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**From Editor's desk**

*"Investing in yourself is the best investment you will ever make.  
It will improve not only your own life but also the life of everyone around you."*

*Robin Sharma*

Reform of the education system in Serbia has caused the scientists to be conditioned to present their research in leading scientific journals on the *Science Citation Index* (SCI) list. Unfortunately, in the Republic of Serbia and its surrounding, no journals in the field of occupational and environmental safety have been included in the list. Given the importance of the protective measures defined by current European legislation and the fact that we live in a time when it is imperative to preserve the quality of the working environment, the editorial staff of the journal "Safety Engineering" cordially invites everyone who has directed their scientific research towards this field to publish their results and increase their citedness and the journal's impact. This would improve the entire system of education in the field of occupational and environmental safety. In a year when the city of Niš celebrates the 1700-year anniversary of the Edict of Milan, the document that proclaimed religious tolerance, which was a new step in European history and culture, we are confident that the research results published in this issue of the journal will be another step forward in achieving our ultimate goal - promotion and exchange of experiences between scientists and professionals in the fields of safety engineering.

*"Ulaganje u samog sebe je najbolje ulaganje koje ćeš ikada da učiniš.  
To neće unaprediti samo tvoj život, već i život svih oko tebe."*

*Robin Sharma*

Reforma obrazovnog sistema u Republici Srbiji učinila je da su naučni radnici uslovljeni da svoja istraživanja predstavljaju u vodećim naučnim časopisima koji se nalaze na *Science Citation Index* (SCI) listi. Nažalost, u Republici Srbiji i njenom okruženju, nijedan časopis iz oblasti zaštite radne i životne sredine nije uvršćen na ovu listu. S obzirom na značaj primene mera zaštite koje su definisane savremenim evropskim zakonodavstvom, kao i na činjenicu da živimo u vremenu u kome je imperativ očuvati kvalitet radne i životne sredine, uređivački kolegijum časopisa „Safety engineering“ poziva sve koji su svoja naučna istraživanja usmerili ka ovoj oblasti, da objavljuju svoje rezultate i povećaju citiranost časopisa. Na taj način bi unapredili i ceo sistem obrazovanja u oblasti zaštite radne i životne sredine. U godini kada grad Niš obeležava 1700 godina Milanskog edikta, dokument kojim je proglašena verska tolerancija, što je predstavljalo novi korak u evropskoj istoriji i kulturi, sigurni smo da će rezultati istraživanja objavljeni u ovom broju časopisa biti još jedan korak napred u ostvarenju našeg konačnog cilja, unapređenja i razmene iskustava između naučnih i stručnih radnika u oblasti inženjerstva zaštite.

On behalf of the editors

*Dr Ivan Krstić*

## Contents

### Scientific Articles

|   |    |
|---|----|
| <b>Zagorka Aćimović Pavlović</b><br><i>Sustainable Solutions for Managing Environmentally Hazardous Waste Materials: Reapplication of Fly Ash</i> ..... | 1  |
| <b>Sukru Aslan</b><br><i>Control Strategies of Nitrite Accumulation in a Submerged Biofilter</i> .....  | 7  |
| <b>Ivana Banković-Ilić</b><br><i>Eco-Friendly Processes for Biodiesel Production from Non-Edible Oils</i> .....   | 11 |
| <b>Amelija Đorđević</b><br><i>Analysis of Gaseous Substance Toxicity Assessment</i> .....   | 17 |
| <b>Ljiljana Živković</b><br><i>Experimental Testing of Tobacco Self-ignition Temperature</i> .....  | 23 |
| <b>Milica Radić</b><br><i>Improving Building Energy Efficiency Using Distributed Artificial Intelligence</i> .....                                      | 27 |
| <b>Nicolaie Varzaru</b><br><i>Implementation of Health and Safety Management System in Automotive Industry</i> .....                                    | 33 |
| <b>Sonja Pavlović-Veselinović</b><br><i>Repetition as a Risk Factor for the Development of Musculoskeletal Disorders</i> .....                          | 39 |
| <b>Duška Pešić</b><br><i>Flammable and Toxic Materials Which are not Allowed to Get in Contact With Water - a Calcium Carbide Case</i> .....            | 47 |

### Professional Articles

|   |    |
|---|----|
| <b>Darko Mihajlov</b><br><i>Rotating Machinery Diagnostics Through Vibrations</i> ..... | 53 |
|---|----|

### Reviews of publications

|   |    |
|---|----|
| <b>Suzana Savić, Miomir Stanković</b><br><i>Technical protection systems 2</i> .....        | 59 |
| <b>Momir Prašević, Dragan Cvetković</b><br><i>Management of environmental quality</i> ..... | 60 |

### Propagation Corner

Joint Stock Company for Quality Testing „KVALITET“ Niš

#### SAFETY IN PRACTICE

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## Sadržaj

### Naučni radovi

|   |    |
|---|----|
| <b>Zagorka Aćimović Pavlović</b><br><i>Održiva rešenja za zbrinjavanje ekološki rizičnih otpadnih materijala: ponovna upotreba letećeg pepela</i> ..... | 1  |
| <b>Sukru Aslan</b><br><i>Strategija kontrole akumulacije nitrita u biofilteru</i> .....   | 7  |
| <b>Ivana Banković-Ilić</b><br><i>Ekološki neškodljivi procesi za proizvodnju biodizela iz nejestivih ulja</i> .....                                     | 11 |
| <b>Amelija Đorđević</b><br><i>Analiza procene toksičnog dejstva gasovitih supstanci</i> .....   | 17 |
| <b>Ljiljana Živković</b><br><i>Eksperimentalno ispitivanje temperatura samopaljenja duvana</i> .....  | 23 |
| <b>Milica Radić</b><br><i>Poboljšanje energetske efikasnosti zgrada primenom distribuirane veštačke inteligencije</i> .....                             | 27 |
| <b>Nicolaie Varzaru</b><br><i>Primena sistema upravljanja za zdrav i bezbedan rad u automobilske industriji</i> .....                                   | 33 |
| <b>Sonja Pavlović-Veselinović</b><br><i>Ponavljanje kao faktor rizika za nastanak mišićno-skeletnih poremećaja</i> .....                                | 39 |
| <b>Duška Pešić</b><br><i>Zapaljivi i toksični materijali koji ne smeju doći u kontakt sa vodom – primer kalcijum karbid</i> .....                       | 47 |

### Stručni radovi

|  |    |
|--|----|
| <b>Darko Mihajlov</b><br><i>Dijagnostika stanja rotacionih mašina pomoću vibracija</i> ... | 53 |
|--|----|

### Prikazi publikacija

|   |    |
|---|----|
| <b>Suzana Savić, Miomir Stanković</b><br><i>Systems theory and risk</i> ..... | 59 |
| <b>Momir Prašević, Dragan Cvetković</b><br><i>Environmental noise</i> .....   | 60 |

### Oglašavanje

Akcionarsko društvo za ispitivanje kvaliteta „KVALITET“

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## SUSTAINABLE SOLUTIONS FOR MANAGING ENVIRONMENTALLY HAZARDOUS WASTE MATERIALS: REAPPLICATION OF FLY ASH

**Abstract:** *The disposal of the fly ash may pose a significant risk to the environment due to the possible leaching of hazardous pollutants. The only sustainable economic solution for the pollution-prevention of the environment is the reuse of fly ash in building materials. Some of building composites, in which fly ash is combined with refractory components can withstand high temperatures. In this investigation testing composites were based on fly ash mixed with high-aluminate cement. Investigated fly ashes were previously subjected to mechano-activation. The leaching behavior and potential environmental impact of hazardous elements were analyzed. Mineral phase analysis by means of XRD was accented due to the fly ash high dependence on its origin. Crystalline phases were investigated by means of DTA. Scanning electron microscopy was used in microstructure analysis. The leachability of toxic elements was within allowed range, thus investigated fly ashes can be replicated in building materials. Investigated fly ash-cement composites proved to have high physico-mechanical performances, but also good thermo-insulation characteristics. The overall results showed that application of the fly ash in building composites is sustainable solution for managing this environmentally hazardous waste material.*

**Key words:** fly ash, thermo-insulation, toxic elements, reapplication, building composites.

## INTRODUCTION

The building materials production is an industry branch which is not completely environmentally friendly because it is constantly depleting natural resources. At the other hand, construction industry is generating large amount of waste that needs to be properly managed in order to avoid pollution and deterioration of landscape. A mutually satisfactory solution should be found in order to create equilibrium between application of the waste material from other industrial branches and reduction of the waste material that construction industry creates. Therefore, the 'three-R' principle (reduction, reuse and recycle) has to be world-wide adopted [1, 2]. Ash from coal combustion is considered as one of the most hazardous environmental pollutants. According to estimation, the annual global fly ash production was more than 600 million tons in past 10 years [3]. The generation of combustion byproducts is a global problem with severe implications for the environment: elements may leach through the soil to the groundwater; ash might cause air pollution if left on open landfills, etc. EU regulations are focused on the recycling of the coal combustion fly ash and reusing it as a component of added-value products [4]. In addition to the fly ash processing and reapplication in new recycled products, there is also an environmental impact that needs to be evaluated before fly ash reapplication. Namely, there is possibility of toxic

metals leaching which could pass through the soil into the ground water, especially when fly ash is used as a construction material. Fly ash may contain some elements of environmental concern, such as arsenic, barium, chromium, cadmium, lead, selenium and mercury, which can limit the potential applications [5-7]. Fly ash usually contains relatively small amounts of heavy metals, particularly volatile metals such as cadmium, zinc and lead [8].

A new possibility for fly ash application could be as raw material for high-temperature application: in thermal insulators or/and refractory material products. As such, fly ash has to adequately answer on mechanical and thermal stability criteria. One of the ways of achieving it is by applying mechanical activation (MA) procedure on fly ash. Fly ash acts as superplasticizing admixture helping the "packing" of composite structure [9]. Superplasticizing ability which leads to reduction of water content needed for optimal mixture consistency and increasing of mechanical strength is only being further enhanced by MA. Although mechanical activation is much more cost effective than application of original sized fly ash results are by far better. Important aspect of construction materials is its behavior at elevated temperatures: its thermo-insulation properties, fire resistance and finally possible refractoriness. The use of fly ash additions in building composites can affect

the material behavior when subjected to elevated temperature [10]. Materials that retain a large quantity of water are more desirable for fire protection and thermal exposure. Namely, when these materials are exposed to a thermal source, part of the water evaporates and is transported from the exposed surface to the interior of the material where the water cools and condenses again. Afterwards, a liquid film forms which is displaced towards the unexposed side. Some commercial products, used as thermal insulation or passive fire protection in buildings and industrial installations, have a chemical composition and properties similar to fly ash mixtures [11].

## 2. MATERIALS AND METHODS

The fly ash used in the investigation originates from the filter systems of coal-fired power plant in Serbia - "Nikola Tesla-Tent A". The fly ash was collected directly from the filter of the power plant. Afterwards the fly ash was transported to a special closed silo for storing. Mechanical activation (MA) of the fly ash was performed by means of laboratory vibrational mechano-activator - planetary ball mill type "Retsch-PM4". 2 kg batch size was used for milling. Material to media ratio of 1:35 was maintained during milling. The fly ash samples were milled for 60 min. Maximal grain size of fly ash was reduced to 0.83 mm by MA. Calcium-aluminate cement (CAC Secar 70/71, Lafarge) was used in the investigation. The composite (labeled as CFA) contained 30 % of fly ash and 70 % of cement.

X-ray fluorescence (XRF) technique was used to conduct chemical element analysis in composites. Analysis was performed by means of XRF spectrophotometer ED 2000 - Oxford. The differential thermal analysis (DTA) of the composites was performed with a Shimadzu DTA – 50 apparatus. The sample was heated under an air atmosphere from 20 up to 1100 °C at heating rate of 10 °C/min. X-ray powder diffraction (XRD) patterns were obtained on a Philips PW-1710 automated diffractometer using a Cu tube operated at 40 kV and 30 mA. All the XRD measurements were performed at room temperature in a stationary sample holder. Potential mobility of trace elements from the composite was determined by means of the batch leaching test, procedure conducted according to Serbian Standard SRPS EN 12457 (1-4) (equivalent to EN 12457 (1-4)). The leaching test was performed at a liquid/solid ratio of 10 L/kg with a stirring time of 24 h and deionized water as the leachant.

## 3. RESULTS AND DISCUSSION

The chemical composition analysis – major and minor elements of the investigated composite CFA is presented in Table 1. and trace elements found are given in Table 2. The investigation showed that composite consists mainly of silica, alumina and calcium oxides. Application of fly ash increased SiO<sub>2</sub> content in the composite in comparison with starting composition of applied cement.

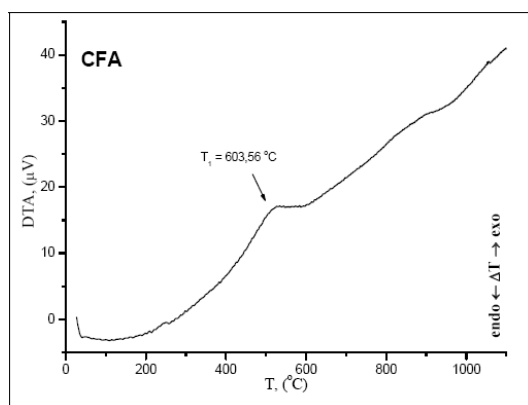
**Table 1.** Chemical analysis of the composite CFA - major and minor elements

| Oxide | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | TiO <sub>2</sub> | CaO   | TiO <sub>2</sub> | SO <sub>3</sub> | Na <sub>2</sub> O | K <sub>2</sub> O |
|-------|------------------|--------------------------------|--------------------------------|------------------|-------|------------------|-----------------|-------------------|------------------|
| %     | 16.08            | 55.30                          | 1.91                           | 0.16             | 22.93 | 0.92             | 0.17            | 0.35              | 0.345            |

**Table 2.** Chemical analysis of the composite CFA - trace elements

| t.e.  | Pb   | Zn   | Zr   | Cu  | Ni   | Cr   | Ba   | Sb    | Se  | Sr   | Co   | V    | W   |
|-------|------|------|------|-----|------|------|------|-------|-----|------|------|------|-----|
| mg/kg | 22.9 | 23.3 | 12.8 | 6.7 | 16.3 | 64.4 | 33.0 | 0.013 | 1.0 | 61.8 | 16.1 | 45.4 | 2.7 |

Processes taking place during composite thermal treatment from 20 up to 1100 °C were identified by means of DTA method (Fig. 1).



**Figure 1.** DTA curve of the CFA composite

The thermal treatment of fly ash normally comprises three separate "regions" that are monitored by three individual peaks. The first peak below 200 °C is attributed to the evaporation of moisture. Such peak normally corresponds to the volatilization of the water mechanically bonded in form of H<sub>2</sub>O molecule. The second "region" occurring within the temperature range 400–700 °C incarnates polymorphic transition. Peak showing at approximately 500 °C is exothermic, corresponding to the transformation of organic matter, the decomposition of CaCO<sub>3</sub> and the burning of residual coal present in the fly ash. Also, it is known that β-quartz undergoes transformation to α-quartz at 573 °C, thus a weak endothermic effect that follows exothermic peak can be assigned to the presence of quartz in fly ash. The third "region" represents the beginning of the fusion of fly ash. The endothermic peak at approximately 900 °C is induced by presence of aluminosilicates.

Detailed interpretation of results obtained for cements is difficult because of complexity of composition of studied samples. The processes of dehydration of individual compounds overlap. In case of CAC the initial amount of water combined with cement is greater than in case of normal Portland cement and a larger amount of this water is retained at elevated temperatures, particularly up to 300 °C. Dehydration of the calcium aluminate and the alumina hydrates is near completion at 500-600 °C which is marked by endothermic peak on DTA curve. The alumina gel passes through several modifications until it is finally transformed at about 1000 °C into  $\alpha$ -alumina. CAH10 can be finally dehydrated to CA but other hexagonal hydrates produce calcium oxide and C12A7 at temperatures from 600-1000 °C. In this temperature range, solid state reactions between calcium aluminates, alumina and lime are induced. This leads to increase in mechanical strength of CAC due to these reactions, which is represented by small endotherms on DTA curve.

Certain, but not significant quality changes in hydrating system of investigated composite are being caused by the addition of 30 % of fly ash. Namely, differences in quantity and quality of hydration products cause small differences in recorded DTA curves of cement and cement-fly ash composite. The first endothermic effect on DTA is slightly shifted towards 120 °C as a consequence of fly ash addition. At higher temperatures addition of fly ash does not cause significant differences in quality composition of referent cement pastes. In this way a new binders based on waste material with equally good thermal properties are obtained. Melting is not recorded at the temperature 1100 °C which attributes to good refractory characteristics of composite.

