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RESEARCH PAPERS

FACULTY OF MATERIALS SCIENCE AND TECHNOLOGY
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CONTENTS

MATERIALS

ENGINEERING

TECHNOLOGY

INDUSTRY ENGINEERING

OTHERS

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

2010 Number 29

THE STUDY INTO THE TRANSITION AREAS OF A SOLDERED JOINT OF ITO CERAMICS

Martin PROVAZNÍK, Roman KOLEŇÁK, Monika KOLEŇÁKOVÁ

Abstract

The paper deals with solderability analysis of ITO ceramics (In_2O_3 / SnO_2) by metals. The soft active solder SnInAgeTi was used for experiments. Solder was actived by power ultrasound in air without flux. The analysis of interface of phases between solder and ceramic was done to discover ultrasonic impacts on active metal and identify creation mechanism of joint on the ceramic side.

Key words

ultrasonic activation, active solder, ITO (indium-tin oxide) ceramics

Introduction

The actual technical practice is characterized by increasing use of ceramic materials. This regards especially electrotechnical area. There are enormous requirements of conductive joining ceramics with metals. Soldering by active solders is a trend in this area on the present. These solders contain an active element, which reacts with surface of the ceramic material. This enables its wetting and reaction layer creation. The solders have a very low wetting angle, they enable soldering at low temperatures, without flux and additionally protection.

The most often used active metal is titanium. The reactive product transforms surface energy of ceramics and enables wetting of the solder. The active element moves from the whole solder volume to both soldered materials. In interface of the soldered joint there a reaction layer with thickness of several μm is created that contains reaction products of active elements and substrate [1].

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Activation of the solder is done mechanically or using a very high temperature effecting on the active element. Mechanical application is done by scraping, spreading by metal brush (soldering of: Cu, Al, CrNi steel), vibrations, ultrasound over 20 kHz (soldering of: ceramics, non-metallic materials). Working cycle of mechanical application is approximately 10 times shorter than high temperature activation and does not need application of vacuum or protective atmosphere.

Experiments

A sample was made by machinery displayed in the picture Fig. 1. The soldering process consists in heating soldered materials by a hot plate to the soldering temperature in the range of 150 – 160 °C. The maximum temperature of soldering is limited by the temperature of 160 °C, when surface oxidation of ITO ceramics increases. Heating by steps is chosen to reach steady heating of both materials. A strap shaped solder made by fast cooling technology is placed on a heated substratum Fig. 2. The solder is activated by a titanium peak of the ultrasonic equipment after melting-down. The activation time was chosen in interval 1 to 5 second in one contact point. In tab.1 are described the parametres of US equipment. The solder is applied on second substratum the same way. Both prepared parties are joined and softly pushed. The present of active solder protects high plasticity of phase interface

Soldering samples were fixed after splitting and prepared by a standard metallographic methodics. Consequently were analyzed by light microscope and scanning electron microscope. For further documentation joint creation mechanism were made analysis concentration profiles separate elements by rtg. diffraction analysis.

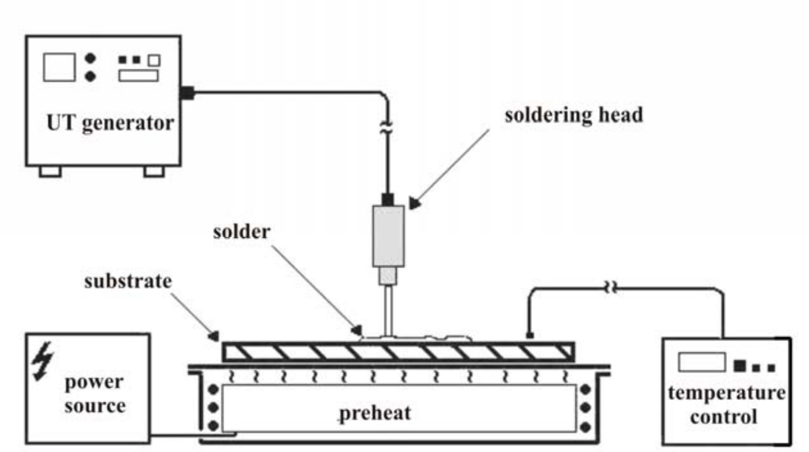


***Fig. 1.** Diagram of equipment for soldering by ultrasound*

PARAMETRES US EQUIPMENT Table 1

Output power – intermittent service	[W]	max. 400
Operative frequency	[kHz]	40
Input power	[W]	max. 600
Time adjustment range	[s]	0,1 - 9,9 for 0,01

Production principle of foil active solder

1. Molten alloy is extrusion by fine pressure of inert gas (argon, helium) trough the rectangular slot of jet placed near cooling shape copper disk.
2. Cooling rotate disk touch gradually molten solder. Outwardly the disk is created thin layer of solid alloy which the roll takes away.

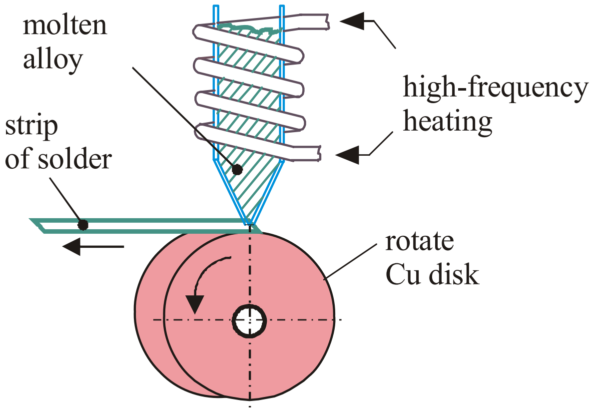


Fig. 2. *Solder production by fast cooling technology [2]*

The solder in foil shape with parameters 0,15 mm x 7 mm, was made by Physical institute SAV Bratislava for an experimental need. Solder was made from foundry alloy ready casting into ingot-mould.

Experiment results

On sample of active solder was made differential thermal analyze. Process of this analysis is recorded on Fig. 3. From DTA graphs we can specify thermal areas, where are phasic metamorphoses. Temperature 116 °C characterizing start of molten eutectic Sn-In. Temperature 156 °C is equivalent to molten temperature of neat indium.

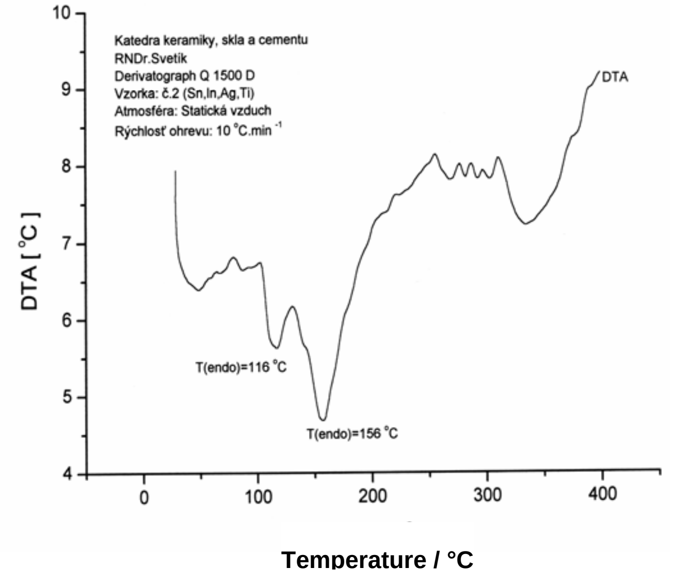
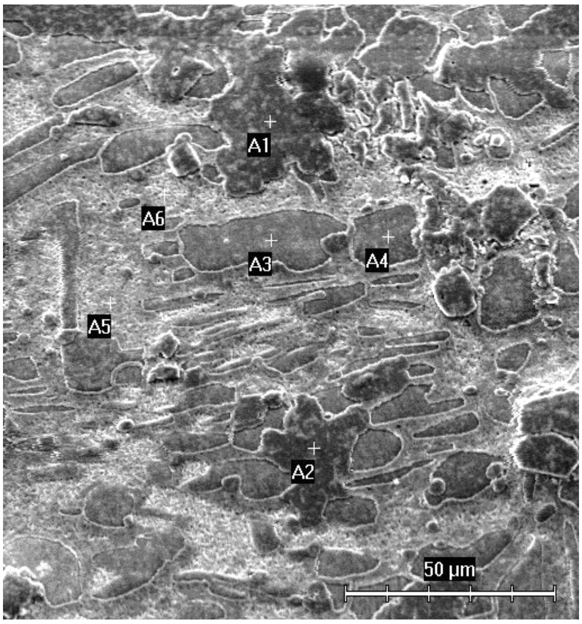


Fig. 3. *DTA of solder SnInAgTi*

Fig. 4 describes heterogeneous microstructure of soft active solder SnInAgTi in the molten status.



	Ti [at.%]	Ag [at.%]	In [at.%]	Sn [at.%]
A1	3,1	27,6	55,1	14,3
A2	1,9	29,3	53	15,8
A3	0	0,3	11,3	88,5
A4	0	0	12,1	87,9
A5	2,7	0	64,7	32,7
A6	0	0	71,4	28,7

Fig. 4. *Microstructure of SnInAgTi active solder [3]*

Quantitative chemical analysis of solder, made in places by Fig. 4. Dark grains, specified positions A1 and A2 are expressively enriched of Ti and Ag. Other pallid grains (areas A3, A4) and matrix (position A5, A6) they are explicitly composite by elements In and Sn.

For identification of phasic composition of solder after molding was made a radiographic diffraction analysis, by Physical institute SAV Bratislava, which identified these phases: In_3Sn, $InSn_4$, Ti_6Sn_5, Ag_3Sn, $AgIn_2$, Ti_3Ag [3]. That is why we can identify dark areas of a solder as a phase Ti_3Ag which demonstrate hight affinity titanium to silver.

On Fig. 5 is phasic interface of solder and ITO ceramics. From concentration profiles of individual elements across the interface is certain that, Ti partly participates on creation of joint, but there is supposition, that the biggest effect has Indium on creation of joint.

Provable effect of power ultrasound is, that the solder is able to fill narrow spaces among grains of ceramics, which proves high degree wetting ceramics by solder.

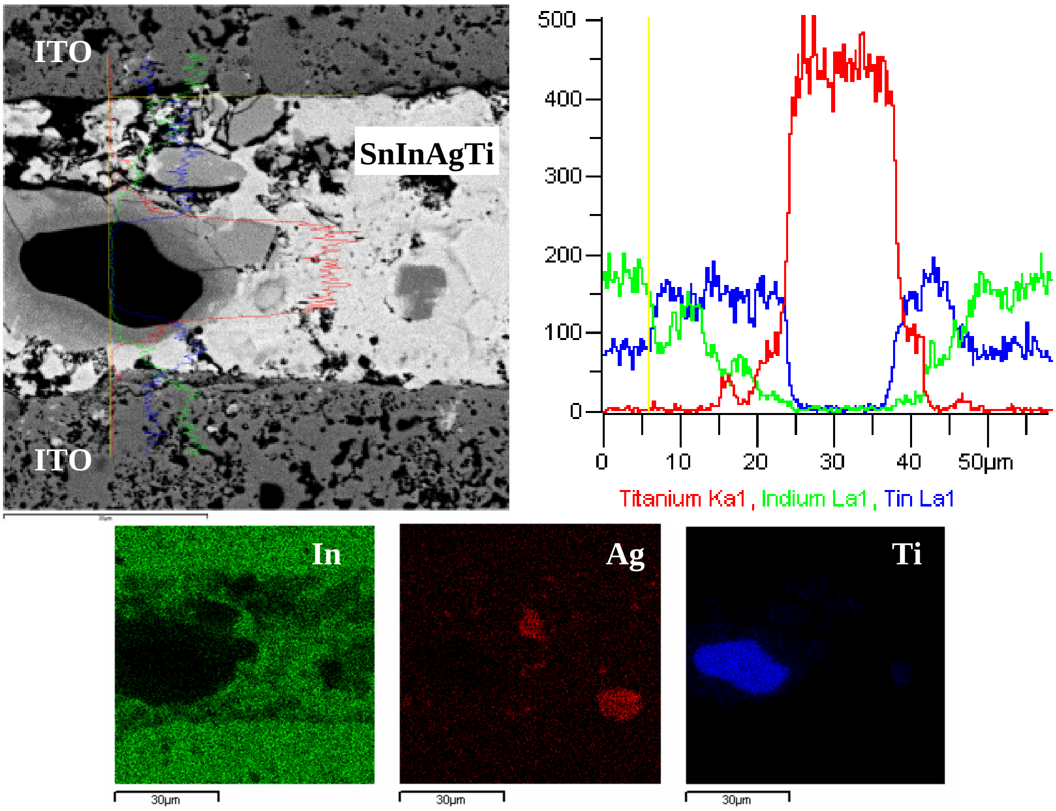


Fig. 5. *Interface SnInAgTi - ITO and concentration profiles of individual elements over the interface*

Indium markedly supports creating of joint in this monitoring interface. From performed experiments is certain that the mission of an active element in solder does not have to appear always. In this case is Ti indifferent (doesn't create any provable phases), it remains fixed in solder (first of all in phase Ti_3Ag) and it does not markedly participate on creation of joint.

As In has a high affinity to oxygen we can assume, that it combines in process of soldering with oxigen from air with complex oxid genesis of indium, which inputs to the reactions with the surface of ITO ceramics by simplified model on Fig.6.

An own contribution to the problem given

Own share to problematic study could be totaled in the folowing points:

- was designed and manufactured by methods of fast cooling development soft active solder SnInAgTi,
- by analyses of phases structure of development solder was identified phases: In_3Sn, $InSn_4$, Ti_6Sn_5, Ag_3Sn, $AgIn_2$, Ti_3Ag,
- development solder SnInAgTi drenched ITO ceramics by using the power ultrasound,
- by studies of interfaces was found out, that on the creation of the joint with ITO ceramics is in preferences participated Indium from the solder.

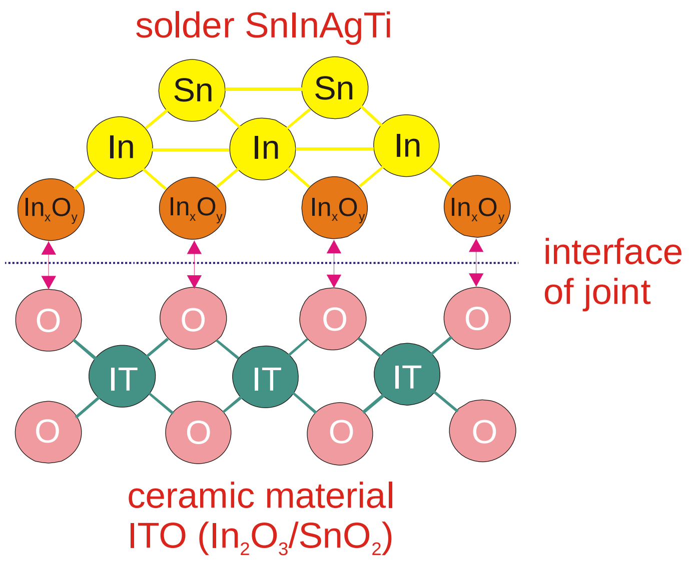


Fig. 6. *Simplified model creation of joint between ITO ceramics and solder SnInAgTi [4]*

Conclusion

Result of experiments was verification of possibility by creation soldering joint between metal and ITO ceramic. Soldering joint arise by using mechanical activation power ultrasound on air, without flux. It was proved that a solder SnInAgTi reacts with surface layers connected metals by the creation of reactive products of various thicknesses and qualities. That proves dissolving solids substrates in solder and creating of diffusion joints.

There is not evident any diffusion area on the interface between solder and ITO ceramics. Solder is able to leak in spaces between grains by which is created the mechanical joint. Important task on creation of joint has the indium, which creates oxides inputs to reaction with ceramics created by chemical bond.

Credits and Acknowledgments

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PRELIMINARY ECOTOXICITY AND BIODEGRADABILITY ASSESSMENT OF METALWORKING FLUIDS

Kristína GERULOVÁ, Peter AMCHA, Slávka FILICKÁ

Abstract

The main aims of this study were to evaluate potential of activated sludge from sewage treatment plant to degrade the selected MWFs (ecotoxicity to bacterial consortium) and preliminary study to evaluate the ecotoxicity by Lemna minor – higher plant. After ecotoxicity evaluation was assessed biodegradations rate with activated sludge by measuring COD. Preliminary study of ecotoxicity measuring according OECD 221 by Lemna minor shows effective concentration of Emulzin H at the rate of 81.6 mg l^{-1}*, for Ecocool 82.9 mg* l^{-1}*, for BC 25 about 99.3 mg* l^{-1}*, and for Dasnobor about 97.3 mg* l^{-1}*. Preliminary study of ecotoxicity measuring by bacterial consortium according to OECD 209 (STN EN ISO 8192) shows effective concentration of Blasocut BC 25 at the rate 227.4 mg* l^{-1}*. According OECD 302B the biodegradations level of Emulzin H, Ecocool and BC 25 achieved 80 % in 10 days. It can be state that these MWFs have potential to ultimate degradation, but it have to be confirm by biodegradability test with other parameters than COD which have some disadvantages in testing O/W emulsions.*

Key words

biodegradability, ecotoxicity, metalworking fluids

Introduction

Metalworking fluids (MWFs) have been introduced into the cutting process with the purpose to improve the characteristics of the tribological processes which are always present on the contact surfaces between the tool and the workpiece [1]. Exposes of the working environment to fluids may cause significant contamination to the environment and health hazards for the workers [2]. Future lubricants have to be more environmentally adapted, have a higher level of performance, and lower total life cycle cost (LCC) than presently used

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lubricants [3]. The use of rapidly biodegradable lubricants could significantly reduce environmental pollution. Environmental friendly alternatives are available for a large variety of mineral oil based lubricants [4]. The most interesting group for formulation of environmentally adapted lubricants is base fluids such as vegetable oils, synthetic fluids (polyglycols, polyalpha olefins (PAO), synthetic ester) [1, 2, 3, 4, 5]. These oils can offer significant environmental advantages thanks to resource renewability, biodegradability and nontoxicity [5]. In Europe predominantly vegetable oils such as rapeseed oil and sunflower oil are used [1, 3]. Chemically these are esters of glycerin and long-chain fatty acids (triglycerides) [3, 4, 6]. Natural triglycerides are very rapidly biodegradable and are highly effective lubricants. The use of vegetable oil in metalworking applications may alleviate problems faced by workers, such as skin cancer and inhalation of toxic mists in the work environments [7]. Biodegradable synthetic esters have much better performance than natural oils especially in the field of low and high temperature application and oxidation stability, but they are more expensive [5]. Properties related to environmental fate of metalworking fluids are toxicity (non toxic against to human beings, fishes, bacteria etc.) [6], degree of biodegradability, bioaccumulability and biomagnification, and relative content of renewable raw material.

Biodegradablity of MWFs

Biodegradation represents a major route for removal of oil from soil and water compartments. Hence, biodegradability studies are of significance for developing eco-friendly lubricants, devising corrective measures for cleanup in case of spillage and meeting the legislation governing the manufacture and use of lubricants in some countries. It is now a common practice in lubricant industry to assess the biodegradability of lubricants in the aquatic environment, and laboratory data are available for a wide range of products [12].

A key performance characteristic when assessing environmental acceptability is the likely fate of the released product (i.e. biodegradation or persistence). Biodegradability is usually determined by measuring either the loss of extractable hydrocarbon (primary biodegradation) in the Coordinating European Council (CEC) L-33-A-93 test or ultimate biodegradation to CO_2, H_2O, inorganic salts and new microbial biomass using tests for ready biodegradability. The CEC test has seen more widespread use as it requires only standard laboratory glassware and an infra-red (IR) spectrophotometer, the latter being available in most oil product laboratories. Although the CEC test is only recommended for use with two-stroke outboard engine lubricants, it has been shown to be applicable to other lubricants. Because the CEC extraction solvent (1,1,2-trichlorotrifluorethane) is an ozone-depleting chemical, its supply and use are restricted by the Montreal Protocol it can be replaced by CCl_4 as extraction solvent [12]. ASTM test method D 5864 determines lubricant biodegradation. This test determines the rate and extent of aerobic aquatic biodegradation of lubricants when exposed to an inoculum under laboratory conditions. The inoculum may be the activated sewage-sludge from a domestic sewage-treatment plant, or it may be derived from soil or natural surface waters, or any combination of the three sources. The degree of biodegradability is measured by calculating the rate of conversion of the lubricant to CO_2. A lubricant, hydraulic fluid or grease is classified as readily biodegradable when 60 % or more of the test material carbon is converted to CO_2 in 28 days, as determined using this test method [13]. In [14] was used as the indicator of biodegradation the COD – chemical oxygen demand and this was used also in this study instead of its disadvantages, according OECD 302 B.

Although microbial deterioration of MWFs during their usage is a problem, such deterioration can be used to advantage for the disposal of operationally exhausted fluids. There is growing interest in exploiting the biocatalytic potential of micro-organisms to biodegrade MWFs in bioreactor-based processes. This can best be achieved by improving our understanding of microbial diversity within metalworking fluids [15]. Recently, genetic engineering has also been employed to specify certain species that can enhance overall treatment performance [16, 17]. The most common extracted bacterial isolates are defined in [15]. In [17] for established bioreactors to be effective for treating chemically mixed wastes such as metal working fluids (MWF) it is essential that they harbor microbial populations that can maintain sufficient active biomass and degrade each of the chemical constituents present. The reduction in the COD by the consortium (*Clavibacter michiganensis, Methylobacterium mesophilicum, Rhodococcus erythropolis* and *Pseudomonas putida*) was approximately 85 % of the total pollution load, and 30 – 40 % more effectively than any other treatment (indigenous MWF community alone or activated sludge). Many chemical components of the MWF proved to be recalcitrant in the other treatments. The results of this study confirm that assemblage of an inoculum, based on a comprehensive knowledge of the indigenous microbial community, in the target habitat, is a highly effective way of selecting microbial populations for bioaugmentation of bioreactors [17].

Toxicity of metalworking fluids

Toxicity to aquatic organisms is generally used to reveal potentially adverse environmental effects of a compound or product [8]. Experience has shown that the toxicological properties of fully formulated lubricants are related to those of the base fluid and additive components. The measured toxicity of mixtures is found to be close to the sum of component toxicities [3]. It is widely recognized that the ecotoxicological effects of the main MWFs components (biocides, corrosion inhibitors, extreme pressure and anti wear agents, emulsifiers, and surfactants) cause a major problem regarding the disposal of MWFs and their environmental impact. Much scientific research indicates the need for wider toxicologic monitoring of industrial effluents and receiving waters [9].

Toxicity of a substance is generally evaluated by conducting an acute toxicity test. The most common test methods used by the lubricant industry for evaluating the acute toxicity and European ecolabelling board of their products are EPA 560/6-82-002 (Sections EG-9 and ES-6); and OECD 201 (Algae growth inhibition test), OECD 202 (Daphnia acute immobilization test) and OECD 203 (Fish acute toxicity test) [1, 2, 8, 9]. The tests are used to determine acute toxicity, and do not evaluate adverse effects after long time exposure. Even so, problems arise from poor water solubility of the test substance. If a hydrophobic compound that is poorly soluble in water is discharged into the natural environment, it will probably end up in sediment and soil rather than remain in the water phase. Development of assays for sediment and soil are underway. The following scales of toxicity have been used: $EC_{50}<1$ mg l^{-1} highly toxic, $1-10$ mg l^{-1} toxic, $10-100$ mg l^{-1} hazardous, and >100 mg l^{-1} without acute toxicity [8].

Before starting the OECD 302B test, it exist a presumption with appropriate methods that no inhibition of sludge occurs at the chosen concentration of test substance if this is not already known [22]. If an inhibitory effect is found, reduce the concentration of test substance to a level which is unlikely to be inhibitory. The test of activated sludge inhibition of respiration is recommended also when OECD 301A-F for primary biodegradation is realized. Compounds with an EC_{50} value greater than 300 mg l^{-1} are not likely to have toxic effects in ready biodegradability testing [18].

Materials and methods

In the first test was used *Lemna minor* as the organism for ecotoxicity testing and this was obtained from the ECOTOX s. r. o. Bratislava in 2008. It was cultivated in Hoagland E medium by [10] in axenic condition before test started according OECD 221 [11]. For evaluating EC_{50} value was applied linear regression. Inhibition was calculated by the area under the growth curve to control groups as it is described in [10]. In the first test were used four types of MWF´s such as Emulzin H, Ecocool, Blasocut BC 25 and Dasnobor.

As inoculums for the second test (toxicity and degradability by activated sludge) was used fresh activated sludge from sewage treatment plant from Jaslovské Bohunice the same day as the experiment start. In each test was used 0.1 g of dry matter per liter in final volume for toxicity and 0.5 g of dry matter per liter in final volume for degradability evaluation. In this test were preliminary tested Blasocut BC 25 and Adrana D407. The toxic effect of tested substance signified decrease of oxygen consumption according OECD 209 [19]. The degradability evaluation was realized according OECD 302B.

Result and discussion

Preliminary study of selected MWFs ecotoxicity on *Lemna minor* is shown in the Fig. 1a-d. For the test to be valid, the doubling time of frond number in the control must be less than 2.5 days (60 h), corresponding to approximately a seven-fold increase in seven days and an average specific growth rate of 0.275 d^{-1}. Average specific growth rate were evaluated for all tests in the range 0.23 – 0.24 d^{-1} and pass the criteria for the test. In the Fig. 3 a-d there are shown dependences of growth inhibition from logarithms of concentration of three tested metalworking fluids such as Emulzin H, Ecocool, BC 25 and Dasnobor.

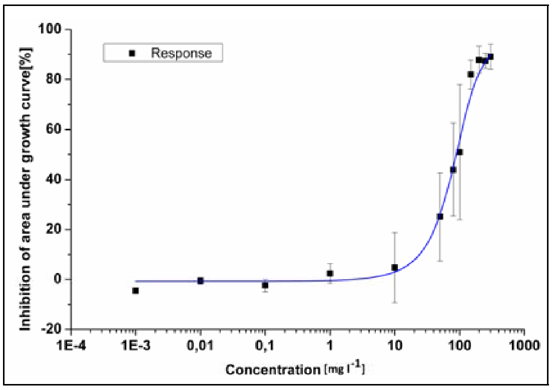

Fig. 1a *– Dose-response (concentration-response) curve of Emulzin H for all tested concentrations*

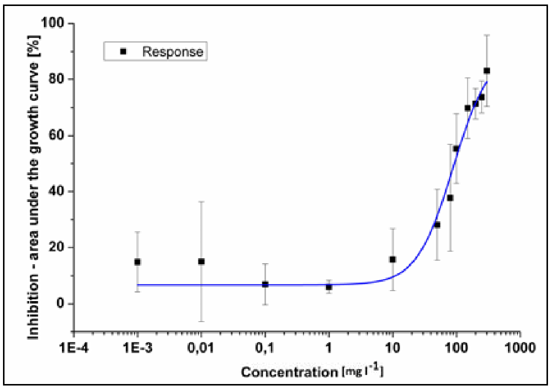

Fig. 2b *– Dose-response (concentration-response) curve of Ecocool for all tested concentrations*

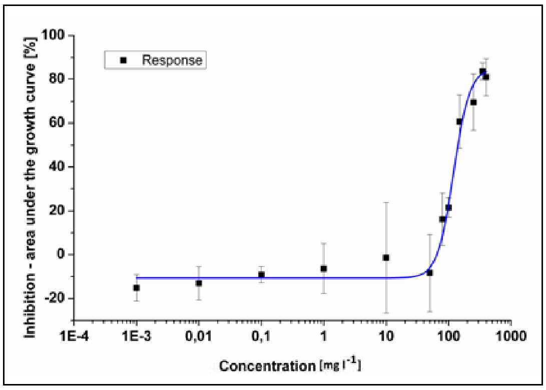

Fig. 1c – Dose-response (concentration-response) curve of BC 25 for all tested concentrations

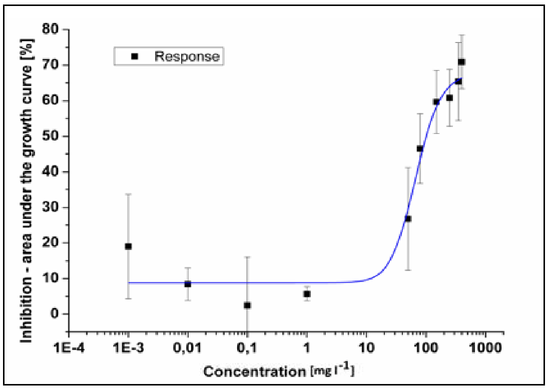

Fig. 1d – Dose-response (concentration-response) curve of Dasnobor for all tested concentrations

Hormesis effect was shown in the presence of small concentration of Blasocut BC 25. In the concentration 0.001 mg l^{-1}; 0.01 mg l^{-1}; and 0.1 mg l^{-1} of all tested MWFs were observed hormesis – stimulatory effect on growth. Effective concentration of tested MWFs that effect 50 % of growth inhibition was evaluated from the area under the growth curves and for Emulzin H was about 99.19 mg l^{-1}, for Ecocool 99.66 mg l^{-1}. BC 25 has affected inhibition about 99.3 mg l^{-1} and Dasnobor a little bit lower than the others – 97.3 mg l^{-1}. The Tab. 1 compare evaluated effective concentrations and the Tab. 2 listed effective concentrations cause 20, 50 and 80 % of growth inhibition.

