_3]^-$ ,  $[CdCO_3(aq)]^0$ ,  $[Cd(CO_3)_2]^{2^-}$ ,  $[CdSO_4]^0$ , as well as in the form of organic complexes with various organic ligands (Pitter 1990). The proportion of sorbed Cd(II) on clay minerals shows an important increase at pH 6.5 – 9.0, while on illite it is sorbed more intensively than on caolinite (Reid and McDuffie, 2005).

## Conclusions

Heavy metal distribution in technogenous sediments and ores of the dump-field L'ubietová – Podlipa is variable and reflects the original concentration of metals in technogenous sediments as well as their migration abilities. Rtg-diffraction analysis proved that the main prevailing natural sorbents are illite, muscovite and smectite, and less so caolinite and chlorites. Hydrogoethite is relatively rare. Results of the sorption properties of clay minerals and hydrogoethitised rocks show that the studied dumps are disposed to a certain level of

"self-cleaning ability." A substantional part of heavy metals and contaminants is caught in porous substances, in Fe-hydroxides (hydrogoethite) and in clay minerals (mainly K, Na, Li, Al, Rb, Sr, Hf, V, Cr, Ti, W, Zr, Nb, Ta and Th), which, in the case of Fe, As, Sb, Ag, Pb, Zn, Mn, Mo, Bi and U, show important free sorption capacity. The mentioned data enables expression of the following result: The arrangement (opening) of the dumps could cause massive release in this way of fixed heavy metals to the environment.

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## **RESEARCH PAPERS** FACULTY OF MATERIALS SCIENCE AND TECHNOLOGY IN TRNAVA SLOVAK UNIVERSITY OF TECHNOLOGY IN BRATISLAVA

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## **RATE OF NON-BIODEGRADABLE GRAVEYARD WASTE FRACTION**

Miroslav RUSKO, Bohdan STEJSKAL

### Abstract

An analysis of graveyard waste composition has been carried out, where, by repeated measurements of samples weighing more than 500 kg (the total amount of analyzed waste was 3107 kg), it was found that the graveyard waste consists of almost 77 % of bio-degradable matter. It is operationally impossible to separate bio-degradable matter from non-bio-degradable materials. It is desirable to collect compostable graveyard green waste separately from the waste coming from the decoration of gravestones that may be energetically utilized.

### Key words

biodegradable waste, graveyard waste

### Introduction

Landfilling is the most common method of municipal waste disposal in the Czech Republic. The percentage of biodegradable waste (biowaste) in municipal waste is in the range of 40 - 47% [1], [2], [3]. Garden and park waste, including graveyard waste, belongs to the category of municipal waste [4].

Effective management and rational utilization of biodegradable municipal waste is still a subject of much discussion. The most serious problems are caused by the heterogeneous biodegradable wastes which contain too many biodegradable components to be landfilled, but also contain too many non-biodegradable components and foreign materials to be composted. The typical example of such waste is cemetery waste.

The Czech Republic must comply with the legislative requirements set for waste management. In this particular case that means the EU Council Directive 1999/31/EC "On the

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Waste Landfills". The Directive requires EU member states to limit the amount of BRW in landfills. The main purpose of this restriction is to reduce the amount of emitted gases, particularly methane as a greenhouse gas, into the atmosphere. Therefore, the Plan of Waste Management of the Czech Republic includes the requirement to reduce the quantity of biodegradable waste deposited into landfills to (at least) 75  $\%_{weight}$  in 2010, to 50  $\%_{weight}$  in 2013, and to 35  $\%_{weight}$  in 2020 as compared to 1995 [5]. These objectives are not able to be reached, and it is clear that there will be a lot of biodegradable waste deposited into landfills.

To achieve the above-mentioned objectives, various methods have been proposed. Prior to the waste processing, it is necessary to know the waste material's composition, and after that to select the most appropriate method and procedure for waste utilization or disposal. The aim of this project was to determine the ratio of the biodegradable fraction and nonbiodegradable fraction of graveyard waste and, on the basis of this analysis, to find an optimal method for utilization of such waste.

In both Czech and foreign publications, similar data have not been published yet; therefore it is not possible to compare the results obtained in the project with other studies.

### Materials and methods

The analysed graveyard waste was collected from the Central Cemetery in Brno. The analysis itself was carried out at the temporary dump very close to the Central Cemetery. Large quantities of the graveyard waste are stored there for a long time. The samples were always collected from the newly deposited waste. For practical reasons the waste from other cemeteries was not analysed, but we do not expect big differences (i.e. differences in the tens of percent) in the waste composition coming from different cemeteries.

The sample was at first sorted in accordance with the Waste Catalogue, i.e. to 20 02 01 "Biodegradable Waste" and 20 02 03 "Other Non-biodegradable Waste". The waste 20 02 02 "Soil and Stones" was rarely found in the samples (<2%) and therefore it was not taken into consideration.

The sorted ingredients were then put into bags of the volume of  $0.16 \text{ m}^3$  and weighed by mechanical weight hanging (steelyard). In this way the approximate volume ratio of the particular graveyard waste components was simultaneously recorded.

The measurements were repeated six times. The size of each analysed sample was at least 500 kg.

Due to the climatic conditions immediately preceding some of the measurements, the weight of such components was slightly affected by the presence of precipitation water. The measured values proved them to be irrelevant for the objective of this project.

### Measurement results and comments

The aim of this project was to determine the proportion of biodegradable fraction and nonbiodegradable fraction of graveyard waste in regard to its further utilization. Due to the research methodology, the mass analysis has a higher value; the measured and calculated values of the mass analysis are shown both in tabular and graphical form for better clarity. The volumetric analysis may be flawed, as just *an approximate* volume of waste bulk has been measured. Therefore, the results of volumetric analysis are expressed only in tabular form. For a more precise assessment and elimination of differences in the sample size for each measurement of the mass and volume analysis, the data results were converted into weight and volume percentages ( $\%_w$ ,  $\%_v$ ) of the particular components.

It is apparent that the particular measurements show only small differences in composition, with the unmatched content to biowaste variability in mixed municipal waste. For measurement II, i.e. on April 3, 2009, there was a greater proportion of green waste from the cemetery maintenance in the sample; the other samples were very well balanced. It appeared that the proportion of biowaste and non-biowaste does not depend on weather conditions or the season (winter - spring).

Biodegradable wastes (Cat. No 20 02 01) are largely made up of branches from conifer trees and cones; composting is possible though difficult and lengthy. Another waste component is flowers, where composting is smooth.

All non-biodegradable waste fractions come from the city residents - from the decoration and maintenance of graves, and the minimum degree is made up of mixed municipal waste, i.e. non-graveyard waste. The largest portion is made up of plastic materials while pieces of paraffin, glass, and metal represent only a small part of it. Other components of nonbiodegradable fraction (such as ceramic pots) are negligible. There is no possibility for efficient material utilization of non-biodegradable graveyard waste, but it can be used to produce energy.

In some cases, the biodegradable and non-biodegradable wastes make up a unit which is difficult to disconnect (e.g. funeral wreaths). Such waste is only suitable for producing energy.

The measured values from particular measurements and conversion of them to volume percentage are listed in Table No. 1 and Table No 2. Relevant graphs correspond to the results of the mass analysis.

## MASS OF GRAVEYARD WASTE COMPONENTS

Table 1

Measurement/ Date	Non-biowaste	Biowaste [kg]	In total	Non-biowaste	Biowaste
Dutt	L81	[ <del>8</del> ]	[kg]	[,,,,,,]	[, , , , , ]
I/11 Mar	138	379,5	517,5	27	73
II/3 Apr	68,5	454,5	523	13	87
III/21 Apr	122,5	390	512,5	24	76
IV/30 Apr	135	405	540	25	75
V/4 May	136	297	500	27	73
VI/7 May	123	391	514	24	76



Graph 1a. Weight of graveyard waste portions



Graph 1b. Percentage of weight of graveyard waste portions

Measurement/ date	Non-biowaste [m <sup>3</sup> ]	Biowaste [m <sup>3</sup> ]	In total [m <sup>3</sup> ]	Non-biowaste [% <sub>v</sub> ]	Biowaste [% <sub>v</sub> ]
I/11 Mar	1,01	2,67	3,68	28	72
II/3 Apr	0,64	4,27	4,91	13	87
III/21 Apr	1,2	3,36	4,56	26	74
IV/30 Apr	1,28	4,12	5,4	24	76
V/4 May	1,12	3,2	4,32	26	74
VI/7 May	1,04	352	4,56	23	77

Table 2

### THE VOLUME OF GRAVEYARD WASTE COMPONENTS

Measurement/ date	Non-biowaste [kg]	Biowaste [kg]	In total [kg]	Non-biowaste [% <sub>w</sub> ]	Biowaste [% <sub>w</sub> ]
I/11 Mar	138	379,5	517,5	27	73
II/3 Apr	68,5	454,5	523	13	87
III/21 Apr	122,5	390	512,5	24	76
IV/30 Apr	135	405	540	25	75
V/4 May	136	297	500	27	73
VI/7 May	123	391	514	24	76

#### Conclusion

The analysis of graveyard waste composition was carried out with regard to its further processing and utilization, especially composting.