XRD diffractograms of investigated composite as result of the mineralogical analysis are given in Figure 2. Major phases normally present in CAC are: monocalcium aluminate and monocalcium dialuminate. Fly ash samples contain aluminosilicate glass, quartz and mullite. Magnetite, hematite, fluorite and anhydrite are usually present in relatively negligible amounts.

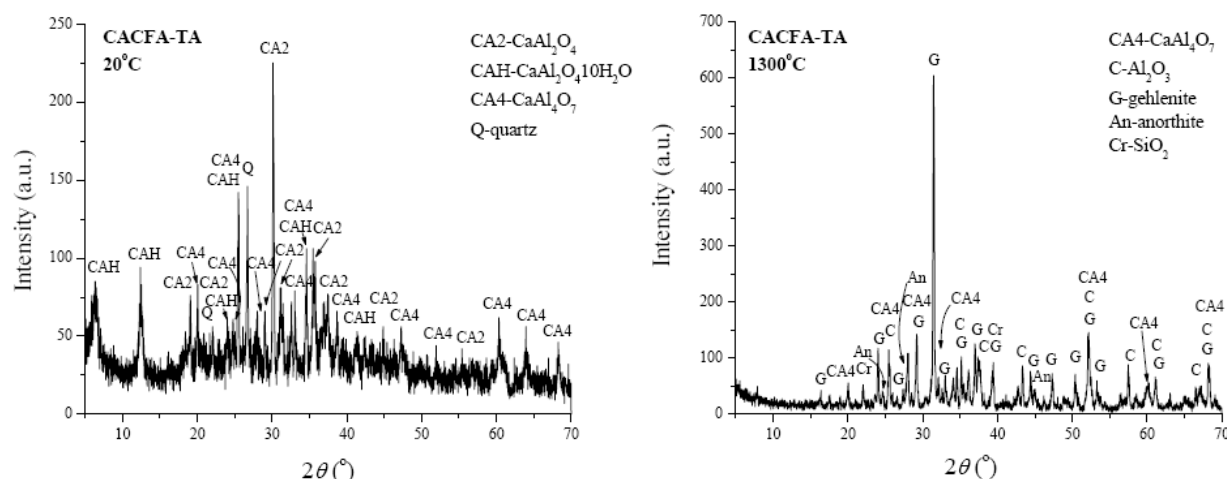


Figure 2. XRD diffractograms of CFA at temperatures 20 and 1300 °C

At  $T = 20$  °C, phase composition of CFA is as follows: monocalcium aluminate, grossite ( $\text{CaAl}_4\text{O}_7$ ), calcium aluminium decahydrate ( $\text{CaAl}_2\text{O}_4 \cdot 10\text{H}_2\text{O}$ ), quartz and amorphous matter. The most abundant phase is  $\text{CaAl}_2\text{O}_4$ ,  $\text{CaAl}_4\text{O}_7$  is less abundant.  $\text{CaAl}_2\text{O}_4 \cdot 10\text{H}_2\text{O}$  and quartz are present in small amount. Crystallinity degree of all present phases is very low. At  $T = 1300$  °C phase composition is: gehlenite,  $\text{Al}_2\text{O}_3$  (corundum),  $\text{CaAl}_4\text{O}_7$ , anorthite,  $\text{SiO}_2$  (cristobalite). The most abundant phase is gehlenite, while less present phases are  $\text{CaAl}_4\text{O}_7$ , corundum and anorthite. There is also possibility of presence of cristobalite but in very small amounts. Crystallinity degree is significantly higher than on the initial sample.

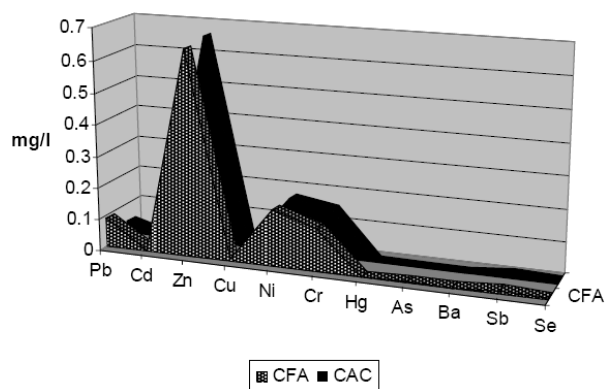
XRD analysis of the composite pointed out to certain phase changes occurring with increasing temperature. The XRD spectra in all cases were very complex, usually containing 40–60 peaks. The XRD patterns revealed that with an increase of sintering temperature,

more complex aluminosilicates were newly formed. It is possible that simple minerals were gradually incorporated into the complex aluminosilicates when the sintering temperature increased. The original ash contains a significant amount of siliceous glass together with the crystalline phases - quartz, hematite and mullite. Sintering reduces the amount of glassy phase and quartz, and promotes formation of anorthite, mullite, hematite and cristobalite. However, the diffraction peaks of these compounds in sintered samples were broad or poorly developed and in some cases overlap. It was observed that, the peak intensities of these compounds slightly increase and their crystallinity improves with increasing temperature. The formation of rankinite, gehlenite, anorthite and cristobalite in the composites is important because they are thermally stable (i.e. have high melting point) and therefore they contribute to the thermal stability of the concrete mixtures. Although most of the peak



intensities of these compounds are relatively small - when gathered and combined with peaks of refractory aggregate minerals they influence creating heat enduring material. These results are in a good agreement with the retained compressive strength after exposure to high temperatures.

The results of the leaching test performed on the composite and comparison with cement sample without addition of fly ash is given in Figure 3. It can be seen that level of toxic elements - Cu, Zn, Se and Cr is lower in the composite than in cement. Addition of fly ash increased level of Pb, Ni and As, while the level of Sb did not change.



**Figure 3.** Results of leaching test performed on CFA and CAC samples

#### 4. CONCLUSION

The developed fly ash-cement composite seems to be a promising thermal-insulation and high temperature resistant material which can be used as bonding agent in concretes or mortars for structures and structural elements that are exposed to high temperatures. The investigation highlighted following:

- Mechano-activation promoted long-term strength enhancement and improved over-all performances of investigated composites by minimizing the chemical and microstructural incompatibility of fly ashes and employing it as superplasticizer.
- Fly ash, as raw material, showed positive thermal insulation or temperature protection properties and behavior in the cementitious composite.
- DTA pointed to the slight shifting of the high temperature peaks (above 900 °C) which means that mechano-activation influenced decreasing of fly ash sintering temperature. Melting of the material is not recorded at the temperature 1300 °C which attributes to good refractory characteristics investigated composite.
- XRD showed that crystallinity of the composite improved with increasing temperature. The formation of rankinite, gehlenite, anorthite and cristobalite in the composites is important because they are thermally stable and therefore they contribute to the thermal stability of the composites.

- Despite the level of toxic elements in fly ash composition it is safe to reapply this nus-product in building materials. Potentially toxic and/or leachable elements in leachate of fly ash based building composite were under upper value limit assigned by official regulative. The following potential pollutants - Pb, Cd, Zn, Cu, Ni, Cr, Hg, As, Ba, Sb and Se are proved to be of low concern when fly ash is exposed to standard environmental conditions approximated by laboratory batch water leaching test.
- As the leaching tests carried out on the composite denied possibility of potential larger scale transition of toxic elements from the building material in contact with water, this fly ash reapplication might be regarded as safe process.

#### 5. ACKNOWLEDGEMENTS

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## ODRŽIVA REŠENJA ZA ZBRINJAVANJE EKOLOŠKI RIZIČNIH OTPADNIH MATERIJALA: PONOVA UPOTREBA LETEĆEG PEPELA

Zagorka Acimović Pavlović, Anja Terzić, Ljiljana Miličić, Zagorka Radojević, Ljubica Pavlović

**Rezime:** Odlaganje letećeg pepela može da predstavlja značajan rizik po životnu sredinu usled mogućeg ispuštanja opasnih zagađujućih materija. Jedino ekonomski održivo rešenje za sprečavanje zagađenja životne sredine je ponovna upotreba pepela u građevinskim materijalima. Neki od građevinskih kompozita, u kojima se leteći pepeo kombinuje sa vatrostalnim komponentama, mogu da izdrže visoke temperature. Kompoziti testirani u ovom istraživanju su se bazirali na pepelu koji je pomešan sa aluminatnim cementom. Ispitivani pepeo je prethodno podvrgnuti mehaničkoj aktivaciji. Analizirani su modeli curenja i potencijalni uticaji opasnih elemenata na životnu sredinu. Kristalin faze su ispitivane pomoću DTA. Elektronska mikroskopija je korišćena za analizu mikrostrukture. Mogućnost curenja toksičnih elemenata je bila u dozvoljenim granicama, čime se pokazalo da se ispitivani leteći pepeo može primeniti u građevinskim materijalima. Pokazalo se da ispitivani pepeo/cement kompoziti imaju visoke fizičko - mehaničke performanse, ali i dobre termoizolacione karakteristike. Ukupni rezultati su pokazali da je primena pepela u dobijanju građevinskih kompozita održivo rešenje za upravljanje ovim ekološki opasnim otpadom.

**Ključne reči:** leteći pepeo, termoizolacija, toksični elementi, ponovna upotreba, građevinski kompoziti.

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## CONTROL STRATEGIES OF NITRITE ACCUMULATION IN A SUBMERGED BIOFILTER

**Abstract:** Short-cut nitrification under various Nitrogen Loading Rate (NLR), dissolved oxygen (DO) concentrations and pHs at a constant temperature of  $25 \pm 1$  °C was investigated in a submerged biofilter reactor. The lowest  $\text{NO}_2\text{-N}/\text{NO}_x\text{-N}$  ratio was observed when the NLR was up to  $160 \text{ g/m}^3\cdot\text{day}$ . Further increase the NLR resulted in incomplete oxidation of ammonium and the effluent  $\text{NH}_4\text{-N}$  and  $\text{NO}_2\text{-N}$  concentration increased. Although the highest  $\text{NO}_2\text{-N}/\text{NO}_x\text{-N}$  ratio of 0.61 was achieved, the  $\text{NH}_4\text{-N}$  removal efficiency was drastically dropped to 48% at the NLR of  $294 \text{ g NH}_4\text{-N/m}^3\cdot\text{day}$ . The highest  $\text{NO}_2\text{-N}/\text{NO}_x\text{-N}$  ratio of 0.68 was achieved at the pH of 9.0 and  $1.0 \text{ mg O}_2/\text{l}$ . However,  $\text{NN}_4\text{-N}$  removal efficiency and the  $\text{NO}_2\text{-N}/\text{NO}_x\text{-N}$  ratio were sharply dropped to 33% and 0.55 by getting the NLR to  $381 \text{ g NH}_4\text{-N/m}^3\cdot\text{day}$  at the DO concentrations of  $2.0 \text{ mg/l}$ .

**Key words:** partial nitrification,  $\text{NO}_2\text{-N}/\text{NO}_x\text{-N}$  ratio.

## INTRODUCTION

In order to eliminate ammonium in the wastewater, biological method is widely applied because; the low cost and the nitrogen compounds are converted to the biomass and nitrogen gas. A recirculated supernatant generated from the wastewater treatment plants (WWTP) with anaerobic sludge digestion, contributes to 15-20% of the influent nitrogen load [1]. Currently, many municipal wastewater treatment plants encounter the problem of overload of  $\text{NH}_4\text{-N}$ , which makes it difficult to be biologically nitrified generated in side-stream wastewaters such as nitrified municipal sludge decants. This high level of ammonium makes it difficult to be biologically nitrified due to the ammonia toxicity to nitrifiers and the extensive oxygen requirement for nitrification. Therefore it is desirable to treat ammonium rich supernatant before returning to the head of wastewater treatment plant [2]. In the partial nitrification processes, since  $\text{NO}_2\text{-N}$  and  $\text{NO}_3\text{-N}$  are intermediary compounds in nitrification and denitrification, a partial nitrification to  $\text{NO}_2\text{-N}$  and denitrification from accumulated  $\text{NO}_2\text{-N}$ , instead from  $\text{NO}_3\text{-N}$ , would be feasible [3]. In recent years, partial nitrification process has been great attention for nitrogen compounds removal because of the low operational cost of this process considering the DO and organic carbon requirements [4-8]. Accumulation of  $\text{NO}_2\text{-N}$  in the effluent water could be achieved by operating the experimental set-up under high pH, low DO concentrations, short sludge retention time, etc.

In this study, the environmental factors such as DO concentrations and pH affects on the  $\text{NH}_4\text{-N}$  removal efficiency and  $\text{NO}_2\text{-N}/\text{NO}_x\text{-N}$  ratio were investigated at various nitrogen loading rate (NLR).

The experiments were carried out at constant temperature of  $25^\circ\text{C}$  in the submerged biofilter.

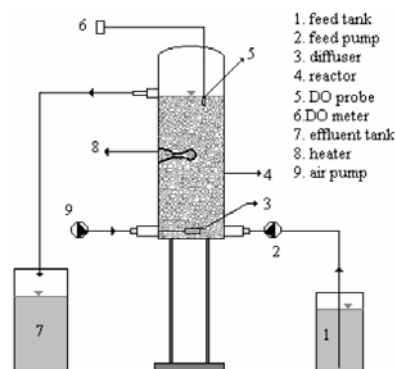
## 2. MATERIALS AND METHODS

### 2.1. FEED WASTEWATER

The synthetic wastewater, which was contained trace metals and vitamins necessary to maintain bacterial growth, was used in the experimental study. The synthetic wastewater constituents was presented in the Table 1 [2].

### 2.2. REACTOR SET-UP AND OPERATION

The PNBR had a liquid volume of 2.6 liter and was filled with plastic coils which was provided  $0.5 \text{ m}^2$  resulting in  $188.5 \text{ m}^2$  surface area/ $\text{m}^3$  for bacterial growth and completely submerged. The influent wastewater was pumped continuously to the bottom of PNBR using peristaltic pump and discharged from the top of reactor to an effluent tank. The PNBR was operated at the temperature of  $25^\circ\text{C} \pm 1$  and an air diffuser was installed directly at the bottom and the DO concentration was measured periodically at the top of reactor by using a DO meter (YSI 5100). The schematic diagram of experimental set-up was presented in the Figure 1.



**Figure 1.** Schematic diagram of the PNBR

The partial nitrification bioreactor (PNBR) was inoculated with microorganisms taken from the nitrification batch reactor in the laboratory of Environmental Engineering Department.

**Table 1.** Synthetic wastewater constituents [2]

| Chemicals                            | Concent. (mg/l) | Chemicals   | Concent. (mg/l) |
|--------------------------------------|-----------------|---|-----------------|
| NH <sub>4</sub> Cl                   | 100–400         | CoCl <sub>2</sub> ·6H <sub>2</sub> O                | 0,0119          |
| Na <sub>2</sub> EDTA                 | 4,83            | Na <sub>2</sub> MoO <sub>4</sub> ·2H <sub>2</sub> O | 0,066           |
| CuSO <sub>4</sub>                    | 0,0046          | MgSO <sub>4</sub> ·7H <sub>2</sub> O                | 36,97           |
| ZnSO <sub>4</sub> ·7H <sub>2</sub> O | 0,023           | NaHCO <sub>3</sub>                                  | 226             |
| CaCl <sub>2</sub> ·2H <sub>2</sub> O | 36,74           | FeCl <sub>3</sub> ·6H <sub>2</sub> O                | 0,316           |
| H <sub>3</sub> BO <sub>3</sub>       | 1,0             | KH <sub>2</sub> PO <sub>4</sub>                     | 1920            |

The initial pH value of feeding wastewater was adjusted to be 7.5, 8.0, 8.5, and 9.0 at the DO concentration of  $1.0 \pm 0.2$  mg/l. The DO concentration affects on the NO<sub>2</sub>-N accumulation and NH<sub>4</sub>-N oxidation was also tested for  $1.0 \pm 0.2$  and  $2.0 \pm 0.2$  mg/l at constant pH value. The NLR was increased gradually by varying the influent NH<sub>4</sub>-N concentration of PNBR.

### 2.3. ANALYTICAL METHODS

The PNBR effluents were collected daily and filtered using 0.45 µm, white, 47 mm radius filters to remove impurities. The concentrations of NH<sub>4</sub>-N, NO<sub>3</sub>-N and NO<sub>2</sub>-N were tested by using analytical kits; NH<sub>4</sub>-N (14752), NO<sub>2</sub>-N (14776) and NO<sub>3</sub>-N (14773) with the Merck photometer (Nova 60 Model). The analysis of samples was carried out at room temperature.