EC$_{50}$ OF EMULZIN H, ECOCOOL, BC 25 AND DASNOBOR ACCORDING TO OECD 221, TESTING ORGANISM WAS *LEMNA MINOR*

Table1

MWF	EC$_{50}$ [mg l^{-1}]	R^2	95% confidence interval [mg l^{-1}]
Emulzin H	81.6	99.19	75.6 - 86.9
Ecocool	82.9	99.66	73.5 – 85.5
BC 25	133.6	99.3	112.0 – 201.3
Dasnobor	108.4	97.3	75.5 – 193.6

CALCULATED VALUES OF EC$_{20}$, EC$_{50}$ AND EC$_{80}$ FOR THE MWFs

Table 2

MWF	EC$_{20}$ [mg l^{-1}]	EC$_{50}$ [mg l^{-1}]	EC$_{80}$ [mg l^{-1}]
Emulzin H	28.2	81.6	223.9
Ecocool	22,4	82.9	281.8
BC 25	89.1	99.3	316.2

By the test it seems that all tested MWFs have comparable toxic effect on higher plant – *Lemna minor* in the range 97.3 – 99.66 mg l^{-1}. The test was realized in static condition but it shows to be advantageous to study effect on *Lemna minor* in semi-static or flow-through condition with renewal of testing solution due observed little precipitation during the test.

Preliminary study of selected MWFs ecotoxicity with bacterial consortium is shown in the Fig. 2 – 3. The purpose of the method is to provide the quick screening test to identify substances that have unfavorable influence on sewage treatment plant and identify noninhibition concentration of tested substances applicable in biodegradability test according OECD 301 A-D. Respiration rate is calculated from the oxygen decrease curves for all of tested substances concentrations approximately between 6.5 – 2.5 mg l^{-1} O_2. A part of the respiration curve above which the respiration rate is calculated has to be linear.

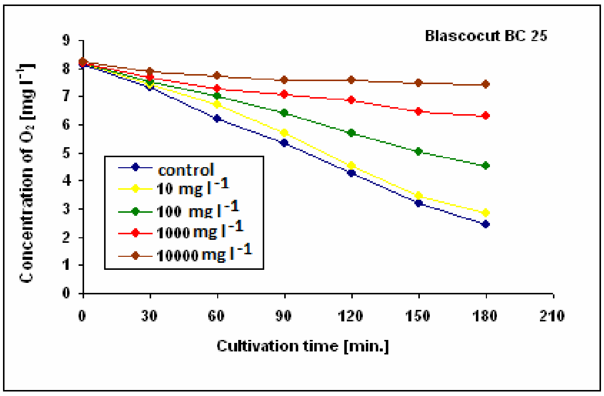

Fig. 2. *Oxygen decreased curves in the range finding test of BC 25, part of the curve between 6.5 and 2.5 mg O_2 per liter has to be linear*

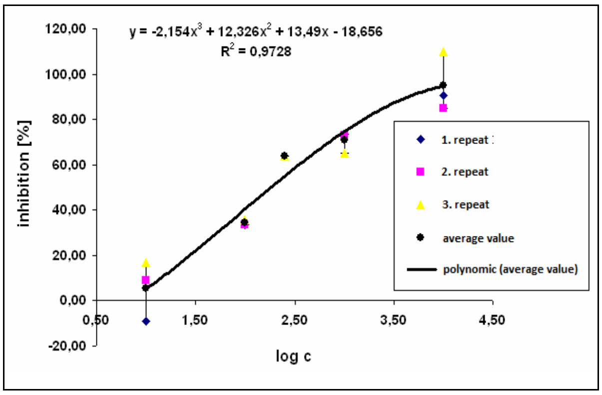

Fig. 3. *EC_{50} evaluation of BC 25with bacterial consortium become from sewage treatment plant activated sludge*

In the next – Tab. 3 there are shown calculated values of EC_{20}, EC_{50}, EC_{80} for the MWFs Blasocut BC 25. EC_{20} of BC 25 was calculated to 30.3 mg l^{-1}; EC_{50} was calculated to 227.4 mg l^{-1} and EC_{80} for the MWFs Blasocut BC 25 was calculated to 3 293.1 mg l^{-1}.

CALCULATED VALUES OF EC_{20}, EC_{50} AND EC_{80}
FOR THE MWFs BLASOCUT BC 25

Table 3

	EC_{20} [mg l^{-1}]	**EC_{50} [mg l^{-1}]**	**EC_{80} [mg l^{-1}]**
Average value	30.3	227.4	3293.1

According to the regulation OECD 209 it is sufficient to ordering tested substance into one of four classes (<1 mg l^{-1}, 1 – 10 mg l^{-1}, 10 – 100 mg l^{-1} and <100 mg l^{-1}). BC 25 come under 4th category and it is possible observe that BC 25 is relatively low toxic to the activated sludge bacteria from sewage treatment plant. In the case of using concentration like this it is presumably that it won't be toxic for the biodegradability test according OECD 301 A-F. It is recommended to realized also test to the reference compound such as 3,5-dichlorphenol to state right activity of the bacteria in the sludge and also the physical-chemical test for the inorganic elimination of the oxygen by the testing substance. The same test was repeated also for Adrana D407. The EC_{50} of Adrana is much higher than Blascocut BC 25 − 3 288.5 mg l^{-1} instead of it belongs to the group > 100 mg l^{-1}.

The preliminary ecotoxicity study were followed by the biodegradability evaluation according to OECD 302 B. Validity and interpretation of the test is considered valid if the procedural control shows the removal of the reference compound by at least 70 % within 14 day and if the removal of DOC (or COD) in the test suspension took place relatively gradually over days or weeks, since this indicates biodegradation. Ultimate degradation degree of a reference compound was 95 % in 10 days window (started concentration of COD was in the required range up to 1000 mg l^{-1} and was 772 mg $l^{-1}$of COD). Starting concentration of MWFs samples passed COD 1101 – 1225 mg l^{-1}. As it is presented in the Fig. 4a-4d all tested cutting fluids satisfy 80% of degradation in 10 days. *Lag phase* were shown in the cases of Emulzin H and Ecocool and extend 2 days (Tab. 4).

SUMMARIZED RESULTS FROM ZAHN-WELLENS TEST OF EMULZIN H STANDARD

Table 4

	Cultivation	**Starting concentration of COD [mg l^{-1}]**	**lag phase t_l [day]**	**adsorption [%]**	**total decrease D_t' (if >20 % of adsorption)**	**ultimate degradation degree D_t [%]**	**Biodegradation time t_2 [day]**	**ultimate biodegradability (pass 80 %)**
Emulzin H	1	1 203	no	13	-	95	3	**yes (3 days)**
	2	1 333	no	8	-	85	no	**yes (8 days)**
	3	959	no	15	-	76	no	**no**
	4	1 101	2	1	-	96	11	**yes (10 days)**
Ecocool	1	1 220	no	16	-	94	6	**yes (5 days)**
	2	1 358	1	9	-	90	11	**yes (8 days)**
	3	1 552	no	33	91	88	no	**yes (7 days)**
	4	1 125	2	3	-	85	no	**yes (10 days)**
BC 25	1	1 252	no	44	90	83	no	**yes (5 days)**
	2	1 497	no	36	90	85	no	**yes (8 days)**
	3	776	no	7	-	72	no	**no**
	4	1 043	no	28	86	82	no	**yes (10 days)**
Dasnobor	1	1 120	No	18	-	78	**no**	**no**
	2	872	no	24	93	91	13	yes (4 day)

Lag phase t_l – time from inoculation until the biodegradation percentage increase up 10 % from initial COD (or DOC). Lag phase is variable and repeat with difficulties. It is measured in days. *Ultimate biodegradation degree* – it is the degree of biodegradation, above no other biodegradation occurs. *Biodegradation time t_2* – degradation time from the end of lag phase until 90 % of biodegradation occurs.

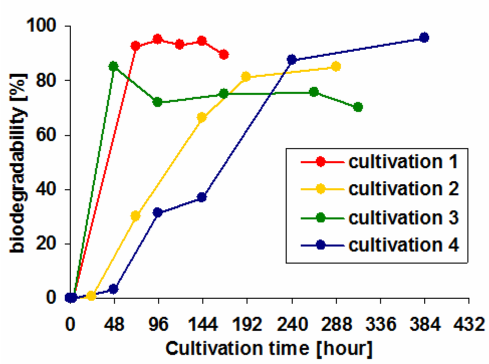

Fig. 4a – *Biodegradability curves of Emulzin H*

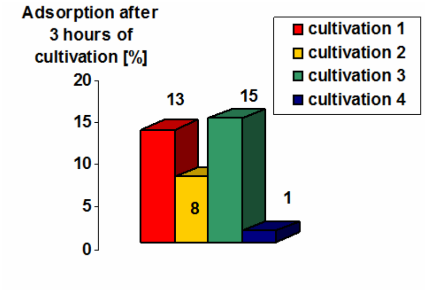

Fig. 5a – *Adsorption after 3 hours of cultivating of Emulzin H*

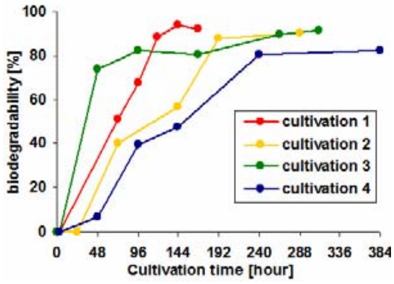

Fig. 4b – *Biodegradability curves of Ecocool*

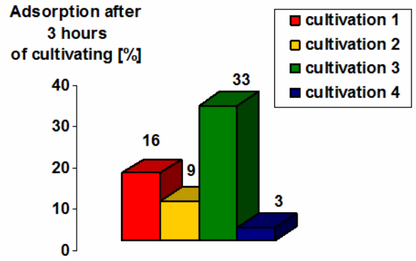

Fig. 5b – *Adsorption after 3 hours of cultivating of Ecocool*

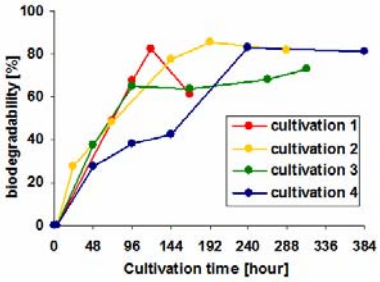

Fig. 4c – *Biodegradability curves of BC 25*

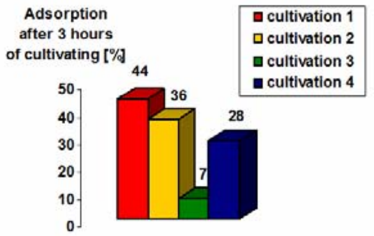

Fig. 5c – *Adsorption after 3 hours of cultivating of BC 25*

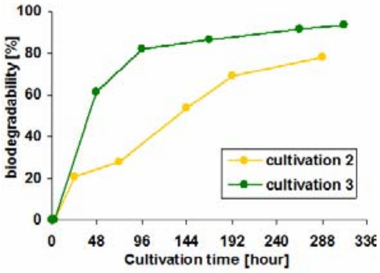

Fig. 4d – *Biodegradability curves of Dasnobor*

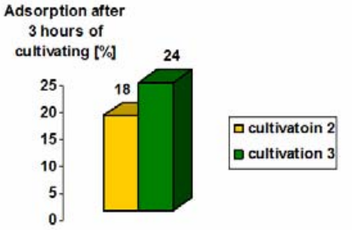

Fig. 5d – *Adsorption after 3 hours of cultivating of Dasnobor*

All tested MWFs standards shows to be good ultimate degradability by the Zahn-Wellens test even when the concentration of COD was higher about 43 – 125 mg l^{-1} than is required for this test. However, physico-chemical adsorption can, in some cases, play a role and this is indicated when there is complete or substantial removal in the first 3h and the difference between blanks and test solutions remains at an unexpected low value. In such cases additional information is obtained from a comparison between the 3h value and initial value of test measured before the inoculum is added. If a more precise distinction between biodegradation (and partial degradation) and adsorption is to be drawn, carry out further tests, preferably a respirometric test for ready biodegradation, using the supernatant of the acclimatized sludge as inoculums.

Tab. 4 shows the adsorption of tested emulsions after 3 hours of the test (+/- 30 min.). Decrease of COD of tested MWFs in testing vessel were higher than 20 % in Ecocool, where presented 33 % of COD decrease and in the case of BC 25 it was 28 %, 36 % and 44 % of COD decrease, so there were no possibility to evaluate if the decrease was realized with the microbial activity, or by other adsorption kinetics (physico-chemical). It is required to evaluate the level of biodegradation by other biodegradation method for BC 25 e.g. OECD 301 B or by CEC-L-33-A-93. Emulzin H and Ecocool standards has the decrease of COD in the limits of Zahn-Wellens test validation (< 20 %).

Conclusion

Preliminary study of ecotoxicity measuring by *Lemna minor* shows effective concentration of Emulzin H at the rate of 93.1 mg l^{-1}, for Ecocool 99.7 mg l^{-1}, for BC 25 about 99.3 mg l^{-1} and for Dasnobor 97.3 mg l^{-1}. The toxicity effect to *Lemna minor* of tested MWFs was comparable. Small concentrations of testing fluids indicate hormetic effect. It is required to test Emulzin H, Ecocool, BC 25 and Dasnobor by semi-static or flow-through condition. Preliminary study of ecotoxicity measuring to the consortium of activated sludge bacteria shows effective concentration of BC 25 is 227.4 mg l^{-1} and Adrana D 407 is 3 288.5 mg l^{-1}. By the results Adrana is less toxic than BC 25, both of belong to the fourth category > 100 mg l^{-1} so the concentrations about EC_{50} values didn't cause problems in tests of biodegradability according OECD 301 A-F. Evaluated level of tested MWFs (Emulzin H, Ecocool, BC 25 and Dasnobor) biodegradation by Zahn-Wellens test achieved 80 % in 10 days, so they have potential to ultimate degradation by this test. Disadvantages of Zahn-Wellens test are DOC measurement by which is not able to evaluate all presented organics, even when they are in insoluble form (in the case of COD there is evaluating with oxidable forms also inorganic). At high rate of adsorption it is impossible to differentiate between biotic degradation and other form of abiotic elimination, which was shown in the case of BC 25 (28 and 38 % of COD decrease after 3 hours of cultivating). This method is also discontinuing. It will be in next study, use the modified test method of Zahn-Wellens test, by measuring of CO_2 production and O_2 consumption, by continual measuring or replace by modifications of CEC test.

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RESEARCH PAPERS
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THE STUDY INTO THE CERAMIC-TO-METAL SOLDERED JOINTS INTERFACE FOR Al_2O_3 AND SiO_2 MATERIALS

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Abstract

The conditions of joining a ceramic-metal configuration by active metal soldering using tin-based (SnTi3) alloys are presented. Active metal (Ti) was alloyed in a low concentration of 3 weight percent. The joining process was done in a vacuum (10^{-2} Pa) at a peak temperature of 860 °C with a short holding period (t = 9 min). The ceramic-metal soldered interface was examined using optical microscopy, scanning and transmission electron microscopy (SEM, TEM). The natures of the interfacial reactions and the reaction products have been identified using X-ray diffraction (XRD). The thickness of reaction layers and X-ray maps of the same region were measured.

Key words

active soldering, oxide ceramics, reaction layers, intermetallic compounds, fracture surface

Introduction

Lately, combined engineering materials have been used in a wide range of technical applications. Their advantage is that their extraordinary properties can be used in demanding technical applications in a controlled or targeted manner. Ceramic and metal combined in the form of a soldered joint [2] are doubtlessly one of such combinations. From the perspective of joint production, the critical factor is the selection of suitable solder. The first condition for the production of a high-quality joint is the substrate's wettability with molten solder. The wettability of a ceramic material with common solders is difficult without having the substrate sufficiently coated with metal. Another solution is to use solder with a small amount of an active element (Ti, Zr or Hf) that has a strong affinity for the ceramic substrate's anions. Inside molten solder, an active element migrates to the interface between the solder and the

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ceramic substrate where it generates intermediary compounds, thus catalyzing oxidation or reduction reactions [3]. By adding an active element into soft solder, the metal content of which offsets the differences in thermal expansivity of the parts being united, metals can be joined with various non-metallic materials such as quartz (SiO_2), ceramics, carbon or the like [4-6]. Soldering ceramic materials using an active solder alloy is therefore economically advantageous. Various methods of preparing ductile active solders, primarily the option to produce a solder of a desired composition during the soldering process, substantially extend the range of applicability of said technology.

The study analyzed the interface of a soldered joint between ceramic and solder attained by uniting a ceramic-metal combination using the active SnTi3 soft solder. The issue in question is whether the use of the SnTi3 solder is suitable in the context of soldering parameters optimization.

Experiment Preparation

The combination of a soldered part studied in this study consisted of a ceramic substrate, the active SnTi3 solder, and a metallic pad. A metallic pad made of CrNi steel (18/8) 5 mm in thickness has been used for the experiment and two types of ceramic substrates: Corundum Al_2O_3 and melted SiO_2. These materials were joined using active Sn-based solder with an addition of 3 wt pct of active Ti (Fig. 1). The active SnTi3 solder was prepared by the Slovak Academy of Sciences' Institute of Physics, Bratislava, using the method of rapid cooling of the melt into the form of a tape 30 μm in thickness. To produce a joint of the required thickness, four SnTi3 solder layers were used.

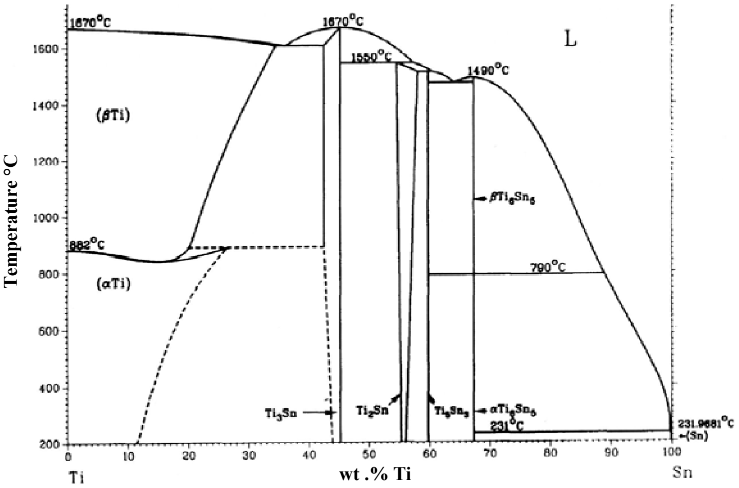


Fig. 1. Ti – Sn binary diagram

Soldering Design and Performance

All samples intended for the study of the interface of soldered joints between ceramic-metal combined materials have been prepared by soldering in a vacuum brazing furnace (TESLA PZ 803). Before being actually soldered, the joint components' surface layers were gently abraded and cleaned using an ultrasonic acetone bath. Shown in Table 1, the soldering process parameters have been designed with respect to the wettability and diffusion capacity of the solder's active element at the given temperature.

VACUUM SOLDERING PARAMETERS AS DESIGNED

Table 1

Soldering temperature	860 °C
Working vacuum	10^{-2} Pa
Dwell time	9 min

The temperature cycle shown in Figure 2 consisted of heating to a working temperature of 860 °C and a holding period of 9 minutes at that temperature. The process of cooling went on in a furnace at a medium cooling speed of 2 °C/s. All samples intended for the experimental analysis were prepared within a single cycle at the above-stated parameters.

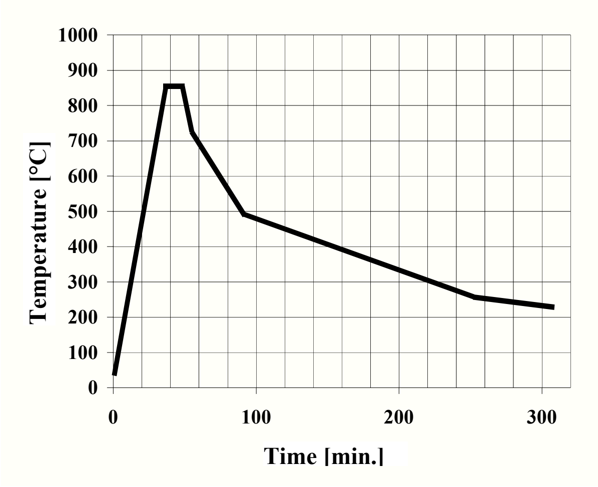


Fig. 2. *Temperature Regime Record*

Metallographic Sample Preparation

For the purposes of metallographic analysis by a light microscope, the soldered joints were cut crosswise into slices 15 mm in thickness and then sealed into a copper handle.

Using a light microscope and a CCD camera with an output to an Impor Pro2 image analyzer, the ceramic-metal interface's reaction layer was examined under both polished and corroded state conditions. The polishing of the surface was done using a chemical polishing with Struers OP-S, a commercially available suspension. The reaction layer and the solder's grain boundaries were corroded with a 3-percent solution of Nital.

Electron Microscopy and Microanalysis

The solder-ceramic interface was analyzed using reflection electron microscopy (SEM) and transmission electron microscopy (TEM). The morphology of the transition zone and the reaction layer on corroded metallographic sections was observed using SEM TESLA BS300. The chemical microanalysis – linear profile, the surface distribution of elements, was conducted through a solder-ceramic reaction layer using the EDAX analyzer, which was a component of the SEM JEOL JXA-840A. To supplement the study, an identification of the phases extracted from fracture surfaces by electron diffraction has been completed on TEM JEOL 200CX.

X-ray Diffraction Analysis

To conduct an X-ray diffraction analysis of the solder-ceramic interface, ceramic substrates of cylindrical shape with dimensions of 8,5 x 10 mm were used after their surfaces were previously wetted by molten SnTi3 active solder. After metallographic preparation, they were analyzed using an X-ray diffractometer (DRON 3M) with a goniometer operated in Bragg-Brentano geometry.

One prerequisite for a successful analysis of products in a reaction layer was polishing away a sufficient amount of the solder from the surface without further influencing the solder-substrate interface. The scanning parameters were as follows: $\lambda CuK\alpha = 0{,}1541$ nm, $U = 35$ kV, $I = 30$ mA, secondary LiF monochromator.

Experimental Results

Metallographic Analysis, SEM, TEM

Figures 3 through 6 show the interfaces of ceramic-metal soldered joints in both polished and corroded state condition. The polished interface between SiO_2 and solder is characteristic for its steady reaction layer; the dominant features are the intermediary phases with different morphologies (Fig. 3) that were generated in the steel-to-solder transition zone and filled the SnTi3 solder's volume. After the solder was etched, the thickness of the SiO_2-solder interface's reaction layer was 6 μm (Fig. 4).

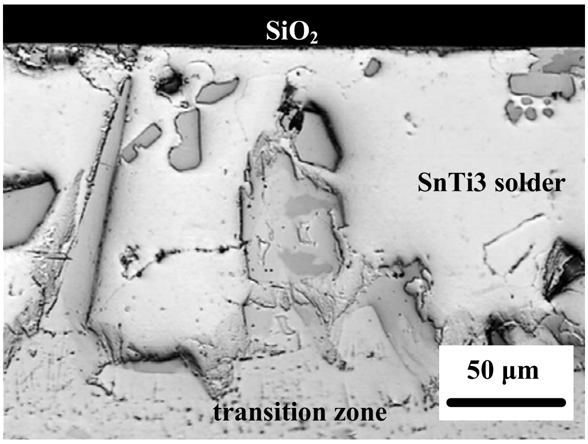


***Fig. 3.** Ceramic-solder-metal composition polished interface*

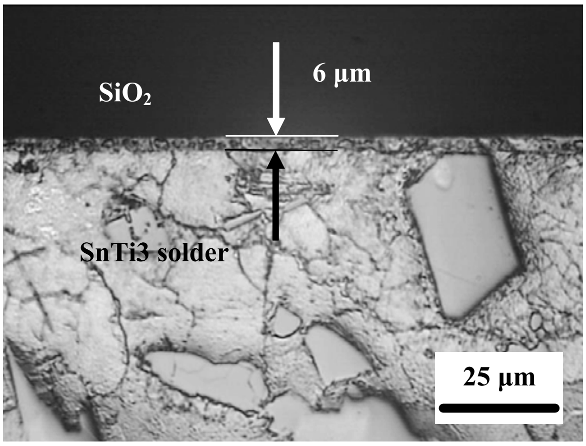


***Fig. 4.** Etched SnTi3 solder with a continuous reaction layer*

Figure 5 shows a polished joint between a ceramic-metal combination with a visible solder-steel transition layer and some occurrences of intermediary phases in the SnTi3 solder. The reaction layer between the solder and Al_2O_3 was discontinuous and considerably thinner than that of the joint with SiO_2. A detailed investigation into the solder-ceramic interface (SEM) showed the local concentration of the products formed by the reaction between the SnTi3 solder and Al_2O_3 solder (in Fig. 6, these products are denoted with arrows).

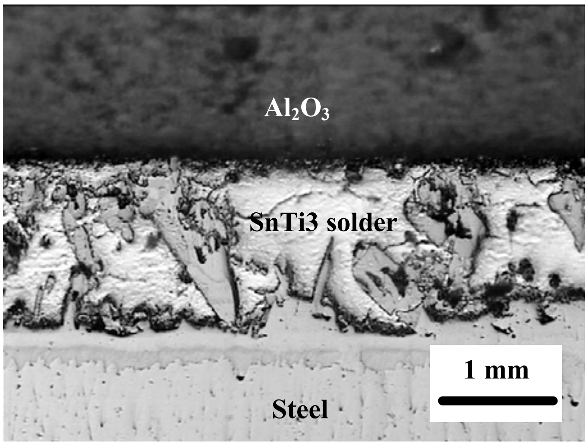


Fig. 5. Polished ceramic solder metal composition with distinct reaction products

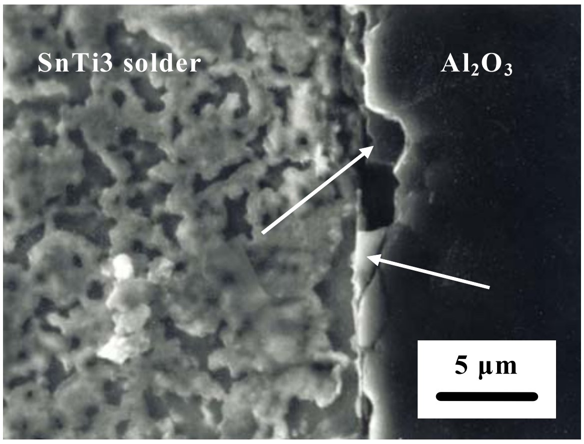


Fig. 6. A detail of the reaction layer with the denotation of fragile phases

A linear and areal X-ray microanalysis was conducted on the SiO_2-solder interface. The results appearing in Fig. 7 show that the maximum concentrations of both Sn and the active element (Ti) are present in the SiO_2-solder interface's reaction layer. The distribution of the active element the highest concentration of which was detected in the reaction layer indicates the union of the SiO_2 substrate with the active solder. Fig. 8 shows the results of an analysis made to examine the solder-Al_2O_3 reaction layer. The figure indicates the active element's maximum concentration at the interface between solder and Al_2O_3. As can be seen from the detailed analysis shown in Figure 6, no continuous reaction layer formation occurred at the soldering temperature of 860 °C.