The graveyard waste (mixed) contains approximately 26% of the non-biodegradable component which does not allow use of the waste as a raw material for composting or in biogas stations for biogas production.

For better utilization of graveyard waste, the most appropriate way is to introduce sorting of the waste generated by the citizens as well as the waste that comes from the maintenance of cemetry green (this waste is less contaminated by litter than the city maintenance green waste). The separated waste from the cemetery green maintenance can be composted; the waste generated by the citizens in untreated form can only be used as an alternative fuel. Another possibility for its disposal is composting and then landfilling as stabilized waste.

Owing to the difficulty of sorting graveyard waste and poor economic performance of its incineration, it can be expected that graveyard waste will mostly be deposited into landfills.

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## **RESEARCH PAPERS FACULTY OF MATERIALS SCIENCE AND TECHNOLOGY IN TRNAVA** SLOVAK UNIVERSITY OF TECHNOLOGY IN BRATISLAVA

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# **TIME-DRIVEN PRODUCT DEVELOPMENT**

# Rudolf RYBANSKÝ, Michal REŠETA

#### Abstract

The product realization process consists of product planning, design, process planning, and manufacturing. The development time is an important factor. Accelerated development of the product results in a longer sales life, a marketplace advantage by early acquisition of customers, a pricing advantage for the company, and the ability to use more up-to-date technology in the product. An increase in development time has a much greater effect on profits than an increase in production costs or development costs. The decision regarding accelerated product development must consider the trade-off among the parameters of interest such as product features, product cost, development speed, and development expense. Often, the development of a product is delayed in the early stages because no one in the company realizes its importance. Another factor that can cause delays is when a company tries to develop an entirely new product, often using new technology. There is less risk if a product is improved in stages, using only tried and tested technology. The chief factors that facilitate faster development of products are better communication between departments, which also leads to lower cost and higher quality products. The company increases its market share and enjoys higher profits through the early introduction of a product.

### Key words

manufacturing, product, time-driven development

#### **Time-driven product development**

There is more competitiveness in manufacturing over the last years. The key ingredients of product innovation and quick development actuate products to market. The time from the moment that a company realizes that a product should be developed to the time it is in the customer's hands can be reduced by applying certain techniques of time-driven development.

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This is a procedure used by management to focus on reduction of the time taken to develop a product. There is the possibility of a 50 percent time reduction by companies that have applied the method of time-driven product development. Competition on the market requires that producers be able to present to customers products that are low in cost with attributes such as short delivery time and high quality. There are several steps in the production process, such as engineering aspects including planning, design, and manufacturing. The product specifications list and the product structure are important factors of a product's characteristics set during the planning phase. A management point of view must include a compromise study to determine the economic acceptability of rapid product development, product innovation by stages, and the overlapping of activities in planning, design, and manufacture.

### **Conventional product realization process**

The product realization process consists of two steps: design and manufacturing. In order to understand the process, it is necessary to look at the whole life of a product, which begins with its planning and ends with its disposal.

### Steps in the Product Realization Process

The *need* for a product must exist, and may come from external or internal sources. The external causes are a direct order from a customer, an outdated existing product, the availability of new technologies, or a variation in market demands. Internal to the company, new product ideas may come from developments within the company or the needs identified by the marketing department. After the need is established, the product has to be designed and manufactured. It must be said that in this process, which is sequential, each step must be completed before the next step begins, and this fact shows that this procedure can lead to delays, mistakes, poor quality, and high costs. Activities in the successive stages can be concurrent or overlap.

*Product Planning* is the selection and development of ideas for new products. A systematic approach to product planning should lead to a better means of meeting the constraints of cost and time. There are several activities like establishment of goals, market analysis, detailing of the customer's benefits from the product, deciding on the product's features, establishment of product performance parameters, economic analysis and setting the cost target, setting the expected sales volume, setting deadlines for completion of tasks, such as design, prototype building, and setting up the manufacturing line. The two most important entities involved in making the decisions are the company and the market. The company needs to define its objectives and examine its capabilities. An evaluation of resources and objectives will help focus the company on the type of product it should develop.

*Design.* The first major step in the design of a product is the preparation of the requirements or specifications list. The specific requirements are classified according to the life phases of the product and types of requirements (technical, economic, ergonomic, legal). Most important are the technical requirements for the product use. Conceptual design is the most important phase of design; it has the single largest influence on costs. Embodiment design leads the process through a more concrete stage, as the shapes and materials are determined. The final design phase leads to production drawings. The final decisions on dimensions, arrangement, shapes of individual components, and materials are made. The design proceeds

from the more abstract level of task clarification to the more concrete form as it approaches this phase.

*Process Planning*. Known also as production or manufacturing planning, process planning involves decisions on how the product is to be manufactured, the manufacturing processes, the machines required, and how the parts are to be mounted. The steps in process planning are producibility analysis, process design, vendor selection, and tooling design.

*Manufacturing* includes material handling, production of parts, quality control, and related activities. Items such as overall design arrangement of the manufacturing process, form design of components, materials for components, and purchased parts related to production capacity have the largest influence on manufacturing. There are also additional steps of the process, such as marketing and product disposal.

## Accelerated product development

A shorter time to market does not necessarily mean higher costs. A well managed program can produce products at a low cost and under the allowed time. It also depends on how the development process is managed.

## Cost and Price

From the time when the development of a product begins, its cost starts to grow because of the resources used for its production (personnel, facilities, equipment). The price of a competitor's product decreases with time. There are several reasons for the optimization of the production and manufacturing processes, cost-driven development in design, and increased knowledge about the product.

## Benefits of rapid product development

Time-driven product development, in comparison to the conventional development process, yields benefits to a company in many ways, as does extension of the product's sales life. Early introduction of the product gives a marketplace advantage by gaining early customers who lock on to it, develop loyalty, and who are less likely to switch to another product. Also, the company gains a pricing advantage ahead of the competitors. A company that applies rapid development methods on a product later than a traditional company will use more up-todate technology in the product. The status of the technology indicates what advantage the technology has according to time. The state of technology is advancing. Companies may reach the market with their products in the same time. But there is a difference between the companies, and the company that applies rapid development methods with newer and more advanced technology is at an advantage compared to the company preferring the traditional development process which starts at the same time with technology obtained a longer time ago. The market is a moving target. The length of time it takes for product development is very critical. The longer the time to product introduction, the more uncertain the market forecast will be, and therefore the greater the risk. The effect on profits due to deviations in development time, production costs, and development costs shows, for example, that an increase of 50 percent in development costs can decrease profits by 10 percent, but an

increase of 10 percent in development time can reduce profits by up to 30 percent. Therefore, it benefits a company to shorten the development time, even at the expense of some increased development costs.

## Management for rapid product development

The primary initiatives in achieving rapid product development must come from the top management of the company. There are several decisions that must be made and procedures to be implemented, for example economic decisions, decisions regarding product innovations, project management, etc.

## Economics of Rapid Product Development

Decisions regarding the product development project must be based on facts rather than intuition. It may appear at first that it is difficult to quantify the costs and benefits of the various development goals. Nevertheless, even the use of gross estimations is better and more easily justifiable than an instinctive decision.

The four primary elements to be considered in the product development decision are the following:

- a) The characteristics of the product relating to its performance, which is an important determinant of its market success. The product's public presentation is determined by the customer and the marketplace, not only by satisfying what is in the specifications.
- b) Product cost over its life cycle, including the purchase price and the operating, maintenance, and disposal costs.
- c) Development speed. Time to market is obviously the most critical factor. This is the total time from the moment when someone thinks about developing the product to the time it is in the customer's hands. The speed of product development determines the time to market; it can be important to the success of the product. It pertains to all of the company's departments, not just design engineering.
- d) Development expenses are the one-time costs associated with the development of the product, including the one-time costs associated with the product and extra expenses for items such as overtime, facilities, and consultants. Although rarely an overriding concern, this expense must be justified to the upper management. Rapid product development will show extra costs on the balance sheet and must be justified by savings in time that would otherwise be spent.

Each of these factors needs to be weighed against the other three on the basis of costs and benefits before the decision to proceed can be made. It leads to better decisions and is usually preferable to more sophisticated and complex approaches and is certainly an improvement over a decision based on intuition only.