## 3. RESULTS AND DISCUSSION

### 3.1. START-UP PERIOD

The main goal of start-up period was to promote nitrification organisms growth to obtain attachment and biofilm formation onto the filling materials. The PNBR was operated in a batch mode with water recycling. The influent wastewater pH and DO concentrations at the top of PNBR was adjusted to 7.5 and 2.0 mg/l, respectively. The NH<sub>4</sub>-N removal efficiency of 80% achieved during the first two weeks operation. During the start-up periods NO<sub>2</sub>-N was not detected and nitrification was quickly completed to nitrate. After the start-up period, the PNBR was operated in a continuous mode and the NH<sub>4</sub>-N concentration in the influent water was increased gradually.

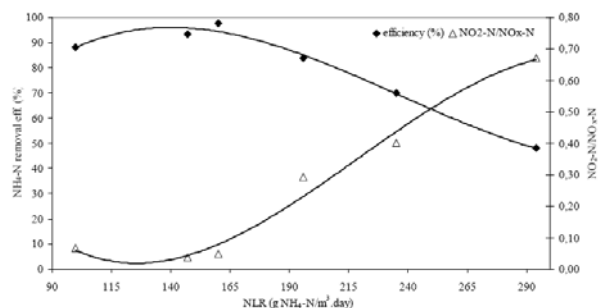
The PNBR was operated at various pH values, DO concentrations, and NLRs to determine optimal operational condition to achieve the highest NO<sub>2</sub>-N/NO<sub>x</sub>-N ratio and NH<sub>4</sub>-N removal efficiency.

### 3.2. THE NLR EFFECTS ON THE NO<sub>2</sub>-N/NO<sub>x</sub>-N RATIO

Variation of the NLR was provided with changing influent NH<sub>4</sub>-N concentrations and flow rate of water between 50–260 mg NH<sub>4</sub>-N/l and 3.3–5.0 l/day

(hydraulic retention time (HRT) was between 12.2 and 18.5 hour), respectively.

The NLR was gradually increased from about 100 to 160 g/m<sup>3</sup>·day by varying the influent NH<sub>4</sub>-N concentration in the feeding wastewater. This change resulted in complete oxidation of NH<sub>4</sub>-N, the NH<sub>4</sub>-N removal efficiency was increased from 88 to about 98% and the NO<sub>2</sub>-N concentration slightly increased to 5.0 mg/l in the effluent water. The lowest NO<sub>2</sub>-N/NO<sub>x</sub>-N ratio was observed when the NLR was up to 160 g/m<sup>3</sup>·day. Further increase the NLR caused partial nitrification and resulted in incomplete oxidation of ammonium and the effluent NH<sub>4</sub>-N and NO<sub>2</sub>-N concentration increased. The NO<sub>2</sub>-N accumulated in effluent water and the NO<sub>2</sub>-N/NO<sub>x</sub>-N ratio was increased to 0.293 at the NLR of 196 g NH<sub>4</sub>-N/m<sup>3</sup>·day. Although the highest NO<sub>2</sub>-N/NO<sub>x</sub>-N ratio of 0.61 was achieved, the NH<sub>4</sub>-N removal efficiency was drastically dropped to 48% at the NLR of 294 g NH<sub>4</sub>-N/m<sup>3</sup>·day (Figure 2). As shown in Figure 2, it was evident that the PNBR was unable to provide high NH<sub>4</sub>-N oxidation when the NLR was higher than 196 g NH<sub>4</sub>-N/m<sup>3</sup>·day under experimental conditions. During the NLR experimental studies, free ammonia (FA) concentrations were between 1.0–3.2 mg/l and the free nitric acid (FNA) (HNO<sub>2</sub>) concentrations were lower than the inhibition level.



**Figure 2.** NO<sub>2</sub>-N/NO<sub>x</sub>-N ratio and removal efficiency variation at different NLR

### 3.3. EFFECTS OF pH VARIATION ON THE NO<sub>2</sub>-N/NO<sub>x</sub>-N RATIO

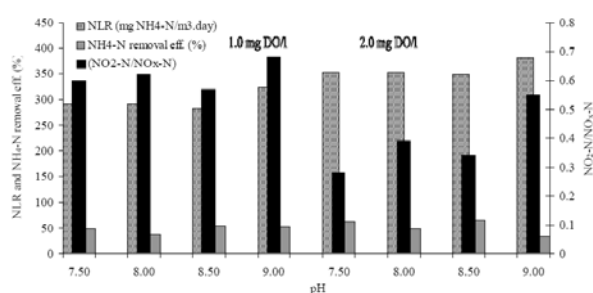
The pH and DO concentration effects on the NO<sub>2</sub>-N accumulation were investigated to achieve the highest NO<sub>2</sub>-N/NO<sub>x</sub>-N ratio under operational conditions. The ammonium-oxidizing bacteria (AOB) and the nitrite oxidizing bacteria (NOB) were inhibited 10–150 mg/l and 0.1–1.0 mg/l of free ammonia (FA), respectively and all nitrifying bacteria were inhibited above 0.2 mg/l of free nitric acid (FNA) (HNO<sub>2</sub>) [9]. The equation 1 and 2 are used for the calculations of FA and (FNA) concentrations [9]. Since the NO<sub>2</sub>-N accumulation is achieved by FA, the feeding solutions of pHs was varying between 7.5 and 9.0 at DO concentrations of 1.0 and 2.0 mg/l, respectively.

$$FA(\text{mg/l}) = \frac{17 \sum NH_4 - N(\text{mg/l}) \cdot 10^{pH}}{14 e^{6344/(273+T)} + 10^{pH}} \quad (1)$$

$$HNO_2(\text{mg/l}) = \frac{47 \sum NO_2 - N(\text{mg/l})}{14 e^{-(2300/273+T)} \cdot 10^{pH}} \quad (2)$$

Effect of operational conditions on the  $NO_2\text{-N}/NO_x\text{-N}$  ratio was presented in the Figure 3. Under the operational conditions, the PNBR was operated at higher NLR for the DO concentration of 2.0 mg/l than 1.0 mg/l. The pH affects the NOB and the  $NO_2\text{-N}/NO_x\text{-N}$  ratio in the effluent water was increased by increasing the pH value to 9.0 in the feeding wastewater for both DO concentrations. The highest  $NO_2\text{-N}/NO_x\text{-N}$  ratio of 0.68 and 0.55 were achieved for the DO concentrations of 1.0 and 2.0 mg/l at the applied NLR for the 325 and 381 g/m<sup>3</sup>·day, respectively. Increasing DO concentration from 1.0 to 2.0 mg/l decreased the  $NO_2\text{-N}$  accumulation and  $NH_4\text{-N}$  removal efficiency.

The results indicated that pH had a clear effect on the NLR and  $NO_2\text{-N}/NO_x\text{-N}$  ratio even at DO concentration as high as 2.0 mg/l. Although the ratio of  $NO_2\text{-N}/NO_x\text{-N}$  was 0.6 at the pH of 7.5, increasing the pH value from 7.5 to 8.0, the removal efficiency was slightly decreased from 48 to 38 % at the NLR of 292  $NH_4\text{-N}/m^3\cdot\text{day}$ . In order to increase the  $NH_4\text{-N}$  removal efficiency, the NLR of 282 g  $NH_4\text{-N}/m^3\cdot\text{day}$  was tested at the pH of 8.5. The  $NH_4\text{-N}$  removal efficiency and  $NO_2\text{-N}$  oxidation increased to 54% and 0.57, respectively. The highest  $NO_2\text{-N}/NO_x\text{-N}$  ratio of 0.68 was achieved at the pH of 9.0 and NLR of 325 g  $NH_4\text{-N}/m^3\cdot\text{day}$ . However, the  $NH_4\text{-N}$  removal efficiency decreased slightly to 52%. Anthonisen et al. (1976) reported that the NOB is more sensitive than the AOB to the FA. The activity of NOB was inhibited at high pH due to the FA concentration increases with increase in pH value.



**Figure 3.** Variations of the  $NO_2\text{-N}/NO_x\text{-N}$  ratio at various DO, pH and NLR

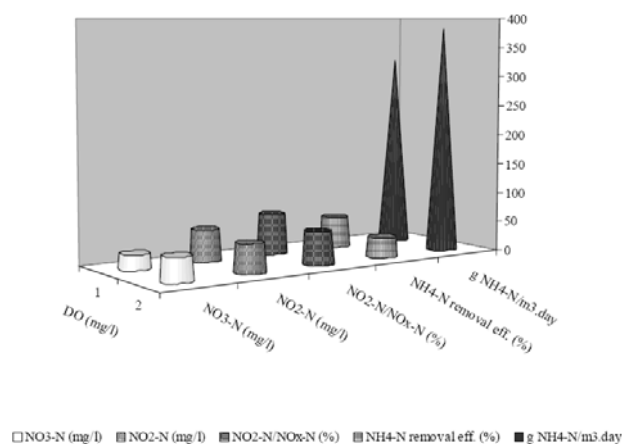
The experimental studies confirmed that  $NO_2\text{-N}$  accumulation could be achieved by regulating pH to control FA concentration. But the threshold inhibition concentrations of FA found in the literature were different [10] and Kim et al [11] reported that the  $NO_2\text{-N}$  accumulation can not be provided for a long time by using only pH for control strategies.

### 3.4. DO CONCENTRATIONS EFFECTS ON THE $NO_2\text{-N}/NO_x\text{-N}$ RATIO

Effects of DO on the  $NO_2\text{-N}$  accumulation were tested for concentrations of 1.0 and 2.0±0.2 mg  $O_2/l$  at constant pH of 9.0. The growth rate of NOB at low DO concentration was lower than the AOB, which will result in  $NO_2\text{-N}$  accumulation [6]. It is known from the Figure 2 that, 48 %  $NH_4\text{-N}$  removal efficiency and 0.67  $NO_2\text{-N}/NO_x\text{-N}$  ratios was obtained at the NLR of 294 g  $NH_4\text{-N}/m^3\cdot\text{day}$ . The biofilter was operated at the NLR of 325 and 381 at the DO concentrations of 1.0 and 2.0 mg/l, respectively (Figure 4). The highest  $NO_2\text{-N}/NO_x\text{-N}$  ratio of 0.68 was achieved at the pH of 9.0 and 1.0 mg  $O_2/l$ . However,  $NH_4\text{-N}$  removal efficiency and the  $NO_2\text{-N}/NO_x\text{-N}$  ratio were drastically dropped to 33% and 0.55 by getting the NLR to 381 g  $NH_4\text{-N}/m^3\cdot\text{day}$ .

Low concentrations of DO, inhibited the NOB and the  $NO_2\text{-N}/NO_x\text{-N}$  ratio was ascending by accumulating the  $NO_2\text{-N}$  concentrations in the effluent water, the previous experimental study carried out at the biofilm system was confirmed this results [1, 12]. The accumulation of  $NO_2\text{-N}$  in the effluent water could be controlled also by varying the biological reaction time by the HRT and NLR.

The previous experimental study indicated that the HRT positively affects the  $NO_2\text{-N}/NO_x\text{-N}$  ratio by decreasing the HRT [13 and 14]. This change resulted in incomplete oxidation of  $NH_4\text{-N}$  and the effluent  $NH_4\text{-N}$  concentration increased. Although, the  $NO_2\text{-N}$  accumulation was greater at the short reaction time compared to longer one, the  $NH_4\text{-N}$  oxidation was limited and the  $NH_4\text{-N}$  concentrations were increased in the effluent water. As a result it could be determined that the HRT and NLR have significant effect on the  $NO_2\text{-N}/NO_x\text{-N}$  ratio in the PNBR. A convenient HRT and NLR should be applied to achieve partial nitrification. Due to the DO half-saturation coefficients of AOB is lower than the NOB, low DO concentration is more restrictive for the growth of NOB than AOB, which will result in nitrite accumulation [15].



**Figure 4.** DO effects on the oxidation of  $NH_4\text{-N}$  and  $NO_2\text{-N}/NO_x\text{-N}$  ratio

## CONCLUSION

The PNBR was operated at various pH, DO, and NLR at constant temperature to determine the highest  $\text{NH}_4\text{-N}$  oxidation and  $\text{NO}_2\text{-N}/\text{NO}_x\text{-N}$  ratio. The AOB grow faster than the NOB at elevated temperatures ( $>15^\circ\text{C}$ ). Although the PNBR was operated at low temperature considering the optimal temperature for the NOB, considerable  $\text{NO}_2\text{-N}$  accumulation was obtained by using submerged biofilter at the temperature of  $25^\circ\text{C}$ . The highest  $\text{NO}_2\text{-N}/\text{NO}_x\text{-N}$  ratios was achieved at the pH and DO concentrations 9.0 and 1.0 mg/l, respectively. However, the PNBR could be operated at high NLR by ascending the DO concentrations to 2.0 mg/l. The effluent water of PNBR can be used for the Anammox processes which needs about 1/1  $\text{NH}_4\text{-N}/\text{NO}_2\text{-N}$  ratio.

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## ECO-FRIENDLY PROCESSES FOR BIODIESEL PRODUCTION FROM NON-EDIBLE OILS

**Abstract:** *At present, edible vegetable oils are most often used feedstocks for industrial biodiesel production. In this paper, the various non-edible oils and usually used processes for biodiesel production are analyzed from the ecological and economic aspects. The aim of the paper is to present the possibilities for improving the biodiesel synthesis by employing the heterogeneous catalysts, the novel catalysts obtained from waste materials and continuous process development, especially taking into account their impact on the environment.*

**Key words:** alcoholysis, biodiesel, non-edible oils.

### INTRODUCTION

The world's oil reserves depletion and environmental concerns increase caused a great demand for alternative sources of oil-based fuels. The most popular alternative energy sources fulfilling sustainability and economic feasibility criterions are biofuels particularly that made from readily available biomass feedstocks [1]. The best fossil diesel substituent is biodiesel, a clean renewable fuel that can be used in a compression ignition engine without or with small modifications. Comparing to fossil diesel, biodiesel is non-explosive, biodegradable, less toxic and with lower exhaust emission of smoke, dust, carbon (II) and (IV) oxides and hydrocarbon. Therefore, biodiesel is considered to be an environmentally friendly fuel [2].

Chemically, biodiesel is a mixture of alkyl esters of low aliphatic alcohols and high fatty acids obtained by the alcoholysis process of biological feedstocks rich in triacylglycerols (TAG). The most used alcohol for biodiesel production is methanol, so biodiesel is usually defined as a mixture of fatty acid methyl esters (FAME). Vegetable oils are the main feedstocks for biodiesel production. In current technologies, more than 95% of biodiesel production feedstocks come from edible vegetable oils such as rapeseed and sunflower seed oil in Europe, soybean oil in USA and palm oil in tropical countries [3]. However, this causes the competition at edible oil market, which increases both the price of edible oils and biodiesel [4]. Furthermore, environmentalists have discussed the negative impact of biodiesel production from edible oil on our planet, especially deforestation and destruction of ecosystem. Expansion of oil crop plantations for biodiesel production on a large scale has already caused deforestation in some countries [5].

In order to overcome these disadvantages, researchers have suggested using alternative oily feedstocks such as non-edible oils, used oils and fats, waste fats, side-stream products of refined edible oil production and algae oils. In this paper non-edible oils as feedstocks for

biodiesel production and the alcoholysis processes for their conversion into biodiesel are analyzed. The aim is to present the advantages and disadvantages of non-edible oil using and the characteristics of commonly used processes for biodiesel synthesis along with a critical review in terms of environmental protection. The special attention is paid to the possibilities for improving the biodiesel production processes by using the heterogeneous catalysts.

### NON-EDIBLE OILS AS FEEDSTOCKS FOR BIODIESEL PRODUCTION

Based on the previously investigation there are a lot of plant feedstocks, which can be exploited for biodiesel production: jatropha, karanja (pinnata), mahua, linseed, rubber seed, cottonseed, neem, tobacco seed, fodder radish, see mango, cardoon, putranjiba, moringa, castor, jojoba, crambe, tung, etc. [6]. Of these feedstocks, jatropha, karanja, mahua and castor oils are most often used in biodiesel synthesis. In terms of ecological and economical requirements, non-edible oil crop cultivation demands must be known. Non-edible oil crops such as jatropha, castor and karanja have unique ecological requirements and botanical features that make it suitable to be cultivated in lands that are unsuitable for food crops. For instance, jatropha plant can grow almost anywhere, even on gravelly, sandy and saline soils and its cultivation is easy, without intensive care and minimal efforts. It has a healthy life cycle of 30–50 years, which eliminates the yearly re-plantation. Castor is another plant that is easily grown and has similar ecological requirements as jatropha. On the other hand, karanja is one of the few nitrogen-fixing trees that produce seeds with significant oil content. It can be cultivated to improve the soil quality, and the exhausted land can be reused for the agricultural purpose in future [5]. The biodiesel fuel characteristics depend on the fatty acid composition of the oily feedstocks. Generally, most of the fuel properties of biodiesel obtained from frequently investigated non-edible oil are within the standard limits [6].