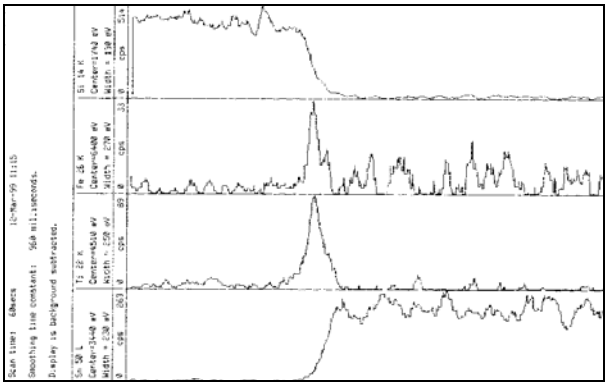


Fig. 7. Chemical analysis through SiO_2-solder interface's reaction layer

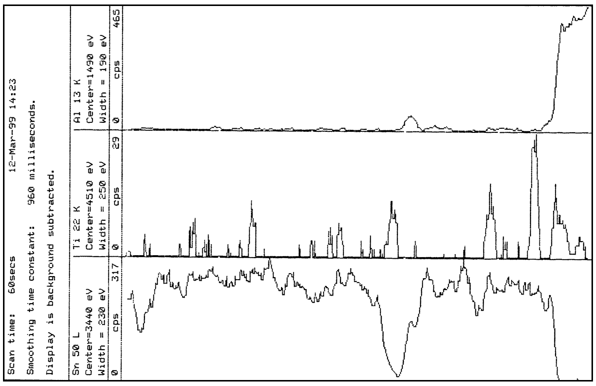


Fig. 8. Chemical analysis through Al_2O_3-solder interface

Due to shortcomings stemming from the analysis of a planar surface, the solder-Al_2O_3 was analyzed using fractographic investigation methods. The interface between Al_2O_3 and the solder was notched, then fractured by rotary bending in a fragile condition. Figures 9a,b show a typical appearance of ruptures attained in this way. The surface of the fracture shown in Fig. 9a indicates cleavage break with a greater proportion of non-fragmented surface, which attest to the SnTi3 substrate's insufficient wetting with the solder. The proportion of the perfectly wetted area computed from the overall fragmented solder layer area on the separated portion of the ceramic substrate only represented 20 percent. Fig. 9b shows the decohesion of a part of the Sn+Ti_6Sn_5 eutectic in the matrix. Figure 10a shows a detailed view of the Ti_6Sn_5 formations. Along the tin solder's grain boundaries a Ti_5Sn_3 phase segregates. The phase identification was conducted using the method of electron diffraction after the phases had been extracted into a carbon replica. Also, foil Ti_2Sn (Fig. 10c) and α-Al_2O_3 oxidic films were identified in the same manner from the solder-Al_2O_3 interface (Fig. 10d).

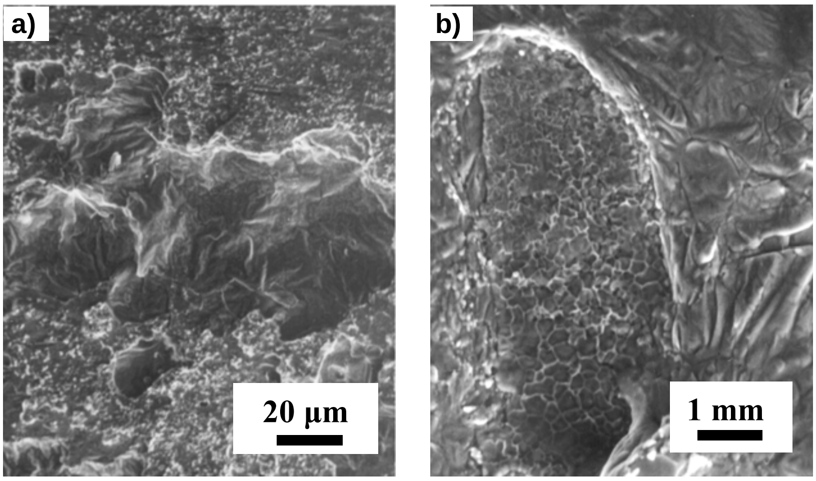
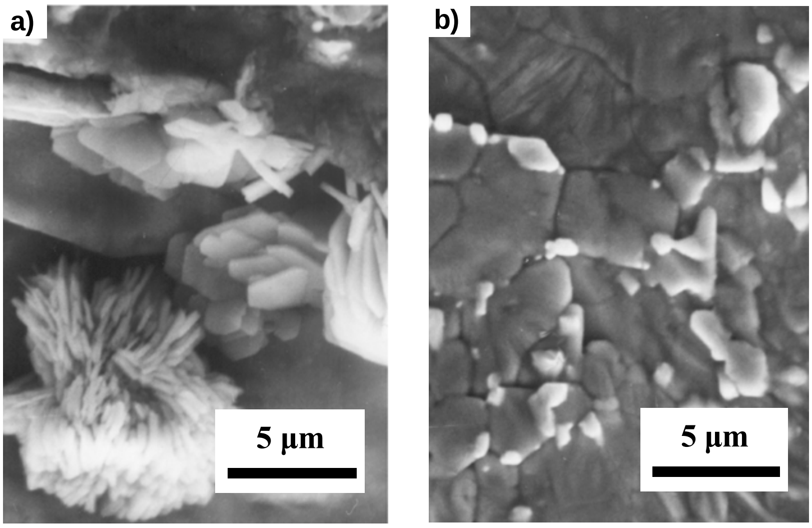


Fig. 9a-b. *Morphology of fracture areas in solder- Al_2O_3 reaction layer*



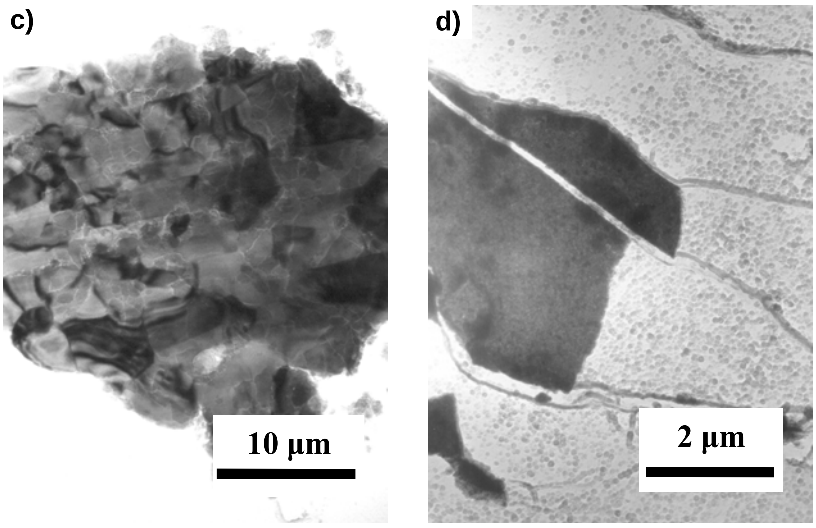


Fig. 10 a-d. *Fragmented solder-Al_2O_3 interface*

X-ray Diffraction Analysis

A quantitative X-ray phase analyses detected modifications of Sn and Ti based phases in the interface between solder and ceramic substrate: tetragonal Ti_2Sn, hexagonal Ti_5Sn_3, Ti_6Sn_5, and Ti_3Sn. The Ti_6Sn_5 phase with a hexagonal lattice shown in Fig. 10a was part of the $Sn+Ti_6Sn_5$ eutectic. All of the above-mentioned phases occurred in both ceramic substrates previously superficially wetted with SnTi3 solder. The solder-SiO_2 interface's reaction layer also contained a product of the active element's (TiO with a cubic lattice) reaction.

An own contribution to the problem given

The pieces of knowledge derived from the uniting of a ceramic-metal combination using the SnTi3 active solder can be summarized as follows:

- Combinations of ceramic and metallic materials can be soldered using the SnTi3 soft solder.
- The soldering temperature of 860 °C/9 min. was sufficient to fabricate the joints; in both cases, the maximum active element (Ti) concentration was detected at the solder-ceramic substrate interface.
- Using SEM, TEM and X-ray diffraction analyses, the morphology, crystalline structures and the types of the solder-ceramic reaction layer's phases were identified.
- At the solder-SiO_2 interface, a continuous reaction layer 6 µm in thickness was formed.
- At the solder-Al_2O_3 interface, no reaction layer formation occurred to the given extent, only discrete points were wetted with the active solder.
- The homogeneity of the active element's (Ti) distribution in the initial SnTi3 solder and a higher soldering temperature are the factors that determine the reactions in the Al_2O_3-solder interface.

Conclusion

The ceramic-metal combination joints were fabricated by vacuum soldering using the soft SnTi3 active solder. The active solder was prepared from 4N purity elements with a composition of 97 wt pct Sn and 3 wt pct Ti. In molten solder, the active element (Ti) migrates towards the solder-ceramic substrate interface where, due to the effect of oxidation reaction, it forms a layer consisting of intermediary phases (i.e. forms a reaction layer). The reaction layer at the solder-ceramic substrate interface was thoroughly studied using metallographic methods of light and electron microscopy, X-ray analysis, and fractographic analysis. The transition layer between SnTi3 active solder and a metal pad (CrNi steel) was examined in another study [7].

Under the conditions of the working mode indicated in Table 1, a continuous reaction layer was formed at the solder-SiO_2 interface. An amorphous SiO_2 structure was used where no temperature-dependent changes occur. This combination's continuous reaction layer indicates perfect wetting with the SnTi3 solder.

The reaction layer at the solder-Al_2O_3 interface was discontinuous and considerably thinner, with discrete points where occurrences of Ti_5Sn_3 and Ti_2Sn -type intermediary phases were detected. Although the distribution of the active element at the solder-Al_2O_3 interface reached its maximum, its effect at the soldering temperature (of 860 °C) did not reach the required quality. A precise measurement of the quantity of the active element present in SnTi3 solder showed a nonhomogeneous distribution of Ti with concentrations ranging from 0.8 to 2.8 wt pct. It was proven that corundum ceramic not only requires an optimized soldering temperature, but it is also necessary that the amount of an active element in a soft Sn-based solder be increased. The above-mentioned pieces of knowledge prove that joints of diffusion quality can also be achieved at a relatively higher temperature (up to 960 °C).

Credits and Acknowledgments

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ANALYSING THE PROPERTIES OF SURFACE LAYERS GENERATED BY SHEET METAL FORMING OPERATIONS

Jana ŠUGÁROVÁ, Peter ŠUGÁR, Peter ZEMKO

Abstract

The paper brings results of surface layers properties analysis of thin wall hollow sheet metal parts, produced by metal spinning and deep drawing. The influence of mandrel (workpiece) frequency of rotation on the spun parts surface layer strainhardening is studied and compared with the quality of the formed part surface layer produced by deep drawing technology.

Key words

surface layer, strainhardening, metal spinning, microhardness

Introduction

Every technological method, which takes part on production of final component, brings in the component specific proprieties that influence its proceeding in whole assembling, i.e. it takes effect on its utility properties. Generated superior parameters of surface layer significantly influence for example wear resistance, fatigue strength, resistant to corrosion etc. These are important aspects, especially for parts that are under dynamic stress or exposed to difficult operative conditions.

Typical parts exposed to such conditions are containers and pressure tanks utilized for holding energy saved in, e.g. compressed gases. Their most important construction elements are the shaped heads (bottoms of the tanks). These are classified as rotary parts, which are for the aspect of shape defined as hollow steel metal components. Heads are components of pressure tank that are manufactured out of boiler-irons, structural steels, aluminum and copper alloys, clad steels and reinforced plastic with carbon fibers [1].

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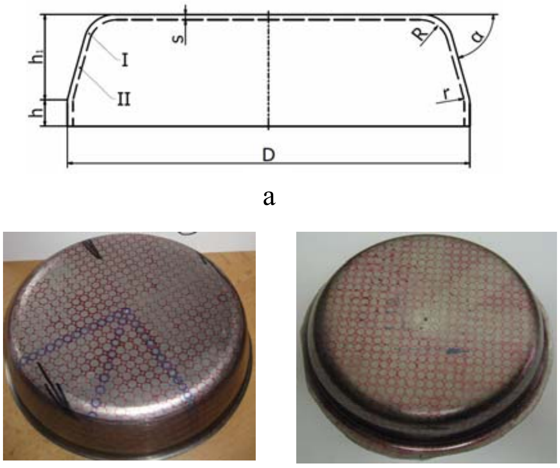
Most applied method of heads manufacturing is deep drawing. However, from the economic aspects and quality indicators is the process of metal spinning better alternative. After application of these operations a typical stress-strain states are generated in material and qualitative proprieties in surface layers [2, 3], which have subsequently effect on the safety index of pressure tanks. Consequential facilities of surface layers determine among other things also material strainhardening that experimental analysis of above mentioned processes is the objective of this contribution.

Experimental procedure of measurement and evaluation

For production of hollow sheet metal part, which dimensions parameters are shown in Fig. 1a and listed in Table 1, was used thin steel sheet made out of material EN 10025-94 (ISO 630-80), thickness s_0 = 1 mm. Chosen basic mechanical proprieties and facilities defining material plasticity are listed in Table 2. The blanks with diameter D_0 = 180 mm were formed by deep drawing (Fig. 1c) and metal spinning (Fig. 1c) processes. Forming was performed by a company Sandrik 1895, spol. s.r.o., Hodruša-Hámre, at technological conditions listed in Table 3.



a

b c

Fig. 1. *Hollow sheet metal part*
a – parts shape and dimensions
b – part manufactured by metal spinning (MS)
c – part manufactured by deep drawing (DD)
I – bottom-wall of part, II – wall of part

FORMED PART DIMENSIONS Table 1

D (mm)	**h** (mm)	**h_1** (mm)	**r**	**R**	**α** (°)	**s** (mm)
140	30	90	10	10	75	1

VALUES OF CHOSEN MECHANICAL PROPERTIES AND PROPERTIES DEFINING MATERIAL PLASTICITY EN 10025-94 Table 2

R_m (MPa)	$R_{p0,2}$ (MPa)	$R_{p0,2} / R_m$	A_5 (%)	r_s	Δr	n	A_{sh}
340	235	0.69	26	1.174	0.34	0.28	27.38

TECHNOLOGICAL PARAMETERS OF DEEP DRAWING AND METAL SPINNING PROCESSES Table 3

Process of deep drawing			**Process of metal spinning**		
Blank-holder force F_P (kN)	**Forming force** F_T (kN)	**Forming velocity** v (m.s^{-1})	**Feed ratio** f (mm)	**Mandrel frequency of rotation** n (min^{-1})	**Maximum circumferential velocity** v (m.min^{-1})
20.11	192.31	0.25	0.80	600	263

Presented experimental observation and evaluation of surface layers properties is aimed at evaluation of material strainhardening, utilizing method of microhardness measuring according to Vickers, method HV 0.025, under STN 42 0375, measured on INDETA Met 1100 device. The measurement was carried out in direction from part's surface to its depth on positions that are from aspect of hollow sheet parts production defined as critical (Fig. 1a), i.e. inter-stage spots of head to wall (I) and conic wall (II). For math formulation of material strainhardening values was the measuring carried out five times, also on base material (BM), whereby the measurement was applied in directions two directions – 0° and 90° refer to the rolling direction of the sheet. Measured and calculated values for base material are listed in Table 4. For metal spinning part in positions I and II are measured and calculated values listed in Table 5.

MICROHARDNESS VALUES OF SURFACE LAYER, MEASURED ON BASE MATERIAL (BM) Table 4

Depth of measure (μm)	***5***	***10***	***15***	***20***	***25***	***Mean average***
HV_{BM-0}	***101.9***	***101.8***	***100.2***	***99.3***	***98.9***	***100.43***
HV_{BM-90}	***101.7***	***99.4***	***99.2***	***98.6***	***98.0***	***99.07***

MICROHARDNESS VALUES OF SURFACE LAYER, MEASURED IN POSITION I AND II OF MS PART Table 5

Depth of measure (μm)	***5***	***10***	***15***	***20***	***25***	***Mean average***
HV_{MS-I-0}	***111.4***	***104.9***	***104.1***	***103.2***	***101.2***	***104.96***
$HV_{MS-II-0}$	***130***	***129.8***	***124.5***	***117.1***	***109.8***	***122.24***

Graphic evaluation of microhardness values of sample's surface layer, made by metal spinning, in positions I and II, under consideration of material rolling direction, is showed in Fig. 2.

Graphic evaluation of microhardness values of sample's surface layer, made by deep drawing, in positions I and II, under consideration of material rolling direction, is showed in Fig. 3.

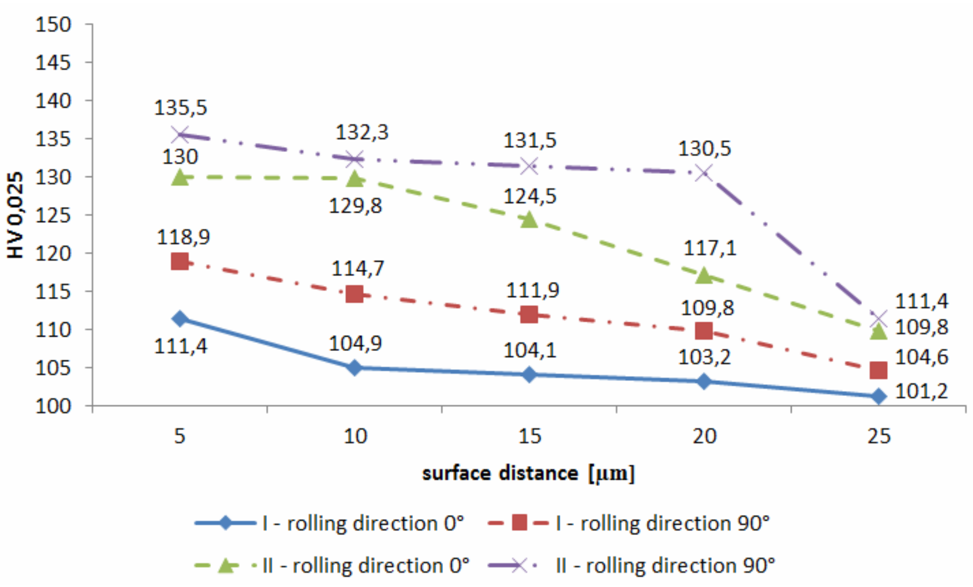


Fig. 2. *Progress of microhardness values in surface layer of MS sample in position I and II, in direction 0^o and 90^o refer to the rolling of the sheet*

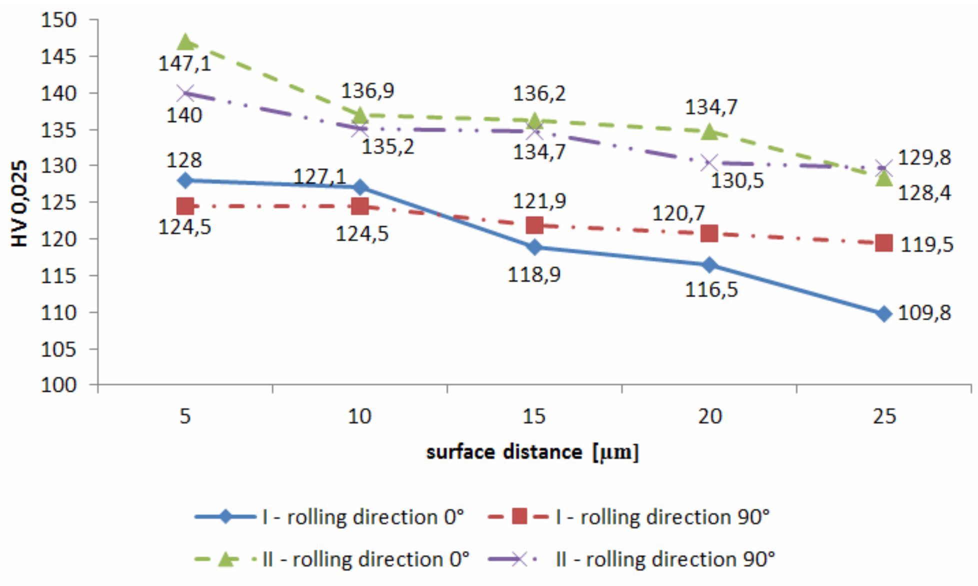


Fig. 3. *Progress of microhardness values in surface layer of DD sample in position I and II, in direction 0^o and 90^o refer to the rolling of the sheet*

Consequently “relative strainhardening of material” (PSM) was interpreted on MS and DD samples considering BM, whereby the material rolling direction was also regarded. Every sample was evaluated twice. The first calculation was aimed at comparison of base material with the inter-stage of head to wall. The second calculation was aimed at comparison of base material with the conic wall. Median calculation example of MS material, in position I, in the direction of material rolling ($PSM_{MS\text{-}I\text{-}0}$), states formula (1) and example of MS material, in position II, in the direction of material rolling ($PSM_{MS\text{-}II\text{-}0}$), states formula (2). Calculations of PSM for maximum values of microhardness, for those same directions and positions, are showed in formulas (3) and (4).

$$PSM_{MS-I-0} = \frac{HV_{MS-I-0} - HV_{BM-0}}{HV_{BM-0}} 100 = \frac{104.96 - 100.43}{100.43} 100 = 4.51 = 5 \ [\%] \tag{1}$$

$$PSM_{MS-II-0} = \frac{HV_{MS-II-0} - HV_{BM-0}}{HV_{BM-0}} 100 = \frac{122.24 - 100.43}{100.43} 100 = 21.72 = 22 \ [\%] \tag{2}$$

$$PSM_{MS-I-0-\max} = \frac{HV_{MS-I-0-\max} - HV_{BM-0}}{HV_{BM-0}} 100 = \frac{111.4 - 100.43}{100.43} 100 = 10.92 = 11 \ [\%] \tag{3}$$

$$PSM_{MS-II-0-\max} = \frac{HV_{MS-II-0-\max} - HV_{BM-0}}{HV_{BM-0}} 100 = \frac{130 - 100.43}{100.43} 100 = 29.44 = 29 \ [\%] \tag{4}$$

Presented procedure evaluates values of PSM for all microhardness values, measured in direction of material rolling. Equal computation was applied for the direction 90^{o} refer to the rolling direction of the sheet. Saturation and comparison of single PSM values of DD and MS samples are showed in Fig. 4 and 5.

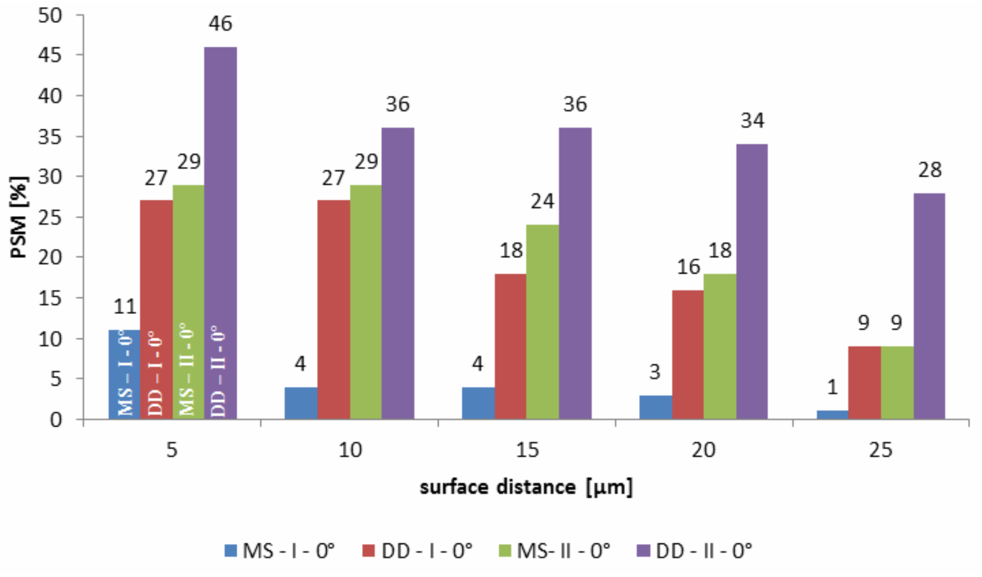


Fig. 4. *Comparison of PSM values of DD and MS samples in positions I and II, in direction of material rolling*

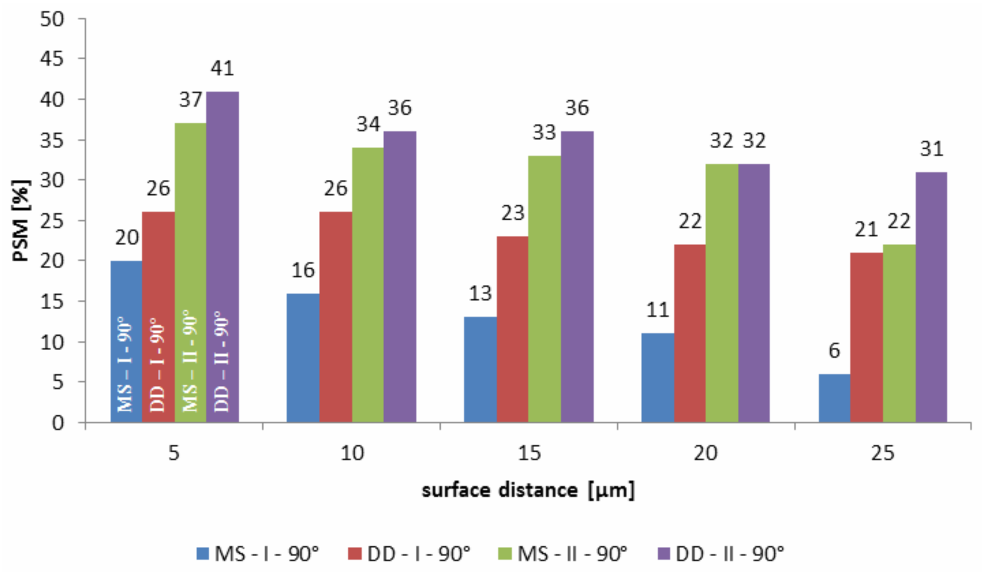


Fig. 5. *Comparison of PSM values of DD and MS samples in positions I and II, in direction 90^o refer to the rolling direction of the sheet*

Conclusion

From published results follow that the maximum values of PSM in both directions, refer to the direction of rolling, is on DD sample, whereby its average value in position I-0 is 19.4 %, in I-90 it’s 23.8 %, in II-0 the average PSM value is 36 % and in II-90 it’s 35.2 %. The average PSM value of MS sample in positions I-0 is 4.6 %, in I-90 it’s 13.2 %, in II-0 the average PSM value is 21.8 % and in II-90 it’s 29.8 %. These values are at average higher in position I over 12.7 % and in position II over 9.8 %. Likewise is interesting fact that the PSM values distinction in single measuring positions of DD and MS samples (Fig. 4 and 5) are moving in the same values. Namely, on DD sample it’s 14 % and on MS it’s 16.9 %, which we can consider as relatively equal values for both forming processes.

Based on observation of strainhardening values and their average PSM surface layers values of deep drawing and metal spinning samples it is possible to state that the different stress-strain conditions, parallel in material, generated different values of material strainhardening. In the DD sample were values about 10 % higher. Equal values of PSM are possible to achieve putting into the manufacturing process a calibration process, or modifying of technological parameters, i.e. choosing higher frequencies of mandrel rotation, or higher feed ratio of forming tool.

Besides propitious values of material strainhardening on surface layers, typical stress-strain condition of material after spinning, effects also wear intensity positively, increases corrosion resistance and also some other values of mechanical properties and properties defining formability of materials, e.g. increases fracture limit [4], which is important aspect in process of exploitation.

Further we can state, that the final important properties of surface layers are influenced by initial direction of material rolling, since the values of PSM after spinning are almost equal to those made by deep drawing in perpendicular direction to the direction of material rolling

(6%, 4%). However difference between both directions values is higher (16%, 17%); therefor we can predict, in theoretical line, places of potential failure in components exploitation process.

Following the carried out experimental measurement and its evaluation it is possible to state, that the technology of metal spinning is supposable to produce components with suitable surface staining as technology of deep drawing, whereby the character of material deformation in spinning process determines other facilities that are more convenient from aspect of their working qualities.

Thanks

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2010 Number 29

3D MODEL GENERATION FROM THE ENGINEERING DRAWING

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Ladislav IZAKOVIČ[2]

Abstract

The contribution deals with the transformation of engineering drawings in a paper form into a 3D computer representation. 3D computer model can be further processed in a CAD/CAM system, it can be modified, archived and a technical drawing can be generated from it as well. The transformation process from paper form to the data one is a complex and difficult problem, particularly because of the different types of drawings, forms of displayed objects and encountered errors and deviations from technical standards. The algorithm for 3D model generating from an orthogonal vector input representing a simplified technical drawing of the rotational part is described in this contribution. The algorithm was experimentally implemented as ObjectARX application in the AutoCAD system and the test sample as the representation of the rotational part was used for verificaton.

Key words

3D Model, AutoCAD, ObjectARX, rotational part, reconstruction, engineering drawing

Introduction

There are several forms of archiving and exchange of the products information: a classic paper engineering drawing, an electronic raster and vector drawing and 3D model. Processing in the direction 3D model - paper drawing is a commonly used procedure in modern CAD/CAM systems.

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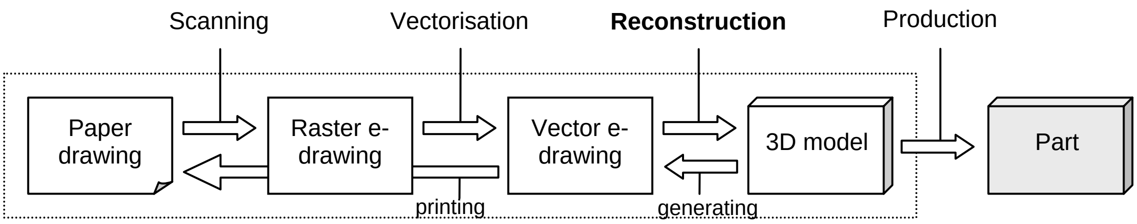


Fig. 1. *Forms of the part representation and transformation drawing-model and vice versa*

The aim of this article is to introduce an algorithm for 3D model generating for rotational parts from the vector record of its orthogonal projections. The result of the processing is a solid model described with the CSG representation.