## Early Stages of a Project

The lack of management of a product in its earliest phases can account for the greatest loss of time. A project can become inactive without people realizing it, as there is no one responsible to keep track of it; there may be several reasons for this. There might be a perceived need for the product but not enough importance is dedicated to it. The company might be not sure it

has the technology for all parts of the product, or is not sure the expenses of the product increase only after its importance is recognized, while the market window of opportunity is closing.

## Product Innovation by Phases

In all new projects, there is a certain level of novelty, which includes unknowns and therefore more risk is attached to the product's development. Rather than innovation on the whole product, as far as possible it is better to improve only on parts of the product one at a time.

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# OCCURRENCE, DISTRIBUTION AND POTENTIAL SOURCE OF ORGANOCHLORINE POLLUTANTS IN BOTTOM SEDIMENTS OF THREE WATER RESERVOIRS, SLOVAKIA

## Maroš SIROTIAK

## Abstract

Bottom sediments are a specific type of water management waste. Mainly hydrophobic organic matter reported in sediments and particles with high surface area can leach more persistent organic pollutants. Thirty-four bottom sediments samples was collected from three water reservoirs – Zemplinska Sirava, Ruzin (at Hnilec and Hornad puller) and Velke Kozmalovce. 14 congeners of polychlorinated biphenyls and 10 organochlorinated pesticides (OCPs) were analyzed. The concentrations in dry weight samples of  $\Sigma$  PCB were in the ranges of 20,28 ng/g (Ruzin/Hnilec) – 2530,00 ng/g (Zemplinska Sirava); of  $\Sigma$  DDT in the ranges 5,47 ng/g (Zemplinska Sirava) – 525,7 ng/g (Zemplinska Sirava). Hexachlorbenzene was reported in the ranges of 0,27 – 9,24 ng/g (Velke Kozmalovce). Lindan, Heptachlor and Mirex were under the detection limit. Sources of these OCPs are mainly agriculture and forestry in their catchments. The major source of PCBs is industrial wastewater and in the case of the Zemplinska Sirava water reservoir, land contamination caused by Chemko Strazske.

## Key words

polychlorinated biphenyls, organochlorine pesticides, bottom sediments

## Introduction

Persistent organic pollutants (POPs) are characterized by slow rates of environmental degradation, low water solubility, and high sorption to suspended particles. Once these chemicals are dispersed, they are capable of persisting for many years, with environmental half-lives often of the order of years to decades [1]. Long environmental half-lives and high particle sorption of POPs also mean that lake sediments are natural archives of these

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chemicals. Due to persistence and lipophilic properties, they are able to accumulate in the ecosystem. In addition to carcinogenetic / mutagenic potential, they may cause toxic effects on animal reproduction, development, and immunological functions [2]. Since POPs can enter fishponds and persist for a long period, they can be transferred into food chains, accumulated in fish, and finally reach human beings. In a biological system, several of these chemicals may also cause alterations in endocrine and nervous systems [3, 4, 5]. For these reasons, most countries have restricted or banned the use of PCBs and OCPs.

#### Polychlorinated biphenyls (PCB)

Chemically, PCBs are chlorinated, aromatic compounds. There are 209 congeners, containing from 1 to 10 chlorine (Cl) substituted on a biphenyl structure (monochlorobiphenyl to decachlorobiphenyl). Approximately 150 congeners are found in the environment [6]. PCBs are thermally stable and resistant to degradation by oxidation or chemical agents. PCBs also have excellent dielectric properties, which led to their widespread use as dielectric fluids in capacitors and transformers. They were also utilized as industrial fluids in various systems, in fire retardants, and in plasticizers used in adhesives, textiles, surface coatings sealants, printing and copy paper. The names of common PCB technical mixtures are Aroclor, Kanechlor, Clophen and Sovol [7]. The physico-chemical properties of chlorobiphenyl homologues are shown at Tab.1.

	IUPAC No.	Molecular	Water solubility	Vapour pressure	log K <sub>OW</sub>
		weight (g.mol <sup>-1</sup> )	( <b>mg.l</b> <sup>-1</sup> )	(Pa)	
Monochlorobiphenyl	1 – 3	188,7	1,21 – 5,5	0,9 - 2,5	4,3-4,6
Dichlorobiphenyl	4 – 15	223,1	0,06 - 2,0	0,008 - 0,60	4,9 - 5,3
Trichlorobiphenyl	16 – 39	257,5	0,015 - 0,4	0,003 - 0,22	5,5 - 5,9
Tetrachlorobiphenyl	40 - 81	292,0	0,043 - 0,010	0,002	5,5-6,3
Pentachlorobiphenyl	82 - 127	326,4	0,004 - 0,020	0,0023 - 0,051	6,0-6,5
Hexachlorobiphenyl	128 – 169	360,9	$4,0.10^{-4} - 7,0.10^{-4}$	$7.10^{-4} - 12.10^{-3}$	6,9 - 7,3
Heptachlorobiphenyl	170 – 193	395,3	$4,5.10^{-5} - 2,0.10^{-4}$	2,5.10-4	6,7-7,0
Oktachlorobiphenyl	194 - 206	429,8	$2,0.10^{-4} - 3,0.10^{-4}$	6.10 <sup>-4</sup>	7,1 – 7,4
Nonachlorobiphenyl	207 - 208	464,2	$1,8.10^{-5} - 7,9.10^{-5}$	-	7,2-8,16
Dekachlorobinhenvl	209	498 7	$1  10^{-6}$	$3.10^{-5}$	8 26

SELECTED PROPERTIES OF CHLOROBIPHENYL HOMOLOGUES [8]

Table 1

PCBs were also produced as Delor (Delotherm, Hydelor) by Chemko Strážske in eastern Slovakia (Michalovce District in the former Czechoslovakia) from 1959 to 1984. The production of Delor 106 was started in 1959 for use in a paint factory. In 1967 and 1968, the production of Delors 103 and 105 was initiated for use in transformers and capacitors. Delor 103 was used as a dielectric fluid in capacitors and Delor 105 was used in transformers manufactured in the Czech Republic. It has been estimated that Chemko produced 21 500 metric tons of PCBs. About 46% of the PCBs were exported to the former East Germany, whereas the rest were used in the territory of former Czechoslovakia. High concentrations of PCBs have been found in humans and wildlife sampled in the area of former PCB manufacture in Slovakia [9,10]. The production of Delors was based on the direct catalytic (FeCl<sub>3</sub>) chlorination of pure biphenyl, which was manufactured by Chemko through the high-temperature pyrolysis of benzene. When the expected stage of chlorination was achieved, the

reaction mixture was neutralized with sodium hydroxide and vacuum distilled. Less chlorinated compounds were distilled out of the mixture using steam-jet air pumps. Distilled residues contained highly chlorinated biphenyls and terphenyls. Because the residues were heated at high temperatures (500°C), formation of PCDFs and other dioxin-like compounds could be expected [11]. The compositions of chlorobiphenyl homologues in Delor mixtures in comparison with those in Aroclors PCB mixtures are shown in Figure 1.



Fig. 1. Composition (%) of chlorobiphenyl homologues in PCB commercial mixtures [11]

## DDT

DDT has been widely used throughout the world to control arthropod disease-vectors and agricultural pests. As a result DDT residues are widely distributed and are persistent environmental contaminants. Although DDT is banned in developed nations it is still being used in developing nations [12] due to its cost effectiveness and broad-spectrum activity. In Slovakia it was manufactured in a Bratislava chemical plant in the 60's and 70's. Its use for agriculture was banned in 1976, however, in spite of that fact it was used until the depletion of DDT stockpiles. For example, in 1970 about 140 t of active ingredient was used. Currently, there is almost no information on obsolete DDT stockpiles in Slovakia. One can expect that limited amounts of obsolete DDT could be still stored at cooperative farms and by individuals. A certain amount is in the landfill site of the former producer outside Bratislava [13]. Commercial grade DDT generally contains 75% p,p'-DDT, 15% o,p'-DDT, 5% p,p'-DDE, <0,5% p,p'-DDD, <0,5% o,p'-DDD, <0,5% o,p'-DDE and <0,5% unidentified compounds [14]. DDE and DDD are the two major metabolites of DDT usually present together with their parent compound in DDT-contaminated soils and sediments. It is a common notion that DDT is biodegraded to DDE under aerobic conditions or to DDD under anaerobic conditions in the environment. Combined with the fact that DDT (sum of p,p'-DDT and o,p'-DDT) accounts for more than 90% of the technical DDT formulation, the ratio of DDT/(DDE+ DDD) is often used to indicate whether fresh technical DDT input is viable [15]. In addition, o,p'-DDT/p,p'-DDT is close to 7 in dicofol and 0,2 in technical DDT mixture; hence, a ratio of o,p'-/p,p'-DDT close to 7 suggests the likelihood of dicofol-related inputs [16].