## TRADITIONAL PROCESSES FOR NON-EDIBLE OIL BIODIESEL PRODUCTION

Homogeneously catalyzed vegetable oil methanolysis is the subject of most FAME synthesis researches and is a widely used process for industrial biodiesel production. Homogeneous base catalysts are attractive due to its higher activity in mild reaction conditions and a high FAME yield obtained in a short reaction time. Base catalysts used most frequently are sodium and potassium hydroxides and alkoxides [7]. Acid catalysts are rarely investigated but they are suitable for feedstocks with high free fatty acid (FFA) content.

The type of a catalyst for the biodiesel production from non-edible vegetable oils mostly depends on the FFA content in the oily feedstock which is influenced by the oil source, the type of cultivation and storage mechanism. A wide range of acid value data of non-edible oil has been reported in the literature. For example, for jatropha oil acid value varies from 0.92 mg KOH/g [8] to 28 mg KOH/g [9]. Therefore, researchers suggest a different catalyst type for non-edible oils alcoholysis. As expected, base catalysts are preferable in the case of oil with a lower FFA content. FFAs in the presence of base catalysts form soaps which reduce FAME yield, cause catalyst loss and complicate phase separation. Acid catalysts have low susceptibility to the presence of FFA in the starting feedstock due to their ability to simultaneously catalyze FFA esterification and TAG alcoholysis reactions. On the other hand, the acid catalyzed alcoholysis reaction is slow and long time is required to obtain high FAME yield, so acid catalysts have been rarely applied. Table 1 summarizes the catalyst type and optimal reaction conditions for some homogeneously catalyzed alcoholysis of non-edible oils.

To take advantages of both base and acid catalysts, two-step processes for the biodiesel production from the oils with the high FFA content have been developed. The two-step process, consisting of acid catalyzed FFA esterification and base catalyzed TAG alcoholysis is an effective way to achieve a high biodiesel yield within a short reaction time and at mild reaction conditions comparing to acid catalyzed process. A review of some two-step alcoholysis processes employing different non-edible oils is presented in Table 2.

From an ecological point of view, the use of homogeneous catalysts have many disadvantages. Working problems are related to the catalyst type (potassium and sodium hydroxide) because they are hazardous, caustic and hygroscopic [10]. Additionally, in order to meet the specified product quality the process involved a number of washing and purification steps producing a large amount of wastewater, which is environmentally unfavourable and required appropriate treatment. The high amount of water used in washing and consequent treatment of the resulting effluent increased the overall process cost. For these reasons, homogeneously catalyzed alcoholysis could be

considered as a traditional method for biodiesel synthesis, and alternative methods have been developed.

**Table 1** A review of the homogeneously catalyzed alcoholysis processes using different non-edible oils

| Feedstock    | Alcohol             | Type, volume of reactor, cm <sup>3</sup> /<br>Type of agitator, agitation<br>intensity, rpm | Alcohol:oil molar<br>ratio, mol/mol | Catalyst / loading,<br>%wt to the oil   | Temperature,<br>°C | Yield (Conversion),<br>% / Time, min | Ref. |
|--------------|---------------------|---|-------------------------------------|---|--------------------|--------------------------------------|------|
| Jatropha oil | Methanol            | Batch reactor, - / -, 300   | 9:1                                 | NaOH / 0.8  | 45                 | (96.3) / 30                          | [11] |
| Jatropha oil | Methanol            | Batch reactor, 224 /<br>Mechanical, 900   | 6:1                                 | KOH / 1   | 50                 | 97.1 / 120                           | [12] |
| Jatropha oil | Methanol            | Flask, 1000 / -   | 5.6:1                               | NaOH / 1  | 60                 | 98 / 60                              | [13] |
| Jatropha oil | Methanol            | Flask, 100 / Magnetic, -  | 6:1                                 | KOH / 1   | 45                 | (≈100) / 30                          | [14] |
| Karanja oil  | Methanol            | -   | 10:1                                | KOH / 1   | 60                 | (92) / 90                            | [15] |
| Mahua oil    | Methanol            | Flask, 100 / Magnetic,  | 6:1                                 | KOH / 1   | 45                 | (95) / 180                           | [14] |
| Castor oil   | Ethanol             | Flask, 250 / Magnetic, 600  | 16:1                                | NaOC <sub>2</sub> H <sub>5</sub> / 1  | 30                 | 93.1 / 30                            | [16] |
| Castor oil   | Methanol<br>Ethanol | Batch reactor, 250 / Magnetic, -  | 6:1                                 | KOCH <sub>3</sub> / 0.2 <sup>a</sup><br>NaOCH <sub>3</sub> / 0.2 <sup>a</sup> | 60<br>80           | 85 / 60<br>80 / 360                  | [17] |

<sup>a</sup> - molar ratio catalyst: oil

**Table 2** A review of the two-step (acid/base) homogeneously catalyzed alcoholysis of different non-edible oils

| Feedstock        | Alcohol  | Type, volume of reactor, cm <sup>3</sup> / Type of agitator, rpm | Step <sup>a</sup> | Alcohol:oil molar ratio, mol/mol | Catalyst/ loading, %wt to the oil    | Temperature, °C | Yield (Conversion), % / Time, min | Ref. |
|------------------|----------|--|-------------------|----------------------------------|--------------------------------------|-----------------|-----------------------------------|------|
| Jatropha oil     | Methanol | Flask, - / Magnetic, 1000  | I                 | 6:1                              | H <sub>2</sub> SO <sub>4</sub> / 0.5 | 45              | (93) <sup>b</sup> / 120           | [18] |
|                  |          |  | II                | 9:1                              | KOH / 2                              | 60              | 95 / 120                          |      |
| Jatropha oil     | Methanol | Flask, 1000 / Mechanical, 600                                    | I                 | 8:1                              | H <sub>2</sub> SO <sub>4</sub> / 0.4 | 60              | (92) <sup>b</sup> / 30            | [19] |
|                  |          |  | II                | 6:1                              | KOH / 1                              | 60              | 86.2 / 30                         |      |
| Karanja oil      | Methanol | Flask, - / Magnetic, 1000  | I                 | 6:1                              | H <sub>2</sub> SO <sub>4</sub> / 1   | 50              | (94) <sup>b</sup> / 45            | [20] |
|                  |          |  | II                | 9:1                              | KOH / 0.5                            | 50              | 80 / 30                           |      |
| Tobacco seed oil | Methanol | Flask, - / Magnetic, 400   | I                 | 13:1                             | H <sub>2</sub> SO <sub>4</sub> / 2   | 60              | (97) <sup>b</sup> / 50            | [21] |
|                  |          |  | II                | 6:1                              | KOH / 1                              | 60              | 91 / 30                           |      |

<sup>a</sup> – I- first step: acid pretreatment, II- second step: base-catalyzed alcoholysis; <sup>b</sup> – FFA conversion

## HETEROGENEOUSLY CATALYZED PROCESSES FOR NON-EDIBLE OIL BIODIESEL PRODUCTION

Attempts at improving the biodiesel production process have been ongoing for years. Development of biodiesel production methods has aimed at reducing the biodiesel production cost in environmentally favorable processes. Among them, special attention has been attributed to the heterogeneously catalyzed alcoholysis which is referred as green process. The use of heterogeneous catalysts improves biodiesel synthesis for several reasons. These catalysts can be separated more easily from the reaction mixture, and thus the process does not demand catalyst neutralization in reaction products. Accordingly, the purification of the products is much more simplified and does not require a large amount of water, which makes the process environmentally and economically advantageous. The additional benefit of the solid catalysts using is their easy regeneration and reuse that further make the biodiesel synthesis process cost-effective. The disadvantages of heterogeneously catalyzed processes are the formation of three phases leading to diffusion limitations, thus lowering the reaction rate, and the complex catalyst preparation in some cases.

The catalytic activity of a heterogeneous catalyst depends on its nature, specific surface area, pore size and volume and active site concentration. Their catalytic activity could be improved by catalyst support on the carriers, which provide a higher specific surface area [22] or by applying the appropriate treatment in order to increase the catalyst acidity or basicity [23, 24].

A short review of the catalyst type and reaction conditions applied in heterogeneously catalyzed alcoholysis of non-edible oils is given in Table 3. The type of a heterogeneous catalyst for the biodiesel production from non-edible vegetable oils depends on the FFA content in the oily feedstock. Solid acid catalysts have been more often used in alcoholysis of non-edible oils with the high FFA content because they contain a variety of acid sites with different strength of Bronsted or Lewis acidity. Some researchers also employ the modified catalysts which exhibit dual basic and acidic sites [25] or the mixture of acid and base catalysts [26], which allow oil conversion to biodiesel in a one-step process of simultaneous esterification and alcoholysis. Previous researches of heterogeneously catalyzed alcoholysis of non-edible oils have been aimed at developing a catalyst with a high catalytic activity, which is generally, attributed to the presence of the large amount of strong basic [27, 28], acid [29] or both basic and acid [25] sites.

Several studies deal with the use of heterogeneous catalysts in the two-step (acid-base) process, and they are reviewed in Table 4.

**Table 3** A review of the heterogeneously catalyzed alcoholysis of different non-edible oils

| Feedstock          | Alcohol  | Type, volume of reactor, cm <sup>3</sup> /<br>Type of agitator, agitation<br>intensity, rpm | Alcohol:oil<br>molar ratio,<br>mol/mol | Catalyst / loading, %wt to the<br>oil  | Temperature,<br>°C | Yield<br>(Conversion), % /<br>Time, h | Ref. |
|--------------------|----------|---|--|--|--------------------|---------------------------------------|------|
| Jatropha oil       | Methanol | Round-bottom flask, 50 /  | 55:1                                   | Mg-Zr mixed oxide with<br>Mg/Zr weight ratios of 2:1 / 10  | 65                 | ≈(100) / 0.75                         | [28] |
| Jatropha oil       | Methanol | Flask, 100  | 9:1                                    | CaO / 1.5  | 70                 | (93) / 2.5                            | [24] |
| Cottonseed oil     | Methanol | Autoclave, 250 / Magnetic   | 9:1                                    | SO <sub>4</sub> <sup>2-</sup> /TiO <sub>2</sub> -SiO <sub>2</sub> / 3  | 200                | 92 / 6                                | [30] |
| Castor oil         | Methanol | Round-bottom quartz flask, 250,<br>Microwave / Magnetic, 600                                | 12:1                                   | 55% H <sub>2</sub> SO <sub>4</sub> /C / 5  | 65                 | 94 / 1                                | [31] |
| Rubber seed<br>oil | Methanol | Teflon-lined steel autoclave, 100 /<br>rotating, 50   | 15:1                                   | K <sub>4</sub> Zn <sub>4</sub> [Fe(CN) <sub>6</sub> ] <sub>6</sub> ·6H <sub>2</sub> O·2(tert-<br>BuOH) / 3           | 170                | (97) / 8                              | [29] |
| Jatropha oil       | Methanol | Batch reactor Parr 4842, 300 /<br>Mechanical  | 11:1                                   | Mg <sub>0.7</sub> Zn <sub>1.3</sub> Al <sub>2/3</sub> O <sub>3</sub> / 8.68  | 182                | 94 / 6                                | [25] |
| Jatropha oil       | Methanol | Round-bottom flask / Mechanical,<br>300   | 6:1                                    | CaO+Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ; Li-CaO+<br>Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> / 5 | 60                 | ≈100 / 3                              | [26] |

**Table 4** A review of the two-step (acid/base) heterogeneously catalyzed alcoholysis of different non-edible oils

| Feedstock    | Alcohol  | Type, volume of reactor, cm <sup>3</sup> /<br>Type of agitator, agitation<br>intensity, rpm | Step <sup>a</sup> | Alcohol:oil<br>molar ratio,<br>mol/mol | Catalyst / loading, %wt to the oil                               | Temperature,<br>°C | Yield<br>(Conversion), % /<br>Time, h | Ref. |
|--------------|----------|---|-------------------|--|--|--------------------|---------------------------------------|------|
| Jatropha oil | Methanol | Flask, 1000 / Magnetic, 400   | I<br>II           | 12:1<br>6:1                            | SiO <sub>2</sub> -HF / 10<br>NaOH / 1                            | 60<br>60           | (96) <sup>b</sup> / 2<br>≈99.6 / 2    | [23] |
| Jatropha oil | Methanol | Three-neck flask, 250 / Mechanical<br>Autoclave / Mechanical, 1500                          | I<br>II           | 20:1 <sup>c</sup><br>6:1               | SO <sub>4</sub> <sup>2-</sup> /TiO <sub>2</sub> / 4<br>KOH / 1.3 | 90<br>64           | (≈97) <sup>b</sup> / 2<br>98 / 0.33   | [32] |
| Karanja oil  | Methanol | Round-bottom flask, 1000 /<br>Mechanical, 600   | I<br>II           | 6:1<br>8:1                             | H <sub>2</sub> SO <sub>4</sub> / 1.5 v/v<br>CaO / 2.5            | 65<br>65           | (≈91) <sup>b</sup> / 1<br>95 / 2.5    | [33] |
| Mahua oil    | Methanol | Round-bottom flask, 1000 /<br>Mechanical, 1000  | I<br>II           | 6:1<br>8:1                             | H <sub>2</sub> SO <sub>4</sub> / 1.5 v/v<br>CaO / 2.5            | 55<br>65           | (91) <sup>b</sup> / 1<br>95 / 2.5     | [34] |

<sup>a</sup> - I- first step: acid pretreatment, II- second step: base-catalyzed alcoholysis; <sup>b</sup> - FFA conversion <sup>c</sup> - methanol:FFA molar ratio

Heterogeneous catalysts are used either to catalyze FFA esterification or TGA alcoholysis. According to best authors' knowledge a completely heterogeneous two-step process has not been developed yet.

Generally, heterogeneous catalysts could exhibit high activity but the reactions are slow and time consuming. Therefore, recent researches have been focused towards an ideal heterogeneous catalyst which is low cost, eco-friendly and with high catalytic activity. Such a novel catalyst could be prepared either from biomass or from waste generated in the households. Recently, high efficient catalysts for the methanolysis reaction with CaO as the main component have been obtained from waste egg, oyster, shrimp and lime stone. Using wastes as raw materials for catalyst synthesis could eliminate the wastes and simultaneously produced the catalysts enabling sustainable process development. The use of cheap and efficient catalyst makes the process economic and fully ecologically friendly. For example, CaO obtained from waste chicken eggshells was used as a methanolysis catalyst in the two-step biodiesel production process from karanja [33] and mahua [34] oil. The catalyst preparation involves eggshells washing, drying at 105°C, powdering and finally calcinating at 900°C for 2 h. The FAME yields obtained in those processes were 95%. It is expected that further investigations could be aimed at applications of the high-effective heterogeneous catalysts derived from various natural or waste resources, development of continuous heterogeneous catalyzed processes and optimization on reaction parameters.

The possibility of reusing heterogeneous catalysts is another of its advantages, which enables the continuous process development. Continuous processes facilitate the larger biodiesel productivity and the improvements in the equipment design for the optimization of the biodiesel quality. Additionally, continuous processes could reduce the production cost, making the price of biodiesel competitive with respect to fossil fuels.

The laboratory scale continuous process of heterogeneously catalyzed alcoholysis of non-edible oil was developed by Sreepersanth et al. [29]. The process was conducted in a fixed-bed, down flow reactor with  $K_4Zn_4[Fe(CN)_6] \cdot 6H_2O \cdot 2(tert-BuOH)$  as the catalyst. The unrefined rubber seed oil and *n*-octanol at the alcohol:oil molar ratio 15:1 were fed with the total flow rate 2 ml/h. The obtained rubber seed conversion was 89.2%, and no loss in the catalytic activity was noticed after 52 h [29]. Peng et al. [30] proposed a continuous biodiesel production process from cheap raw feedstocks by solid acid catalysis. The production process was carried out in a sequence of three reactors with the countercurrent flow of vaporized methanol. Using the proposed continuous process, a 10,000 tonnes/year industrial biodiesel demonstration product plant was built [30].

## CONCLUSION

The mostly applied process for the industrial biodiesel production is homogeneously base catalyzed methanolysis of edible oils. Due to the competition at edible oil market and negative environmental impact of large scale edible oil crop plantations, investigations have been focused towards non-edible oils. The non-edible oil crop cultivation is generally easy and with minimal requirements, making them attractive as sources for biodiesel production. The biodiesel production development is directed towards simple, environmentally and economically advantageous processes; among them, heterogeneously catalyzed alcoholysis is the most promising method. Due to simple catalyst separation and reaction products purification heterogeneously catalyzed processes are referred as green processes. Novel high-performance catalysts have been prepared from waste materials allowing their utilization in a useful product. Continuous process technologies based on heterogeneously catalyzed process is expected to get a wider application in the future industrial biodiesel production.