The solution procedure and algorithm

The solution procedure that deals with the 3D model reconstruction of the rotational part from 2D vector drawing has been divided into the following steps:

1. Determination of input conditions and restrictive criteria.
2. Selection of an implementation form of the algorithm for verification of a proposed solution.
3. Loading input data from the vector e-drawing of the part.
4. Processing of each view.
5. Building of 3D model.
6. Visualization of the reconstructed 3D model.

When choosing the input and output format of the vector record several options were compared:

- publicly available standard formats (DXF, STEP, IGES),
- proprietary formats of selected CAD/CAM systems (there is a problem with their exact specification - for the most it is unknown and patent),
- use of format and API host CAD or CAD/CAM system.

API allows using the services of the system for prosessing input vector data or for creating 3D objects as well. The another advantage is that we can work with its native file format, possibly with some standard format for product data exchange and do not need to be addressed by implementing the file inputs and outputs. This approach with appropriate application of the proposal can create input/output modules into several CAD/CAM systems and the whole process of the processing vector data up to the reconstruction of the 3D model can be carried out in a common module. Alternatively the module can be then supplemented with processing of input/output interface for reading and recording of standard formats.

Autodesk AutoCAD was selected from several CAD and CAD/CAM systems for this phase of the project implementation. The API ObjectARX and integrated development environment Visual C ++ were used for implementation.

The algorithm presented in this paper can handle e-drawings that meet the following conditions and limitations.

The drawing of the part can contain three primary orthogonal views – front, side and top. All views must be placed in one layer where no other drawing elements, such as dimensions, separate sections and cross-sections, hatching, text information etc. are occured. The following types of lines are accepted:

- bold continuous – for visible edges
- thin dashed (short dashes) - for hidden edges
- thin dot-and-dash - for axis.

These elements must be placed in the first layer of the drawing.

Edges and axis of the part displayed in orthogonal projections may comprise only the elements of the type of line segment, circle and circular arc. Geometric shapes that can be divided into the elements above are after data reading from a vector drawing replaced automatically. Dimensioning was excluded from the processing for now. But, it is not possible to transform the drawing to the 3D model automatically without information from them; therefore, they will need to be considered in subsequent stages of the processing. All dimensions are processed as they were drawn on the drawing, namely 1:1. Three primary orthogonal projections are automatically recognized. If the drawing contains only a front view, the part is created by operation of profile rotation around the main axis. If there is more than one view on the drawing, there is a high probability, that it is not possible to reconstruct the rotational part by using only profile rotation, because it contains either elements axially and potentially symmetrically distributed around the perimeter (e.g. coaxial holes, grooves, etc.) or ones located radially around the perimeter (eg, radial holes, cuts, grooves, etc.).

The proposed algorithm for 3D model generating using reconstruction from 2D vector drawing was divided into the following steps:

- Input of vector data
- Line segmentation
- Recognition of line groups and views
- Front view processing
- Identifying of the major axis and other axises of rotation
- Recognition of distance circles
- Detection of the contour
- Identification of internal edges
- Processing of additional views.

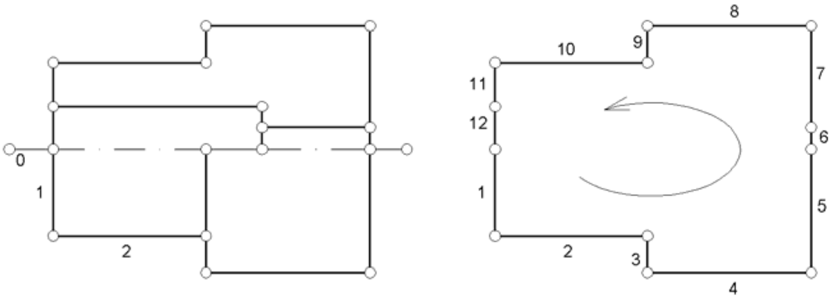
Recognition of distance circles

Besides axis consisting of abscissa-segments also the distance circles or their parts can be at the drawing, so in our case there are dot-and-dash circular arcs. These sequences of arcs are detected in the same way as abscissa-segments of straight axis.

Detection of the contour

The outer edge contour is detected by the smallest angle method, because only lines with the smallest angle towards the current segment are included in the boundary area (Fig. 3).

This way of projection lines scanning leads to the acquisition of area borders represented as a oriented graph, where the internal surface area is located on the left from the direction of the border traversing.



a) b)

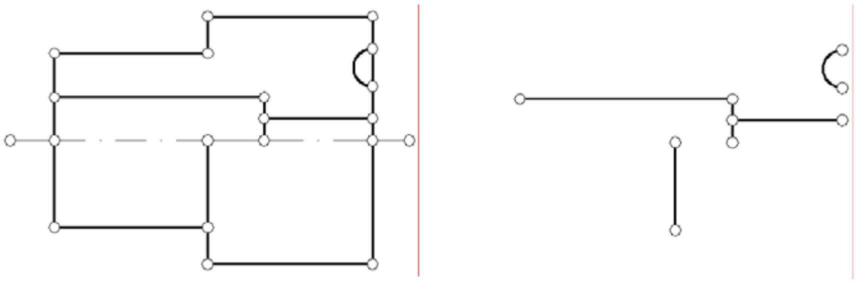
Fig. 2. Outer contour detection: a) the source b) the result

Identification of internal edges

All lines which are not constituent of the contour are scanned using the similar manner as the search of groups of lines is running throughout the whole drawing. The lines forming individual groups of edges inside are called islands. These inner islands, separately from each half of the projection are analyzed in order to find out how they have been created.

Algorithm distinguishes the following types of inner islands:

- A - Hole through in the axis of rotation
- B – Blind hole in the axis of rotation
- C – Side taking-out in the edge of the part away from the axis
- D – Side taking-out of the another part
- E – Line through away from the axis of rotation
- F – Hole through away from the axis of rotation
- G – Inner island in the axis of rotation
- H – Inner closed island away from the axis of rotation
- I – Inner island connected to another line that is different from perpendicular contour line
- J - Perpendicular abscisses associated with the contour and the axis
- K - Other types of internal lines.



a) b)

Fig. 3. Inner edges detection: a) the source b) the result

Each island is categorized and then compared with the lines islands in the other half of the projection and in the other projections. Thus their inclusion has been confirmed, or if is necessary, it can be adjusted and made more accurate. Elements that were not successfully detected haven't been used in the reconstructed 3D model.

At the present stage of development only coaxial holes and rings, therefore, the elements A, B, C and D are subsequently processed. These elements must have their projection in the direction of the main axis of rotation in the form of one or more concentric circles centered on the central axis.

The islands, successfully detected as parts we are able to create by rotation around the main axis of rotation, are supplemented with the missing segments that have completed the contour of enclosed area. The axis line and the line of the outer edge are used as the missing segments. Finally, the outer contour of these internal areas is detected.

The interior areas acquired this way can be used as a template to create a 3D model by profile rotation method. Created solids and rings with the respective cross-section are successively taken away from the main solid made by rotation of the outer profile of the part.

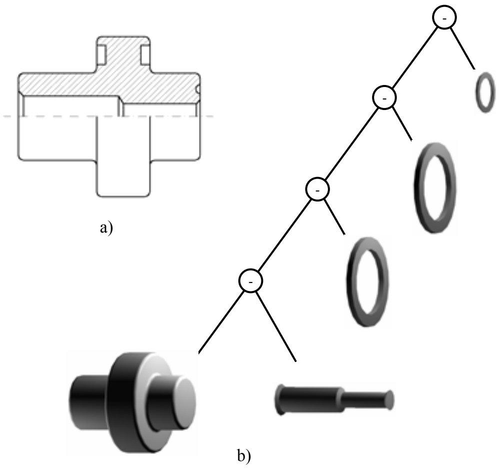
Processing of additional views

Side elevation and top view are processed only as a supplement to the front one. They serve mainly as a source of decision-making elements in assessing the elements identified in front elevation. Next, they provide additional information on the dimensions of structural elements and their location on the perimeter, respectively their distribution along the perimeter of the rotary solid.

CSG representation

The part is composed of objects created in the previous steps, using the Boolean volume operations. The main solid is made up by operation of rotation of the outer half-contour of the part around the main axis of rotation. The volumes resulting from the processing of internal edges are subsequently subtracted from it. These units are placed into a binary representation of the CSG tree.

This processing is based on a postorder method for tree processing [1] [2]. It starts in the lowest left arm of the whole tree. Coming back to the root of the tree all right nodes and their possible nodes on the left side is subsequently gone through. The part is completely reconstructed after reaching the root node.



a)

b)

Fig. 4. CSG part representation: a) the original projection b) CSG tree

Visualisation of 3D model

Visualization of 3D model is implemented using the appropriate graphics API from AutoCAD. Module intermediated communication between this graphics system and the performing module will get a command to draw the object, along with the CSG tree structure entirely describing the complete 3D model delivered to. Then the actual graphics output is executed by processing the CSG tree and the successive building of the resulted model of the part using means of the graphics system.

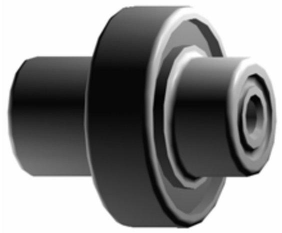


Fig. 5. *The visualization of the part*

Possibilities of a future development

The proposed methods and created application will be considered as a pilot project, which awaits further enlargement, especially the implementation of processing of various types of construction elements. Of course other development possibilities of automation of 3D model reconstruction can be outlined as follows:

- To process dimensions. This is one of the most important elements that will be required to be resolved. If there are not 2 or 3 projections, we are not able to identify and reconstruct some construction elements correctly. We are talking mainly about the cylindrical elements whose projection is identical to the prism projection.
- To process sections and cross-sections, which do not occupy the position of the primary view. This is the question of the sections location, which are marked with the cutting plane (eg. A-A) and their detection at the drawing.
- Automatically verify the successful reconstruction of 3D model by generating of projections and comparing them with the original vector record.
- To design and implement I/O modules for some other CAD/CAM systems, such as eg. Inventor, SolidWorks, ProEngineer.
- To design and implement I/O modules for separate processing of standard file formats DXF, STEP, IGES.

Conclusion

The solved problem is very complex, even after the significant limitation of elements of engineering drawing that entry to the processing are taken into account. Just about class of rotational parts, at which is presented the work aimed, involves a number of shape elements that should be taken away from the basic solid. At the same time each additional design element bringing about the rise in asymmetries increases the difficulty of 3D reconstruction of the object.

The contribution deals with a partial problem solved in the frame of the project ***VEGA 1/0282/08 with the name “3D model generation from the orthogonal views of the engineering part drawing for using in CAD and visualization”.***

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RESEARCH PAPERS
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2010 Number 29

EMPLOYER BRANDING – SOURCE OF COMPETITIVENESS OF THE INDUSTRIAL PLANTS

Dagmar BABČANOVÁ [1], Miroslav BABČAN [2], Eva ODLEROVÁ [3]

Abstract

The paper deals with the concept of employer branding, which is very important to follow, because an employer brand represents core values of an organization. Organizations that are considered good employers have a strong identity and a positive image in the marketplace. Organizations need to attract employee market to be successful. Marketing disciplines associated with Brand Management have been applied by the HR (Human Resources) to attract, engage and retain employees, in the same way that marketing applies such tools to attracting and retaining customers.

Key words

employer branding, employer image, employee, human resources management, marketing

Introduction

The term *"Employer Brand"* was first used in the early 1990s to denote an organization's reputation as an employer. [3] Employer brand is understood as a brand which differentiates it from other competitors in the employment market. The term also includes long term strategy that establishes an organization's identity as an employer in the employment market. Ambler and Barrow define employer brand as: "The package of functional, economic, and psychological benefits provided by employment, and identified with the employing company" [1]. Minchington defines employer brand as "the image of organization as a great place to work in the mind of current employees and key stakeholders in the external market (active and passive candidates, clients, customers and other key stakeholders). The art and science of

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employer branding is concerned with the attraction, engagement and retention initiatives targeted at enhancing company's employer brand. [9]

Employer branding is central to the concept in HR Marketing. It defines the personality of a company as a preferred employer. [10]

The employer brand is the most powerful tool for attracting; engaging and retaining the right talent/culture fit that will help leaders grow their organization. Like any brand, employer brand is about perception. [10]

As mentioned, branding has moved into the field of Human Resources from the discipline of marketing. In principle, brands can be seen as a set of symbols which represents a variety of idea and attributes the net result of which is the public image, character or personality of an organization. As such, branding activities involve constructing particular attributes (e. g. the values on an organization) that are considered to represent the image that a company wishes to communicate to potential employees, current staff and the public. [2] Employee and employer branding are distinct activities due to the difference in what has been branded. Employee branding is targeted at the existing workforce, but employer branding by highlighting that the organization is an employer of choice, reinforces the employee branding message to the existing workforce. Nonetheless, it is important to note that the two activities have a different emphasis. (Table 1)

FEATURES OF EMPLOYER AND EMPLOYEE BRANDING [2] Table 1

Area of employer and employee branding	**Employer branding**	**Employee branding**
Direction of branding activities	External and internal	Internal
Branded entity	The organization	The employee
Target of branding	Current and potential employee	Customers who interact with brandy employees
Roots	Personnel/ HR management Marketing literature	The management of culture literature Organizational socialization literature Marketing literature
HR activities	Recruitment and selection Advertising External and internal communication Benchmarking	Induction Training and development Performance management Competency-based HR systems Internal communication
Aim	To ensure the company attracts new recruits of quality and retains existing employees	To ensure employees act „on brand“ and share the values of the organization’s brand
Intended outcomes	Winning the war for talent High quality, motivated and high performing work force Having the competitive edge	Increased employee commitment and identification Increased customer satisfaction and loyalty/identification

Employer brand management expands the scope of this brand intervention beyond communication to incorporate every aspect of the employment experience, and the people management processes and practices that shape the perceptions of existing and prospective employees. [3]

Housden divides human resource levers to the following ones (Figure 1): 1. Employer Brand (What do people think of the organization?); 2. Talent Management (How does organization manage its talents?); 3. Reward & Recognition (What keeps organization's talent with the organization?); 4. Communication (How does organization talk to its talented people?); 5. Recruitment Processes (How organization does attract talented people to it?); 6. Performance Management (Where is a talent in the organization?). [8]

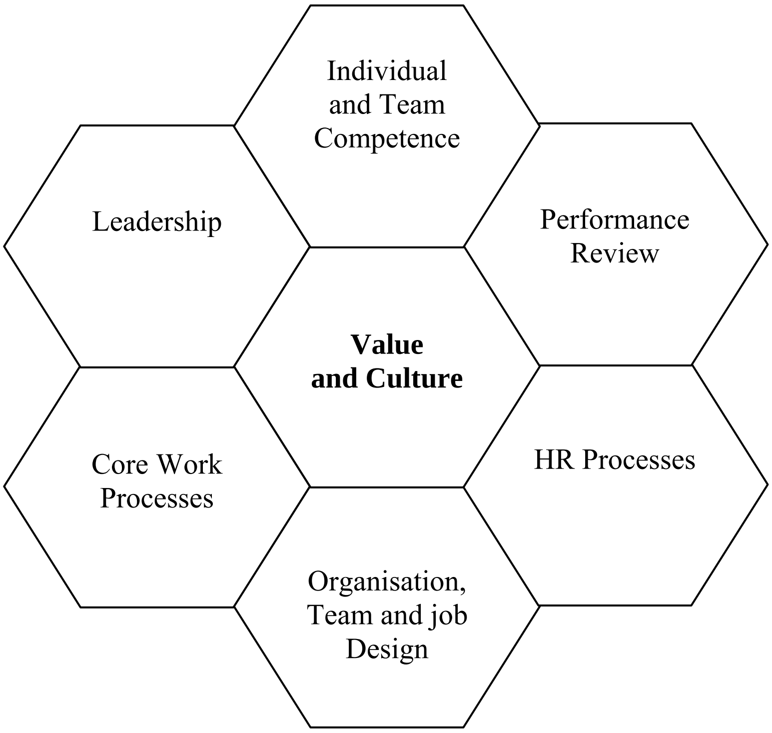

Fig. 1. Human Resources Levers [8]

There is a proven relationship between excellence in key components of employer branding and the level of market premium organizations enjoy. Harris considers the main components of employer branding are: employee engagement, employee communication, training and development, external reputation. [7]

Nowadays the global employer branding leader in the market is called Universum. Universum drives the industry forward having focused exclusively on employer branding (EB) for over 20 years. In September 2010 Universum presented the world's Top 50 most attractive employers. Universum releases the global talent attraction index: *"The World's Most Attractive Employers 2010"*, based on close to 130,000 career seekers (students at top academic institutions chose their ideal companies to work), with a business or engineering background. [6]

This is the first global index of employer attractiveness and highlights the world's most powerful employer brands of those companies that excel in talent attraction and retention. The global rankings are based on the employer preferences of students from Brazil, Canada, China, France, Germany, India, Italy, Japan, Russia, Spain, U.K., and U.S. Following the unprecedented world release in 2009, Google still manages to keep the no. one position, but this time facing growing competition from the big four auditing firms. In the business category, 2010 has been a good year for the auditing industry, as the top four companies now take four out of the top five places in the ranking. On a less positive note, the companies in the Banking and Investment industry, Management Consulting, and Oil & Gas, now encounter the problem of being perceived as less attractive employers [6].

In the engineering category (Table 2), however, the IT-sector companies continue to dominate: the top three employers – Google, Microsoft, and IBM – maintain their positions from last year. The notable changes are Japan's Sony at no. four and Apple's new entry. German car manufacturer BMW is still the most powerful employer brand in the automotive industry [6].

THE WORLD'S MOST ATTRACTIVE EMPLOYERS 2010 –
– TOP 10 ENGINEERING [5]

Table 2

TOP 10 - Engineering	**Rank 2010**	**Rank 2009**
Google	1	1
Microsoft	2	2
IBM	3	3
Sony	4	7
BMW	5	4
Intel	6	5
General Electric	7	6
Siemens	8	8
Procter & Gamble	9	10
Apple	10	New

THE WORLD'S MOST ATTRACTIVE EMPLOYERS 2010 –
– TOP 10 BUSINESS [5]

Table 3

TOP 10 - Business	**Rank 2010**	**Rank 2009**
Google	1	1
KPMG	2	8
Ernst & Young	3	5
PricewaterhouseCoopers	4	2
Deloitte	5	10
Procter & Gamble	6	6
Microsoft	7	3
The Coca-Cola Company	8	13
J. P. Morgan	9	7
Goldman Sachs	10	4

AIESEC (Association Internationale des Étudiants En Sciences Économiques et Commerciales) in Slovakia organises events to support relationship between potential employees and employers. (e. g. National Career Days, Talents of Tomorrow, AIESEC Symposium, recruitment campaigns, webportal Chcemkarieru.sk.). [4] Companies from the TOP 10 of The World's Most Attractive Employers 2010 (Table 3, business field) like Deloitte, Ernst & Young, Procter & Gamble, PricewaterhouseCoopers, KPMG presented their activities at the National Career Days 2010. Participating companies understand the need of presenting their activities at such events to get attention of potential talented employees.

Within employer branding program of AIESEC organizations conducting their business in the Slovak Republic have the opportunity to reinforce organization's brand among students and recent graduates. With products aimed at the employer brand, organizations get direct access to university students [4].

Influencing candidates to join the company requires a targeted recruitment strategy and communications approach according to a wide-ranging new survey from Employer Brand International (EBI). The "Influencers of Employment Choice Global Research Study" surveyed more than 400 employees worldwide on what influences their employment choice. Research study investigated the "Influencers of Employment Choice", specifically which of 15 employer brand attributes have the strongest influence on why employees choose to join an organization over another. The report includes global segmented results for gender, age, organization type, country, position in company and tenure. One of the research issues was related to the employer brand strategy. Just 16 % of respondents have a clear employer brand strategy and 13 % of studied employers confirmed no developed employer brand strategy (Figure 2) [6].

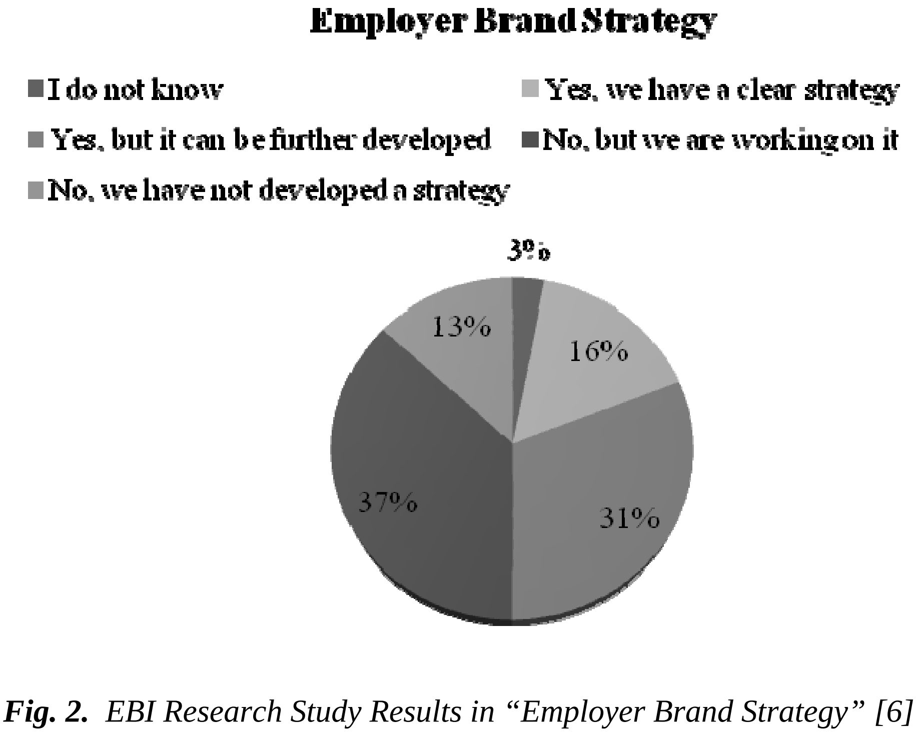

Fig. 2. EBI Research Study Results in "Employer Brand Strategy" [6]

The study found if employer wants to influence women in their employment choice they need to communicate flexible working patterns and a friendly working environment. Compared to men, flexible working patterns are six times more likely to influence women in their employment choice. The opportunity to work with thought leaders, an organization with a culture of innovation and a clearly defined mission has a stronger influence on employment choice for males. The research shows employees in private companies can be influenced to join companies who value leadership, reward for performance and a global perspective in their work much more than not-for-profit and government sector employees. On the other hand, government employees are more influenced in their employment choice by companies that offer flexible work patterns and who can demonstrate an authentic approach towards corporate social responsibility. *Other key findings of the global survey include [6]:*

1. Being rewarded for performance decreases in strength of influence of employment choice as age increases.
2. Working for a company that provides a high level of customer service increases in influence of employment choice as age increases. It is nearly 5 times as strong an influence for 50+ years compared to 18-29 years.
3. A friendly working environment is also a stronger influencer of employment choice for younger age groups and declines with age (nearly 3 times stronger for 18-29 years compared to 50+ years).
4. The opportunity to work with thought leaders is nearly twice as strong an influencer of employment choice for employees in the private sector compared to government.
5. Working for a company with inspiring leadership is three times a stronger influence for employees in the private sector compared to not-for-profit and government employees.

The results of the research assist to inform and guide organisations in their talent attraction and retention practices.

Conclusion

Employer branding is the response of Human Resources Management to the particular market circumstances. Very important factor in achieving employer branding objectives is to have a clearly defined employer brand strategy. Regarding the career seekers in the field of engineering, potential hires find companies that are innovative, produce exciting products and offer exciting services.

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POSSIBILITIES OF UTILIZING THE METHOD OF ANALYTICAL HIERARCHY PROCESS WITHIN THE STRATEGY OF CORPORATE SOCIAL BUSINESS

Katarína DRIENIKOVÁ, Gabriela HRDINOVÁ, Tomáš NAŇO, Peter SAKÁL

Abstract

The paper deals with analysis of the theory of corporate social responsibility, risk management and with the exact method of analytic hierarchic process that is used in the decision-making processes. The second and third chapter focused on presentation the experiences with the application of the method in the formulating the stakeholders´ strategic goals within the CSR and simultaneously its utilization in minimalization environmental risks. The major benefit of this paper is mentioned application of AHP. ***This work was supported by the Slovak Research and Development Agency under the contract No. LPP-0384-09: "Koncept HCS modelu 3E vs. koncept Corporate Social Responsibility (CSR)."***

Key words

corporate social responsibility, risk management, method of analytic hierarchic process

Introduction

Every day each of us must decide between a lot of choices of our action. Of course we have some criterions connected to the solution that impact our action. They can be both objective and subjective. To objective solution of social problems was developed Analytic Hierarchic Process (AHP) method - a sample tool for solution of our goal or problems. In the article we want to even roughly show how to use AHP method and how does it work in praxis.

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CSR and AHP

Corporate social responsibility (CSR)

There are too many definitions of corporate social responsibility (CSR) in a literature but we can mention the definition according to EU where the CSR is: “A concept whereby companies integrate social and environmental concerns in their business operations and in their interaction with their stakeholders on a voluntary basis.“

Socially responsible business includes all the activities that are beyond the legitimate requirements of maximum and beyond the activities that helps companies to understand and satisfied the stakeholders´ expectations. **Definitions of CSR relies on general ethical principles like neutrality, engagement, active cooperation with stakeholders, transparency and usually are characterized with common features:**

- ***are universal,***
- ***emphasize voluntary,***
- ***are based on active cooperation with its stakeholders,***
- ***are committed to contributing to the development of quality of life,***
- ***are focused on development, not only growth,***
- ***mention three areas that are crucial and specifically,*** *the company operates with respect to triple-bottom-line (it focuses on economic growth, social and environmental consequences).*

Economic pillar of CSR is mainly concerned with questions of corporate transparency, creating good relationship with stakeholders that have an impact on economic activity of the company (investors, owners, customers, suppliers, business partners, etc.)

Social pillar of CSR can be divided into internal and external areas. Internal area concern social policy and external business area focuses mainly philanthropy, altruism and cooperation with local community.

In **environmental pillar** of CSR companies focus to reduce the negative impact of its activities on the environment.

Analytic hierarchic process

The AHP method characterization

Analytic hierarchic process is a structured technique to manage complex decisions. Provides a comprehensive and coherent approach to structuring the problem, quantifying its elements, related to the overall objectives and for evaluating alternative solutions. AHP is used in various fields. It is used worldwide in fields as government, commerce, industry, health, education.

It was used in many decisions in the field of economy, energy management, environmental, transport, agriculture, industry and the military [2].

Structure of AHP method

AHP method as a flexible model for decision making, clarifies issues, which have several possible solutions. AHP is performed by expert and then by performed mathematical method, which divides the main problem into smaller and more detailed elements.

Decision by AHP method can be divided into 3 different levels [2]:
1. hierarchy,
2. priorities,
3. consistency.

Explanation of the AHP hierarchy

When you create a structured AHP hierarchy it's established a system consisting of optimization objectives, the group of factors or criterions and alternatives, arranged like tree [2].

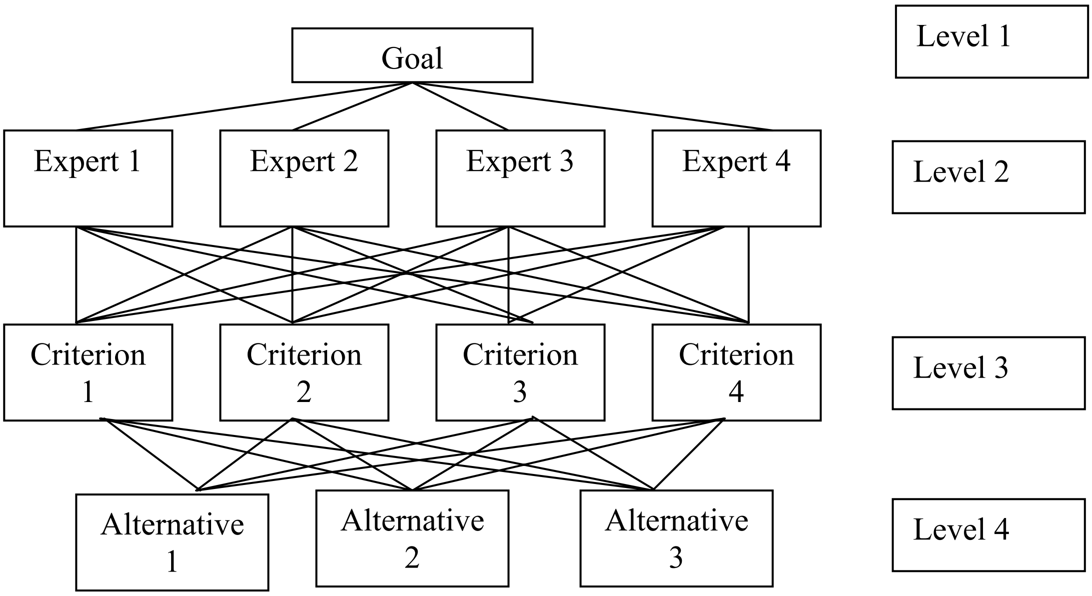

***Fig. 1**. AHP method structure*

Priorities

After sorting their own set of criterions and the establishment of a hierarchical structure at all levels of assessment, various alternatives or criterions that affect the assessment through verbal explanations and figures are compared. The result is given by the weight in proportion to the scale of alternatives and criterions [2].