	IUPAC name	Molecular weight (g.mol <sup>-</sup>	Water solubility 25°C (mg.l <sup>-1</sup> )	Vapour pressure	log K <sub>OW</sub>
o,p´-DDT	1,1,1-trichloro-2,2-bis (p-chlorophenyl)ethane	354.49	0,085	1,1.10 <sup>-7</sup> torr (20°C)	6,79
o,p´-DDE	1,1-dichloro-2,2-bis (p-chlorophenyl)ethylene	318,03	0,14	6,2.10 <sup>-6</sup> torr (25°C)	6,00
o,p'-DDD	1,1-dichloro-2,2-bis (p-chlorophenyl)ethane	320,05	0,1	1,94.10 <sup>-6</sup> torr(30°C)	5,87
HCB	hexachlorobenzene	284,78	0,006	1,09.10 <sup>-5</sup> mmHg (20°C)	5,73
Alpha HCH	alpha-1,2,3,4,5,6- hexachlorocyclohexane	290,83	10	4,5.10 <sup>-5</sup> mmHg (25°C)	3,8
Beta HCH	1-alpha, 2-beta, 3-alpha, 4-beta, 5-aplha, 6-beta- hexachlorocyclohexane	290,83	5	3,6.10 <sup>-7</sup> mmHg (20°C)	3,78
Gamma HCH	1-alpha, 2-alpha, 3-beta, 4-alpha, 5-alpha, 6-beta- hexachlorocyclohexane;	290,83	17	4,2.10 <sup>-5</sup> mmHg (20°C)	3,2
Delta HCH	1-alpha,2-alpha,3-alpha, 4-beta, 5-alpha, 6-beta- hexachlorocyclohexane	290,83	10	3,5.10 <sup>-5</sup> mmHg (25°C)	4,14
Heptachlor	1,4,5,6,7,8,8-heptachloro- 3a,4,7,7a-tetrahydro-4,7- methanoindene	372,32	0,05	3.10 <sup>-4</sup> mmHg (20°C)	6,10
Mirex	1,4,5,6,7,8,8-heptachloro- 3a,4,7,7a-tetrahydro-4,7- methanoindene	372,32	0,05	3.10 <sup>-4</sup> mmHg (20°C)	6,10

SELECTED PROPERTIES OF CHOSEN ORGANOCHLORINE PESTICIDES [8]

### Hexachlorobenzene (HCB)

This compound does not occur naturally. It is formed as a by-product during the manufacture of chemicals used as solvents (substances used to dissolve other substances), other chlorine-containing compounds, and pesticides. Small amounts of hexachlorobenzene can also be produced during combustion processes such as burning of city wastes. It may also be produced as a by-product in waste streams of chlor-alkali and wood-preserving plants. It was also used to make fireworks, ammunition, and synthetic rubber [17]. Hexachlorobenzene was widely used as a pesticide until 1965. In Slovakia HCB was manufactured in a Bratislava chemical plant in the 60's and 70's. It was used mainly as a pesticide until its use was banned in 1976. For example, in 1971 about 4.5 t of active ingredient was used in agriculture [13].

### Hexachlorocyklohexane (HCH)

An insecticide on fruit, vegetables, and forest crops, and animals and animal premises - hexachlorocyclohexane (HCH) is a synthetic chemical that exists in eight chemical forms called isomers. The different isomers are named according to the position of the hydrogen atoms in the structure of the chemical [18]. Amongst the hexachlorocyclohexane isomers, lindane (gamma HCH) was consistently present in higher concentrations than alpha- and beta-HCH. This suggests that lindane has been used instead of technical HCH, a mixture that contains several HCH isomers, generally with high percentages of alpha-HCH [19]. Commercial HCH contains 55–80% alpha-HCH, 5–14% beta-HCH, 12–15% gamma-HCH, 2–10% delta-HCH and other chloroorganic compounds [20]. In soils, the average half-life of

delta-HCH is 20–50 days, while that for alpha-HCH is 20 weeks [19]. Because the ratio of alpha-HCH/gamma-HCH (4–7 in commercial grade HCH) is relatively stable, it can be used as an indicator of the level of degradation or use of HCHs [20].

### *Heptachlor*

Heptachlor is a manufactured chemical and doesn't occur naturally. It is produced via the Diels-Alder reaction of hexachlorocyclopentadiene and cyclopentadiene. The resulting adduct is brominated followed by treatment with hydrogen chloride in nitromethane in the presence of aluminum trichloride or with iodine monochloride. Pure heptachlor is a white powder that smells like camphor (mothballs). Heptachlor was used extensively in the past for killing insects in homes, buildings, and on food crops, especially corn. These uses stopped in 1988. Currently it can only be used for fire ant control in power transformers [21].

### Mirex

Mirex is not known to occur in the environment as a natural product. Mirex was produced as a result of the dimerization of hexachlorocyclopentadiene in the presence of an aluminum chloride catalyst. Technical grade preparations of mirex contained 95,18% mirex, with chlordecone as a contaminant. Mirex was most commonly used in the 1960s as an insecticide. Because it is nonflammable, mirex was marketed primarily as a flame retardant additive for use in various coatings, plastics, rubber, paint, paper, and electrical supplies [22].

### **Samples and methods**

## Sample collection

Thirty–four samples of surface sediments were collected from three water reservoirs – Zemplinska Sirava, Ruzin (at Hnilec and Hornad puller) and Velke Kozmalovce in July – Spetember 2003. Details of the sampling sites are shown in Fig. 2. These sampling sites were recorded using the global position system (GPS). The sediments of the Ruzin water reservoir were collected using a stainless steel box corer (developed by Czech Geology Survey, Brno). Other sediments were collected using UWITEC sediment sampling equipment (Austria). Sediment samples were stored in glass bottles, capped with aluminum foil and transported inside ice-chest boxes to the laboratory at the Czech Geology Survey, Brno. They were dried, ground, homogenized and stored to prior analysis. Detailed information is reported in Hiller et al. [23].

### Extraction and analysis

Extractable organic matter (EOM) was extracted by agitation with a mixture of n-hexane and acetone (1 : 1, v/v), supported by an ultrasound. Evaporation residues of EOM were used for the determination of the organochlorinated pollutants of interest (PCB, OCP). Hexane leachates of EOM evaporation residues were chromatographically purified on a column with silica gel, impregnated with concentrated H<sub>2</sub>SO<sub>4</sub>, NaOH and AgNO<sub>3</sub>. Pentane eluates, concentrated using the TurboVap evaporator (Zymark, USA), were analysed on an HP 5890 (Hewlett-Packard, USA) gas chromatograph equipped with an electron capture detector (ECD) and HP ChemStation software package. The basic parameters of the HRGC experimental arrangement for analysis of halogenated substances were: capillary column HP-5 (length 60 m, inner diameter 0,25 mm, phase film thickness 0,25  $\mu$ m), hydrogen as carrier gas, automated pulsed splitless sample injection. This way, altogether 14 components (congeners) of PCB and 8 components of OCP were determined, with LOD values of about 0,1 ng/g for the majority of the analyzed analytes with relative standard deviations of about 15 %.