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## EKOLOŠKI NEŠKODLJIVI PROCESI ZA PROIZVODNJU BIODIZELA IZ NEJESTIVIH ULJA

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**Rezime:** *Jestiva biljna ulja predstavljaju danas najčešće korišćene sirovine za industrijsku proizvodnju biodizela. U ovom radu analizirana su ekološkog i sa ekonomskog aspekta različita nejestiva ulja, kao i uobičajeni procesi za proizvodnju biodizela procesi. Cilj rada je da predstavi mogućnosti za unapređenje sinteze biodizela upotrebom heterogenih katalizatora, novih katalizatora dobijenih od otpadnog materijala i da prikaže kontinuirani razvoj procesa, posebno uzimajući u obzir njihov uticaj na životnu sredinu.*

**Ključne reči:** alkoholiza, biodizel, nejestiva ulja.



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## ANALYSIS OF GASEOUS SUBSTANCE TOXICITY ASSESSMENT

**Abstract:** Exposure to pollutants from the air indirectly affects the health risk level for the exposed population. This dependency is manifested through harmful health effects conditioned by the level of exposure and occurring after the interaction between the pollutant and the biological molecules-receptors in the human body. To fully grasp and assess health risk it is necessary to know the relationship and conditionality between toxic substance doses and the occurrence of unwanted biological and health effects. Consequently, this paper focuses on the application of adequate parameters in health risk assessment in the form of physical equations used to quantify the potential dose, the received dose, and the internal dose of pollutants from the air that are inhaled into the body. The paper also provides the assessment of substance toxicity as a function of exposure duration and dose.

**Key words:** potential dose, received dose, internal dose, biologically effective dose, exposure, health risk.

### INTRODUCTION

Toxicity assessment involves determining the chemical and physical effects of agents under certain conditions, which causes pathological changes and unwanted health effects in the exposed individual. Analysis of chemical agent toxicity assessment is performed by determining the quantitative value of the effect the chemical agent has per given uptake concentration – the dose and the occurrence of specific reactions in the exposed individual's body (the dose-response process). In addition to other purposes, this analysis can also be used to determine causality between individuals exposed to airborne pollutants and the occurrence of negative health effects per unit of air quality change.

Scientific study of the negative health effects of pollutants includes a broad spectrum of methods and procedures. In time, the methods used in the study of health effects have become more precise and will continue to evolve. Such progress is the result of improved available research and data processing techniques, as well as of the possibility that the future studies could be more focused on the key remaining issues, which were identified owing to the previous work in the field. The available studies of health effects that are potentially useful as the assessment basis are categorized as epidemiological studies, clinical studies, and animal experimentation studies.

### DOSE-RESPONSE RELATIONSHIP ASSESSMENT

The dose-response relationship assessment is a quantification of hazard in the identification stage of health risk assessment. It determines the relationship between different doses and the occurrence of unwanted health effects in humans (Figure 1). This relationship is determined by the use of experimental

doses on animals and people, with the required prediction of unwanted effects for the people. An extrapolation with two variability categories is performed in the process:

1. Differences between animal species used in experimental studies and humans in terms of species variability and
2. Differences in sensitivity that can be expected among the humans in terms of certain individual subgroups (gender, age, health, etc.).

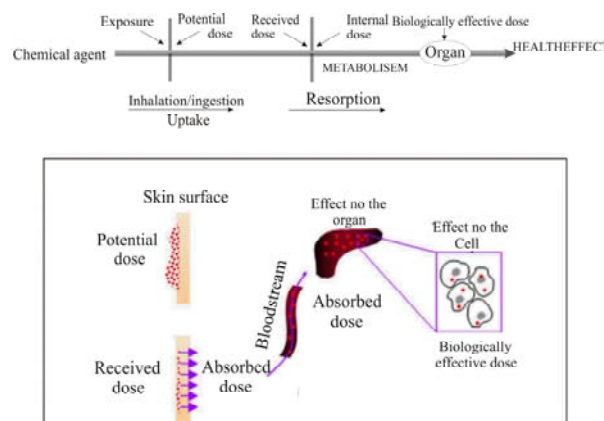


Figure 1. Exposure-dose schematic

It is difficult to determine with complete certainty the relationship between a received dose and the response it causes (response or internal dose) because there are certain absorption barriers inside the exposed individual's body that are inaccessible for direct determination of dose level (Figure 1).

## POTENTIAL DOSE

Received doses can be calculated by approximation, but the focus is on the potential dose when determining the dose-response relationship. The potential dose is the quantity of the inhaled chemical agent inside the body whose effect is considered as separate from the further effect of the agent in the body.

The general equation for potential dose calculation is:

$$D_{pot} = \int_{t_1}^{t_2} C(t) \cdot IR(t) dt \quad (1)$$

where  $D_{pot}$  – potential dose [mg/kg/day],  $IR$  – respiratory rate per unit time [ $m^3/day$ ],  $C(t)$  – exposure agent concentration per unit time [ $m^3/kg/h$ ], and  $t_1$  – exposure duration [h].

Equation (1) can be explicitly expressed as the sum effect of chemical agent  $i$ , which results in known or expected reactions:

$$D_{pot} = \sum_i C_i \cdot IR_i \cdot ED_i \quad (2)$$

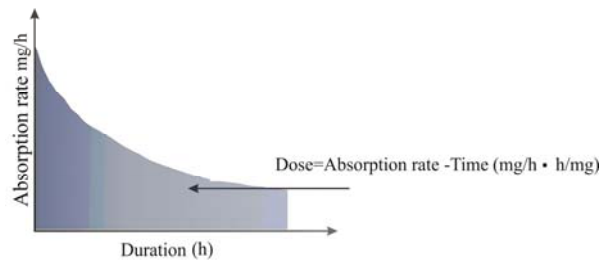
If the exposure duration is short, concentration  $C_i$  and the respiratory rate per unit time  $IR_i$  can be taken as approximately constant values, in which case the following equation is used:

$$D_{pot} = \bar{C} \cdot \bar{IR} \cdot ED \quad (3)$$

where  $ED$  – exposure sum duration for a specific

response to the chemical agent effect,  $\bar{C}$  and  $\bar{IR}$  – arithmetic value of the  $C_i$  and  $IR_i$ . Equation (3) is not considered as valid in case of large oscillatory values of the  $C$  and  $IR$  parameters. In that case, the values of the aforementioned parameters in Eq. (2) are taken as approximate constants. If it is not possible to apply the equations (2) and (3), the potential dose is calculated with the basic form of Eq. (1).

To assess the risk, it is important to know the calculated doses that include the dose-response relationship. The dose-response relationship is often based on the potential dose. Nevertheless, there are other approaches in which the dose-response relationship is based on the internal dose. As previously stated, to determine health risk, it is necessary to know the toxicity of the affecting toxic agent. Unequivocally, chemical agent toxicity primarily depends on the dose intensity. Dose per unit time per unit body weight of the exposed individual is expressed as dose intensity. Dose intensity is not a constant quantity because absorption and resorption of a chemical agent can vary to a bigger or smaller extent in the exposed individuals. Equations (1), (2), and (3) provide the total exposure dose for an individual for a given exposure duration (Figure 2).



**Figure 2.** Relationship between chemical agent absorption per individual body weight over exposure time – dose

## AVERAGE DAILY DOSE

Average Daily Dose (ADD) can be calculated starting with Eq. (1) and taking the average potential dose (average exposure time per individual body weight). Specifically, by using Eq. (3) derived from Eq. (1) and considering the dynamic balance of  $C$  and  $IR$  parameters, one can obtain the Average Daily Potential Dose ( $ADD_{pot}$ ).

$$ADD_{pot} = \frac{[\bar{C} \cdot \bar{IR} \cdot ED]}{[BW \cdot AT]} \quad (4)$$

where  $ADD_{pot}$  – average daily potential dose [mg/kg/day],  $BW$  – body weight of the individual [kg],  $AT$  – time expressed by days over the averaged exposure duration.

Arithmetic values of  $C$  and  $IR$  parameters in Eq. (4) are considered as approximate constants.

In case the exposed individual is afflicted with cancer, the average daily potential dose is calculated by substituting the  $AT$  parameter with the  $LT$  parameter in Eq. (4).

$$ADD_{pot} = \frac{[\bar{C} \cdot \bar{IR} \cdot ED]}{[BW \cdot LT]} \quad (5)$$

where  $LT$  – probability of duration of life.

When assessing the unwanted effects of environmental (or, in this case, atmospheric) chemical agent exposure, it is also necessary to define the received dose. The entire dose inhaled into the body is not subject to tissue absorption. The dose that is absorbed, available for interaction with a biologically determined receptor and subject to further resorption is called the received dose. A portion of the received dose that penetrates the absorption barriers is subject to resorption and is known as the internal dose (Figure 1.). The internal dose influences the chemical agent reaction with a tissue cell and/or bodily fluids causing the actual health effect. A fraction of the internal dose that enables this reaction is called the biologically effective dose.

### Internal dose

If we use the expression for potential dose calculation and substitute  $IR$  with the product of the absorption coefficient ( $K_p$ ) and the specific barrier contact area ( $SA$ ), we obtain the expression that defines the internal dose ( $D_{int}$ ):

$$D_{int} = \int_{t_1}^{t_2} C(t) \cdot K_p \cdot SA(t) dt \quad (6)$$

The rate of chemical agent transport through the barrier is not directly quantifiable, as it depends on several factors, such as the chemical nature of the agent; current physicochemical conditions of transport; chemical properties of the barrier; presence of other chemical agents with which the observed agent is mixed; etc. The relationship between the transport rate and the concentration of the chemical agent is commonly explicitly expressed as the absorption coefficient, which can be determined experimentally. The relationship between the concentration and the absorption coefficient is expressed by Fick's law:

$$J = K_p \cdot C \quad (7)$$

where  $J$  – dynamic balance of the chemical agent's transport rate and its concentration in a given environment,  $K_p$  – absorption coefficient, which is determined experimentally for a given chemical agent and barrier and expressed as the chemical agent mass penetrating the barrier per unit time per unit barrier area [ $\text{mg/s} \cdot \text{cm}^2$ ], and  $C$  – internal dose, which is analogous to the potential dose as defined according to Eq. (3):

$$D_{int} = \bar{C} \cdot K_p \cdot \bar{SA} \cdot ED \quad (8)$$

where  $\bar{SA}$  – the magnitude of average exposure of a specific barrier area.

The internal dose can also be expressed analogously to Eq. (3) for the potential dose, by which the average daily internal dose can be obtained:

$$ADD_{int} = \frac{[\bar{C} \cdot K_p \cdot \bar{SA} \cdot ED]}{[BW \cdot LT]} \quad (9)$$

To calculate the internal doses, it is important to establish a relationship between the potential, the received, and the internal dose. These doses are unidirectionally influenced, so the potential dose influences the received dose and the received dose influences the internal dose. Determination of this inter-relationship is possible only theoretically, based on the knowledge of toxicokinetics of a given chemical agent. The following equations can represent the relationship between the internal and the received dose:

$$D_{int} = D_{app} \int_{t_1}^{t_2} f(t) dt \quad (10)$$

where:  $D_{app}$  – received dose,  $f[t]$  – complex non-linear absorption function expressed as the quotient of the chemical agent's absorbed mass and its received mass per unit time:

$$D_{int} = D_{app} \cdot AF \quad (11)$$

where:  $AF$  – fraction of the absorbed chemical agent expressed as the quotient of the mass of the absorbed chemical agent (fraction mass) per received dose mass.

Combination of equations (1), (2), (3), (10), and (11) can yield the expression that defines the relationship between the doses:

$$D_{int} = D_{app} \cdot AF \cong D_{pot} \cdot AF = \bar{C} \cdot \bar{IR} \cdot ED \cdot AF$$

$$ADD_{int} \cong ADD_{pot} \cdot AF = \frac{[\bar{C} \cdot \bar{IR} \cdot ED \cdot AF]}{[BW \cdot AT]}$$

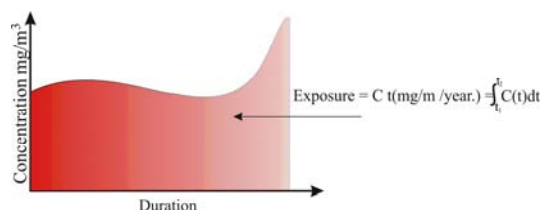
## EXPOSURE ASSESSMENT AND HEALTH RISK ASSESSMENT

Exposure assessment, as a part of health risk assessment, begins after the chemical agent (pollutant), which is regarded as potentially causing unwanted health effects, has been identified.

Exposure assessment is performed by means of a qualitative-quantitative evaluation of the exposure magnitude and a determination of the exposure duration frequency and exposure effects manifestations. The magnitude of exposure is a function of the chemical agent exposure concentration and the time interval of its effect, and it is expressed with the following equation (Figure 3):

$$E = \int_{t_1}^{t_2} C(t) dt \quad (12)$$

where:  $E$  – magnitude of exposure [ $\text{mg/m}^3/\text{duration}$ ];  $C(t)$  – concentration of agent as a function of time [ $\text{mg/m}^3$ ]; and  $t_2 - t_1$  – exposure duration [ED]. ED is a continuous period of exposure (e.g. a day, a week, a year, etc.).



**Figure 3.** Functional dependence of exposure on concentration and effect time

Exposure concentration of the agent  $C(t)$  can be equal to zero during an interval of the exposure time. The total exposure is calculated for a given individual of a designated subgroup, for a specific chemical agent, and

for the corresponding exposure dose for the given period of time.

Exposure assessment is most often based on the reasonable maximum exposure (RME), which is defined as the maximum exposure present in the designated area. RME is assessed for each identified exposure pathway. In case the population becomes exposed to the same chemical agent through different exposure pathways, the RME has to reflect the actual impact of multiple exposure pathways.

Determination of general exposure conditions includes obtaining the general physical-spatial data on the location and the characteristics/habits of the potentially exposed population. General location data include, among other things, the data about the climate, vegetation, and surface and ground waters. The data on the potentially exposed population include the location of residential/occupational zones in relation to the pollution source location, as well as the habits and activities of the threatened population.

Identification of exposure pathways includes determining the ways in which the predefined population subgroups could be exposed to chemical agents. Each identified exposure pathway describes a unique mechanism by which the given subgroup could be exposed to chemical agents within or outside the pollution source location.

Exposure pathways are determined based on the types and locations of pollution sources, the manner of pollutant emission, physicochemical and chemical transformations of pollutants, as well as the living conditions of the observed subgroups in the exposed population.

Exposure quantification includes determination of the size, frequency, and duration of each identified exposure pathway. Exposure quantification is conducted by assessment of concentrations and calculation of toxic agent uptake.

Assessment of concentrations involves determination of concentrations of the identified chemical agents in an environmental medium, to which an individual of a given subgroup is exposed during a certain period of time. Concentration of chemical agents in a given environmental medium is established by use of standardized measuring methods; if measuring is not possible, the adequate mathematical models for concentration prediction can be used.

Uptake calculation involves calculation of the quantity of chemical agent coming into contact with the exposed person's body per unit body weight per unit time (expressed as mg/kg/day), according to the defined uptake pathway:

$$Uptak\ dose = C_{i,x} \left( \frac{IR_y}{BW_y} \right) \left( \frac{ED_i \cdot ET_i \cdot EF_i}{AT_x} \right) [mg/kg/day] \quad (13)$$

where:  $C_{i,x}$  – concentration of pollutant  $x$  in environment  $i$  [mg/m<sup>3</sup>];  $IR_y$  – individual respiratory rate at rest per unit time for a representative individual in subgroup  $y$  in environment  $i$  [m<sup>3</sup>/day];  $ET_i$  –

exposure time of the representative individual in environment  $i$  [days/years];  $BW_y$  – body weight of the representative individual in the observed subgroup, represented as  $y$  [kg];  $ED_i$  – exposure duration for the representative individual in environment  $i$  [year]; and  $AT_x$  – average time of effect duration of pollutant  $x$  [days].