Weight allocation

The correct and responsible determination of the individual sub-scales of assessment criteria is one of the key tasks in solving multicriterial problems. Therefore it's necessary to know solved issue well and know the importance and impact of the criterions which evaluate the result achieved [2].

AHP in stakeholders´ strategic goals formulation

The aforementioned AHP method is designed to deal with such decision-making situations that are repeated and where the relationships between elements are expressed quantitatively. This method, inter alia, can be used in formulating of the stakeholders´ strategic goals in CSR too.

In dealing with this method, we used the software program Expert Choice, whose output is a wide range of materials for an explicit reasoning of the best alternatives choice. Expert Choice is a software tool that supports decision making in the selection of alternatives that are characterized by hierarchical layout of criterions and priorities for selection

Corporate stakeholders represent the decision making subject. Decision making about the stakeholders´ strategic goals is one of the most serious issues company solves within the strategic planning.

From the many alternative goals were selected in the decision making process the following goals:

- ***realization of ergonomic audit in the manufacturing process,***
- ***eco-effective project implementation,***
- ***do nothing.***

We realized the decision making process in a company where it was necessary to determine which of the proposed alternatives - the CSR goals, would be the most useful for the stakeholders. A group of experts were considered to be shareholders, managers and employees (internal stakeholders). There were assigned three criterions to each expert, which have an impact on decision making in selecting the best alternatives.

The goal was to find a through strategic stakeholders´ goal within the CSR. We proceed as follows, at first we set the main objective solution (to find a trough strategic goal), then we set various alternatives (strategic goals) and created the hierarchic structure see Fig. 2 (4 levels – the goal, the experts, criterions and alternatives). We identified the importance of experts and their criterions by the pairwise comparison, after that we decided about the alternative importance according to rated criterions by the pairwise comparison too.

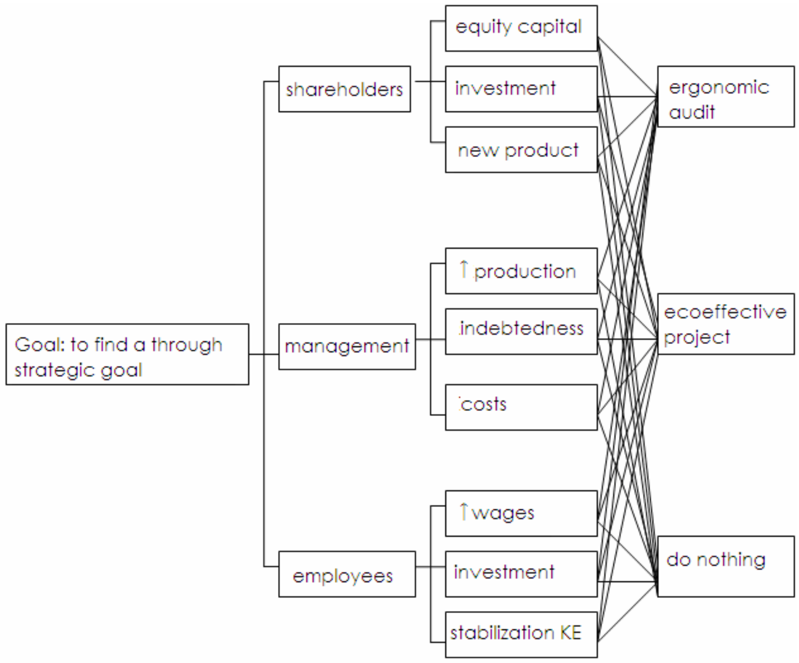

***Fig. 2.** Hierarchical structure of decision-making process*

After the creating a hierarchical structure, we continued in the decision making process and its most important part of the paired comparisons. First, using an analytical form, we found out the experts importance in finding a strategic goal. According to the matrix that was compiled (Table 1) on base of the form it can determined that shareholders are 4 times more important than the managers and employees and managers that are 2 times more important than employees. Based on the matrix software Expert Choice assessed that the most important word in deciding takes the shareholders with more than 66 %, followed by management with nearly 21 % and the smallest word have employees with 13 %.

MATRIX OF PAIRWISE EXPERT COMPARISON

Table 1

	shareholders	**management**	**employees**
shareholders	1	4	4
management	¼	1	2
employees	¼	1/2	1

We continued in the criterion evaluation (by alternatives) by the same way as the previous, it was necessary to draw 3 matrixes.

And the result was:

- ***Shareholders*** *- the most important criterion for them seems to be the equity capital with 66%, followed by investments with more than 18% and finally the implementation of a new product with almost 16% importance.*
- ***Management*** *- for them is essential to ensure the growth of labor productivity with 55%, followed by the cost of claims with 24% and the remaining 21% is company's indebtedness.*
- ***Employees*** *–they prefer the wage increase with 61%, then require investment to the working environment with nearly 27% and only 12% is to the key personnel stabilization.*

Finally, it was necessary to evaluate the alternatives according to individual criterions and the 9 matrixes were created (because there are 9 criterions) of the size 3x3 (alternatives were compared between), that were compiled on a base of the evaluated analytical forms. Because of too many matrixes, we decided to show at least 1, that shows a comparison of alternatives according to criteria of equity capital (Tab. 2). When evaluating alternatives, we counted with local and global weight of individual criterions too.

COMPARISON OF ALTERNATIVES ACCORDING TO THE CRITERION – EQUITY CAPITAL

Table 2

criterion equity capital	**ergon. audit**	**ecoeffective project**	**do nothing**
ergonomic audit	1	4	2
eco effective project	1/4	1	1/5
do nothing	1/2	5	1

The result of the decision making process was to determine the alternative with the highest priority. **Software Expert Choice determined the order according to the calculations follows:**

1. ***realization of ergonomic audit in manufacturing process***
2. ***nothing to do – do not realize any project with priority 29,4%***
3. ***implementation of eco- effective project with 25,5 % priority***

The output of decision making process is that was found a through stakeholders´ strategic goal within the CSR strategy – the realization of ergonomic audit in manufacturing process. The whole process of deciding was verified by mathematical calculation.

AHP in minimalization of environmental risks

We tried to build the application of AHP method for environmentally oriented risk management on the company orientation in the environmental protection and safety and occupational health. The reason of this orientation is that this company where we did the verification produces electric energy. Next, we describe the procedure for resolving this method step by step as it was implemented.

In a first step we had to define the goal or problem solution. This was in connection with the examination of environmental risk management defined as follows: "Minimalization of environmental risks". The goal is specifically bound to the problem, we have identified in the company and to the need or intend to minimize or eliminate the use of hydrazine substances. The substance is highly toxic, carcinogenic and also has a toxic effect to aquatic organisms. Effective solution of the problem should therefore results in effective elimination of environmental risks and risks associated with protection and safety and occupational health of employees who are exposed to effect of the substance.

The second step was to design alternatives. Although the suggestion of alternatives was on the last level of the hierarchical structure of AHP we made it in the second step. It is an important part of the result by the reason that the alternatives must be realistic and feasible to use them. They also must be designed by experts because of efficiency of the resulting alternatives in terms of goal applications.

In this case we used following alternatives of solving:

- ***A1- volume changes in purchasing and handling of hydrazine,***
- ***A2- hydrazine replacement or technology change,***
- ***A3- to do nothing.***

The role of the suggested alternatives was to cover the full range of options to solve this problem. We considered the keeping the substance in the company in the first alternative, but with some changes we tried to minimize or eliminate its potential risks. The second one is when we wanted to completely remove the substance from company and the last option was designed to examine what would happen if we did nothing.

In the third step we suggested the criterions that are restrictions for the alternatives. So they limited the outputs of problem solving or goal. There are criterions that were designed for our application in the last table Tab.4.

The calculations of standardized scale and tests of consistency and following finding the optimal alternative or the most important criterion are in the next steps. This can be done both manually and with the use of the software tool for solving of AHP method – Expert Choice 11.5. Because of the size of this article it's not possible to describe the whole process solutions punctually. This can be found in following publication: NAŇO, T. *The Utilization of the AHP Method in Decision Making in Environmental Risk Management of SE, a.s. EBO.* In *SSC 51: 51th International Student´s Scientific Conference. 6th May 2010, Zvolen*. Zvolen: Technical University in Zvolen, 2010, ISBN 978-80-228-2053-0.

In the fourth step we compared criterions by pairwise comparison (Tab. 3) of criterions using Saaty assessment matrix which compared all the criterions among themselves.

CRITERIONS PAIRWISE COMPARISON MATRIX

Table 3

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**C10**
C1	1	1/3	3	1/7	3	1/4	1/7	1/9	1/8	1/2
C2	3	1	3	1/4	3	1/3	1/5	1/8	1/8	1/2
C3	1/3	1/3	1	1/3	2	1/3	1/5	1/9	1/8	1/4
C4	7	4	3	1	7	4	1/3	1/9	1/8	1/2
C5	1/3	1/3	1/2	1/7	1	1	1/7	1/9	1/8	1/6
C6	4	3	3	1/4	1	1	1/5	1/5	1/4	1/4
C7	7	5	5	3	7	5	1	1/2	1	2
C8	9	8	9	9	9	5	2	1	2	2
C9	8	8	8	8	8	4	1	1/2	1	2
C10	2	2	4	2	6	4	1/2	1/2	1/2	1

The result of the comparison was finding the order of the criterions importance. **The three most important criterions were the following:**

1. ***ensuring protection and safety and occupational health,***
2. ***ensuring environmental safety solutions,***
3. ***reality and sustainability of solution.***

We equivalently compared the alternatives each based on any other criterion in the final fifth step. The result of the comparison was to find optimal solution to the defined goal. There's a final assessment and finding optimal solution in the Tab. 4.

There is an optimal alternative for the defined goal – to minimize environmental risks – is an alternative A2 - **hydrazine replacement or technology change** in the Tab. 4.

ALTERNATIVE FINAL ASSESSMENT Table 4

Criterion	**Weight**	**Weight in %**	**A1**	**A2**	**A3**
Ensuring protection and safety and occupational health	0,270	27,05	0,03	**0,21**	0,03
Ensuring environmental safety solutions	0,204	20,39	0,051	**0,102**	0,051
Reality and sustainability of solution	0,166	16,57	0,1123	**0,032**	0,0217
Company standards compliance	0,103	10,25	0,054	**0,0146**	0,0344
Possibility of exemption from the law 261/2002 statute	0,089	8,9	0,0209	**0,0612**	0,0069
Possibility of measuring and regulation	0,051	5,07	0,0053	**0,0325**	0,0132
Economic effectiveness of solution	0,042	4,18	0,0089	**0,0056**	0,0275
Staff preparation in direct and indirect contact with hydrazine	0,033	3,27	0,0024	**0,0053**	0,0252
Time effectiveness of solution	0,023	2,33	0,0034	**0,0016**	0,0181
IT requests	0,020	1,99	0,0040	**0,0013**	0,0147
Total:	1	100%	**0,292**	**0,466**	**0,243**

Conclusion

When applying AHP method in the field of stakeholders´ strategic goals formulation can be stated that the most suitable alternative goal oriented to the CSR was realization of ergonomic audit according to the estimates of company experts. According to the selected criterions it was also found that on the second rank was the alternative – do nothing and for the least suitable alternative was considered eco effective project. It should be noted that sequence of these alternatives was influenced by the established criterions of individual experts.

Furthermore, in the minimization of environmental risks was a recommendation for the application and effective functioning alternative replacement substances and changing technologies, the second place was alternative the change of the volume purchasing and handling with the substance and on the last rank was the alternative which examined what happens when we would do nothing and the state remained unchanged.

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APPLYING THE THEORY OF CONSTRAINTS IN THE COURSE OF PROCESS IMPROVEMENT

Michal MARTON, Iveta PAULOVÁ

Abstract

Theory of constraints (TOC) is about thinking in logical, systematic, or structured processes similar to the PDCA learning loop. It is about analyzing cause and effect, verifying basic assumptions, exploring alternatives and process improvement. The goal of TOC is to maximize the efficiency of a process selectively at the most critical points and thereby maximize profitability, quality, or other corporate objectives. This paper include basic theoretical information about TOC and following application during process improvement.

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Key words

theory of constraints (TOC), process improvement, critical chain

Introduction

Theory of Constraints (TOC) is an overall management philosophy introduced by Dr. Eliyahu M. Goldratt in his 1984 book titled *The Goal*, that is geared to help organizations continually achieve their goal. The title comes from the contention that any manageable system is limited in achieving more of its goal by a very small number of constraints, and that there is always at least one constraint. A constraint is anything that prevents the system from achieving more of its goal.

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Theory of constraints assumption

TOC methodology operates on several assumptions:

- As in the case of lean, the organization places a value on the speed at which its product or service travels through the system. Speed and volume are the main determinants of success.
- Current processes are essential to produce the desired output.
- The product or service design is stable.

Value added workers do not need to have an in-depth understanding of this improvement methodology. Suggestions by the workforce are not considered vital for successful implementation of the theory of constraints. Organizations with hierarchical structure and centralized knowledge value this approach.

Systems as chains

A system is generally defined as a collection of interrelated, independent processes that work together to turn inputs into outputs in the pursuit of some goal. As pictured above, the chain has one “weakest link.” If force is applied to the chain at an increasing rate, it would eventually break at this point. Therefore, the weakest link is the constraint that prevents the chain (system) from doing any better at achieving its goal (transmitting force).

Fig. 1. *Weakest link in the chain*

Goldratt states that there is only one constraint in a system at any given time limiting the output of the entire system. The remaining “links” are known as nonconstraints.

When one constraint is strengthened, however, the system does not become infinitely stronger. The constraint simply migrates to a different component of the system, i.e., some other link is now the weakest and all other links are nonconstraints. The system is stronger than it was but still not as strong as it could be.

To better understand the theory of Constraints and nonconstraints, consider a sample production system that runs raw materials through three component processes and turns them into a finished product, as pictured on figure 2.

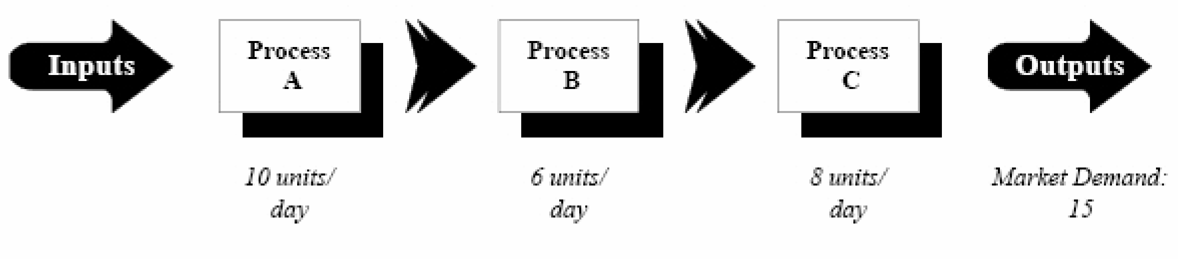

Fig. 2. *Standard process flow in organization*

Within the system, each process is equivalent to a link in the production chain. Where is the constraint in this chain? Process B is the weakest link since it produces only six units per day no matter how many the rest of the components produce. Where are the nonconstraints? Everywhere else.

Imagine that the manufacturer improves process B until it can produce 18 units per day. Now, process C becomes the system constraint while the nonconstraints are everywhere else. If process improvements continue until all processes are producing 18 units/day or higher, the system constraint becomes the marketplace, which can accept only 15 units per day.

At this point, internal constraints have been replaced by an external constraint. Overall, the theory of constraints emphasizes fixing the weakest link in the chain—the system constraint—and temporarily ignoring the nonconstraints. In this way, the theory has a profound impact on process improvement.

Rather than spreading limited time, energy, and resources across an entire system (which may or may not result in tangible results), teams focus on that part of the system with the potential to produce immediate system improvement.

The five focusing steps of TOC

Step 1: Identify the system constraint.

In the first step, an organization identifies what part of the system constitutes the weakest link and determines whether it is a physical constraint or a policy-related issue.

Step 2: Decide how to exploit the constraint.

Organizations “exploit” the constraint by utilizing every bit of the constraining component without committing to potentially expensive changes and/or upgrades.

Step 3: Subordinate everything else.

With a plan in place for exploiting the constraint, organizations adjust the rest of the system to enable the constraint to operate at maximum effectiveness and then evaluate the results to see if the constraint is still holding back system performance. If it is, the organization proceeds to Step 4. It it’s not, the constraint has been eliminated and the organization skips ahead to Step 5.

Step 4: Elevate the constraint.

If an organization reaches Step 4, it means that Steps 2 and 3 were not sufficient in eliminating the constraint. At this point, the organization elevates the constraint by taking whatever action is needed to eliminate it. This may involve major changes to the existing system, such as reorganization, divestiture, or capital improvements. Since these typically require a substantial up-front investment, the organization should be certain that the constraint cannot be broken in Steps 1 through 3 before proceeding.

Step 5: Go back to Step 1

But beware of inertia. After a constraint is broken, the organization repeats the steps all over again, looking for the next thing constraining system performance. At the same time, it monitors how changes related to subsequent constraints may impact the constraints that are already broken, thus preventing solution inertia.

Advantages and disadvantages of application Theory of constraints

Advantages:

- Potential for tremendous increases in productivity with minimal changes to operations.
- Most powerful and cost effective tool for increasing production capacity.
- Very simple to communicate and apply, making it ideal for shop floor teams.
- Great for fostering teamwork as different areas become aware of the constraint and the need to work together to assist the constraint process.
- Great process for kick starting improvement efforts as it provides immediate and very tangible benefits.
- Allows growth of turnover/productivity without the need for additional space or staff.
- Provides a means to evaluate the true value of changes (using T, O, I), and utilize this to select the best options, and drive the right behaviour/decisions.

Disadvantages:

- Can be difficult to apply if the constraint process is constantly moving (for example if the nature of the work sees dramatically different and difficult to predict demands on various production resources).
- Can be difficult to apply in a jobbing environment (however it is still very applicable).

Possible conflicts of application TOC at Slovak industrial practice

We can meet often at industrial practice that exists situation or process which is not coordinated. We can immediately find root cause of this problem, but is possible that in the future we find out that root cause was incorrect.

Typical situation at production:

- Low profit, low economic return of invest.
- Delivery time and through time of production are long than can customer wait.
- Delivery precision is not followed.
- Not enough time for good decision.
- Moving bottlenecks on another place, etc.

All of these symptoms have a root from exist so called General conflict at production. His logic is displayed on the next figure.

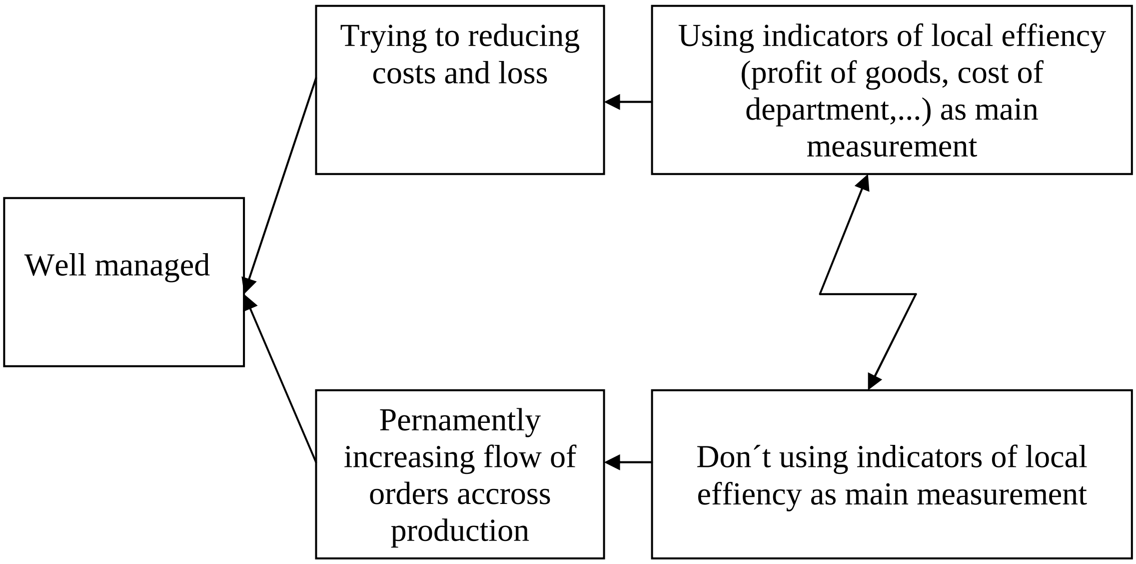

Fig. 3. *General conflict at production*

I would like to mention some other aspects of possible conflict at Slovak industrial practice. It is important consider about human factor. During application we can meet often with following problems:

- Resistance to change - human don't accept radical change at company.
- Disagreement on the issue - the same problem human understand different.
- Disagreement about problem solving - every person has idea for solving problem.
- Solution has sometimes unwanted risk - it is normal process, during application human must be informed about this risk.
- Unspoken concerns - of course, this concerns can occurred or not but doesn't exist clear answer for solution.

Research contribution

The authors described in this research theoretical and practical knowledge about Theory of constraints. Consequently, this article pointed to the possible problems and barriers at Slovak industry during application. Results from this research give an impulse for next working out about continues process improvement at Slovak industry. At the present is solving doctoral thesis about interconnection TOC, LEAN and Six Sigma and output from this research will regard in the further research.

Conclusion

So far this paper has focused on maximizing throughput as the end goal. Actual manufacturing is a trade off between throughput, the number of units through the factory per unit time, and cycle time, the start to finish length of the process. Short cycle times allow you to be more responsive to customers and can allow more rapid process improvement, an important consideration in rapidly changing processes. However, short cycle times are incompatible with high throughput: if you're going to make sure that the bottleneck tool is available when the hot lot gets to it, then you risk having the bottleneck tool sitting idle while it waits. For maximum throughput, you always want the bottleneck tool to run at full capacity. That's one reason why *Just In Time* isn't really compatible with mass customization and other agile manufacturing requirements. Goldratt's approach *should* be flexible enough to work in a low cycle time environment, simply by redefining the constraints.

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THE KNOWLEDGE ACCELERATING THE SOCIETY DEVELOPMENT

Jaroslav ŠMÍD, Peter SAKÁL

Abstract

The creation of appropriate conditions can accelerate the society development. According to existing definitions the society can be viewed as mankind as a whole, or a state, a region or a group of businessmen. This paper extends and supplements the previous paper [1]. It deals with knowledge, which accelerates the society development using the modified formal notation of the society development according to [2].

The open innovation concept [3] presents the intentional use of external knowledge flow. This paper deals with the intentional use of knowledge in time.

Key words

society development, pyramid of knowledge, knowledge

Pyramid of knowledge

Every branch accumulates certain amount of knowledge. The picture 1 shows the knowledge model using a pyramid. Every building unit in the pyramid shows the single knowledge. The units at the top of the pyramid present the top level of knowledge. Every unit was at certain time placed at the top and presented the top level of knowledge. The pyramid develops in real time in such a way, that every unit with the human invention generates the new knowledge, which becomes the new top knowledge [1].

Some knowledge, progressive knowledge is so important, that a new branch appears or the development transfers rapidly [1].

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The pyramid of knowledge can be visualized as a multidimensional one - some knowledge is a part of pyramids of knowledge from several branches. It can be marked as section knowledge. Any progress and the new knowledge, which can be used in various fields influences the development of various fields at the same time, thus accelerating the society development more than the knowledge acquired and used in one field [1].

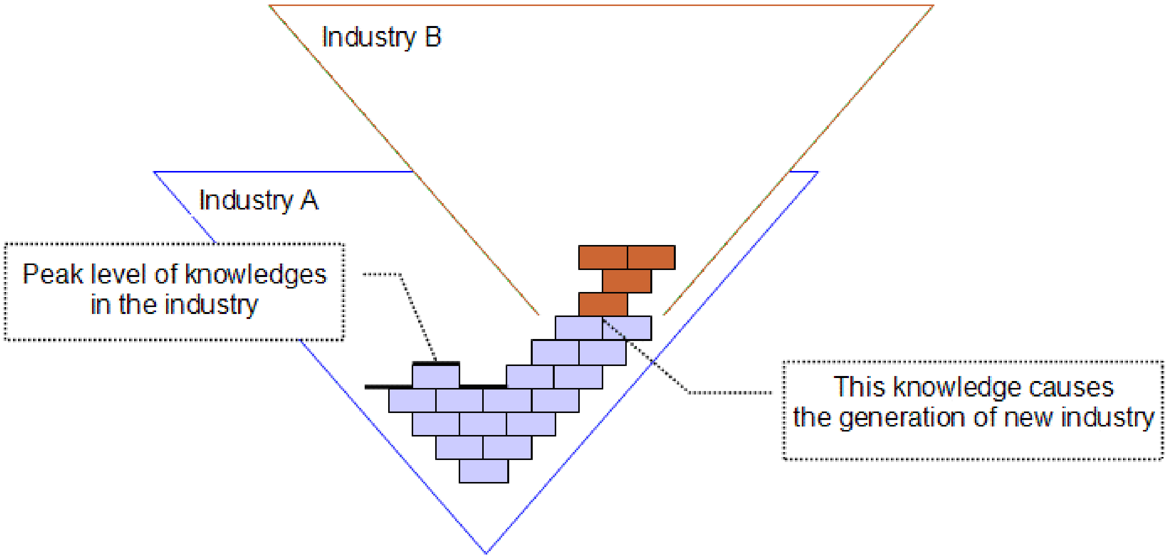


Fig. 1. *Pyramid of knowledge*
Source: Accelerating the society development level of innovation and ... [1].

Society development model

A symbolically denoted branch (discipline) D_i {i=1,m}, where m is the number of branches. For example, Engineering D_1, Electrotechnics D_2. The single knowledge is denoted by the symbol V. The time order of the single knowledge acquiring in single branches can be expressed by the following notation:

D_1	Electrotechnics	$V_{1,1}$	$V_{1,2}$	$V_{1,3}$	...	$V_{1,k1}$
D_2	Engineering	$V_{2,1}$	$V_{2,2}$	$V_{2,3}$	...	$V_{2,k2}$

The knowledge $V_{1,k1}$ represents the top knowledge level in the branch D_1, the knowledge $V_{2,k2}$ represents the top knowledge level in the branch D_2. According to the model - Pyramid of knowledge, the acquired knowledge with the prior branch knowledge generates the new knowledge.

The new knowledge formation is not only caused by the previous knowledge from a given area and by the invention expressed by the knowledge growth coefficient. It is caused as well by the knowledge from the nearest related branches.

The society development can be expressed as a gradual knowledge acquiring from different branches in time. The society development can be generally expressed by the following notation:

D_1	$V_{1,1}$	$V_{1,2}$	$V_{1,3}$	$V_{1,4}$	$V_{1,5}$	...	$V_{1,k1}$
D_2		$V_{2,2}$	$V_{2,3}$	$V_{2,4}$	$V_{2,5}$	...	$V_{2,k2}$
...							
D_m			$V_{m,3}$	$V_{m,4}$	$V_{m,5}$	...	$V_{m,k3}$
	⟶ Time						

Branches D_2 a D_m emerged later than the branch D_1. This is the reason why the knowledge $V_{2,1}$ $V_{m,1}$ $V_{m,2}$ do not exist. The first knowledge in the branch D_2 is $V_{2,2}$. The branch D_m emerged as the last and its first knowledge is $V_{m,3}$.

Apart from the common society development by the gradual knowledge acquiring the special knowledge occurrence could come into existence:
- knowledge, which was ahead of the society development,
- knowledge, which influences the development of various branches,
- knowledge, which broadens the existing branch or gives rise to a new branch.

Knowledge, which was ahead of the society development

The society development presents knowledge, which was ahead of its time and which will be used in the future. A typical example is the binary system use. M. Leibnitz was the first person, who introduced the binary system and its use in the year 1703 [5]. The binary system was practically used later in the computing technology though. It is the knowledge, which does not appear to be ahead of the society development in the time of discovery. It appears to be the knowledge, which does not have a practical use. It was necessary to acquire deep knowledge from other branches to find the practical use of the binary system.

D_1	$V_{1,1}$	$V_{1,2}$	$V_{1,3}$	$V_{1,4}$			
D_2		$V_{2,2}$	$V_{2,3}$	⟶	⟶	⟶	$V_{2,4}$
...							
D_m			$V_{m,3}$	$V_{m,4}$			

$P_{2,4}$ is the knowledge, which was ahead of its time in the branch 2.

This knowledge causes to reinvent the knowledge in its branch and other branches acceleratingly.