Fig. 2. Map of sampling sites



Fig. 3. The sampling equipment

### **Results and discussion**

#### PCB concentrations and source identification

COr	NCEN	IKA	HON	S OF	PCBS	s (ng/g	, DK Y	WEI	GHT)	IN B	0110	JM 21	EDIM	ENIS	<u>s 1ac</u>	ne s
	Velke Kozmalovce Zemplinska Sirava		a	Ruzin / Hnilec				Ruzin / Hornad								
	min.	max.	mean	med.	min.	max.	mean	med.	min.	max.	mean	med.	min.	max.	mean	med.
CB8	0,29	1,10	0,88	0,93	0,96	181,00	44,53	30,00	0,38	1,83	1,41	1,02	0,22	1,20	0,42	0,24
CB18	0,81	2,87	2,03	2,05	1,31	209,00	54,16	30,50	1,19	5,11	4,64	3,75	0,52	4,90	1,29	0,58
CB28	1,59	4,66	3,66	3,88	3,35	501,00	137,76	87,50	2,50	8,42	8,61	7,83	1,33	8,20	2,55	1,45
CB31	1,34	3,95	3,14	3,30	2,18	378,00	95,62	65,00	1,80	6,27	6,04	5,56	0,89	6,00	1,82	1,04
CB44	1,01	2,69	1,95	1,93	1,19	113,00	39,59	31,90	1,27	4,10	3,77	3,84	0,54	3,70	1,10	0,63
CB52	1,52	3,51	2,64	2,66	2,12	205,00	68,69	57,90	1,64	4,91	4,44	4,55	0,93	4,20	1,52	1,04
CB101	2,77	5,67	4,16	4,13	2,27	149,00	58,93	52,80	1,59	4,36	3,20	3,27	2,14	3,10	2,63	2,78
CB118	1,17	2,16	1,68	1,71	1,04	85,10	31,88	27,50	0,64	1,77	1,39	1,42	0,68	1,20	0,87	0,83
CB138	4,32	6,79	5,95	6,18	2,61	176,00	69,32	63,20	2,27	7,00	4,09	4,02	3,70	6,78	5,19	5,42
CB149	3,39	6,00	4,98	5,07	2,51	165,00	63,87	54,90	2,00	5,40	3,43	3,49	3,20	5,37	4,31	4,60
CB153	4,48	7,19	6,28	6,53	2,79	197,00	72,44	63,90	2,47	7,26	4,42	4,40	4,10	7,14	5,58	5,86
CB180	3,20	4,99	4,15	4,12	1,65	121,00	48,22	40,60	1,70	5,29	3,11	2,98	3,20	5,24	4,07	4,08
CB194	0,66	1,03	0,82	0,78	0,41	25,40	11,07	9,96	0,46	1,03	0,64	0,61	0,66	0,99	0,80	0,75
CB203	0,76	1,02	0,87	0,84	0,51	24,50	10,86	9,32	0,37	1,05	0,75	0,75	0,72	1,10	0,91	0,90
SUM PCB	27,31	53,63	43,20	44,07	24,90	2530,00	806,94	624,98	20,28	63,80	49,95	47,45	22,83	59,12	33,05	30,21

CONCENTRATIONS OF PCBs (ng/g DRY WEIGHT) IN BOTTOM SEDIMENTS Table 3

The concentrations of  $\Sigma$  PCB (the sum of measured 14 congeners) in the bottom sediments from three Slovak water reservoirs ranged from 20,28 ng/g (Ruzin/Hnilec) to 2530,00 ng/g dry weight (Zemplinska Sirava) with a mean value 233,28 ng/g. The highest concentration of  $\Sigma$  PCB was found at site ZS2 – S, and the second highest at site ZS3 – S (1135,60 ng/g). The source of these higher concentrations is Chemko Strazske. In sediment samples, the most abundant PCB congeners were 28, 31, 153,138 comprising up to 46,35% of the total amount of PCB. The PCB concentrations in sediments from three Slovak water reservoirs were found to be lower than the maximum of those in the sediments of other lakes and rivers in Slovakia. In 1997 - 1998 the Institute of Preventive and Clinical Medicine (IPCM) in Bratislava analyzed 53 samples of stream and lake sediments taken from the surroundings of the chemical plant Chemko Strážske. All results were positive. The maximum sum value of PCBs was registered in the waste canal from the chemical plant with PCB concentrations achieving 4100 ng/g. The State Hydrometeorological Institute analyzed PCBs in sediments from the Slovak rivers Danube, Hron, Ipel and Vah in 2001. Altogether 21 samples were analyzed. Positive values were discovered in 4 samples from the Danube and 1 sample from the Vah [13]. In comparison to other regions and countries, Kang et al. [24] reported  $\Sigma$  PCB 11,5 – 485 ng/g dry weight from the Perl River Estuary, South China, Xing et al. [25] 15.1 - 58 ng/g dry weight from Minjiang River, Southeast China and 0.62 - 337 ng/g dry weight from Songhua River, Northeast China. Hartmann et al. [26] reported  $\Sigma$  PCB 20,8 - 1760 ng/g dry weight from Narragansett bay, USA, Barakat et al. [27] 0,9-1210 ng/g dry weight from Alexandria harbour, Egypt, Sprovieri et al [28] 10 - 899 ng/g dry weight from Neaple harbour, Southern Italy. He et al. [29] reported  $\Sigma$ PCB nd – 6,0 ng/g dry weight from the mid- and down-steam of the Yellow River, North China and Shen et al. [30] 0,92 - 9,7 ng/g dry weight from the lower reaches of the Yangtze River, East China.



Fig. 4a) Concentrations of  $\Sigma PCB$  (ng/g dry weight) and 4b) percentage compositions of PCBs in sediments

Our sediment investigation revealed the general prevalence of lower molecular weight PCBs. The proportion of different PCBs in sediment samples from Zemplinska Sirava and Ruzin / Hnilec decreased in the following order: trichlorobiphenyls, hexachlorobiphenyls, tetrachlorobiphenyls, pentachlorobiphenyls, heptachlorobophenyls, diand octachlorobiphenyls in Zemplinska Sirava / octa- and dichlorophenyls in Hnilec. The dominant congeners in Velke Kozmalovce and Ruzin / Hornad are hexachlorobiphenyls, trichlorobiphenyls and pentachlorobiphenyls. A number of previous studies show the production of low molecular weight PCBs during steel manufacturing processes. This is due to the presence of PCBs in fly ash generated from burning coal during the iron ore sintering process [31, 32]. A relatively higher percentage of high chlorinated congeners, such us heptachlorobiphenyl and octachlorobiphenyl in our sediments indicates near-source emissions of PCBs from industrial wastewater and domestic sewage. Congener composition indicates that the PCBs in sediments originated from sources like Delor 106 (used mainly as paint additive) or Delor 103 retrospectively (used primarily in power capacitors as dielectricum). The result is also consistent with the fact that the heavier PCBs are deposited nearer the source while lower chlorinated PCBs are more mobile and easily biodegraded [33, 34, 35].

## **OCP** concentrations and source identification

## CONCENTRATIONS OF OCPS (NG/G DRY WEIGHT) IN BOTTOM SEDIMENTS

Table 4

	V	elke Ko	zmalovo	e	7	Cemplins	ka Sirav	a		Ruzin	/ Hnilec			Ruzin /	Hornad	
	min.	max.	mean	med.	min.	max.	mean	med.	min.	max.	mean	med.	min.	max.	mean	med.
p,p'- DDT	2,25	13,00	6,58	4,35	0,40	8,50	3,38	3,00	0,40	1,70	0,69	0,50	0,40	15,10	2,77	0,50
o,p'- DDT	0,38	0,92	0,69	0,73	0,50	5,30	1,03	0,50	0,30	0,30	0,43	0,30	0,30	0,70	0,36	0,30
p,p'- DDE	5,51	9,79	8,47	8,95	1,27	410,00	54,46	9,92	2,36	8,60	6,35	6,88	4,60	13,20	10,18	10,70
o,p'- DDE	0,20	0,22	0,21	0,21	1,00	7,57	1,73	1,00	0,17	0,23	0,21	0,21	0,20	0,54	0,32	0,29
P,p'- DDD	0,31	1,29	0,60	0,47	0,30	53,30	6,58	0,70	0,30	0,50	0,32	0,30	0,30	6,00	1,57	0,50
o,p'- DDD	2,00	2,00	2,00	2,00	2,00	41,20	6,36	2,00	2,00	2,00	2,00	2,00	2,00	2,00	2,00	2,00
HCB	0,66	9,24	3,44	2,59	0,27	2,64	1,09	1,01	0,53	9,00	1,73	1,06	0,90	2,80	2,29	2,51
Lindan	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50
Hepta chlor	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50
Mirex	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40



Fig. 5a) Concentrations of  $\Sigma DDT$  (ng/g dry weight), 5b) percentage compositions of DDT and its metabolites 5c) Concentrations of hexachlorbenzene in sediments

It is still possible to prove the presence of DDT in the environment together with the DDT degradation products DDE and DDD. The total concentrations of DDTs (sum p,p'-DDT, o,p'-DDT, p,p'-DDE, o,p'-DDE, p,p'-DDD, o,p'-DDD) ranged from 5,47 to 525,7 ng/g dry weight, with a mean of 29,81 ng/g. The highest concentration of DDTs was found at site ZS3 – P and the lowest concentration was detected at ZS4 – S (Zemplinska Sirava). In comparison to other reports, the DDT pollution was relatively comparable. Amongst 73 samples taken in the Spiš-Gemer Mountains, 7 were positive - with the maximum concentration of 208 ng/g. Samples of water sediments were taken in the frame of the project TIBREG in districts Sobrance, Vranov, Michalovce and Trebisov. The content of DDT in the sediments was low even though agricultural activities are widespread in this region. Of 125 samples, only 2 were above the detection limit - 90 and 20 ng/g. The highest DDT concentration was discovered in the district of Levice: 940 ng/kg in the sample taken near the village Horsa [13]. May et al. [36] reported  $\Sigma$  DDT 35,1 – 91,1 ng/g dry weight from Zhujiang River, China, 22,9 – 40,41 ng/g dry weight from Shiziyang River, China, 5,0 – 16,6 1 ng/g dry weight from Xijiang, China, and 26 – 115,6 1 ng/g dry weight from Lingding Bay, China.