Inhalation rate, distribution, and resorption of the inhaled air pollutant vary according to the features of individuals in a subgroup. Accordingly, the average uptake of air pollutants is assessed through parameters for a representative individual in a subgroup. Exposure in relation to average uptake of airborne pollutant  $x$  and in relation to the representative individual with average anatomical and physiological features in their subgroup, in environment  $i$ , is calculated with the following physical equation:

$$E_{i,x,y} = 0,001 \cdot C_{i,x} \left( \frac{IR_y}{BW_y} \right) \left( \frac{ED_i \cdot ET_i \cdot EF_i}{AT_x} \right) \quad (14)$$

where:  $E_{i,x,y}$  – exposure, or the average uptake of pollutant  $x$  as a function of time, for the representative individual  $y$  in the observed subgroup in environment  $i$  [mg/kg per day].

When assessing the respiratory rate, the following are to be considered: physical properties of the air (temperature, humidity, and pressure), as well as the physiological properties of the representative individual in the subgroup. Equation (14) implies total retention of the pollutant in the exposed individual's respiratory system. This takes into account the probability of harmful health effects due to exposure, and the value of risk in risk assessment includes all the receptors of the exposed individual.

In health risk assessment, exposure is implemented into the equation for the assessment of potential carcinogenic effects and the hazard quotient. The probability of potential carcinogenic effects is quantified with the following equation:

$$ICR_{i,x,y} = E_{i,x,y} \cdot SF_x \quad (15)$$

where:  $ICR_{i,x,y}$  – probability of individual cancer risk for individual  $y$  exposed to pollutant  $x$  in environment  $i$ ,  $SF_x$  – carcinogenic coefficient of pollutant  $x$  [mg/kg/day].

The increased probability of health risk in individual  $y$  exposed to non-carcinogenic pollutant  $x$  in a given subgroup in environment  $i$  can be obtained by calculating the health risk hazard quotient ( $HQ$ ):

$$HQ_{i,x,y} = \frac{E_{i,x,y}}{RfD} \quad (16)$$

where:  $HQ_{i,x,y}$  – health risk hazard quotient for non-carcinogenic substances (dimensionless quantity).

## CONCLUSION

Based on the data presented in the paper, the following conclusions can be drawn:

- In order to quantify the magnitude of health risk, it is necessary to determine the functional dependency of exposure and relevant dose. The relevant dose refers to the internal dose and the biologically effective dose, which are responsible for the harmful health effects. However, the relationship between the potential, the received, the internal, and the biologically effective dose is difficult to establish with complete certainty.
- In practice, exposure is regarded as the uptake dose and is accordingly determined by the adequate physical equation, which is implemented in the quantification of health risk through the determination of the hazard quotient and the probability of risk from carcinogenic diseases.
- Exposure implies contact of individuals (recipients) with pollutants (toxicants) and it is a function of pollutant concentration and their effect duration. If an individual is exposed to the air (exposure medium) of a given location, the concentration of pollutants in that location determines the level of exposure.
- In order to quantify the doses of toxic substances in the best possible manner, it is necessary to consider not only the pollutant properties, exposure duration, and the mean time of agent effects, but also the respiratory rate and the body weight of a representative individual.

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## BIOGRAPHY

**Amelija Đorđević** was born in Niš. She graduated from the Faculty of Science and Mathematics in Niš, Department of Chemistry and received her master and PhD (technical sciences – environmental protection) degrees from the Faculty of Occupational Safety in Niš.



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## ANALIZA PROCENE TOKSIČNOG DEJSTVA GASOVITIH SUPSTANCI

Amelija Đorđević, Lidija Milošević, Marija Rašić

**Rezime:** Ekspozicija ili izloženost zagađujućim supstancama iz vazduha indirektno utiče na stepen zdravstvenog rizika kod eksponirane populacije. Ova zavisnost se ostvaruje preko nepovoljnih zdravstvenih efekata koji su uslovljeni stepenom ekspozicije, a nastaju nakon interakcije zagađujuće supstance sa biološkim molekulima-receptorima u organizmu čoveka. Za potpuno razumevanje i procenu zdravstvenog rizika potrebno je poznavati odnos i uslovljenost doza toksične supstance na pojavu bioloških efekata i pojave neželjenih zdravstvenih efekata. Zbog toga je u radu dat poseban akcenat na primeni odgovarajućih parametara u proceni zdravstvenog rizika u vidu primene fizičkih jednačina koje se koriste za kvantifikovanje potencijalne doze, primljene doze i interne doze zagađujućih supstanci iz vazduha koje se unose inhalacijom u organizam. Takođe u radu je procenjena toksičnost supstanci koja je u funkciji dužine ekspozicije i doze.

**Cljučne reči:** potencijalna doza, primljena doza, interna doza, biološki efektivna doza, ekspozicija, zdravstveni rizik.



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## EXPERIMENTAL TESTING OF TOBACCO SELF-IGNITION TEMPERATURE

**Abstract:** Fires caused by spontaneous ignition represent a serious occupational and environmental hazard. The process of tobacco self-ignition is slow but it results in tobacco combustion that is hard to extinguish, causing loss and other harmful effects. This is what motivated us to conduct research on the causes and mechanisms of this phenomenon. The results obtained depend on the methods and equipment used. This paper describes the procedure to specify specimen temperature versus ambient temperature on the basis of time. The equipment used and the measuring process are also described in the paper. We concluded that the values of self-ignition temperature are not laboratory constants for certain species of tobacco but variables, which primarily depend on the temperature of the working environment. The data we obtained in the experiment was used to train an RBF (Radial Basis Function) network. After training, the RBF network was able to predict self-ignition temperature for some cases of working environment temperatures that were not considered.

**Key words:** self-ignition, experiment, tobacco samples.

### 1. INTRODUCTION

Since recently, the attest of exported or imported products worldwide includes the temperature of self-ignition, as an important characteristic of a product. For safety reasons, this property is of great importance when tobacco is stored, transported, or technologically treated.

Tobacco storage in warehouses has always been a problem because of the fact that spontaneous heating of the mass sometimes occurs in warehouses.

It is well-known that the quality of cigarettes produced from tobacco that had been heated will be far worse than from regular tobacco. Spontaneous heating does not always have to cause self-ignition of tobacco, but can result in poor quality of the tobacco, making it unusable for the manufacture of final products.

The process of spontaneous heating may eventually lead to self-ignition.

Based on literature sources, we can conclude that there are several ways in which the process of spontaneous heating of tobacco may occur while it is stored in a warehouse.

First, it is possible that microorganisms, usually mold, have developed on the tobacco. This process is conditioned by the amount of water content in the system; the greater the water content, the more probable the development of microorganisms. During their development, microorganisms release heat in the tobacco mass and this heat is slowly taken out of the mass and retained in the system, leading to gradual heating of the mass to 60-65°C, when microorganisms die.

The second possibility of a heat-releasing process is oxidation of unsaturated compounds present in tobacco, with oxygen from the air or water from the tobacco.

Spontaneous heating of a mass is a phenomenon in which there is an increase in temperature from within and not from the surrounding.

All processes of self-ignition have the same time diagram. In the initial phase of the process, reactions occur slowly and temperature also increases slowly. The process begins to accelerate when it reaches a certain temperature, and the diagram shows that the temperature change of the mass exceeds the temperature of self-ignition of a material in a system, which leads to smoldering or classical ignition.

The time from the beginning of temperature increase to the temperature level of self-ignition is the induction period, and this is the period when harmful consequences should be prevented. It can last from several hours to several months.

Since the harmful consequences are obvious, the authors propose a methodology and the apparatus for testing the process of tobacco self-ignition.

### Experimental testing of the process of self-ignition of tobacco layers

Literature offers some methods and apparatuses to test self-ignition. The authors designed the experimental apparatus based on analyses of a number of different apparatuses found in literature, ensuring that the working conditions are similar to those in actual warehouses.

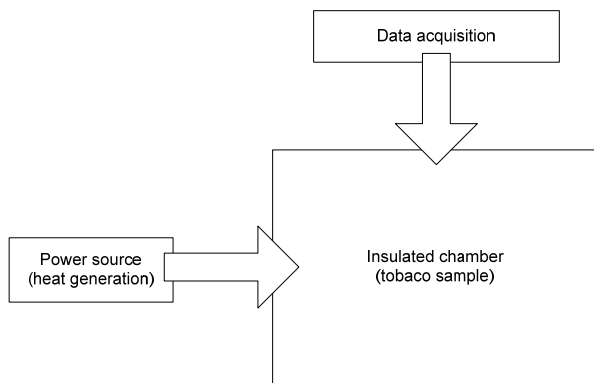
The apparatus is designed to contain a heating chamber with radiation and low convection.



The experimental apparatus consists of:

- the experimental chamber;
- the system for temperature regulation;
- the system for measuring the working environment and sample temperature; and
- the sample holder.

The block diagram of the experimental setup is shown in figure 1.



**Figure 1.** Block diagram of the experimental setup for testing tobacco self-ignition

The main part of experimental setup is the insulated chamber equipped with thermocouples for measuring ambient and sample temperatures, the sample holder, the chamber heater, the insulated chamber door, and the chimney. The external modules are the power source module and the data acquisition module.

The insulated chamber is actually a dryer with a volume of 0.02 m<sup>3</sup>. The chamber has the ability to control the temperature from 100°C to 300°C, which can be maintained constant with an accuracy of  $\pm 1^\circ\text{C}$ . At the top of the dryer there is a 2 cm vent. The sample should be placed at half the height of the chamber space. We used an insulated thermocouple (Chromel/Alumel) to measure the temperature of the sample.

The sample is formed in a cylindrical vessel, with the dimensions  $d=40$  mm, and  $H=50$  mm, made of fine wire mesh, with a diameter smaller than the smallest examined granulation. The container manages the tobacco and tobacco dust that we have to examine ("dry in air"). A sample thus prepared is then exposed to elevated temperature ranges of 100-300°C and the temperature change in the sample is recorded.

The duration of the experiment amounted to 3 hours, since the previously performed experiments showed that it is a sufficiently long period of time to ascertain whether self-ignition can occur in the sample tested at specific conditions, as well as to establish the point of self-ignition.

The main principle of experimental research is the monitoring of the temperature change in a tested tobacco layer sample.

For the experiment, the sample is placed into the experimental chamber, which has already been heated to a certain temperature. The process of heating, the phenomenon of self-heating, and self-ignition are registered by means of thermocouples.

Definitions of self-ignition temperatures vary in literature, but all of them agree on the notion that the temperature of self-ignition is the lowest temperature of experimental material, at which self-heating causes a sudden increase of reaction speed accompanied by a release of heat. This is the temperature of experimental material at which tobacco temperature suddenly increases after a time period called the period of induction. Self-ignition temperature is the lowest temperature in the sample that is high enough to cause self-ignition.

Possible tobacco layer samples affect the shape of the sample holder, which works with layers of different thickness.

In every conducted experiment, the inclination towards self-ignition is determined either by the slow increase in the temperature of the working environment or by placement of the sample in an enclosed heat source for a certain time period.

In this paper, we opted for the latter research method because it is a relatively simple method that yields acceptable results.

In all the existing methods, the temperature of self-ignition is required, but the proposed method indirectly involves the temperature of the working environment, which causes self-ignition after a certain time period. The focus is on this temperature because, under working conditions, it is the only parameter that can be controlled and manipulated easily. We could say that temperature change is one of the possible parameters that are supposed to say whether self-ignition will occur under given conditions.

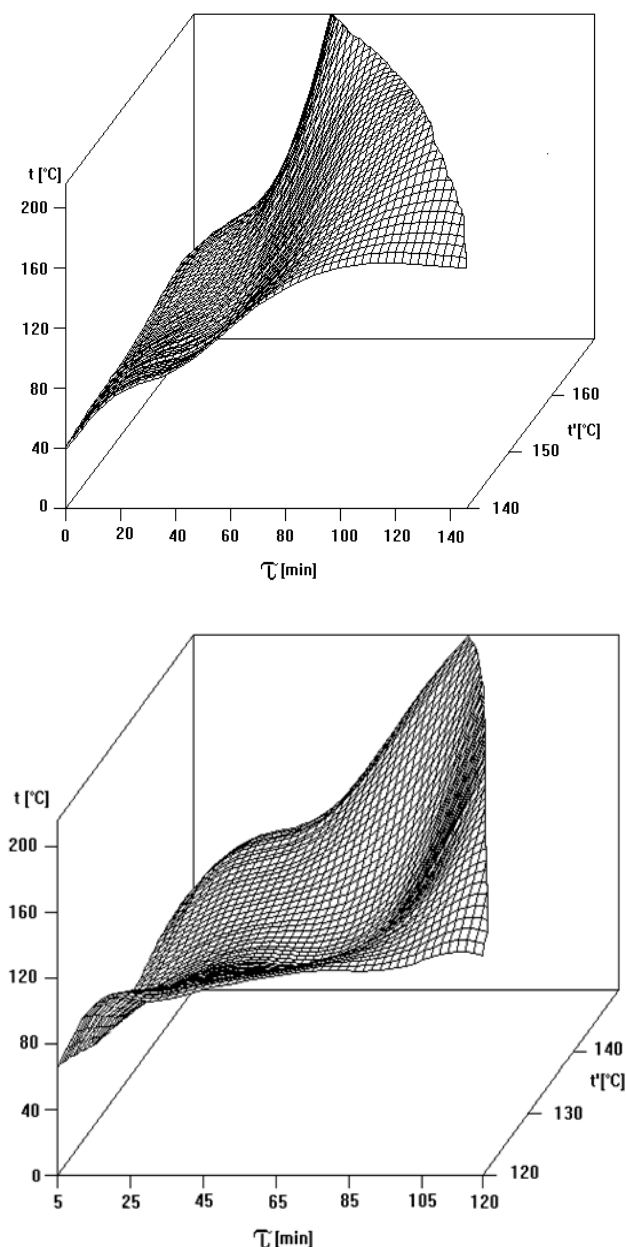
In the analyses performed until today, the following factors influencing self-ignition of tobacco have been registered:

- the system for temperature regulation;
- temperature of the working environment;
- thickness and shape of tested tobacco layer;
- chemical structure of tobacco.

The conducted experimental research yields data on the temperature change of the sample over time for a given temperature of the working environment.

The diagram of temperature change over time is given in figure 2, on the basis of experimental data. The use of neural network in the treatment of experimental data is warranted due to its ability to approximate nonlinear mapping.

Figure 2 represents a three-dimensional diagram with three independent variables:  $\tau$  - time of tobacco sample exposure to the ambient temperature,  $t'$  - ambient temperature, and  $t$  - tobacco sample temperature.



**Figure 2.** Approximation of tobacco samples temperature dependence on ambient temperature over time

In this paper Radial basis function network (RBF network) is applied to functional approximation problem.

Like neural network with sigmoidal nonlinearities, RBF networks have the capability to represent arbitrary function but they can be trained more rapidly [4,5].

The networks we shall discuss have two linear inputs and none linear output unit (in general RBF network can have  $n$  input units and  $p$  output units). The internal units are a single layer of  $m$  receptive fields which can give localized response function in the input space. The overall response function of the network is:

$$f_k(\vec{x}) = \sum_{i=1}^m w_{ki} g_i(\vec{x}), \quad k = 1, \dots, p$$

$$g_i(\vec{x}) = \exp \left( - \sum_{j=1}^n \left( \frac{x_j - m_{ij}}{\sigma_{ij}} \right)^2 \right)$$

Here,  $\vec{x} = [x_1, \dots, x_n]^T$  is real-valued vector in input space,  $g_i$  is  $i$ -th receptive field response function (is gaussian in our case). Parameter  $w_{ki}$  is function value associated with each receptive field;  $m_{ij}$  and  $\sigma_{ij}$  are the center and width of the  $i$ -th receptive field for  $j$ -th input.

The purpose of learning algorithm is to tune the parameters  $w_{ki}$ ,  $m_{ij}$  and  $\sigma_{ij}$ , in order to minimize the quadratic error defined as:

$$E = \frac{1}{2} \sum_{\lambda} \sum_{k=1}^p \left( f_k^{\lambda}(\vec{x}) - f_k^{*,\lambda} \right)^2,$$

where  $\Lambda$  is number of training samples,  $S_p^{\lambda} = (x_1^{\lambda}, \dots, x_n^{\lambda}, f_1^{*,\lambda}, \dots, f_p^{*,\lambda})$  is  $\lambda$ -th training sample ( $x_1^{\lambda}, \dots, x_n^{\lambda}$  is training sample input and  $f_1^{*,\lambda}, \dots, f_p^{*,\lambda}$  is training sample output). In our case training set consist of samples  $(\tau, t'; t)$  where  $\tau$  is time of exposing a coal sample to the ambient temperature,  $t'$  is measured ambient temperature and  $t$  is measured temperature of coal sample.