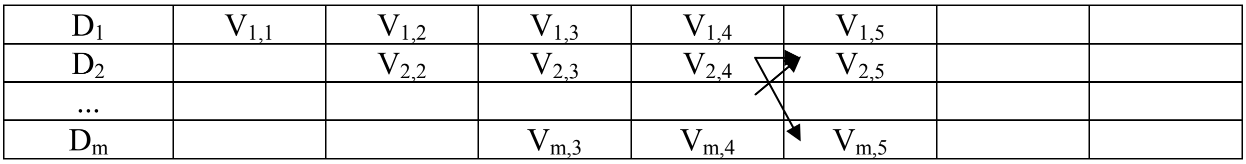
D_1	$V_{1,1}$	$V_{1,2}$	$V_{1,3}$	$V_{1,4}$	$V_{1,5}$ ←	←	
D_2		$V_{2,2}$	$V_{2,3}$		$V_{2,5}$ ←	←	$V_{2,4}$
...							
D_m			$V_{m,3}$	$V_{m,4}$	$V_{m,5}$ ←	←	

The binary system use as well, which was not of any practical use in its time, accelerated the society development. The development in certain period, which considers using two states of data transmission and processing was accelerated by the existing knowledge of the binary system and basic mathematic operations, which were run in this system. The extent to which the knowledge accelerated the society development was in this case low though.

To use this knowledge to accelerate the knowledge, it is necessary to preserve and develop it for future and search for and use the knowledge from the past.

Knowledge, which influences the development of various branches

The electronic microscope, which enables to study materials on the atomic level, opened up new development possibilities of all branches. It enables to observe the surface of materials and manipulate single atoms and molecules, which facilitates research of new areas for example nanotechnology.

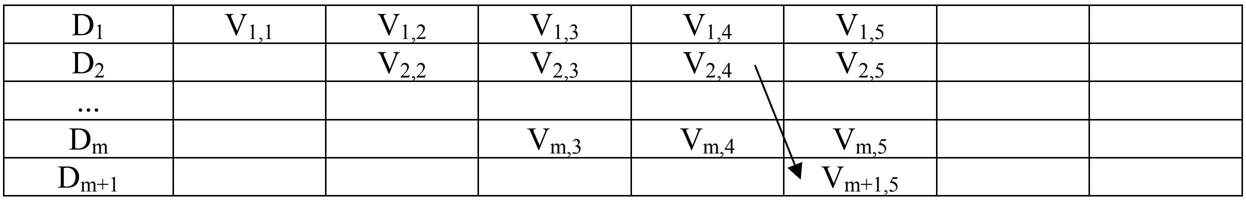


D_1	$V_{1,1}$	$V_{1,2}$	$V_{1,3}$	$V_{1,4}$	$V_{1,5}$		
D_2		$V_{2,2}$	$V_{2,3}$	$V_{2,4}$	$V_{2,5}$		
...							
D_m			$V_{m,3}$	$V_{m,4}$	$V_{m,5}$		

The knowledge $V_{2,4}$ is the section knowledge and influenced and accelerated the development of different braches.

Knowledge, which broadens the existing branch or gives rise to a new branch

The most precious knowledge is such, which causes to broaden the boundaries of the existing branch or gives rise to a new branch.



D_1	$V_{1,1}$	$V_{1,2}$	$V_{1,3}$	$V_{1,4}$	$V_{1,5}$		
D_2		$V_{2,2}$	$V_{2,3}$	$V_{2,4}$	$V_{2,5}$		
...							
D_m			$V_{m,3}$	$V_{m,4}$	$V_{m,5}$		
D_{m+1}					$V_{m+1,5}$		

A good example could be the laser discovery and development, which helped to broaden boundaries of many branches.

Conclusion

It is possible to generalize this concept and to a certain level consider every knowledge to be the knowledge, which:

- was ahead of its time and retrospectively accelerates the society development,
- influences the development of various branches,
- broadens boundaries of the existing branch or causes a new branch creation

The knowledge, which has these qualities can be considered to be the knowledge which accelerates the society development.

In the sense of this paper and previous paper it is necessary:

- to support knowledge, which influences the development of various branches or gives rise to a new branch – support cooperation between branches, support technologies development, new materials, measurement methods and other section areas.
- to preserve or develop the knowledge which does not have in the present time any commercial use and search for existing knowledge, which in the past was not commercially used.

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2010 Number 29

ECONOMICAL ASPECTS OF ENVIRONMENTAL SAFETY

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Abstract

By transition to market economy information about environment condition has been accessed and stepwise findings of such "inventory control" are published. There is a space for slowing-down the growth of economics damages on environment and for disposal of old environmental loads, solution of which requires in conditions of Slovak Republic around 100 – 130 mld. Sk. This space is forming in difficult socioeconomic conditions. Ongoing problems are related not only to wherewithal shortage for solving these problems, but also to insufficient legislative and its adjusting to European Union requirements, and to insufficient environmental appreciation and unawareness of "satiation of our own future", us all.

Key words

environment, economic,

Introduction

Economic activities in recent decades have brought side-effect that also consist in abuse of particular elements of environment and others negative consequences on natural environment connected with this. Critical (Main) effect on the condition and quality of environment has economic process of reproduction that is affect backwards by quality of environment (production and consumption). During industrialization some industries heightened their production regardless of environment, whereby negative consequences in the form of economic effects – externalities are produced.

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Even if most of Slovak soils are clean – not contaminated, there are some areas in Slovak Republic (SR), which we indicate as problem areas, where in the past following different human economic activities soil fund was and still is contaminated especially by air pollutants of industry and energetic, but also by another effects. Thereby ecological disturbances, economic and safety problems, which we also call "environmental loads", are formalized.

In the areas like this, with acreage of approximately 4470 km^2 (12 % of Slovak Republic area), live almost 40 % of Slovak inhabitants. These areas are mostly bigger urban territorial units with concentrate economic activities. Refine on allocation of endangered areas led to determination of 9, later 10, and in present 8 endangered areas more or less interconnected.

Sources and methods

Environment (living and natural) in Slovak republic was harmed mainly by intensive development of heavy industry and power industry, improper structure and location of particular types of productions. We analyze human economic activities and their impacts on environment in our contribution. We will dissertate about so called loads at environment, removal of which takes around 100 – 130 mld. Sk.

In our analyses we follow accessible current sources relating to implementation of analyzed problem on national level as well as on international. We use home internet information sources, and sources of European Commission, National allocation plan (program) for the years 2005-2007. We use methods of synthesis, analysis, guided (controlled, instructed) interview; we use subscripted analysis out of mathematic-statistical methods. We brink ourown ideas of solution of given problem. We use results of our own research – grant tasks VEGA, APVV.

Results and discussion

Environmental policy, which is a part of economic policy, is aim at coming into production and consumption decisions of business sphere and consumers, with a view to achieve changes in behavior of subjects that damage environment. As main economic incentives for solving environmental problems we consider those instruments of environmental policy that work in order to desirable behavior of subjects, which are conductive to environmental deterioration by their activity.

EXTERNALITIES – MARKET FAILURES

Externalities, or external effects, affect production of certain product, or work in consumer favor or disadvantage, whereby producer neither consumer can control them. It means infliction of costs, or benefits of one subject to another, which are not included in decision-making. In relation to *externalities* market is being evaluate, market and its price structure as their defection. It rather would be say, that externalities are concerned as relations between economic subjects, which are not solving by market prices. It means that they are not market internal loads, but to the market they are external whereupon we call them *externalities*. *Positive externalities* positively affect subject's economic activity at the market (they are a product of economic activities of one subject and they bring benefit to another subject, which did not endeavor to this benefit and it doesn't need to meet the costs related to this benefit), contrariwise *negative externalities* have adversive – detrimental impacts especially on environment (economic activities of one subject bring costs de incrimento to another one). This “harmed” subject doesn’t earn benefit, but it makes higher costs and shows a loss. That is one of the reasons why we talk about two essentially different approaches to externalities and solving of them. One of the solutions is through national economic policy by using of *taxes and subsidies*. This solution is based on fact, that market doesn’t solve externalities. A second solution is through negotiation between companies, by using theory of transaction costs. In the next we will analyze impact of industry and energetic air pollutants {which show themselves as negative externalities) in relation to agricultural products. They become evident as constraints founded from impaired quality of soil, what leads to impaired quality and quantity of grown production. They also become evident in decrease of animal production efficiency parameters and last but not least in posse of food web contamination.

As an example of negative externalities we can illustrate magnesite factories, which mine magnesite ores and at the same time they produce emission into atmosphere by processing these magnesite ores. Firms of polluters form those negative effects in relation to surrounding natural environment by the continuous instrumentality of pollutants. Those emission strike upon soil (as pollutants), and their excessive accumulation leads to high increase of soil reaction (pH 9). Soil, that is so heavy over-alkalized become unfit stall for agricultural crops. Along with this landscape stability was disrupted, because of soil structure disturbance and strong erosion. We have observed analogical situation in areas of iron ores processing, where converting plants produce some element chain into atmosphere, that from the beginning were useful for plants and soil (positive externality), but by their continuous input into the soil their content increase above the level of toxicity. In consequence of changed externality (to negative one) soils are starting place for extraneous substances to enter food web.

These are examples of negative externalities stem in productive activity of manufacturing or energetics plants. It appears form this that company in addition to produce regular products is also a producer of externalities, which are not included in prices of the goods that company produces. [6]

ENVIRONMENTAL MANAGEMENT OF THE COMPANIES

Economics and ecological problems in Slovak republic, as well as in other countries, could be consistently solve by using of EMS or EMAS system according to the ISO 14 000. As evidence we can use tens of organizations with certified system that accepted this “challenge”, but also those ones, that are preparing for process of certification. We have observed this voluntary trend in change of approach of biggest companies - the polluters of environment as well in our country. Within the frame of their environmental policy those companies “pull” with them their supplier and business partners. Competitiveness and successes of products at world markets is dependent on increasing requests on quality, that is in relation to sustainable development understand as optimization of raw consumption, decreasing of energy intensity of raw (in production as well as in consumption), minimization of emission and processing scrap production as well as production of negative effects on environment within product life cycle at all (LCA). As a result of environmentally appropriate realization of production would be “environmentally appropriate product life cycle” what apart from the “environmentally appropriate product” would definitely mean also abatement of environmental ecological load. This process applies to our biggest polluters of environment, which existence and activity (past or ongoing) has led to determination of problems – ecologically disrupted areas. By contrast, management of the companies, which operate in problems areas, should look for such solutions that would eliminate at least in part this unwanted condition, and government have to contribute in this areas by active environmental policy and financial compensation of aggrieved subjects by using direct and indirect instruments of environmental policy. Managements of companies should look for optimum of quality at macro and micro level [7].

Management of agricultural companies is constraint to apply measures that will, at least partly, eliminate unwanted effect in advance (good soil – good plants – health of people). Amount of damage on 1 hectare agricultural land depends on degree of soil damage as well as on concentration of harmful pollutants in air. According to our calculation the amount of damage ranges from 300 to 2 500 Sk on 1 hectare agricultural land, depending on degree of damage.

Environmental as well as top management has to conduce to find solution of harmony between economics activities and quality of environs components. It will be also necessary to monitor divided responsibility at that, if every polluter is paying for his share of pollution [1].

EMISSION RIGHTS AND PERMISSION TRADING

In the connection it is necessary to see problem of so-called "greenhouse effect", wherewith global warming is connected. This movement is required by need for solving the exploitation of exhaustible and non-renewable resources. At the present time to this group of resources belong mainly fossil fuels, such a coal, oil and natural gas. Nearly 90 % of industrially produced power in the world comes from fossil fuels. By their combustion we acquire necessary power, which also developed emission of greenhouse gases – especially of carbon dioxide - CO_2, that cause climate change. United Nations Framework Convention on Climate Change from 1992 (UN FCCC), and International Convention so-called Kyoto Protocol are dealing with this problem. Emission of greenhouse gases of state are mainly designate by these factors: trend in HDP, in number of the population, trend in energy intensity to HDP unit, in carbon-fuel quantities in energetics (power industry). Reduction of greenhouse gases emission and their improvement in future lead up to low carbon techniques. In the connection, market with greenhouse gases emission is formed, which measurable indicators are *"quantified emission limitation, emission rights, unit price for tonne of CO_2 equivalent"*, which has been changed significant since it was started-up to trading at EU market on 1. 1. 2005.

Market system with quantified emission limitation connects mechanism of financial market with environmental objectives. It determines "upper limit" of total greenhouse gases emissions quantity, therefore it is needed for companies to reduce quantity of emissions emit to air. This upper limit will be flare up to assigned amount of emissions units. In this system company is allowed to exceed assigned amount of greenhouse gases emission provided that it will buy missing quotas at the emission market. By contrast, company that will aim to reduce emission can sell redundant quotas at the end of the period, or keep them. Those companies, which won't be able to reduce emission up to assigned amount, will have to be prepared to pay for needed emissions rights, and those companies, which will be able to control their emissions, should trade with surpluses.

Mechanism of IET (International Emissions Trading) allows industrialized countries, which emissions are under the assigned amount of Kyoto Protocol, by reason of reduction of emission under this amount of commitment, sell their units within the frame of annex I to the other country, which is not able to carry out its commitment by its self.
Trading is the scantiest of mechanisms of flexibility listed in Kyoto Protocol. Principles, rules and regulations for trading are defined by particular conferences of COP. Some countries already made progress in this area – Slovak Republic has presented financial structure to support companies that reduced their greenhouse gases emissions, whereby profits on AAU (Assigned Amount Units) selling are allocated to this companies. We will probably see those structures in several countries of Central and East Europe.

Mechanism of CDM (Clean Development Mechanism) allows governments or private subjects in industrialized countries to accomplish their objectives in reducing of emissions. Industrialized countries obtain units for these projects in form of CER (Certified Emission Reductions) units. The purpose of CDM is to support "sustainable development" and at the same time to contribute for accomplishment of United Nations Framework Convention on Climate Change objectives. Inconsistent with this is objective of JI, by Kyoto Protocol, to support only counties listed in annex I in pursuance of their commitments in reducing emissions.
Each quota or credit represents metric tonne of CO_2 equivalent, which is calculated following the effect of 6 gases listed in Kyoto Protocol. European Unit Allowances (EUA) is one of them. European quotas are the only one that is consists with this type of units. Assigned Amount Units (AAU) are the quotas formed within the conditions of -/CMP.1 annex (account procedures of assigned units). Emission Reduction Units (ERU – emission credits) represents metric tonne of CO_2 equivalent. They embody in transferred credits that were obtained from Joint Implementation (JI) project, which has been accomplished in one of the countries listed in annex B of Kyoto Protocol.

Mechanism of Kyoto Protocol known as JI allows governments and companies in industrialized countries to buy ERU * (Emissions Reduction Units - represents metric tonne of CO_2 equivalent, * there are several types of quotes and credits, that are defined in international conventions) from the projects that has been realized in underdeveloped countries that reduce greenhouse gases emissions. Joint Implementation is reasonable instrument, because it is possible to reduce financing costs and capital by means of it. That is how the following project can be realized: *Changes in greenhouse gases emission technologies – Reduction of methane emissions in coal-mines – Stock gas collection – Promotion of renewable power resource – Transformation of power stations fuel basis and cogeneration units building – Measures for rising of energy intensity at industry and municipal sphere – Fuel change of central heating system and measurer for efficiency increase.*

Since January 1st, 2005 approximately 15 000 plant come under emissions trading scheme of EU (EU ETS). The objective of this scheme, which is an important element in EU strategy for attain the objectives of Kyoto protocol, is to reduce emissions of carbon dioxide in member states by regulation of CO_2 emissions from big sources in each of member states. Technical possibilities associated with CO_2 collection and storage is in the centre of attention for the first time. Nevertheless it is hard to achieve 5 % reduction of greenhouse gases emission in years 2008 till 2012 in compare with year 1990. Emissions in industrial countries in 2003 were overall about 5,9 % lower (1,08 milliard tonne CO_2) than in 1990, because reports included countries of former eastern block, in which production has tumbled, whereupon they temporary got under the assigned amount of Kyoto Protocol. Estimated growth of emissions in industrial countries in 2010 in regard to negative present trend is almost 11 % (instead of minus 5 %).

Price for opportunity to pollute air with CO_2 emissions still grows up. While in last year emissions trading price was 5 €, since the beginning of the year, even because of rise in the price of energies, price has increased. Price of the one tonne of carbon dioxide emissions attain approximately 26, 55 € for EUA in March of this year (spot price – March 31st.2006). Large companies can prosper from this new system, if they will have good planning. Quotes, that company will save, can be used in the future as extraordinary reserves (etc. Slovak power plants).

In the connection penetrative change needs to be made in the area of energy policy conception at European as well as at international level. New conception has to expressly support power production of renewable resources, too. Lot of companies has stepped out in the way of biomass; in our country it is especially Lesy SR, š.p. who pursue this policy. Our Slovak producers, in comparison to e.g. Austrian ones, are highly disadvantaged at support, at the rate 1:5 for unit (kWh). Even the biomass is cheaper by half as gas; there is the way for 7 mld. SK. In setting of Slovak Republic it seems to be profitable only in surrounding of 30 km [8], [9], [12].

Conclusion

Externalities as said effect of production and consumption are related to price system, which doesn't respond to some effects. This is typical for environment, because for its elements there is no market, as there is nobody who owns them as well as nobody who would offer them. It is one of the reasons why society looks for new market instruments that are *emissions rights* and *emissions permissions*, through which negative trends in trading and international conventions would be reduced, but also financial situation of countries and companies that have invested into relevant measures would be improved. Creation of global carbon market that should be formed after 2012, when Kyoto Protocol will end, by the scheme of emission trading in EU, is under consideration. Economics instruments become very powerful instrument, which will lead to air pollution condition improvement, in company practice it will lead to looking for the ways of their effect and activities improvement, to goodwill improvement and of course to gained sufficient wherewithal for companies that invest in air conservation. Do not invest – it is step back for management, it is the way that leads to loss in production.

With old environmental loads consistent inventory control of area should take place. It is very hard to apply for resources for something we don't know thoroughly. Otherwise erasure of ecological debt would stay only on good will of company's owners and on ecological thinking of local government, what is not in-step with TUR. Economic knows possibility of "Smith's invisible hand of market", through foreign investors. One can not count on this. If investor finds, that additional ecological costs will markedly raise price, we can alternate by purchase in purer environment, without loads.

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RESEARCH PAPERS
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AN OVERVIEW OF GEOGRAPHIC INFORMATION SYSTEM AND ITS ROLE AND APPLICABILITY IN ENVIRONMENTAL MONITORING AND PROCESS MODELING

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Abstract

The geographical information system (GIS) is a tool used generically for any computer-based capability for manipulating of geographical data. The hardware and software functions of a GIS includes data input, data storage, data management (data manipulation, updating, changing, exchange), data reporting (retrieval, presentation, analysis, combination, etc.). All of these actions and operations are applied to a GIS as a tool that forms its database. The paper describes types of the GIS data formats (vector, raster), database object definitions, relationships, and geometric features, the data organization structure. Some GIS applications and examples are given for better understanding of how GIS data can be used in GIS applications, with the respect on data formats, including surface elevation and slope from digital elevation model data (DEM), with the applicability on water industry.

Key words

Geographical Information System (GIS), data vector, data raster, GIS data management, digital elevation model (DEM)

Introduction

Geographical Information System (GIS) is computer based tool for collecting, storing, transforming, retrieving and displaying spatial data from the real GIS world. GIS provides facilities for data capture, data management, data manipulation, analysis, and the presentation

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of geographical data. GIS is not simply system for making maps (although it can create maps at different scales, in different projects), a GIS is an analysis tool as well.

The geographical (or spatial) data represent phenomena from the real world in terms of their position with respect to a known coordinate system; their attributes that are unrelated to position (such as color, pH, incidence of disease, etc.); their spatial interrelations with each other which describe how they are linked together (this is known as topology and describes space and spatial properties such as connectivity which are unaffected by continuous distortions) [12].

GIS is appearing in almost every industry, used for education, land management, natural resource management, environmental and aeronautical applications. Examples of the different kinds of geographical data collected for different purposes from different disciplines (planning zones, land parcelles utilities, soil surveys maps, groundwater levels and quality), are shown in Section 2.

Application of GIS

GIS is appearing in almost every industry. Is used for education, land management, natural resource management, environmental and aeronautical applications (data on rocks, water, soil, atmosphere, biological activity, natural hazards, and disasters collected for wide range of spatial levels of resolution) [12].

Although it is easy to purchase the parts of GIS (hardware and software), the system functions only when the requisite expertise is available, the data are compiled, the necessary routines are organized and the programs are properly modified to suit the application, and/or organization's needs. GIS system suitability chain is shown in Fig. 1 [5].

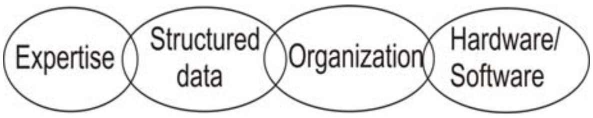

Fig. 1. *GIS system suitability chain*

Geographical information attaches a variety of qualities and characteristics to geographical locations. These qualities are physical parameters such as ground elevation, soil moisture, atmospheric temperature, as well as classifications according type of vegetation, ownership of land, zoning, floods, environmental accidents, water sources, waste water, storm water, air quality, etc.

GIS are powerful and cost effective tools for creating intelligent maps for water, wastewater, and storm water systems. In next we will describe storm water system management, and will give some system application examples as well.

A storm water management practice is one that reduces the quantity and/or quality of water being discharged into a land or water area.

Effective storm water management requires the linking of specialized computer models to the GIS. Also integration of engineering, environmental, and socioeconomic objectives into storm water management could be included.

In local storm water management different areas of a watershed implement different storm water management plans locally to solve the problems as flooding, sedimentation, erosion, etc.

Most of the physical, social, and economic problems associated with storm water are attributable to unwise land use, insufficient attention to land drainage in urban planning, and ineffective updating of existing storm water control systems. An effective solution to storm water management is the watershed wide approach. This approach implements a comprehensive storm water plan throughout the watershed to prevent the adverse effects of storm water, both at a particular site and anywhere downstream where the potential for harm can be reasonably identified [10].

Typical applications of GIS for storm water systems include: (1) Watershed storm water management; (2) Floodplain mapping and flood hazard management; (3) Hydrologic and hydraulic modeling of combined and storm sewer systems (Fig. 8), including estimating surface elevation and slope from digital elevation model data (DEM) (Fig. 2); (4) Documenting field work; (5) Planning, assessment of the feasibility and impact of system expansion; (6) Estimating storm water runoff from the physical characteristics of the watershed, e.g., land use, soil, surface imperviousness and slop [4], [6].

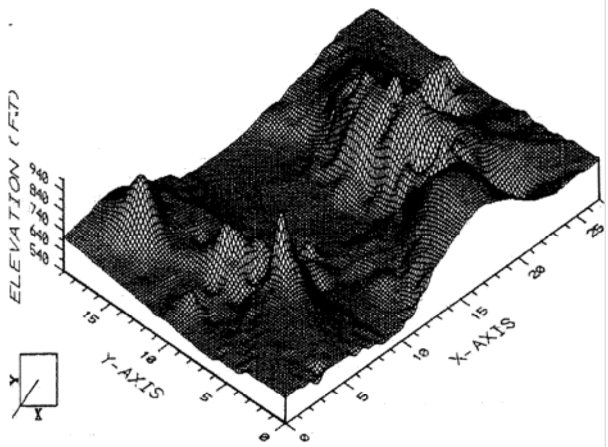

Fig. 2. *Digital elevation model data (DEM) [1]*

Topography influences many processes associated with the geography of the Earth, such as temperature and precipitation, GIS application professionals must be able to represent the Earth surface accurately because any inaccuracies can lead to poor decisions that may adversely impact the Earth environment.

A DEM model (Fig. 2) is a numerical representation of terrain elevation. It stores terrain data in a grid format for coordinates and corresponding elevation values. DEM data files contain information for the digital representation of evaluation values in a raster form. Cell-based raster data sets (or grids), are very suitable for representing geographical phenomena that vary continuously over space such as elevation, slope, precipitation, etc. Grids are also ideal for spatial modeling and analysis of data trends that can be represented by continuous surfaces, such as rainfall and storm water runoff.

Regardless of the data structure, DEM models can be defined in terms of (x, y, z) data values, where *x* and *y* represent the location coordinates and *z* represents the elevation values. Grid DEM model consists of a sampled array of elevations for a number of ground positions at regularly spaced intervals. This data structure creates a square grid matrix with the elevation of each grid square, called a pixel, stored in a matrix format.

Fig. 2 shows a 3D plot of the grid-type of digital terrain models (DEM) data. Usually, some interpolation is required to determine the elevation value from a DEM for a given point. The DEM based point elevations are most accurate in relatively flat areas with smooth slopes. DEM models produce low-accuracy point elevation values in areas with large and abrupt changes in elevation, such as cliffs and road cuts [1], [12].

Major DEM applications include: delineating watershed boundaries and streams, developing parameters for hydrologic models, modeling terrain gravity data for use in locating energy resources, determining the volume of proposed reservoirs, calculating the amount of material removed during strip mining, determine landslide probability. DEM can be used for automatic delineation of watershed and sewershed boundaries. DEM data can be processed to calculate various watershed and sewershed characteristics that are used for Hydrologic and Hydraulic model (H&H) modeling (Fig. 3) of watersheds and sewersheds [1].

DEM can create relief maps that can be used as base maps in a GIS for overlaying vector layers such as water and sewer lines. DEM files may be used in the generation of graphics such as isometric projections displaying slope, direction of slope (aspect), and terrain profiles between designated points. The aspect identifies the steepest down-slope direction from each cell to its neighbors.

Raster GIS software packages can convert the DEM into image for visual display as layers in a GIS. DEM data may be combined with other data types such as stream locations and weather data to assist in forest fire control, or they may be combined with remote sensing data to aid in the classification of vegetation.

Possibility to use GIS to modify the configuration of the water distribution network, compile model input files reflecting those changes, run the hydraulic model from within the GIS, use the GIS to map the model results, and graphically display the results of the simulation on a geo-referenced base map. The integration method of interrelationships among the user, the Hydrologic and Hydraulic model (H&H), and the GIS software is shown in Fig. 3 [1]. Also detailed description of H$H model can be found in [1].

GIS is intended to be a means of improving everyday life. Geographical information attaches a variety of qualities and characteristics to geographical locations. These qualify for physical parameters are such as ground elevation, soil moisture, atmospheric temperature, as well as classifications according to type of vegetation, floods, environmental accidents, water sources (waste water, storm water), ownership of land, etc.

We described common geographical data model structures - a grid-based structure (raster), and a coordinate point structure (vector). Also we gave a view at a database management system DBMS as a program (or collection of programs formalized description of real world phenomena, database structures and methods of database organization) that enables the user to save, modify, classify, select, and extract information for a central database.

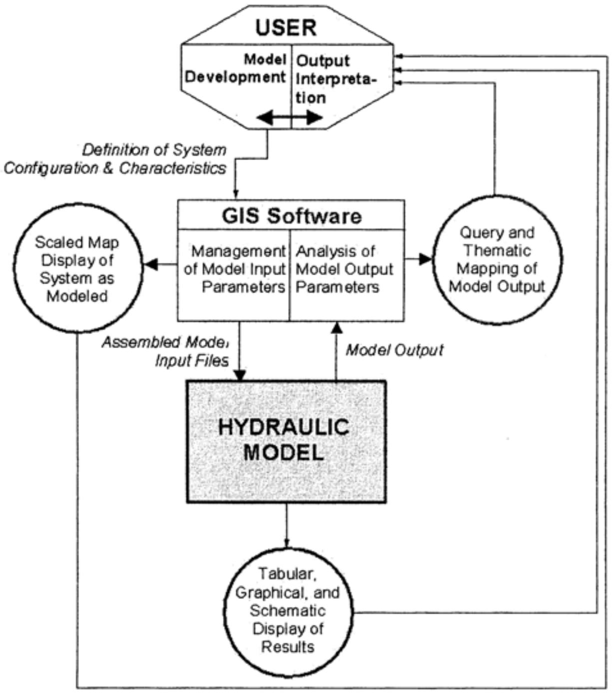

Fig. 3. *Integration of GIS Software, End User, and H&H model [1]*

Conclusion

We have shown the GIS system as the powerful and effective tool for creating intelligent maps for, e.g., water, wastewater, and storm water systems. Although it is very easy to purchase the constituent parts of GIS (hardware and software), the system functions only when the requisite expertise is available, the data are compiled, the necessary routines are organized, and the programs are modified to suit the application, and/or the organization's needs.

GIS integrates all kinds of information and applications with a geographic component into one manageable system. Therefore, a benefit of GIS applications is their ability to integrate and analyze all spatial data to support a decision-making process. A GIS system has to be built up within an organization. The integration capability of GIS technology empowers organizations to make better and informed decision based on all relevant factors.

We must be aware of the fact that the digital representation of geography is not equal to the geography itself. Any digital representation involves some degree of approximation. It is therefore important that the information that results from data processing be applied to guide the real world in the right direction.