Among DDT and its metabolites in our sediment samples, p,p'-DDE was most dominant and its concentrations were in the range of 1,27 - 410 ng/g dry weight with a mean value 20,25 ng/g dry weight, accounting for 68% of the total DDTs. o, p'-DDD was the second highest. This composition indicated an aerobic pathway of metabolism of DDT, probably after its application on agricultural soil. Evaluating the o,p'-DDT/p,p'-DDT ratio in all samples, there were used a technical DDT mixture, and using the DDT/(DDE+ DDD) ratio we can determine historical application.

Hexachlorbenzene (HCB) was detected in all soil samples collected, and the concentrations ranged from 0,27 (Zemplinska Sirava) to 9,24 ng/g dry weight (Velke Kozmalovce) with a mean 1,98 ng/g. The higher concentrations were detected in the sediment samples VK3 – S (9,24) and HN3-L (9,0). Some previous studies reported the existence of HCB in sediments near the Chemko Strazske chemical plant, in the water reservoirs of Domaša, Sirava, Laborec and Ondava. The highest concentrations were found in the western part of the water reservoir Sírava: 1100 mg/kg, in the central part of Zemplinska Sirava: 100 mg/kg, Domaša – Turany nad Ondavou: 1100 mg/kg, Domaša-Bžany 2500 mg/kg. The content of HCB in other samples was below 1 mg/kg. [13] By comparison with other countries, our levels of HCB were similar to or higher than those of others studies as follows: Han river (main stream): 1,43 ng/g, Bukhan river: 1,74 ng/g and Namhan river: 1,34 ng/g [37]

Lindan, heptachlor and Mirex was analyzed in all sediment samples, but their concentrations were under the concentration limit.

#### Conclusions

The present study examined the occurrence, distribution and possible sources of 14 congeners of PCBs and 10 OCPs in bottom sediments from three Slovak water reservoirs. Although the use of these POPs is banned, it is still possible to prove their presence in the environment. The most frequently occurring POPs in three Slovak water reservoirs – Zemplinska Sirava, Velke Kozmalovce and Ruzin are PCBs, DDT and hexachlorobenzene.

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## **RESEARCH PAPERS FACULTY OF MATERIALS SCIENCE AND TECHNOLOGY IN TRNAVA** SLOVAK UNIVERSITY OF TECHNOLOGY IN BRATISLAVA

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# THE IDEAS AND EXPECTATIONS OF NEW UNIVERSITY STUDENTS TOWARDS UNIVERSITY TEACHERS

## Jozef STRAKOŠ

### Abstract

The article presents the results of an inquiry focused on new university students' ideas and expectations about their schooling, and especially about the university teachers during their first days at university. The method of inquiry -"unfinished sentences" technique - was used to collect data. There were 208 respondents aged from 19 to 47, including both males and females. The results gained describe the situation on this matter at the Faculty of Materials Science and Technology of Slovak University of Technology in Trnava, and they can also serve as self-reflection material for all university teachers. Two possible ways of further continuing the research work are described by the author.

## Key words

university students, ideas and expectation inquiry, unfinished sentences, university teacher, quality of schooling

#### Introduction

Quality of education is very often discussed in conferences and contemporary educational literature. What is its core?

The quality of the educational process is based on the reaching of instructional goals, achievement of educational standards and requirements of its customers, and especially reaching of students' satisfaction [1].

The first step to achieve the satisfaction of students is recognising their expectations.

But what are the expectations of students at our universities? There are many good examples of students' evaluation of their university studies, but there has still been a special group of university students here that has not been attracting the attention of our researchers

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yet: the new students at universities ("novices"). Our faculty – the Faculty of Materials Science and Technology of Slovak University of Technology in Trnava – offers to all new undergraduates at the beginning of their university career an intensive course called "An *Introduction to the University Studies*". This academic year (2009/2010) we used the frame of this course to do a qualitative study – an analysis of new university students' ideas and expectations about their schooling. We have specifically focused on their ideas and expectations about university teachers.

#### Methods

We decided to use the projective method of inquiry – the "unfinished sentences" technique. Our respondents – 208 new university students, aged from 19 to 47 – were asked to complete a set of 7 unfinished sentences specifically designed for this purpose. The printed form of the items was distributed by their teachers to them in the beginning of their first seminar. Our respondents completed writing the sentences in 15 minutes.

The next steps were analysis of the verbal categories of the conclusions (words, phrases and sentences filled in), sorting them according to their similarities, and creating consistent groups. This was a quite difficult part of our research work. We have found two books, which are listed in the bibliography, very helpful [2, 3]. The distribution (percentage) of the respondents of the inquiry, according to their demographic profiles, is presented in the next table.

Gender/Age	19 - 25 years old	26 - 47 years old	Together
Female	44 (21,15 %)	34 (16,35 %)	78 (37,50 %)
Male	65 (31,25 %)	65 (31,25 %)	130 (62,50 %)
$\mathbf{F} + \mathbf{M}$	109 (52,40 %)	99 (47,60 %)	208 (100 %)

#### **Results**

### Will our new university students like schooling?

An answer to this question was an initial goal of our inquiry. 208 new university students of our faculty were asked to finish this unfinished sentence: "*I will enjoy (be interested in) my schooling if ...*"

Respondents finished the sentence with 272 conclusions. Most of them (134) expressed requirements connected to **what is taught**. Over 36 % of new university students would like to find the content of instruction interesting and attractive; more than 16% of them would like to encounter good examples from practice; and more than 12 % of them would like to find the content useful and meaningful.

There were also many conclusions to the sentence (68) describing the **teacher's instructional skills**. Over 16 % of new university students would like to have the content well explained. This requirement was significantly more preferred by women. More than 9 % of all respondents will enjoy their schooling if the teacher is able to instruct them in an attractive way.
The third biggest group of conclusions to the sentence dealt with the **student's individuality**. Over 17 % of respondents conditioned their enjoyment of their schooling on having their own success. This requirement was significantly more preferred by men. Other conclusions from this group (time management, coping with stress, the ability to concentrate on the instruction, personal vitality) appeared occasionally.

The other 2 groups of conclusions were connected to **teaching aids** (8 conclusions) and the **instructional climate** (5).

We can also arrange the results into a list of the positive expectations of our new university students before starting their university studies (Top 5).

Top 5 positive expectations of new university students:	Incidence
1. I will learn interesting and attractive things	36,05 %
2. I will understand them and I will succeed	17,31 %
3. Everything will be clearly explained to me in detail	16,35 %
4. I will meet good examples from practice	16,35 %
5. I will learn useful and meaningful things	12,02 %

#### What are our new university students' ideas about effective methods of instruction?

Answering this question was the next item of our inquiry. Our new students were asked to finish this unfinished sentence: *"From the methods of instruction point of view it is important to ..."* 

Respondents finished the sentence with 232 conclusions. Most of them expressed requirements connected to **attractiveness and dynamics** (66) and to **simplicity and intelligibility** (61) of instruction.

The results also showed that use of **visual and schematic tools**, implementation of **up to date content**, maintenance of a suitable **tempo of the instruction**, and use of **dialogue methods** were also important for our new university students.

Here is the list of important requirements of new university students on methods of instruction before their university studies start.

Im	Incidence	
1.	Attractiveness and dynamics of instruction	31,73 %
2.	Simplicity and intelligibility of instruction	29,33 %
3.	Use of visual and schematic tools	14,42 %
4.	Implementation of up to date content	13,94 %
5.	Maintenance of suitable tempo of the instruction	8,65 %
6.	Use of dialogue methods	7,69 %

#### What should a good university teacher know, be able and willing to do?

Our new university students were also asked to finish 3 unfinished sentences: "A good university teacher is one who knows ...", "A good university teacher is one who is able to ..." and "A good university teacher is one who is willing to ..."

208 respondents finished the sentences with 690 conclusions (225 about knowledge, 233 about abilities, and 232 about willingness).

Their portrait of a good university teacher, based on their conclusions, is described below:

A good university teacher is one who	Incidence
knows the subject taught well	65,86 %
is able to explain things simply and clearly	42,79 %
is willing to help students (also outside the official time of instruction)	37,50 %
is able to attract and draw attention	35,58 %
is willing to explain things once more	27,88 %
is willing to give individual advice (individual consultation)	24,04 %
knows the students (their needs, abilities, feelings,)	18,75 %
knows effective ways how to teach (to motivate, to explain, to	17,31 %
communicate,)	

#### What should a good university teacher avoid?

Respondents were asked to finish this unfinished sentence: "A good university teacher is one who is able to avoid ...".