The Gradient Descent method consists in applying the following formulae:

$$w_{ki}(l+1) = w_{ki}(l) - \eta_w \frac{\partial E}{\partial w_{ki}},$$

$$m_{ij}(l+1) = m_{ij}(l) - \eta_m \frac{\partial E}{\partial m_{ij}},$$

$$\sigma_{ij}(l+1) = \sigma_{ij}(l) - \eta_{\sigma} \frac{\partial E}{\partial \sigma_{ij}(l+1)},$$

where  $\eta_w$ ,  $\eta_m$ ,  $\eta_{\sigma}$  are Gradient Descent speeds.

## CONCLUSION

Since every obtained temperature depends on the layer thickness and the type of sample, it can be concluded that the temperature is not a constant value for certain species of tobacco. Thus, it is possible to determine the tobacco sample temperature dependence on ambient temperature over time from a certain number of usual values that can be used for neural network training. In other words, we can predict the behavior of another (untested) tobacco sample, or layer thickness, or temperature of the working environment.

Using some of the mathematical predictive procedures, such as neural network, it is possible to predict and analyze the process of self-ignition and self-heating of tobacco in temperature periods in which no measuring was done.

The literature uses the definition of self-ignition temperature as the temperature at curve inflection point ( $\tau$ ,  $t$ ), which is a necessary, but insufficient condition for the occurrence of combustion processes. The additional requirement would be as follows: the ignition ensues if the rate of temperature increase is greater than critical [ $^{\circ}\text{C}/\text{min}$ ]. This additional criterion is proposed for the assessment of self-ignition.

While testing self-ignition, we gave special attention to the rate of temperature increase at the moment of passing through the operating ambient temperature  $v = \Delta t / \Delta \tau$  [ $^{\circ}\text{C}/\text{min}$ ]. We discovered that there were occurrences of self-ignition in experiments in which the subject rate, called critical rate, was not under 1.29 [ $^{\circ}\text{C}/\text{min}$ ].

## ACKNOWLEDGEMENTS

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## BIOGRAPHY

**Ljiljana Živković** was born in Vranje, Serbia, in 1949. She received the diploma in mechanical engineering, master and the Ph.D. degree in thermal science from the University of Nis, Faculty of Mechanical Engineering. Her main areas of research include safety engineering in thermal science and energetics, etc. She is currently working as the dean of Faculty of occupational safety in Nis, as well as full professor on several subject related with mentioned scientific areas.



## EXPERIMENTALNO ISPITIVANJE TEMPERATURA SAMOPALJENJA DUVANA

**Ljiljana Živković, Miomir Raos, Jasmina Radosavljević,  
Nenad Živković, Emina Mihjalović**

**Apstrakt:** Požari izazvani spontanom paljenjem predstavljaju ozbiljnu opasnost u radnoj i životnoj sredini. Proces samozapaljenja duvana je u osnovi polagan ali rezultira požarnim stanjem koga je teško ugasiti, pri čemu može doći do žrtava i materijalnih šteta. To je bio razlog što su autori sprovedi istraživanje o uzrocima i mehanizmima ovog fenomena. Dobijeni rezultati zavise od metoda i opreme koja se koristi. Ovaj rad opisuje postupak određivanja temperature uzorka u odnosu na temperaturu okoline u funkciji vremena. Oprema koja se koristi u eksperimentu i postupak merenja su takođe opisani u radu. Zaključak je da vrednosti temperatura samozapaljenja duvana nisu laboratorijske konstante za pojedine vrste duvana, već promenljive veličine koje pre svega zavise od temperature okoline u kojoj se ispitivani uzorak nalazi. Podaci, dobijeni u eksperimentu su korišćeni za obučavanje RBF (Radial Basis Function) neronske mreže. Tako obučena RBF mreža je u stanju da predviđi temperature samozapaljenja duvana I za vrednosti temperature okoline koje nisu uzeti u obzir eksperimentom.

**Ključne reči:** samopaljenje, eksperiment, uzorci duvana.

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## IMPROVING BUILDING ENERGY EFFICIENCY USING DISTRIBUTED ARTIFICIAL INTELLIGENCE

**Abstract:** Saving energy in buildings without losing the comfort of the occupants is contradictory request. It has been shown that the use of smart thermostats to HVAC systems reduce energy consumption as much as thirty percent. Depending on the number of different, pre-defined temperature levels, energy savings might be even greater. The method for determining the coefficient of utilization which is based on a normal time temperature distribution is proposed.

**Key words:** Building energy efficiency, TRIZ matrix, Intelligent agents, Coefficient of utilization.

### INTRODUCTION AND PRELIMINARIES

The coefficient of performance of a thermodynamic system,  $COP$ , is the ratio of the heating or cooling provided over the electrical energy consumed, and is the inverse of thermal efficiency for power cycles,  $\eta$ ,

$$\frac{1}{\eta} = COP = \frac{Q}{W} \quad (1)$$

where  $Q$  is the heat supplied to, or removed from the reservoir and  $W$  is the work done by the system.

A power cycle is the process in which the system performs work on its surrounding, thereby the system acts as a heat engine. Vice versa, all the processes can be reversed, in which case system becomes a refrigeration engine. Obviously, a cycle remains the same, except that the directions of heat transfer and work interactions are reversed. Both are known as Carnot's cycles. Let  $Q_h$  and  $Q_c$  denote the heats of high-temperature and low-temperature reservoir, respectively. Then, according to the first law of thermodynamics, in a reversible system,  $W = Q_h - Q_c$ .

Therefore,

$$COP_h = \frac{Q_h}{W} = \frac{Q_h}{Q_h - Q_c}, \quad COP_c = \frac{Q_c}{W} = \frac{Q_c}{Q_h - Q_c}, \quad (2)$$

holds true.

It can be shown that for a system that works with the theoretical maximum of efficiency (Carnot's efficiency) the following relation is valid

$$\frac{Q_h}{T_h} = \frac{Q_c}{T_c}, \quad (3)$$

where  $T_h$  and  $T_c$  stands for absolute temperatures of hot and cold reservoirs respectively. The expressions for coefficient of performance of a thermodynamic system can be rewritten in the following forms

$$COP_c = \frac{T_c}{T_h - T_c}, \quad COP_h = \frac{T_h}{T_h - T_c}. \quad (4)$$

The  $COP$  of thermodynamic system can be improved by reducing the difference  $T_h - T_c$ . For a heating system, there are just two possibilities to achieve that. The first one is to reduce the output temperature,  $T_h$ , but this solution leads to undesired effects such as subjective thermal discomfort. The second one would be increase of the input temperature,  $T_c$ , which require additional inputs and investments. For the air conditioning system, both temperatures have to be close which is neither possible nor desirable in any case. Therefore, contradictory requests appear in both, heating or cooling modes.

The energy efficiency ratio,  $EER$ , is usually connected to cooling devices and this is the ratio of amount of heat (output energy) to electric energy (input energy).

$$EER = \frac{E_o}{E_i} = \frac{\text{output energy}}{\text{input energy}} \left[ \frac{\text{BTU}}{\text{Wh}} \right] \quad (5)$$

The ratio is expressed with diverse units but they are still in use. The output energy have to be taken in British thermal unit, BTU, ( $1 \text{ BTU} = 1055 \text{ J}$ ) and so,

$$1 \text{ w} = 3.412 \text{ BTU/h} \Rightarrow 1 EER = 3.412 COP. \quad (6)$$

It is more convenient to relate the efficiency of air-conditioners to seasonal energy efficiency ratio,  $SEER$ , which was introduced by Air-Conditioning, Heating and Refrigeration Institute, AHRI. However, the  $SEER$  is a representative measurement of how the system behaves over a season where the outdoor temperature varies.

### TECHNICAL PROBLEM ANALYSIS

The contribution of non-industrial buildings to the total energy consumption is between 20 and 40 percent and tends to increase, [8]. On the other hand, it is well known that conventional energy efficiency technologies, such as thermal insulation and electrochromic windows (smart glass), can be applied to decrease energy use up to 30 percent on average. Conserving energy saves valuable resources and protects the

environment by reducing greenhouse gas emissions. As much as half of the energy used in building goes to heating, ventilating and air conditioning, HVAC. Therefore, a HVAC system has huge impact on energy consumption and comfort. The second largest consumer of energy is the electric light.

This study deals with the elimination of the contradictions that appear in efforts to save energy (and total cost) without making comfort misbalance.

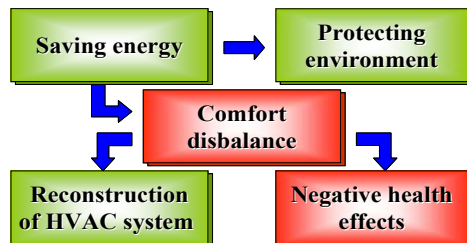


Figure 1. Saving energy without loss of comfort?

The main goal is saving energy that immediately leads to environmental protection through long-term vision such as achieving zero environmental footprints on the global plan. However, saving energy counteracts comfort due to frequent changes in temperature, which consequently produces negative health effects, Fig. 1. The leading question is how to reconcile two opposing uncompromising requests. In other words: how to reconstruct HVAC system that saves energy without worsening of comfort.

## Overcoming technical contradictions

The Theory of Inventive Problem Solving, TIPS, (Russian: ТРИЗ - Теория Решения Изобретательских Задач) is founded on transposition of numerous known solutions from other fields to the field of interest which is not even related to the origin of a problem that has to be solved. In order to obtain an inventive solution, the TRIZ matrix is loaded with knowledge base that is packed in basic technical principles [3]. The analysis of the contradiction is the first step in solving a problem. The second step is search for one or more of the offered principles, which will overcome the contradiction and need for a compromise or trade-off between the opposite requests.

## Technical contradictions

TRIZ matrix contains 39 functions, but only a few are involved in the field of interest, Tab.1. Some of these functions are desired to be improved, and some will be automatically degraded as a result.

In TRIZ terminology these functions are improving and worsening features.

TRIZ Principles for overcoming technical contradictions are obtained at the intersection of rows (Improving feature) and columns (Worsening feature), Tab 2. All technical principles arising from this shift

are not applicable in case of reconstruction of HVAC system.

Table 1. Selected TRIZ functions

| Order | Description                 |
|-------|-----------------------------|
| 17    | Temperature                 |
| 22    | Loss of energy              |
| 25    | Loss of time                |
| 33    | Ease of operation           |
| 35    | Adaptability or versatility |
| 36    | Device complexity           |
| 38    | Extent of automation        |

Table 2. TRIZ Contradiction Matrix

|                   |    | Worsening feature       |                         |                         |                         |
|-------------------|----|-------------------------|-------------------------|-------------------------|-------------------------|
|                   |    | 25                      | 33                      | 36                      | 38                      |
| Improving feature | 17 | 18, 21<br><b>28, 35</b> |                         |                         | 02, 16<br><b>19, 26</b> |
|                   | 22 | <b>07, 10</b><br>19, 32 | 01, 32<br><b>35</b>     | <b>07, 23</b>           |                         |
|                   | 35 | <b>28, 35</b>           | 01, <b>15</b><br>16, 34 | <b>15, 28</b><br>29, 37 | 27, 34<br><b>35</b>     |

Table 3. Adopted TRIZ Principles

| Order | Description           | An idea for resolving contradictions:<br><br>Installation of a thermostat<br>▼<br>Reflex agent<br>▼<br>Learning agent |
|-------|-----------------------|---|
| 07    | Nested doll           |   |
| 10    | Preliminary action    |   |
| 15    | Dynamics              |   |
| 19    | Periodic action       |   |
| 23    | Feedback              |   |
| 28    | Mechanic substitution |   |
| 35    | Parameter change      |   |

In terms of saving energy, adopted TRIZ principles, (Tab. 3), could be described as follows.

*Nested doll* means insertion one control unit into another, e.g. multipurpose detectors.

*Preliminary action* means to perform action before it is needed, e.g. preheating.

*Dynamics* means an optimal operating condition in real time, e.g. not continuous heating/cooling regime i.e. change between the different energy levels.

*Periodic action* means the same as the previous one, e.g. only periodic action can keep up constant temperature.

*Feedback* means improving an action, e.g. sensing room temperature in real time.

*Mechanic substitution* means substitution of mechanical devices with less inertial ones, e.g. microprocessor based thermostats.

*Parameter change* means improving the degree of flexibility, e.g. default temperature value should be variable.

On the basis of the adopted principles for resolving technical contradictions the conclusion is that there is only one way to save energy - Install a smart thermostat, i.e. learning agent.

According to the Environmental Protection Agency, EPA, a smart thermostat can save energy costs up to thirty percent. However, this statement is not documented.

## IMPROVING ENERGY EFFICIENCY

A thermostat is a control element in HVAC systems which sense a temperature of an environment so that a temperature is maintained near setpoint. The sensor technology still changes, from 1883 when the first electric room thermostat was invented until today, but the principle of operation is always the same - two output states: on/off. However, the classic thermostat, which works as reflex automat, is an intelligent agent, IA. In artificial intelligence, AI, intelligent agent is an autonomous system that performs action without immediate presence of humans. IA is capable to carry out tasks on behalf of users, Fig. 2.

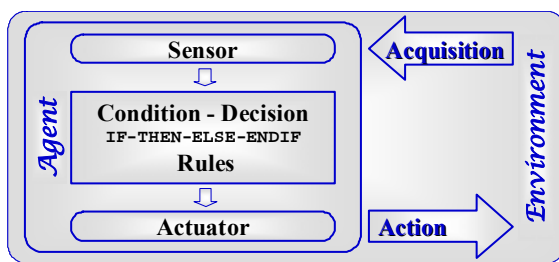


Figure 2. Thermostat - Simple reflex agent

There is a similarity between the computer program and IA. Namely, IA can be described as an abstract functional system. One of the basic problems in the field of designing agent-oriented system is finding an appropriate programming language platform. Various agent-oriented programming languages have been proposed, but no language has become mainstream yet. Hence, for regular thermostat FORTRAN code will be as follows.

```
LOGICAL FUNCTION action(setpoint,temp)
  IF(temp < setpoint) THEN
    action=.true.
  ELSE
    action=.false.
  END IF
END FUNCTION
```

Figure 3. Simple reflex agent - Program

This program is a function that provides transition from acquisition to specific action. In this simple case the setpoint value is unique and specified for heating mode. The same function can be applied for cooling mode

when comparison sign "less than" should be replaced with "greater than". This value has to be compared with perceived (indoor) temperature. The function arguments **setpoint** and **temp** are parameter and independent variable respectively. In this case the action is also simple – activate and deactivate heating or cooling device.

If we define IA as a persistent software entity designed for specific purpose then the term "persistent" will distinguish agents from subroutines. The term "specific" distinguishes agents from variety of multi-functional applications. In essence, IA can be presented by following relationship

$$IA = architecture + program$$

The architecture is some kind of hardware platform such as a simple thermostat or even a computer. The task of AI is to create the program for IA.

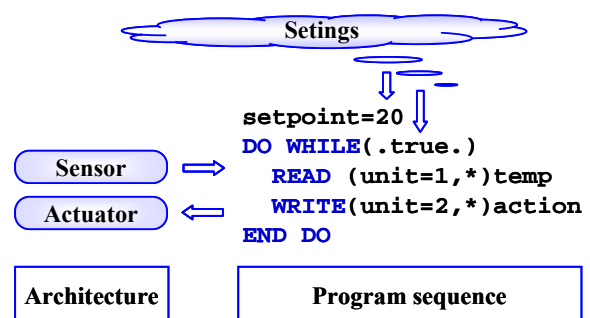


Figure 4. Agent in the environment

Everything that would be necessary to do is calling the proposed function in an infinite time loop, Fig. 4. In real circumstances, it's not an infinite loop. On the very beginning the man turns on a thermostat and adjust the temperature. In the further course of time the thermostat becomes autonomous. Until disconnection, the thermostat **READS** the temperature of the environment, (**unit=1**) calls the function, and if the condition is met, **WRITES** to a particular device (**unit=2**).

Definitely, IA continuously perform three function and those make main difference between IA and a program:

- perceps parameters in the environment,
- cogitates to interpret perceptions,
- acts autonomously to achieve the goal.

## State of the art solution

Basically, each thermostat tends to control and monitor the temperature of the surrounding in order to achieve efficient utilization of energy. To accomplish higher level of energy efficiency and energy optimisation, IA has to be much more than regular thermostat. Furthermore, the perceived intelligence and capability can vary and consequently, since the year 2003, IA are grouped into five categories - Simple reflex agents, Model-based reflex agents, Goal-based agents, Utility-based agents and Learning agents, [6] Concurrently, regular thermostats evolve in two categories.



The first category includes programmable thermostats which control heating and cooling devices to adjust the temperature in accordance with pre-defined values.

One of contemporary solutions is based on even eight temperature setpoint values that define so called energy levels.