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NATURAL RADIONUCLIDES IN THE BUILDING MATERIALS FROM THE REGION OF THE SMALL CARPATHIANS

Miroslav RUSKO[11], Peter ANDRÁŠ[2]

Abstract

Distribution of radionuclides in the main rock types: granodiorites, biotite-gneisses, black shale and amphibolites at the locality Pezinok - Kolársky vrch was studied in samples from two boreholes. Concentrations of ^{238}U, ^{232}Th *and* ^{40}K *in samples were analysed by gamma spectroscopy (concentrations of* ^{238}U *were 0.091 – 37.800 mg/kg,* ^{232}Th *0.534 – 13.234 mg/kg,* ^{40}K *0.116 – 5.162 mg/kg). The highest average* ^{238}U *concentration was in black shale, highest average* ^{232}Th *concentration in granodiorite and highest average* ^{40}K *concentration in granodiorite as well. Activities of* ^{238}U *were determined within the range of 1.092 – 48.960 Bq/kg (with exception of one anomalous value – 453.6 Bq/kg), activities of* ^{232}Th *within the range of 2.189 – 54.298 Bq/kg and activities of* ^{40}K *within the range of 30.933 – 1,376.499 Bq/kg. The source of* ^{238}U *and* ^{232}Th *(and partially also of* ^{40}K*) is in the granodiorite intrusion. Uranium was during the metamorphic process mobilised to the black shales. The concentrations and consequently the total activities of* ^{238}U, ^{232}Th *and* ^{40}K *in studied rock samples exceed the permitted limit values for building materials. It is possible to recommend their utilisation only for external purposes.*

Key words

^{238}U, ^{232}Th, ^{40}K, building material, radioactivity

Introduction

The geological structure of the Malé Karpaty Mts. consists of pre-Alpine fundament, Mesozoic mantle and higher Alpine-age nappes. Volcanic-sedimentary formation of the crystalline complex had originated within Silurian (113 – 416 Ma) and Devonian (416 – 359

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Ma). It consists of pelitic-psammite sequences, carboniferous and black shales (Plašienka et al., 1991).

The overall complex was metamorphosed during the regional Devonian metamorphosis (380 ± 20 Ma; Rb-Sr dating; Finger et al., 2003). Subsequently it was affected by late Variscan peri-plutonic contact metamorphosis (348 ± 4 Ma or 320 ± 3 Ma; Cambel et al., 1980; Rb-Sr and U-Pb dating).

The following rocks participate in the structural-tectonic structure: granitic rocks (mainly granodiorite composition), crystalline shale, amphibolites, limestones and quaternary sediments. The Bratislava Massiv is represented by medium-grained granites – granodiorites which are at the Borinská Unit interface mylonised and sericitised. Crystalline shales represented by phylites, mica schists, gneisses and black shales in the west part of the territory are in the form of fragments and breccia consolidated by calcareous cement and sericitic-chloritic phylites. Phylite layers are alternating with carbonates (Maheľ, 1961).

There are known various ore (mainly pyrite and Sb) deposits in the Malé Karpaty Mts. such as Pezinok and Pernek (Fig. 1), Krížnica, Kuchyňa, Trojárová and etc. Sb mineralisation occurs locally along with Pb-Zn mineralisation (e.g. at the Pod Babou Locality) and Cu-(Au-Ag) ± Ni-Co mineralisation in Častá (Cambel, 1959; Chovan et al., 1992).

Geological and tectonic structure of the Sb-deposits

The most important Sb-deposit in Malé Karpaty Mts. is Pezinok. It is connected with SE-NW tectonic zone known as productive (pyrite zone) about 2 km in length. The deposit covers only 430 m in length from it; tectonic zone width near the surface is barely of 25 – 50 m but deeper its extension can be seen. According to Cambel (1959), the deposit is situated between two amphibole complexes of 50 – 250 m where the ore-bearing volcanic-sedimentary sequence is presented. It is presented mainly by muscovite-clay and black-carboniferous shale which are generally folded in detail and petrologically very variable. Various metamorphosed pyroclastic rocks, apophyses of granitic rocks and tiny loading bodies of amphibolites are less presented.

The deposit consists of two bigger ore bodies of stratiform character of unspecified genesis: central and base. The central deposit is bound to wide dislocation zone inclining about 75° to SW, NW-SE and its width on the surface is within the range of 25 – 60 m. Some younger research works (Andráš, 1983) refer to epigenetic character of the mineralisation.

Antimony mineralisation in the central deposit is tectonically transformed and is uprising in crushed and mylonised rocks where the shale with the organic material addition are of major importance. Exploration works determined the occurrence of smaller accumulations of Sb ores under the antimony adit horizon as well. They consist of small and irregular ore bodies (Cambel, 1959).

The Pernek and Kuchyňa deposits are time-spatially very close to the Pezinok deposit and have the same/similar characteristics of mineralisation genesis as the Pezinok deposit and therefore we do not pay attention to them in more detail.

Cambel and Vilinovič (1987) found out that the contents of U and Th (X – X0 ppm i.e. 0.000X – 0.00X0 wt %) are in the Modra Massiv lower in comparison with analogous granitic rocks in the Bratislava Massiv. Other rock types and relation of U and Th concentrations to ore mineralisation were not studied in more detail.

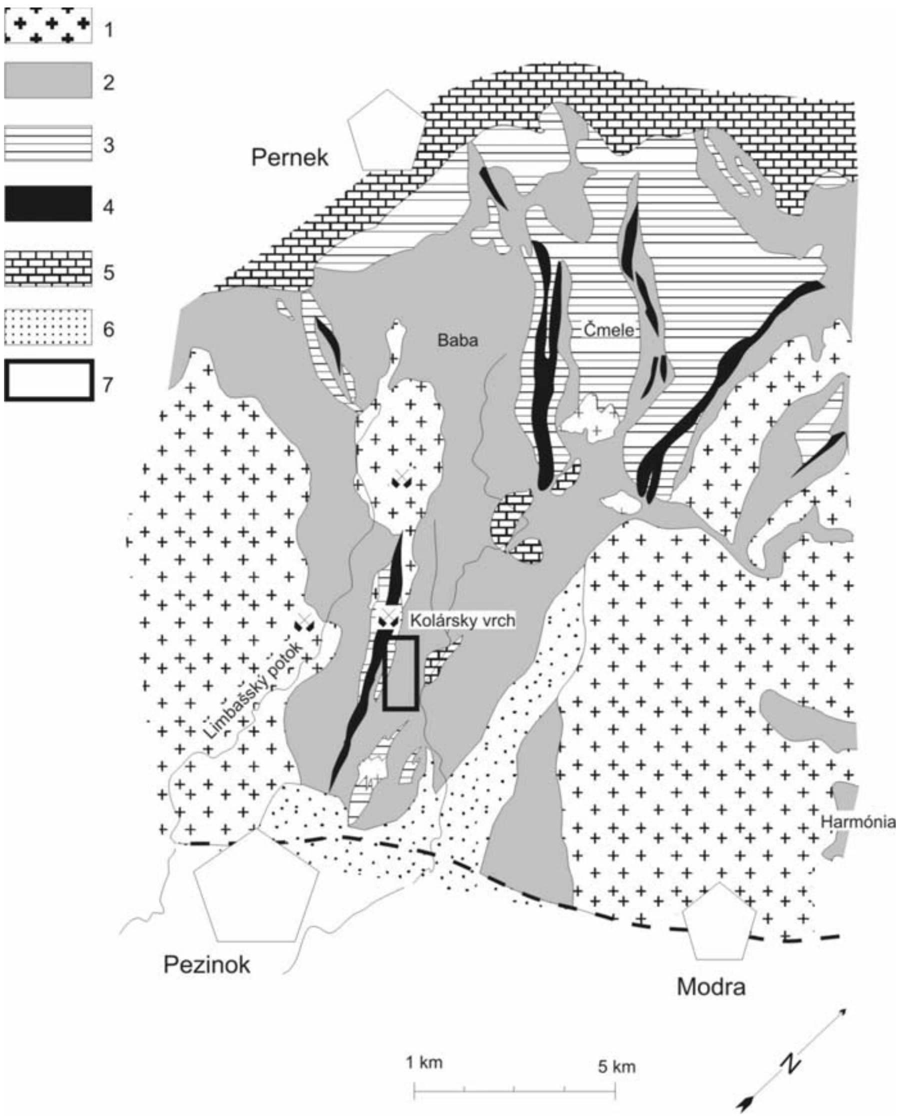

Fig. 1. *Surroundings of the Kolársky Vrch deposit and localisation of KV-44 and KV-46 boreholes*
1 – granitic rocks, 2 – shale strata (phylites – gneiss), 3 – amphibolites, 4 – black shale with mineralisation (so-called productive zones), 5 – carbonates, 6 – quaternary sediments, 7 – area of the boreholes KV-44 and KV-46

Materials and methods

The studied area (Fig. 1) is situated near Pezinok, about 400 m north from a fishpond near the town (about 200 m from vineyards).

The samples from surface boreholes KV-44 and KV-46 were used. They were obtained during research works realised in Pezinok near Kolársky Vrch in 1981 by the Geological

Survey Bratislava, stored in the depository of the Geological Institute of the Slovak Academy of Sciences in Banská Bystrica (Fig. 1 displays localisation of the surface boreholes).

The collected samples reflect all important rock types of the Malé Karpaty Mts. crystalline complex (granodiorites, biotite-gneisses, black shale and amphibolites).

The samples of weight 1 – 5 kg were crushed to size under 0.05 mm, sulphide minerals were separated by flotation and optically repurified under the binocular loupe.

Chemical analysis of the main rock components (silicate analysis) was realised from samples powdered to analytical fineness by X-ray fluorescence analysis (Philips) in the laboratories of the Geological Institute of the Slovak Academy of Sciences in Bratislava (Ing. Boris Toman).

Atomic absorption spectrometry (AAS) of Ba, Pb, Cu, Zr, Co, Ni, V, Ca, Cr, Sr, La, and B was realised from 0.5 g of rock sample gently pulverised and powdered to analytical fineness by single-beam atomic absorption spectrophotometer Philips/Pye Unicam, model PU – 9 000 with deuterium background correction from HCl.

Rock decompositions and their preparation for Au determination according to methodology by Rubeška et al. (1977) were realised from 5 g of sulphide minerals and 10 g of rock samples respectively.

The samples intended for analytical measurements of ^{238}U and ^{232}Th concentrations were crushed to granularity < 50 mm in the laboratories of the Geological Institute of the Slovak Academy of Sciences in Banská Bystrica (Ing. Dana Troppová). Concentrations of U, Th and ^{40}K (and Ra) were determined by gamma spectroscopy (analyzer 1024 NTA-512 B; RNDr. Vlastimil Kátlovský, PhD.).

Correlations among individual elements were calculated according to Hudec (2005):

$$r = \frac{\sum x_i y_i - n \cdot \bar{x} \cdot \bar{y}}{\sqrt{\left(\sum x_i^2 - n \cdot \bar{x}^2\right) \cdot \left(\sum y_i^2 - n \cdot \bar{y}^2\right)}}$$

^{238}U, ^{232}Th and ^{40}K concentrations were calculated to Bq/kg according to methodology by Yousef et al. (2007): ^{238}U mg/kg (ppm) = Bq/kg 80.33 x 10^{-3}; ^{232}Th mg/kg (ppm) = Bq/kg 247 x 10^{-3}; ^{40}K mg/kg (ppm) = Bq/kg 3.862 x 10^{-3}.

Results

^{238}U and ^{232}Th concentrations in individual rocks

^{238}U and ^{232}Th concentrations were determined in all important rock types of the Malé Karpaty Mts. Crystalline Complex (granodiorite, biotite gneiss, black shale and amphibolite). The samples of rocks from the surface boreholes KV-44 and KV-46 from Pezinok (near Kolársky Vrch) were used (Fig. 2).

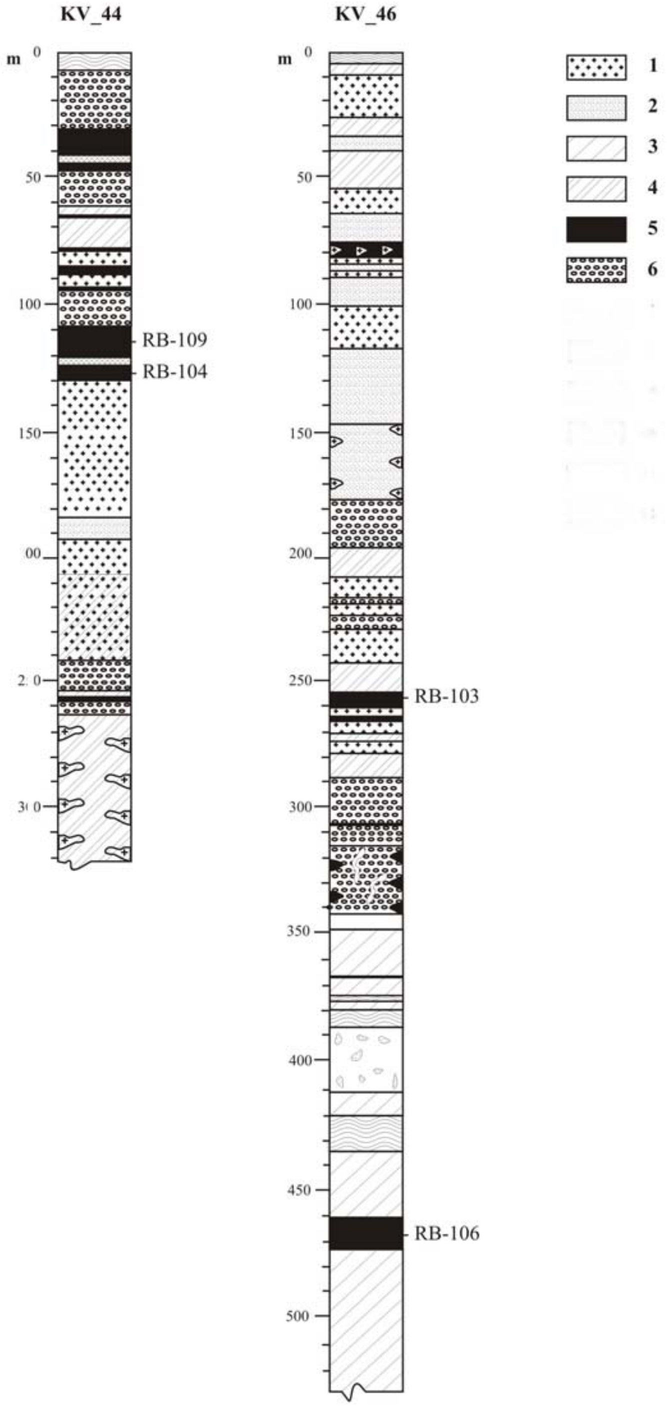

Fig. 2. *Boreholes KV-44 and KV-46; Expanations: 1 – granodiorite, 2 – biotite gneiss, 3- amphibolite, 4- actinolite schist, 5 – black schist, 6 – hydrothermally altered rocks*

Average values of ^{238}U, ^{232}Th and ^{40}K in individual rocks are listed in tab. 1. Concentrations of U, Th and other elements and as well as complete rock analyses are listed in tab. 2 and 3.

AVERAGE VALUES OF U, Th AND ^{40}K IN INDIVIDUAL ROCKS Table 1

Rock	No. of samples	x ^{238}U (mg/kg)	x ^{232}Th (mg/kg)	x ^{40}K (%)
Amphibolite	2	1.78	7.70	1.757
Biotite gneiss	10	7.14	6.56	1.7082
Black shale	3	14.43	3.52	1.463
Granodiorite	11	2.55	7.75	2.319

^{238}U concentrations in granodiorite fluctuated from 1.463 to 4.080 mg/kg and ^{232}Th concentrations fluctuated from 4.702 to 10.913 mg/kg. In biotite gneiss ^{238}U concentrations ranged from 0.091 to 3.341 mg/kg and ^{232}Th concentrations ranged from 0.534 to 9.649 mg/kg. In amphibolites ^{238}U concentrations were determined from 1.746 to 1.806 mg/kg and ^{232}Th concentrations from 7.251 to 8.151 mg/kg. In black shale ^{238}U concentrations ranged from 2.290 to 37.800 mg/kg and ^{232}Th concentrations from 1.524 to 13.234 mg/kg (tab. 2, 3).

The highest average ^{238}U concentrations were determined in black shale (14.43 mg/kg) and the lowest in amphibolite (1.78 mg/kg). In case of ^{232}Th it was possible to observe opposite trend: the lowest average values were determined in black shale (3.52 mg/kg) and the highest in granodiorite (7.75 mg/kg, tab. 1).

In the KV-44 borehole ^{238}U concentrations in granodiorite ranged from 1.463 to 4.080 mg/kg and ^{232}Th concentrations from 4.702 to 10.913 mg/kg. In the KV-46 borehole ^{238}U concentrations in granodiorite fluctuated from 1.645 to 2.274 mg/kg and ^{232}Th concentrations from 5.563 to 8.511 mg/kg. The highest ^{238}U concentrations (4.080 mg/kg) were in the depth of 60 – 70 m and the highest ^{232}Th concentrations (10.913 mg/kg) in the depth of 293 – 294 m. ^{232}Th concentrations in granodiorite were 2 - 3 times higher than ^{238}U concentrations (tab. 2 and 3).

In the KV-44 borehole ^{238}U concentrations in biotite gneiss were measured within the range of 2.440 – 3.088 mg/kg and Th concentrations ranged from 7.275 to 9.649 mg/kg. In the KV-46 borehole ^{238}U concentrations in biotite gneiss were determined within the range of 0.091 – 3.341 mg/kg and ^{232}Th concentrations ranged from 0.534 to 8.788 mg/kg. The highest ^{238}U concentrations (3.341 mg/kg) were in the depth of 299 m and ^{232}Th concentrations (9.649 mg/kg) in the depth of 26 – 27 m. On the basis of comparison of ^{238}U and ^{232}Th concentrations in biotite gneiss it was possible to state that ^{232}Th concentrations were 2 – 3 times higher than ^{238}U concentrations (tab. 2 and 3).

In the KV-44 borehole, in the depth of 236 – 244 m, Th concentrations in black shale were almost 5 times higher (10.801 mg/kg) than ^{238}U concentrations (2.290 mg/kg). In the depth of 310 m, ^{232}Th concentrations in black shale were 4 times higher (13.234 mg/kg) than ^{238}U concentrations (3.188 mg/kg). In the KV-46 borehole, in the depth of 109 – 111 m, ^{238}U concentrations in black shale were 37.800 mg/kg and ^{232}Th concentrations 1.524 mg/kg. The highest ^{238}U concentrations (37.800 mg/kg) were determined in the depth of 109 – 111 m and ^{232}Th concentrations (13.234 mg/kg) in the depth of 310 m (tab. 2 and 3).

^{232}Th concentrations in amphibolite, in the KV-44 borehole ranged from 7.251 to 8.151 mg/kg and were 4 times higher than ^{238}U concentrations (1.746 – 1.806 mg/kg). The highest ^{232}Th and ^{238}U concentrations in amphibolite were determined in the depth of 398 – 402 m (tab. 2, 3).

SILICATE ANALYSIS, GAMMA SPECTROSCOPY OF ^{238}U, ^{232}Th, ^{40}K AND AAS OF SELECTED ELEMENTS IN ROCKS OF THE PEZINOK CRYSTALLINE COMPLEX, BOREHOLE KV-44

Table 2

Rock		Biote gneiss	Biote gneiss	Granodio-rite	Biote gneiss	Granodio-rite	Granodio-rite	Granodio-rite	Black shale	Granodio-rite	Black shale	Granodio-rite	Granodio-rite	Amphibo-lite	Amphibo-lite
Depth (m)		10-15	20	25	26 - 27	60 - 70	142 - 150	150 - 160	236 - 244	293 - 294	310	329 - 330	333 - 368	398 - 402	408 - 409
$\sum Fe_2O_3$	%	8.01	8.37	7.22	9.05	1.97	924	2.50	6.48	1.45	17.21	9.05	6.14	4.11	6.05
MnO		0.20	0.06	0.08	0.05	0.04	0.08	0.03	0.07	0.21	0.12	0.16	0.09	0.08	0.08
TiO_2		0.88	0.92	0.85	0.96	0.26	0.86	9.88	0.99	1.46	0.43	1.58	0.76	0.65	0.71
CoO		0.41	0.65	0.55	0.44	1.21	1.28	1.11	4.14	7.93	6.83	7.31	2.37	2.19	2.39
K_2O		2.80	2.49	2.23	1.90	5.46	2.82	5.83	2.74	1.32	1.38	1.49	2.71	2.08	1.72
SiO_2		60.16	58.56	61.62	58.47	73.89	59.76	66.89	57.59	51.33	49.28	53.62	64.42	69.61	66.97
Al_2O3_3		17.82	17.87	18.65	19.71	12.69	16.91	17.73	19.63	15.58	11.33	15.06	15.30	13.89	15.53
MgO		1.22	2.81	2.85	2.86	1.26	3.69	1.40	2.86	5.41	4.17	7.47	2.51	2.20	2.49
Na_2O		3.43	2.78	3.67	2.64	0.56	1.32	1.03	4.42	3.06	0.31	2.63	2.71	3.76	2.49
dry. los.		1.18	1.08	0.45	0.77	0.22	0.16	0.18	0.30	0.20	0.25	0.19	0.33	0.19	0.08
ann. los.		3.91	4.45	2.24	3.77	2.84	3.88	2.54	0.84	2.05	9.04	1.42	2.68	1.14	1.48
U	ppm (mg/kg)	2.440	3.088	2968	2.831	4.080	2.953	2.539	2.290	3.110	3.188	2.324	1.463	1.806	1.746
Th		7.275	8.497	9.738	9.649	9.596	7.505	8.143	10.801	10.913	13.234	5.980	4.702	8.151	7.251
Th/U		2.981	2.572	3.281	3.407	2.351	2.541	3.206	4.714	3.508	4.131	2.751	3.212	4.513	4.231
^{40}K	%	2.072	1.144	1.576	1.557	5.123	2813	5.162	2.146	1.545	21.125	1.538	1.801	1.765	1.752
Au	ppm (mg/kg)	0.41	0.115	0	0	0	0.050	0.123	0.126	0.023	0	0	0	0.029	0
Ba		710		1,550	890	1,780		1,480	2,630						
Pb		< 10		< 10	< 10	< 10		12.6	49						
Cu		74		46	59	50		< 10	17.4						
Zr		316		500	510	219		251	282						
Co		35		15.1	31.6	25.7		< 10	15.5						
Ni		245		76	117	52.5		14.8	42						
V		95.5		78	95,5	191		22.9	135						
Ca		20.9		20	25.1	<3		11	<3						
Cr		78		89	81	74		15.9	62						
Sr		95.5		245	195	71		151	430						
B		71		29.5	42	288		263	14.1						

Explanatory notes for tab. 2 and 3
dry. los. - drying losses
ann. los. - annealing losses

SILICATE ANALYSIS, GAMMA SPECTROSCOPY OF ^{238}U, ^{232}Th, ^{40}K AND AAS OF SELECTED ELEMENTS IN ROCKS OF THE PEZINOK CRYSTALLINE COMPLEX, BOREHOLE KV-46

Table 3

Rock		Biotite gneiss	Biotite gneiss	Black shale	Granodio-rite	Granodio-rite	Granodio-rite	Granodio-rite	Biotite gneiss	Biotite gneiss	Biotite gneiss	Biotite gneiss	Biotite gneiss
Depth (m)		20	50 - 60	109 - 111	131	139 - 140	173 - 176	194 - 195	180 - 200	287	292	299	300
$\sum Fe_2O_3$	%	8.97	1062	high Fe content	5.70	7.30	6.98	5.45	8.45	8.65	8.62	8.08	8.39
MnO		0.13	0.18		0.08	0.10	0.13	0.10	0.10	0.13	0.13	0.11	0.12
TiO_2		1.03	1.27		0.98	1.45	1.73	0.97	0.98	1.00	1.05	0.80	0.92
CoO		13.08	11.81		5.05	7.45	7.25	4.87	1.87	1.72	1.63	1.22	1.37
K_2O		0.24	0.34		2.03	1.86	1.70	1.81	2.81	2.98	2.61	2.58	2.48
SiO_2		48.76	49.53		60.83	57.54	55.91	61.05	59.05	59.46	58.70	59.71	59.94
Al_2O3_3		19.38	15.01		17.96	15.84	15.44	17.72	17.82	17.58	18.85	18.00	18.18
MgO		5.89	6.85		2.61	3.61	4.91	2.79	3.79	3.37	3.41	3.18	3.38
Na_2O		1.87	2.59		3.79	3.49	3.13	3.39	2.39	2.56	2.89	2.76	2.55
dry. los.		0.18	0.39	0.11	0.22	0.29	0.35	0.28	0.28	0.49	0.35	0.36	0.46
ann. los.		0.88	1.29	8.29	0.91	1.15	2.23	1.49	2.49	2.30	1.88	2.14	2.18
U	ppm (mg/kg)	0.231	0.091	37.800	2.147	2.545	1.646	2.274	2.274	2.097	2.813	3.341	2.219
Th		0.534	0.777	1.524	6.543	8.090	8.511	5.563	5.563	8.690	8.788	7.637	8.208
Th/U		2.313	8.483	0.040	3.046	3.178	5.168	2.445	2.445	4.143	3.123	2.285	3.698
^{40}K	%	0.283	0.561	0.116	1.562	1.355	1.304	1.734	1.700	2.822	2.466	1.776	2.701
Au	ppm (mg/kg)	0.461	0.038	0.219	0.138	0	0	0	0	0	0	0	0
Ba		< 300	< 300		1,230	1,290	1,290			890	890		830
Pb		< 10	< 10		12	10.4	< 10			< 10	13.5		15.9
Cu		71	101		1.2	11.7	17.8			24.5	45		57.5
Zr		123	155		174	340	263			288	224		195
Co		45	62		< 10	13.6	25.7			< 3.4	22.4		18.6
Ni		117	93		9.1	18.6	39			89	87		79
V		288	295		110	138	229			170	170		155
Ca		13.2	24.5		22.9	20.9	10.4			35	17.4		14.1
Cr		200	96		11.7	17.4	74			78	101		79
Sr		330	316		490	600	470			204	224		239
B		7.1	7.4		7.4	11.7	9.8			5.75	31.6		43

^{40}K concentrations in individual rocks

Another radioactive component of the studied rocks is ^{40}K isotope. The highest ^{40}K concentrations were determined in granodiorite (5.123 % and 5.162 %) and in biotite gneiss (2.822 %). The lowest concentrations were determined in black shales (0.116 % and 2.146 %, tab. 2 and 3).

Average values of ^{40}K (tab. 1) were descending in order granodiorite (2.319 %) → amphibolite (1.757 %) → biotite gneiss (1.7082 %) → black shales (1.463 %). This dependency is caused by mineral composition of individual rocks (main carriers of ^{40}K are potassium feldspar and amphibolites).

^{40}K concentrations were determined in the KV-44 borehole within the range of 1.144 % - 5.162 %. In the KV-46 borehole ^{40}K concentrations were within the range of 0.116 % - 2.822 % (tab. 2, 3).

Correlation of distribution of ^{238}U and ^{232}Th with selected ore elements

The correlation among concentrations of ^{238}U/^{232}Th (correlation coefficient is -0.30705), ^{238}U/Cu (correlation coefficient is -0.43582) and ^{238}U/Ni (correlation coefficient is -0.13461) is negative. Similarly, the correlation relations of ^{232}Th/Ni (correlation coefficient is -0.21663) and ^{232}Th/Cu (correlation coefficient is -0.54757) are negative. These findings indicate that the direct positive correlation relation does not exist between ^{238}U and ^{232}Th and not even between metal elements (Ni, Cu) accompanying hydrothermal Sb mineralisation and radioactive elements ^{238}U and ^{232}Th.

The correlation between concentrations of ^{238}U/K (correlation coefficient is -0.258) is negative but between concentrations of ^{40}K and ^{232}Th there was determined correlation dependency (correlation coefficient is 0.4842).

The preferential binding of ^{232}Th to granodiorite indicates that the ^{232}Th addition is in connection with granodiorite intrusion into crystalline shale. ^{238}U is presented in black shale together with Sb mineralisation but its concentrations do not show any positive correlation to metals (Cu, Ni) of hydrothermal mineralisation. This phenomenon is probably connected with ^{238}U mobilisation from granitic rocks. It is highly presumable that the addition of ^{238}U and ^{232}Th is connected with identical geological event (granodiorite intrusion). Because of Th(IV) is considerably less mobile than U(VI) (Polanski and Smulikowski, 1978; Rollinson, 1998) the subsequent U(VI) mobilisation and its reduction and stabilisation occurred in the geochemical barrier which consisted of black shale with syngenetic pyrite-pyrotite mineralisation.

Even though ^{238}U and ores of Sb mineralisation do not show any features of positive correlation of concentrations of individual elements, it is obvious that the addition of U and Th connected with granitic rocks was the mobilisation tool of hydrothermal solutions which brought Sb mineralisation and as well the mobilisation tool of U(VI). Therefore, the age of intrusion, U/Th mineralisation and Sb mineralisation should be about equal.