The conclusions varied quite a lot, but the most common ones were snobbery and arrogance (25,00%), biased assessment (19,71%) and monotony and stuffiness (9,13%).

#### What are the most important characteristics of a university teacher?

The final item of our inquiry was eliciting the most important characteristics of university teacher from our new university students. They were asked to finish this unfinished sentence: *"I think the most important characteristics of a university teacher are..."* 

The most important characteristics of a university teacher are	Incidence
Willingness to help students	32,21 %
Respect for students	23,56 %
Patience	21,15 %
Fair / unbiased assessment	20,19 %
Empathy	16,35 %
Tolerance	12,98 %
Effort, diligence	12,50 %
Professional knowledge	12,02 %
Sense of humour	11,06 %
Wisdom and intelligence	9,62 %

#### **Discussion** (Author's contribution)

The goal of this article was to share research findings with colleagues interested in promoting the quality of education at our universities. The inquiry described was focused on a survey of university students' ideas and expectations about their schooling during their first days at university. They have almost no experience with university instruction or university teachers, so their ideas and expectations are not "loaded" by their own "bad" experience, and we suppose they are quite sensitive to the new situation they are in. The acquired results are quite practical (they have assessed and represent the real situation of the circumstances at our faculty) and they can serve as self-reflection material for university teachers.

We can see 2 ways of further inquiry that can grow from this study:

- 1. long-term research on the changing ideas of students and their expectations about schooling during university study,
- 2. comparison of differences in the results gained by the methods of this inquiry ("unfinished sentences" technique) and the questionnaire method.

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## **RESEARCH PAPERS** FACULTY OF MATERIALS SCIENCE AND TECHNOLOGY IN TRNAVA SLOVAK UNIVERSITY OF TECHNOLOGY IN BRATISLAVA

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# RESEARCH OF METAL FLOW IN CLOSED DIE IN PRECISION FORGING

# Anton ULÍK, Ľuboš KRAVÁRIK, Ľuboš BERNADIČ

#### Abstract

The first part of the article contains the brief characteristics of the precision die forging process. The second part of the article focuses on the design and trials of the press tool for precision die forging of spur gear where aluminum is used as model material. The conclusion gives an evaluation and comparison of material flow in the die cavity, based on the results taken from material experiment and computer simulation.

#### Key words

precision die forging, spur gear, material experiment, simulation of metal flow

#### **Theoretical part**

The process of precision die forging is a separate part of die forging. The technology enables finishing of parts with high dimensional accuracy and high surface quality (near net shape parts) [1].

The main methods of precision die forging which allow for the reduction of material consumption are closed die forging and minimal fillets forging, or forging without fillets. Making cuts in the consumption of material has a serious influence on the final price of the forged piece. This process requires an exact volume of semi-product and exact division of material in the rough forge operations because there is no possibility of displacing surplus material into the flash [3].

There are many factors which have an influence on precision die forging (Fig. 1): the material of the forged piece, tribology, CAD/CAM tools, the forming presses, running, theory

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of plastic simulation. Analysis of these factors is not easy, therefore research in this area is common nowadays [4].

The accuracy and stiffness of the tool, the thermal contraction, the amount of each forging operation, and the parameters give accuracy in forgings. Nowadays these characteristics can be researched with the help of computers (numerical simulation) where technological parameters can be changed, and the optimal conditions of forging and shape of forged pieces can be achieved.



*Fig. 1.* Precision die forging with slot aperture compensation of material surplus [2] 1 – upper die, 2 – lower die, 3 – tool ejector

#### Utilization of the process of simulation

In the experiment the process of material flow simulation in cavity dies was used. This method was based on the division the forged piece into small elements where the path of material flow and the position neutral axis or plane can be defined. Proper characteristics, such as temperature, coefficient of friction, speed of plastic strain, etc., were given to the element. The course of stress and proper force for the element can be obtained by the method of basic equations of equilibrium.

#### **Experimental part**

This part of the article focuses on the design and trials with the tool for precision die forging of the spur gear (Fig. 2) and evaluation and comparison of material flow in the cavity die which is based on the results obtained from material experiment and computer simulation.



*Fig. 2. Forged piece – spur gear* 

Aluminum was used as the material of the forged piece in order to save on experiment costs and energy. The process of the precision die forging was completed by cold forging.

The designed press tool (Fig. 3) was tested on the hydraulic press PYE 160 S under laboratory conditions.



Fig. 3. Designed precision die forging tool [4] 1 – die holder, 2 – die, 3 – lower punch, 4 – ring, 5 – pin of spring ejector, 6 – bullet, 7, 13, 15 – screws, 8 – support plate, 9 – fixing plate, 10 – bushing guide, 11 – punch, 12 – upper punch, 14 – guidepost, 16 – ringled

Material flow of metal in the cavity die in the lower part of the forging die, in connection with the travel of the upper punch, was observed during the material experiment and the course of press force  $F_L$  was obtained.

Note: The forged piece was taken out of the press tool during the process of forging under different values of press force and its dimensions were measured.

#### Realisation of precision die forging simulation

The precision die forging simulation was performed by using the simulation programme MSC.SuperForge [6]. The simulation consisted of one operation – precision die forging of a cylindric aluminum semi-product sized  $\emptyset$ 60 x 25 mm and manufactured by lathe.

The process of entering the input data necessary for starting the simulation:

- forming process: closed die forging, in cold forging, 3D, FVM,
- geometry of the tool and semi-product: designed in Inventor (CAD program) and imported into the programme,
- material of semi-product: DIN AA\_1100 (T =  $18^{\circ}$ C) equivalent of aluminum material for cold forming,
- material of the tool: H-13 equivalent to material 19 554,
- forming press: hydraulic press PYE 160 S (v = 0,2 m/s),
- coefficient of friction: 0,3 (plastic shear friction),
- start temperature of semi-product and temperature of the tool and ambient: 18° C,
- length of the stroke: 20 mm,
- size of the element used in simulation: 1,
- start of simulation,
- evaluation of the results: many quantities such as division of the temperature, effective stress, plastic strain, *material flow*, etc. were observed in different stages of the forming process [2].

An example of visualization of the results in the MSC.SuperForge programme is given in Fig. 4.



Fig. 4. The division of effective stress under stroke z = 10 mm

Evaluation of the results showed that the highest effective stress is on the places where the upper tool is in contact with the semi-product. The lowest intensity is in the upper part of the gearing.

#### Comparison of material experiment and computer simulation

*The material experiment*, based on the tests of metal flow in precision die forging of spur gear in a closed die with a fixed lower die, showed that the process of material flow of a cavity die can be divided into two stages (Tab. 1).



In the first stage the metal (Al) started to flow into tooth spaces of the internal gearing of the die in its lower part, and at the same time the metal started to flow into the hub. After further loading, the metal flowed into the hub and at the same time it started to flow on the whole width of the gearing, while the lower part of the gearing was faster than the upper part.

In the second stage the flow material in the lower part of the tooth spaces was reduced. After further loading the metal filled the radius of the hub and almost the whole width of the gearing, while the tooth spaces were filled with the metal as a result of the friction effect on the contact surfaces of the semi-product and the die. Further loading caused the total filling of the tooth spaces, the radius of the hub, and the radius of the upper punch.

With the *computer experiment* (simulation) of cavity die material, the flow was very similar to the material experiment. The only difference was the following: after the filling of the lower part of the tooth spaces they started to be filled on the whole width. The results of the cavity die filling were influenced by many factors (the entry friction coefficient, the material of the semi-product, the forming press, the tool used, the size of the element used in simulation, etc.).

#### Scientific asset

The verification of the function of the designed forming tool for precision die forging of a spur gear in the experiment showed that the MSC. Super Forge simulation program can be used for simulation of precision die forging, and it can replace material experiments.

#### Conclusion

The comparison of the material experiment and the computer simulation of material flow in the cavity die proved that the results of a physical experiment in real conditions are equal to a theoretical – mathematic model of die forging simulation.

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# **RESEARCH PAPERS FACULTY OF MATERIALS SCIENCE AND TECHNOLOGY IN TRNAVA** SLOVAK UNIVERSITY OF TECHNOLOGY IN BRATISLAVA

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# LEAN LOGISTICS - THE IMPORTANCE AND UTILISATION IN SLOVAK INDUSTRIAL PRACTICE

Helena VIDOVÁ

#### Abstract

Predkladaný článok predstavuje problematiku štíhlosti aplikovanú na oblasť podnikovej logistiky. Jeho zámerom bolo charakterizovať zásadné okruhy problémov logistiky, ktoré je možno práve týmto prístupom eliminovať a dosiahnuť tak pozitívne ekonomické výsledky. Súčasťou príspevku sú parciálne výsledky prieskumu, zameraného na zistenie miery uplatnenia a využívania štíhlej logistiky v priemyselných podnikoch na Slovensku.

#### Key words

optimization, streamlined company, lean logistics, muda debugging ,logistics problems

#### Introduction

The actual worldwide economic situation poses massive need for problem solutions in changing conditions. Many times fundamental changes in business strategy are needed. There are changes concerning all parts of business management. Generally, changes are made by strengthening customer relations, innovation in the production process, eliminating waste, raising production continuity through stock reduction and increasing the turnover ratio, connection of partial processes into logical chains and coordinating them by use of information technology, building up corporate culture through staff education and also supporting product quality and activities at the highest level. Logistics contributes to the fulfillment of these goals because its synthetic approach, oriented to fast and economical customer service, corresponds with the mentioned tasks.

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## Lean Origins

A world financial and economic crisis has affected many businesses. Only those companies which were prepared can resist it. Those which behave rationally and eliminate wasteful expenditures and waste generally can resist it as well.

Toyota realized these facts in the 50's of the last century. It started with their approach to business process management and by limiting all that did not add value to the product or service. They labeled this problem as 3M, or more specifically [1]:

- 1. *Muda waste:* surplus production, waiting, useless transport, needless operation performance, extra stocks, wasted movements, bad quality, under-capacity staff operation.
- 2. *Muri abnormal staff and machinery charging.*
- 3. *Mura operations irregularity*. Mura is the result of these previous two Ms. There is production quantity variation because of internal problems such as dead time or missing material.

Mura and Muri are the basis of the existence of waste (Muda). It is necessary to fix Mura and Muri before starting with removal of Muda. Activities that do not add value to the products and are not necessity to make them are a waste of resources (delay, double handling, raw material accumulation). That is why it is necessary to eliminate them. Toyota put Mura, Muri and Muda into position to eliminate unwanted elements of process execution.

In 1990 the Massachusetts Institute of Technology (MIT) published a survey entitled "The Machinery that Has Changed the World" [2]. They precisely described how the western and Japanese automotive industries differ. Until that time, it was suggested that the right answer to the Japanese challenge is automation (as tried at VW or Fiat). The MIT survey argued that western assembly factories fall behind the Japan ones because of organization innovations.

The result of Japan's innovations was strong control of the organization of work. The employees started to work in teams and therefore they increased their adaptability and their interest in getting better. The process of continual improvement was established. In Japanese philosophy, a lot of small upturns are more important for efficiency than implementation of a completely new and expensive technology. Quality control and maintenance were made the job of line workers and therefore many indirect procedures became obsolete. All levels of company hierarchy were dismantled making the work organization more flexible and transparent. Complex quality control procedures and zero tolerance for sloppiness became leading priorities of business. Many aspects of business inputs were halved – the number of workers, trough time, production stock, area, space, etc. Fast reaction to everything was possible because the work made the employees proactive. Information technologies supplied higher production flexibility in the machine pool. The result was super lean organization of the company with super effective and committed personnel.

#### **Lean Logistics Mission**

Logistics, as the complex of inclusive service activities, has a very important position in management of business tasks. In some cases, it takes a share of 30% of final company costs. It is a fundamental proportion. Therefore it has sense to be interested in it in detail, to analyze the logistics processes, and to measure and evaluate their fruitfulness.

Practical experience shows that many businesses are focus mostly on lean production elements. Production has a massive effect on added value for the customer, but other business activities determine how fast and effectively we finally earn money. The Toyota way, based on the application of lean principles in logistics, is the impulse for improvement in this field.

Lean logistics is a set of complex approaches covering the management of inputs by functional supply relations and also cooperation in the existing company logistics structure. It is a key factor to emphasize the value of flow management, the quality factor, and continuous partial changes and improvement such as Kaizen. This should make harmony between "hard" elements like machines and facilities and "soft" elements such as people's work attitudes, motivation and knowledge, teamwork trends and efforts to communicate and solve specific problems [5].

In harmonizing these components, companies try to find the economic problems hidden in [2]:

- *stocks, excess property, components and spare parts* materials are delivered to companies in an untimely fashion or in excess quantity, the reason being inexact documentation or mistakes made in the planning system or by the supplier,
- redundant handling useless material movements, relocation, transport,
- *waiting* for components, materials, information, vehicles,
- *repair failures* in transport, handling or information system,
- *mistakes* setting out materials and components in incorrect quantity and time,
- *absent transport capacities,*
- *absent skills of the employees.*

In Slovakia, it is a relatively new matter to know and apply the lean conception in logistics. It is mostly an element of companies with participation of foreign ownership. The next chapter will deal with the characteristics and particular method of application in Slovak industry.

#### The Mission of Lean Logistics in Slovak Industrial Businesses

This survey has been carried out in spring of 2009. It was about the detection of the application of lean logistics and the Kaizen principle in Slovak Industrial Businesses. We addressed it to 128 companies. The response rate was 23 %. The survey was sent to logistics staff, quality managers, and to managers of economics departments.

The results show that the highest representation in the survey was big companies having more than 250 employees, mostly with foreign property participation. The respondents to the questionnaire were mostly from the engineering industry (26 %) and the automotive industry

(21 %). Besides that, businesses from the building, glass, electro-technical, textile, printing, and IT industry took part in it.



Fig. 1. Industries Taking Part in the Survey

The most frequent sources of problems in terms of continuity and efficiency of the logistics process were:

- product differentiation, frequent material renewal,
- material flow, utilization and organization of the warehouse area,
- observation of receiving and pick up windows,
- rising efficiency efforts in disharmony with area and staff utilization,
- communication failures, misunderstandings, issues ignored, ignorance, etc.

In discussion of these problems, we were interested in the approaches used for removal of mentioned issues.



Fig. 2. Issues Removal

The situation was not good because 40 % of the respondents do not solve those problems. Another 36 % did not answer this question because of fear or ignorance. Further companies tried to modify the lay-out of the work place, changing the arrangement to optimize material flow in business. Other ones used pull approaches, e.g. JIT, Kanban, to solve the stock issues and their quantity.

We also asked if the companies are familiar with the lean logistics problem at all.



Fig. 3. Problem Understanding

Sixty-four percent of respondents replied that they know the problems of lean logistics and 45 % of them implement it in practice. The most important problems that pertain to application of the principles of lean logistics were related to lack of confidence in this new spirit. Among businesses which have implemented and applied lean logistics, most applied it for more than one year. The median period was 3-4 years.

In evaluating the achieved contributions of lean principles in logistics, we have found that 36 % of the studied businesses achieve positive results, and that is why they proceed in this way. Unfortunately, 44 % of respondents do not evaluate the gained results. It can be concluded that they are missing economic tools and control of logistics activities in the relevant organizations.



Fig. 4. Evaluation of Lean Logistics Impacts

The contribution of lean logistics becomes evident in the following positive ways:

- growth of labour productivity,
- transport reduction (cca. about 15 %),
- efficiency and quality increase,
- faster investments returns,
- workplace organization (20 % 40 %),
- cost saving.

If the contributions of lean logistics are clear, which factors mainly affect its lack of use in practice? The most frequent reasons are: non-acquaintance because of lack of information or experts in this field (20 %) and no-confidence in new management concepts (16 %).



Fig. 5. Barriers to Lean Logistics Utilization

Some respondents explained their answers based on: the ongoing economic and financial crisis, administrative difficulties of the process, the need for continued training, motivation absence, stagnant thinking, non-use of the approaches that could improve the economy of the company, and log time functioning managers refusing the changes [3].

How could we break these barriers? The core solution is to be well-informed and to mention the advantages of lean logistics, e.g. cost and time savings, better area utilization, rising traffic speed, the transparency and organization of working places, increased employee motivation and involvement, faster reaction to customers' requirements, and finally stability development and competitiveness of the company in comparison with other businesses in the marketplace.

#### Conclusion

Now, lean efforts are one of the actual tools of effective business management and are the main ways how to improve business processes, and to clear them from redundant activities and waste at the administrative, production, and logistics level. This topic is important because we live in an era of big changes, economic reductions and money saving. In spite of that fact, we can observe from questionnaire results that there is still fear of new things in the business area that could bring positive effects. Businesses that have applied lean logistics and used it for several years have many positive outcomes. The courage of a competent staff is needed to break the barriers and primary failures too.

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