Discussion

^{238}U and ^{232}Th belong according to classification by Tölgessy et al. (1998) among very toxic elements and therefore the study of their distribution in land is very important. In the presented study the samples from boreholes non-modified by exogenous processes were used to achieve at least deformed data on ^{238}U and ^{232}Th concentrations in individual rock types. Unfortunately, these data are not sufficient to take a stand to radioactive radiation.

^{238}U and ^{232}Th migrate due to the weathering processes into the soil, water and other land components. Their negative impact in the studied area has not been determined yet. It is mainly because of very low concentrations of these elements in rocks.

CALCULATION OF CONCENTRATIONS OF ^{238}U, ^{232}Th AND ^{40}K
to Bq/kg ACTIVITY

Table 4

Rock type	^{238}U mg/kg	Bq/kg	^{232}Th mg/kg	Bq/kg	^{40}K %	Bq/kg	Σ Bq/kg
Granodiorite	2.968	35.616	9.738	38.952	1.576	420.256	494.824
	4.080	48.960	9.596	39.343	5.123	1,366.099	1,454.402
	2.953	35.436	7.505	30.771	2.813	750.115	816.349
	2.539	30.468	8.143	33.386	5.162	1,376.499	1,440.353
	3.110	37.320	10.913	44.743	1.545	411.990	494.053
	2.324	27.880	5.980	24.518	1.538	410.123	462.521
	1.463	17.556	4.702	19.278	1.801	480.255	517.089
	2.147	25.764	6.543	26.826	1.562	416.523	469.113
	2.545	30.540	8.090	33.169	1.355	361.324	425.033
	1.646	19.752	8.511	34.895	1.304	347.725	402.372
	2.274	27.288	5.563	22.808	1.734	462.388	512.484
Biotite gneiss	2.440	29.280	7.275	29.828	2.072	552.519	611.627
	3.088	37.056	8.497	34.838	1.144	305.059	376.953
	2.831	33.972	9.649	39.561	1.557	415.190	488.723
	0.231	2.772	0.534	2.189	0.283	75.465	80.426
	0.091	1.092	0.777	3.186	0.561	149.596	153.874
	2.274	27.288	5.563	22.808	1.700	453.322	503.418
	2.097	25.164	8.690	35.629	2.822	752.514	813.307
	2.813	33.756	8.788	36.031	2.466	657.584	727.371
	3.341	40.092	7.637	31.311	1.776	473.588	544.992
	2.219	26.628	8.208	33.653	2.701	720.249	780.53
Amphibolite	1.806	21.672	8.151	33.419	1.765	470.665	525.756
	1.746	20.952	7.251	29.729	1.752	467.199	517.880
Black shale	2.290	27.480	10.801	44.284	2.146	566.853	638.617
	3.188	38.256	13.234	54.259	2.125	566.665	659.180
	37.800	453.600	1.524	6.248	0.116	30.933	490.781

The samples with the highest ^{238}U concentrations, i.e. black shale, are not utilised in the civil engineering. It is satisfactory to handle with ^{238}U concentrations in other rocks (granodiorite, amphibolite, biote gneiss) on, i.e. maximum to value 4.080 mg/kg determined in granodiorite in the KV-44 borehole in the depth of 60 – 70 m. The highest ^{232}Th concentrations (10.913 mg/kg) were determined in granodiorite in the KV-44 borehole as well.

Concentrations of ^{40}K fluctuated within the range of 0.116 – 5.162 %. The highest values were measured in rocks containing potassium feldspar and amphibolites.

According to Slovak legislative it is not possible to take a definite stand to this issue. Sole legislative source on ^{238}U concentrations is the Resolution of the Government of the Slovak Republic No. 296/2005 Coll. setting requirements on quality and qualitative objectives of surface waters and limit values of pollution parameters of waste waters and particular waters, where the recommended concentration is 50 µg/l.

Activity of radionuclide A is the quantity characterizing the radiation source. It indicates the number of disintegration of radioactive nucleus in material per 1 second. The activity unit is becquerel (Bq = s^{-1}).

Half-life of disintegration of ^{238}U is 4.5 billion years. There are 25,381 disintegrations connected with emission of ά particles in 1 gram of uranium per 1 second (Greenwood and Earnshaw, 1990; Yousef et al., 2007). For comparison, gas-silicates with radiation effect used in home building and urban planning before the year 1985 had the activity higher than 400 Bq/kg (Klicpera, 2003) whereas nowadays the limit value for building materials is 150 Bq/kg (Philippe, 2007).

If we calculate the radiation effect to the highest measured values at the Pezinok deposit (37.800 mg/kg in black shale), the radiation intensity is 453.6 Bq/kg (tab. 4) in comparison with the most used limit values valid in the EU (150 Bq/kg), in the Regulation of the Ministry of Health Service of the Slovak Republic No. 406/1992 Coll. on requirements on limitation of irradiation from radon and other natural radionuclides and in the Act No. 50/1976 Coll. of the Federal Assembly of Czechoslovakia on land-use planning and construction order (Building Act) and on amendments to certain laws (120 Bq/kg). The calculation was realised in case of one anomalous ^{238}U value in rock which is not used in the civil engineering and from the quantitative point of view it presents the insignificant percentage in rock abundance. If we exclude this extreme value, the activity of ^{238}U will fluctuate within the range of 1.092 – 48.960 Bq/kg.

By similar calculation (Ramli et al., 2005; Yousef et al., 2007) of ^{232}Th concentrations to Bq/kg activity can be obtained the interval of values 2.189 – 54.298 Bq/kg for studied rocks of the Pezinok-Pernek crystalline complex. If we exclude ^{232}Th concentrations in black shale which are presented in low quantity and are not used in the civil engineering, the ^{232}Th activity is lower: 2.189 – 44.743 Bq/kg. The activity of ^{40}K is the only one high. The calculation of ^{40}K concentrations to activity was realised according to Yousef et al. (2007). Its values fluctuate within the range of 30.933 – 1,376.499 Bq/kg.

Natural building materials such as building stone, gravel aggregate, gravel, sand, clays, cement, lime and fly ash contain always certain amount of radioactive nuclides (mainly ^{40}K, ^{232}Th and ^{226}Ra) originating by radioactive decomposition of ^{238}U. Mass activities of ^{232}Th a ^{226}Ra in the building materials are usually at tens of Bq/kg and in case of ^{40}K nuclide at hundreds of Bq/kg. Occurrence of such radioactive elements in the building materials in buildings causes man's irradiation in two ways: a) external irradiation (γ radiation) due to radioactive decomposition of natural radionuclides; b) internal irradiation due to inhalation of radioactive nuclides originating in the air from radon which is creating in the construction materials from radium. The activity of building materials and raw materials for their production is limited. Criterion of utilisation of building materials in terms of content of natural radionuclides is stated in the Regulation of the Ministry of Health Service of the Slovak Republic No. 406/1992 Coll. and in the Building Act No. 50/1976 Coll.

On the basis of above listed ideas it is possible to assume that ^{238}U concentrations (and obviously as well ^{232}Th concentrations) are in the studied rocks very low and they do not present any major environmental or health risk. Total radioactivity is significantly influenced by ^{40}K activities (30.933 – 1,376.499 Bq/kg). These induce that majority of investigated rock samples significantly exceed total limit activity values for building materials (120 Bq/kg) and fluctuate within the range of 80.426 – 1,454.402 Bq/kg. This determination enables us to express the negative opinion for their assumed utilisation in the form of building materials. On the other hand, their utilisation for roadworks and similar exterior works does not present any environmental risk.

Conclusions

The highest ^{238}U concentrations were determined in black shale and the lowest in amphibolite. The highest ^{232}Th concentrations were determined in granodiorite and the lowest in black shale.

There was not determined any positive correlation between concentrations of ^{238}U and ^{232}Th. Similarly, there was not verified correlation between ^{238}U and ^{232}Th concentrations and selected ore elements connected with hydrothermal Sb mineralisation.

^{238}U and ^{232}Th source is in granodiorite intrusion but ^{238}U was mobilised from granodiorite during metamorphic process and was accumulated together with synsedimentary pyrite-pyrhotite and hydrothermal Sb mineralisation in black shale presenting geochemical barrier where the ore precipitation occurred.

Concentrations of ^{238}U and ^{232}Th are very low (^{238}U 0.091 – 37.800, ^{232}Th 0.534 – 13.234 mg/kg). Their radiation intensity corresponds to maximum values of ^{238}U = 37.800 Bq/kg (generally to < 3.000 Bq/kg) and ^{232}Th = 13.234 Bq/kg. It is possible to assume that they do not present any environmental risk to land and human activities. They do not exceed permitted limit values for building materials (150 Bq/kg; 120 Bq/kg) as well. The risk for civil engineering presents the total activity of ^{238}U, ^{232}Th and ^{40}K (80.426 – 1,454.402 Bq/kg).

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THE ENVIRONMENTAL IMPACTS OF FIRE-FIGHTING FOAMS

Ivana TUREKOVÁ, Karol BALOG

Abstract

Extinguishing foams are common used by extinguishing fire of flammable liquids, whereby their insulating, choky and refrigerating effect are exploited. The purpose of lecture is to consider and compare foams, that are at present used in fire departments, not only on the part of high extinguishing effect (capability of faster aborted burning on the large surface by little usage) but even to aspect of bearing on the environment in whole stage of their life cycle.

Key words

foams, fire extinguisher, fire

Introduction

Extinguishing agents are different substances and materials using which we can obtain the stop (slow) of combustion process. Basic requirements for extinguishing agents are:

- High fire effects (the ability to quickly break the burning of large areas at low consumption),
- May not be harmful to human (living) organisms, including their use and storage,
- Other criteria such as availability, available price and others.

Significant role among the extinhuishing agents have fire-fighting foams.

Characteristics of fire-fighting foams

Fire-fighting foam is an extinguishing agent composed of numerous bubbles formed mechanically or chemically from liquid. Chemical foam is formed by reaction of alkaline solution with acidic solution in the presence of the foam stabilizer. Mechanical foam rises of introducing air and/or inert gas into a foaming solution [1].

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Foams belong to the two-phase disperse systems consisting of dispersive media (liquid), in which are the dispersed phase - three-dimensional lamellae of permanent structure containing enclosed gas. Plate thickness ranges from 0.001 to 0.01 mm [2].

Foam fire effects consist of the following physical principles (Figure 1):

- Isolation - separate flammable substance from flame,
- Choky - prevents access air oxygen to flammable substance, prevents the evaporation of flammable liquids,
- Refrigerating - reduces the temperature of the burning substance and thus slows burning, which is directly proportional to the water content of the foam [3].

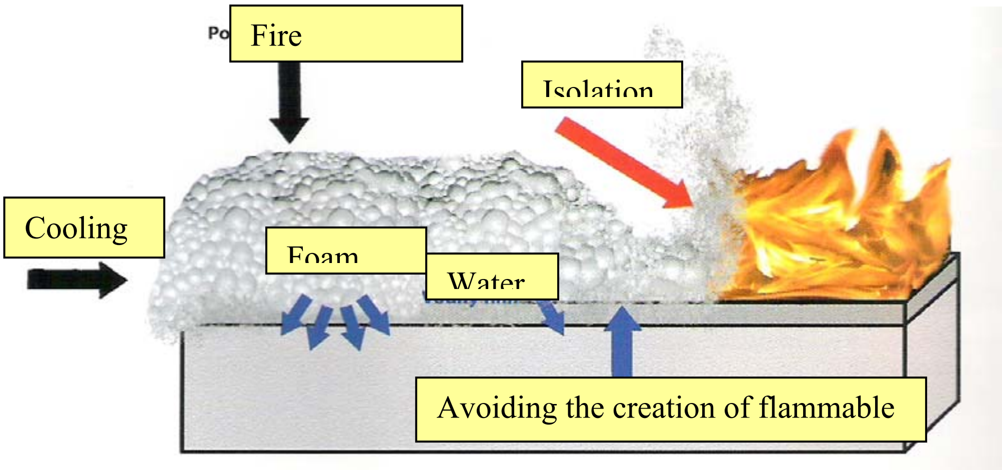

Fig. 1. *Scheme of the mechanism of extinguishing using foam [3]*

Fire fighting foams are commonly used to reduce the spread and extinguishing of Class B fires and to prevent re-ignition. These foams can be used to prevent ignition of flammable liquids and in certain conditions for extinguishing Class A fires. Foams can be used in combination with other extinctive substances, mainly gaseous substances and powders [4]. The first foam fire extinguishers worked on a principe of chemical foam. Currently, the way of development is an air-mechanical foam or foam which arises in the course to a selected group of foaming agents with fire [3]. Air-mechanical foam is prepared at the time of the intervention of a mechanical mixture of solution consisting of water and a foaming solution with atmospheric air in a foaming nozzle. Foaming solution arises in the mixer by injector sucking the foamer into the water. Foamer concentration in water usually ranges from 1 % to 6 %. Gas component in addition to air foams can also be carbon dioxide, nitrogen or other inert gas [2].

Physical properties of foamers

Foamer is a liquid that is mixed with water in a prescribed concentration producing a foaming solution. Foam is a dispersion system in which the dispersing agent gas (air) is and dispersive environment liquid (heterogeneous mixture of gas and liquids). It is an unstable system subject to rapid change. Foam is a cluster of air bubbles generated from a foaming solution. The speed of this transformation is important for assessing the stability of the foam [1]. Stability, properties as well as the effectiveness of foam and foamers determine their physicochemical properties. The monitored physico-chemical properties foamers and foams include:

- **Number of foaming** - the ratio of volume of produced foam to the volume of liquid, by which was this foam produced. This number indicates how many times is the volume of foam larger than the volume of foaming solution. Based on this number foams are divided into three groups (severe, moderate and light foam),
- **Viscosity** - is an expression of fluidity of liquid, it depends on temperature (decreases with increasing, temperature),
- **Foamer frost resistance** - the temperature at which the substance is liquid and does not begin to exclude solid parts,
- **Content of the sediment** - the proportion of solid components in concentrates of foamers expressed in% vol.,
- **Foam stability** - is influenced by excretion of water from the foam, it is defined by half-life, respectively quater-life, which is the time required to eliminate half, respectively fourth water contained in the foam [1],
- **Half-life of foam** - the time at which the foam release 50 % foaming solution, is given in minutes. The conversion speed is an important determinant of quality and stability of foam,
- **pH** - liquid reaction, i.e. acidity, alkalinity or neutrality expressed as the negative decimal logarithm of hydrogen ion activity,
- **A foaming solution spreading factor** - a measure that indicates the ability of one liquid to spontaneously unfold on the surface of another liquid, it is not an indicator of its quality; is given in nM.m^{-1} [3].

Stability of foams depend on the structure of surface films from the so-called foaming agents such as electrolytes, soaps, saponins, proteins, etc. In the process of fire-fighting the foams are constantly disrupted by the influence of heat of ignition, internal force of foam and hot surface of burning liquid. It is proved that the degradation rate of foam by flame heat effect is much smaller than on the actual surface of the heated evaporating liquid. In this process foams have insulating and cooling effect. These effects depend on the type and quality of used foamers. On the quality impact more factors, from a practical point of view are important conditions and storage period of foams [6, 7].

Foam as the extinguishing substance is prepared at the time of intervention. Properties of foam and its quality affect the properties and purity of used chemicals, i.e. water, foaming agents and gas component (usually air). Significant impact on the quality of foam is also used foaming equipment.

According to the nature and use of a foaming agent concentration can be in instant action mousse prepared foam with a special focus on the fire. Foamings with respect to their composition and the resulting properties are divided into the following groups [5]:

- Protein foamers (P),
- Fluorine-protein foamers (FP),
- Synthetic foamers (S),
- Alcohol resistant foamers (AR),
- Aqueous film forming foamers (AFFF),
- Fluorine-protein foamers forming a water film (FFFP) [4, 6].

Summary results of fire skills of faomers are presented in Table 1.

NORMAL FIRE-FIGHTING CAPABILITIES OF DIFFERENT TYPES OF FOAMERS [4]

Table 1

Type of foamer	Extinguishing Class ability	Level of resistance to re-burn	Film-forming
AFFF (no AR)	I	C	+
AFFF (AR)	I	B	+
FFFP (no AR)	I	B	+
FFFP (AR)	I	A	+
FP (no AR)	II	A	-
FP (AR)	II	A	-
P (no AR)	III	B	-
P (AR)	III	B	-
S (no AR)	III	C	-
S (AR)	III	C	-

Storage of foamers

One of the major factors affecting the properties of foamers and foams is their storage life. If foamers are stored in their original packaging according to the manufacturer's instructions they are applicable for several years without changing their original characteristics. However, if a mixture of foramer and water (foaming solution) ready for frothing and is located in the piping system or in vehicle tank, it must be changed each year.

Synthetic foamers must be stored in covering made of stainless steel or plastic. Protein foamers are stored in steel and metal containers. To their storage are not adequate zinc, tin or aluminum containers because foamers are very aggressive and attack these materials.

Valves, pumps and tanks for storage of foamers must be made from one type of metal. If there would have to contact different types of metals, foamers caused electrochemical corrosion. Foamers are very sensitive to temperature changes. Optimal temperatures are in the range +5 to +25 °C. Negative effects on foamers properties were not observed even at the temperature range 15 to + 40 °C. Foamers after re-thawing can be used because there are no changes to their basic physical and chemical properties and no reduce of the fire-fighting effectiveness [3].

Foamer impacts on the environment

Emerging products of combustion and the combustion residues are much more harmful than hand extinguisher. Quickly extinguished fire often outweighs the negative impacts of the extinguishing agent as limiting the formation of toxic products and residues after burning. Putting out fires, for example by water, which is considered to be injurious to the environment, run-off water contaminated by decomposed products of combustion of substances may significantly burden the environment for a long time. In the application of fire-fighting foams and in particular environmentally acceptable, it is possible to extinguish fires earlier and less burden on the environment by products of combustion as in the case of water.

Environmentally acceptable fire-fighting foams should have at least a fire-fighting capability as traditional foams made from protein or AFFF foamers with minimal environmental impacts (water, soil). It is known that the traditional ingredient in foamers (tensides, ethylene glycol, butyldiglykol, propylene glycol, alkylpolyglykozid, nonylalkohol) may cause problems in term of toxicity of the substances themselves, respectively their degradation products. The biggest toxic danger in the application of fire-fighting foams danger is to fish and aquatic organisms. Compared with chemical substances and preparations is indicated low foamer toxicity. Problems arise by secondary toxicity, because the decomposition products have a long bio-degradability in the environment.

Biodegradability of foamers means their ability to degrade by biological or chemical way the original substance to decomposition products environmentally acceptable, for example by assimilation (water and carbon dioxide). Biological degradation is caused by microorganisms and fungi. Foamer degree of degradation is often given as the ratio of biochemical oxygen demand (BOD) and chemical oxygen demand (COD).

Biochemical oxygen demand is the amount of dissolved oxygen consumed by micro-organisms over time, eg. 5 days (BOD5) in the biochemical processes of decomposition of organic substances in water under aerobic conditions. This quantity of oxygen is proportional to the quantity of present degradable organic substances and therefore can be estimated from the BOD level of water pollution by extinguishing foam. Biochemical oxygen demand is determined in the original or a suitably diluted solution of foamer.

Chemical oxygen demand represents the amount of oxygen required for oxidation of organic substances in water using strong oxidants over time (usually two hours). It is the rate of total organic substances in water and thus an indicator of organic pollution of water.

Biodegradability of foamer is expressed as a ratio of COD and BOD5 in percentage (%) biodegradation:

$$\mathbf{BOD5/COD} \tag{1}$$

Ideal foam should have a full-degradability and should not significantly consume dissolved oxygen in water. Environmentally friendly foam (i.e. Green foams) should extinguish fires as effectively as traditionally used foams, but we have to know their degradation, otherwise no significance. They are several times more expensive than conventional foam but on the other hand they may replace by its extinguishing capacity fluorine-protein and AFFF foam (good quenching the flames in AFFF and prevent reoverring in fluorine-protein foams).

EXPERIMENTAL PART

The aim of experiment was to evaluate fire properties foamers in the laboratory and then experimentally verify their impact on the environment. Therefore these measurements were made:

- Tracking numbers frothing and foaming time.
- Determination of half-life.
- Determination of viscosity.
- Determination of biochemical and chemical oxygen demand.
- Ecotoxicological tests on higher plants.

The experiment used following foamers (Table. 2).

USED FOAMERS AND THEIR CHARACTERISTICS Table 2

Name of foamer	Producer	Use for Classes of fires	Recommended concentration	Notes
Sthamex AFFF 1 %	Fabrik chemischer Präparate von Dr. Richard Sthamer GmbH & Co.KG, Hamburg, Germany	A a B	1 %.	specially designed for hydrocarbon fires, plastics and mineral oil products
Sthamex AFFF F-15	Fabrik chemischer Präparate von Dr. Richard Sthamer GmbH & Co.KG, Hamburg,	A a B	3 %.	Specially designed for fires of oil products and plastics
Pyronil	Chemtura Corporation, USA	A a B	3 %	synthetic multipurpose foamer, also light foam
Moussol APS F-15	Výrobca: Fabrik chemischer Präparate von Dr. Richard Sthamer GmbH & Co.KG, Hamburg, Germany	A a B	3 %	fire fighting of liquid of non-polar hydrocarbons
			6 %	fire fighting of liquid of polar hydrocarbons

Their selection was based on research findings available in HZZ. Foamers from each were prepared of five different concentrations (1 %, 3 %, 6 %, 9 % and 12 %).

I. ASSESSMENT OF FOAMERS IN TERM OF EXTINCTIVE AND PHYSICAL PROPERTIES

Number of foaming

To determine the number of foaming (E) made in accordance with STN EN 1568-3: 2002. Technical conditions of foamers for heavy foam on the surface use of the liquid unmixable with water. Questioned the number of frothing of selected foamers different concentrations and the time of a foam formation (Table No.3).

NUMBER OF FROTHING AND TIME OF FOAMING TESTED FOAMERS Table 3

No	Concentration of foamer [%]	Number of frothing E				Time of foaming [s]			
		Sthamex AFFF 1 %	Sthamex AFFF F-15	Pyronil	Moussol APS F-15	Sthamex AFFF 1 %	Sthamex AFFF F-15	Pyronil	Moussol APS F-15
1.	12	4.886	4.909	4.901	4.822	6.61	16.58	17.71	19.23
2.	9	4.894	4.891	4.908	4.854	11.69	19.20	20.34	23.38
3.	6	4.890	4.827	4.878	4.887	13.35	19.25	25.63	26.20
4.	3	4.906	4.826	4.839	4.837	14.70	25.28	30.55	30.24
5.	1	4.827	4.883	4.820	4.807	27.35	35.04	34.44	57.81

Number of frothing ranged around the value 4.9 ± 0.1 for all foamers, allowing a fair comparison foaming time. The fastest foamed foamers Sthamex AFFF 1%, AFFF Sthamex F-15, then Pyronil and the longest foaming time had Moussol APS F-15, in which time foaming at 1% concentration significantly extended.

Half-life

In the half-life testing, as recommended by the manufacturers in safety data sheets, were used 3% solutions and the time, in which 50% of foaming solution released from the foam was monitored. The results of the measured values for each foamer are in the following table 4.

HALF-LIFE OF TESTED FOAMERS (3 % solutions) Table 4

No	Name of foamer	Half-life [s]
1.	**Sthamex AFFF 1 %**	62
2.	**Sthamex AFFF F-15**	166
3.	**Pyronil**	187
4.	**Moussol APS F-15**	187

The most favorable results were achieved using foamers Pyronil and Moussa APS F-15, where the half-life was 187 seconds.

Measurement of foamer viscosity

Viscosity was determined according to DIN 53015:2001 Viscometry - Measurement of viscosity using the Hoeppler falling-ball viscometer for viscosity, etri Höpller KF 3.2, which is designed primarily to measure the dynamic viscosity of Newton‘s liquids. It measured the time of ball fall between two lines and the calculation of the viscosity was calculated from the relation:

$$\eta = t.(\rho_1 - \rho_2).K \,, \tag{2}$$

where

η the dynamic viscosity in mPa.s,

t falls time of balls in s,

$\rho 1$ ball density in g.cm^{-3},

$\rho 2$ density of the fluid in the bath temperature g.cm^{-3},

K the constant mPa.cm^{3}.g^{-1}

The results are shown in Table 5.

MEASUREMENT RESULTS OF FOAMER VISCOSITY Table 5

No	Name of foamer	t [s]	ρ_1 [g.cm^{-3}]	ρ_2 [g.cm^{-3}]	K [mPa.cm^{3}.g^{-1}]	η [mPa.s]
1.	**Sthamex AFFF 1 %**	124	2.224	1.07	0.07293	10.436
2.	**Sthamex AFFF F-15**	70	2.224	1.04	0.07293	6.044
3.	**Pyronil**	76	2.224	1.545	0.07293	3.466
4.	**Moussol APS F-15**	69	8.142	1.170	0.1225	58.931

The lowest viscosity was measured in foamers Pyronil a Sthamex AFFF F-15, the highest had Moussol APS F-15.

II. FOAMER IMPACT ON THE ENVIRONMENT

Determination of biochemical oxygen demand

The essence of the test is treatment and dilution water sample to be analyzed by different amounts of diluent water with a high amount of dissolved oxygen and vaccinic aerobic microorganisms with prevention of nitrification. Incubation was conducted at 20 °C within a defined time of 5 days in the dark in a full closed flask. The dissolved oxygen concentration was setting out before and after incubation according to STN EN 1899-1 Water quality - Determination of biochemical oxygen consumption after n days (BSKn): Part 1: Dilution and inoculation method with the addition of allylurea. Was used vaccinated diluting water and dissolved oxygen was electrochemically determined (Table. 6).

Determination of chemical oxygen demand

The oxidizable substances in the test sample volume are oxidized by a known quantity of potassium dichromate in the presence of mercuric sulfate and silver catalyst in an environment of concentrated sulfuric acid in a defined time interval. COD value is calculated based on the amount of reduced dichromate.

The indicator COD shows the total content of organic substances in water - organic water pollution (Table. 6).

RESULTS OF COD AND BOD5 VALUES TESTED FOAMERS
(3% FOREIGN SOLUTIONS)

Table 6

No	Name of foamer	COD [$mg.l^{-1}$]	BOD5 [$mg.l^{-1}$]	BOD5/COD [%]
1.	**Sthamex AFFF 1 %**	76.23	22 790	0.33
2.	**Sthamex AFFF F-15**	73.68	21 370	0.34
3.	**Pyronil**	79.20	33 530	0.23
4.	**Moussol APS F-15**	83.46	17 470	0.47

The results of foamer biodegradability can be concluded that all foamers have little ability to biologically degrade due to the very small proportion of degradable substances.

Acute toxicity

The acute toxicity is the ability or property of foamer to cause severe biological harm or death of the organism for a relatively short exposure time (24 - 96 hours). IC_{50} was defined as inhibitory concentration of tested substance that causes 50% inhibition of root growth of Sinapis alba plants (pure variety of white mustard, seed germination > 90%, seed size 1.5 mm - 2.5 mm) for 72 hours.

The basic monitored parameter for evaluation of the test is the average length of the roots. As defined in the test solution was compared to control and calculate the percentage inhibition (reduction) or stimulation (extension of the root). Results are listed in the table 7.

RESULTS OF ECOTOXICOLOGICAL TEST FOR SEEDS OF HIGHER PLANTS Table 7

No	Name of foamer	$IC_{0,5}$* %	IC_1 %	IC_2 %	IC_3 %	IC_5 %
1.	**Sthamex AFFF 1 %**	96.2				
2.	**Sthamex AFFF F-15**	87.6	88.3			
3.	**Pyronil**	98.0				
4.	**Moussol APS F-15**	66.2	76.7	87.9	89.6	98.3

** Ecotoxicological test on seeds of higher plants Sinapis alba, subscript reflects the concentration of sample (volume %). empty box = no sprouted seed.*

On the basis of ecotoxicological test shows that the higher concentrations are significantly toxic to the test plant species.

Conclusion

Today we know many types of fire-fighting foams, which have different physical and fire properties. Each has its own fire extinguisher foam pros and cons, as shown by our testing. It is necessary to know their physical characteristics, whether the stability of foams at low and high temperatures, which is defined by a half-life; number of foaming, which specifies whether it is a heavy, medium or light foam and also by the viscosity - a resistance of fluid to internal friction and other properties to be appropriately selected and used in practice to fight fires.

Modern firefighting foams can be considered as very good in term of physical characteristics, but in recent years about the new REACH legislation draws attention to their ecotoxicological properties. If fire-fighting foams are used to extinguish large fires, it is very likely that their products, such as broken water created from foam, to get into the soil, streams and may also affect the purufication of wastewater. All types of foam have different ecological characteristics because its components that determine the rate of biodegradation. Although ecotoxicological testing *Sinapis alba* showed that the already low concentration of foamer is characterized by significant toxicity.

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