- ♦ Energy level *Comfort* is activated if the room is occupied.
- ♦ Energy level *Pre-comfort* is activated for unused room which can be occupied again shortly.
- ♦ Energy level *Economy* is activated for unused room that will only be occupied again in a few hours.
- ♦ Energy level *Protection* is activated in cases of long absence and serves to protect building equipment from damage caused by frost or overheating.

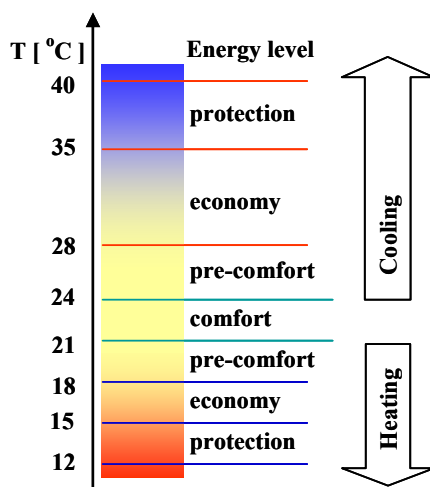


Figure 5. Pre-defined energy levels

The second category comprises smart thermostats which have the same characteristics as previous ones. In addition, the smart thermostats learn about the behavior of the user and reprograms itself according to their habits. Moreover, smart thermostat fine tunes its performance according to ambient temperature, humidity, presence and motion of occupants, etc. Also, smart thermostats use solutions from computer technology and enable control of cooling and heating devices from remote locations. In fact, smart thermostat is a learning agent the concept of which is one of the successful examples of the concept of clean technology. Clean technology assists in building a cleaner environment and contributes in resolving major environmental issues like global warming.

### Necessity of distributed intelligence

Different purposes of rooms and different habits of occupants demands different energy levels and scenarios for temperature regimes. An IA should be installed in every single room. In this case a new problem appears: non-harmonized energy levels and temperature setpoint values in adjacent rooms. There is a necessity that agents communicate and work in

synchronism. In addition, there are many other reasons for introduction of distributed intelligence, DAI, or multiagents system, MAS [2]. Actually, DAI is a predecessor of the MAS which is the system that is composed of coordinated agents including including relationships that exist between them.

Furthermore, the second largest consumer of energy in buildings after HVAC system, is a system of electric lightening. Now, the problem of energy saving and compliance of two subsystems is even more complicated. One IA for one room can be constructed for both subsystems, but IA of this kind is a bottleneck for reliability, maintainability, speed etc. Such an IA would be omnipotent and omniscient, but specialized knowledge is not often available from a single agent. Also, program for single purpose IA is simpler than for multi purpose one. Here, IA can be designed as fine-grained autonomous components of MAS that act in parallel [9]. In the the real time one IA has to know what the other IAs are doing. For example, a presence of occupants that is detected by one IA is the information that has to be forwarded to another IA and it is valid for the both systems (i.e. HVAC and subsystem of electrical lightening). So, MAS can be defined as a network of agents which are loosely coupled.

A special communication protocol and language is needed for this purpose. The Foundation for Intelligent Physical Agents, FIPA, is a body that works on developing and setting standards for computer software for heterogeneous and interacting agents and agent-based systems. Nowadays, two most popular languages are: Knowledge query and manipulation language, KQML, and FIPA's Agent communication language, ACL, although no language is adopted as the leading one, as it is mentioned above. If agents can share knowledge using any agreed language, then the energy saving is expected to occur on all temporal and spatial levels.

In order to ensure proper cooperation of agents in the system they must operate on the following common principles:

- the single IA is at least partially independent,
- no IA has a full global view of the system,
- there is no IA that controls others.

### EXAMPLE AND CONCLUSION

The amount of output energy used during one cooling or heating season is usually calculated as

$$E_o = a \cdot b \cdot c \cdot d, \quad (7)$$

where:

$a$  is a power of HVAC unit in BTU per hour, usually 60000 BTU/h is taken into account as an average value for residential buildings,

$b$  is dimensionless coefficient of utilization, usually the unit runs at two thirds of its capacity,

$c$  is average run time of HVAC unit per day, usually

the unit runs on average eight hours a day during a season. At the end of the season, the unit may run only four hours a day, but at the peak of the season, it is running over 14 hours a day,

$d$  is a number of days in season, typically the season lasts 180 days.

In such a manner,

$$E_o = 60000 \cdot \frac{2}{3} \cdot 8 \cdot 180 = 57.6 \cdot 10^6 \text{ BTU} . \quad (8)$$

In order to calculate the total required electrical energy (input energy)  $SEER$  has to be known. The  $SEER$  tests are done in a laboratory, under conditions that cannot be duplicated on already installed system. In 1992 the minimum  $SEER=10$  was established for units manufactured in the United States. New residential central air conditioner standards went into effect in 2006. Air conditioners manufactured after that year must achieve a  $SEER$  of 13 or higher.

$$E_i = \frac{E_o}{SEER} = 4.43 \text{ MWh} . \quad (9)$$

The calculation like this only gives a very vague and inaccurate idea of what exactly the amount of required electrical energy will be.

Most phenomena in the environment are subject to a normal distribution. Temperature distribution (daily, weekly, monthly) is also subject to the same law. The task of MAS is regulation of temperature that satisfies learned habits of occupants and their needs and save energy at the same time. That can be only possible by avoiding too big temperature difference and by using predefined energy levels. Namely, in a short period, a average person can feel change in temperature of about a 1.5 degree. Respecting these principles, the energy consumption is becoming closer to the normal distribution.

### Introducing the coefficient of utilization

The calculation based on (7) involves empirical data, such as coefficient of utilization and average daily run time of a HVAC system. Bearing in mind the idea of a normal distribution of temperature, the calculation should include the coefficient of utilization which is based on a bell curve,  $f(t, \sigma)$ .

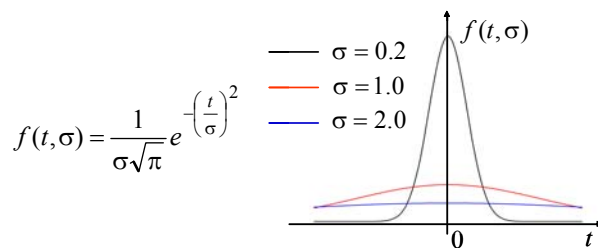


Figure 6. Bell curve  $f(t, \sigma)$

This function is an approximation of Dirac's delta function,  $\delta(t)$ , where  $\sigma$  is stretched factor. The Dirac's

delta function is the limit of sequence of zero-centered normal distributions,

$$\delta(t) = \lim_{\sigma \rightarrow 0} f(t, \sigma) . \quad (10)$$

and the less value of the stretched factor, the better approximation is. Conversely, the HVAC system should be almost equally loaded over time which means that the value of stretched factor should be greater than one.

Coefficient of utilization can be defined now as an integral over run time of HVAC,

$$F(T) = \int_{-T}^T f(t, \sigma) dt = \frac{2}{\sigma\sqrt{\pi}} \int_0^T e^{-\left(\frac{t}{\sigma}\right)^2} dt . \quad (11)$$

The integral above has a value of one for the upper bound tends to infinity, [1],

$$\lim_{T \rightarrow \infty} F(T) = 1 . \quad (12)$$

The efficiency of HVAC systems changes with operating conditions. In real conditions, the value close to one is reached in a finite time. Actual value of the integral, i.e. coefficient of utilization, depends on the exploitation time of the system,  $T$ . Because of the obviousness, the discretized graph of (10) is shown below, Fig. 7.

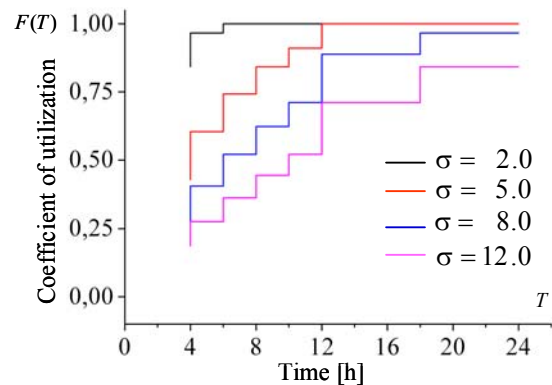


Figure 7.  $F(T)$  - Vertical step discretization

The equation (7) should be rearranged so that a fixed value of  $b$  should be replaced by a functional coefficient,  $F(T)$ .

$$b \sim F(T) \Rightarrow E_o = a \cdot F(T) \cdot c \cdot d \quad (13)$$

In the worst case, the system is active 24 hours, and for sufficiently smooth curve, i.e. small changes in temperature, coefficient of utilization does not exceed two-thirds. Energy saving of around thirty percent was previously mentioned.

Some gaps in the implementation of DAI are still present:

- the choice of the communication language or protocol,
- the ensuring coherence of IA,
- the synthesis of results of IA group.

## APPENDIX

For practical calculation of the coefficient of utilization, the integrand has to be developed in Taylor's series and then integrated. This gives,

$$F(T) = \frac{2}{\sqrt{\pi}} \sum_{n=1}^{\infty} \frac{(-1)^n t^{2n-1}}{(2n-1)(n-1)!} \left(\frac{T}{\sigma}\right)^{2n-1} \quad (14)$$

Because of the factorial function obtained series rapidly converges and for satisfactory accuracy only few first terms have to be taken into account.

## LIST OF ABBREVIATIONS

|             |   |
|-------------|---|
| <b>ACL</b>  | Agent Communication Language                          |
| <b>AHRI</b> | Air Conditioning, Heating and Refrigeration Institute |
| <b>AI</b>   | Artificial Intelligence                               |
| <b>BTU</b>  | British Thermal Unit                                  |
| <b>COP</b>  | Coefficient Of Performance of a thermodynamic system  |
| <b>DAI</b>  | Distributed Artificial Intelligence                   |
| <b>EER</b>  | Energy Efficiency Ratio                               |
| <b>EPA</b>  | Environmental Protection Agency (USA)                 |
| <b>FIPA</b> | Foundation for Intelligent Physical Agents            |
| <b>HVAC</b> | Heating, Ventilating and Air Conditioning             |
| <b>IA</b>   | Intelligent Agent                                     |
| <b>KQML</b> | Knowledge Query and Manipulation Language             |
| <b>MAS</b>  | Multi Agent System                                    |
| <b>SEER</b> | Seasonal Energy Efficiency Ratio                      |
| <b>ТРИЗ</b> | Теория Решения Изобретательских Задач                 |

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## BIOGRAPHY

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## POBOLJŠANJE ENERGETSKE EFIKASNOSTI ZGRADA PRIMENOM DISTRIBUIRANE VEŠTAČKE INTELIGENCIJE

**Milica D. Radić, Dejan M. Petković**

**Apstrakt:** Ušteda energije u zgradama bez gubitka komfora korisnika je kontradiktoran zahtev. Pokazano je da upotreba pametnih termostata u sistemu KGH smanjuje potrošnju energije i do 30 procenata. U zavisnosti od broja različitih, predefinisanih temperaturnih nivoa, ušteda energije može biti i veća. Predložen je metod za određivanje koeficijenta iskorišćenja koji bazira na normalnoj vremenskoj raspodeli temperature.

**Ključne reči:** energetska efikasnost zgrada, TRIZ matrica, Inteligentni agenti, koeficijent iskorišćenja.

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## IMPLEMENTATION OF HEALTH AND SAFETY MANAGEMENT SYSTEM IN AUTOMOTIVE INDUSTRY

**Abstract:** *This work treated the steps for health and safety management implementation, which ensure the increase of responsibility for working environmental with the involvement of employees, customers, governments, capital markets, suppliers.*

*A big step in working environmental increase is systemic approach means using a tool like Healthcare Failure Mode and Effect Analyses (HFMEA), which is a prospective assessment than identify, prevent and improve the process problems before occurring.*

**Key words:** HFMEA, risk, working condition, cause-effect diagram.

### INTRODUCTION

The Failure Modes and Effects Analysis FMEA was use initially for engineering processes in airline and automotive industry.

The main applications were:

- Quality & safety of goods/ services,
- Safety of processes,
- Healthcare application is a recent one.

Systematical analyses of the processes through FMEA have the following benefits:

- Identified the failure mode, effects or results of failures, possible causes of failures,
- Run like an action plan to reduce the failure, which prevent and minimize the possibility of occurrence and minimize the consequence of failures,
- Part of continuous improvement process (CIP),
- Increase effectiveness,
- Increase efficiency,
- Cost avoidance.

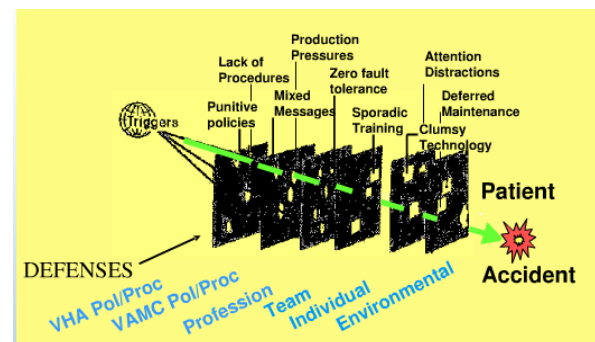
### 1. REASONS MODEL OF THE ACCIDENTS

Before starting analyzing the accidents, it is important to understand the mechanism of these.

The main causes of the accidents come from lack of procedures, systemic approach, leadership and management, resources etc.

The main reasons for accidents and the defenses are presented in figure1 [4].

For defenses implementation is needed the involvement of all organizational chain from customer to supplier and to be aware about the entire governmental and specific healthcare requirement.



**Figure1.** Reasons model of accidents

One of the most complex methods of risk analyses is Healthcare Failure Modes and Effects Analysis (HFMEA).

### 2. THE HEALTHCARE FAILURE MODES AND EFFECTS ANALYSIS APPROACH

The HFMEA is a systematic approached to identify failure modes that could either directly result in, or contribute significantly to, the identified accident scenario by a multi-discipline team familiar with the process and have to follow the next steps:

- Define the topic/ graphically describe a process,
- Establish a multidisciplinary team,
- Analyze the process,
- Identified the risks and strategy for improvement,
- Actions and outcome measures with clear responsible and due date.
- Check and validate the implemented actions,
- Evaluate the effectiveness of implementation.

The champion for action plan implementation has to be the owner of the evaluated area and he is responsible for follow up, until all the actions are closed effective.

The HFMEA is a living document and is working as an action plan.

The failure modes and failure causes are identified initially and are used as the starting point for the FMEA.

Each cause is evaluated for adequate design safety and potential effect on the system. A qualitative risk category is then assigned to each failure cause according to the guidelines given in table 3. This qualitative ranking is determined by considering both the severity and frequency of occurrence.

Critical areas of the process are identified and studied to determine the possibility of a major incident. The management team can then use this information to control the potential risk, and avoid the accident scenario.

The analyses on HFMEA is done base on hazard scoring (HS) which is the multiplication of severity (S) and the probability of occurrence (O) .

$$HS = S * O \quad (1)$$

The evaluation tables for these characteristics are presented in tables 1 and 2 [4].

**Table 1. Severity ranking**

|  |  |
|--|--|
| <b>Catastrophic Event</b><br>(Traditional FMEA Rating of 10 - Failure could cause death or injury)   | <b>Major Event</b><br>(Traditional FMEA Rating of 7 - Failure causes a high degree of customer dissatisfaction.)   |
| <b>Moderate Event</b><br>(Traditional FMEA Rating of "4" – Failure can be overcome with modifications to the process or product, but there is minor performance loss.) | <b>Minor Event</b><br>(Traditional FMEA Rating of "1"– Failure would not be noticeable to the customer and would not affect delivery of the service or product.) |

The probability ranking is described in table 2.

**Table 2. Probability of occurrence ranking**

|   |
|---|
| <b>Frequent</b> - Likely to occur immediately or within a short period (may happen several times in one year) |
| <b>Occasional</b> - Probably will occur (may happen several times in 1 to 2 years)                            |
| <b>Uncommon</b> - Possible to occur (may happen sometime in 2 to 5 years)                                     |
| <b>Remote</b> - Unlikely to occur (may happen sometime in 5 to 30 years)                                      |

Base on characteristics score the hazard scoring matrix is presented in table 3.

**Table 3. Hazard scoring matrix**

| Probability | Severity of effect |    |    |   |
|-------------|--------------------|----|----|---|
|             | Frequent           | 16 | 12 | 8 |
|             | Occasional         | 12 | 9  | 6 |
|             | Uncommon           | 8  | 6  | 4 |
|             | Remote             | 4  | 3  | 2 |

All rates of hazard scoring bigger than 8 must to be immediately treated in problem solving meeting.

The complete evaluation is given by criticality index (CI), which is similar with risk priority number (RPN) and is determined with formula 2:

$$CI = HS * O = S * O * D \quad (2)$$

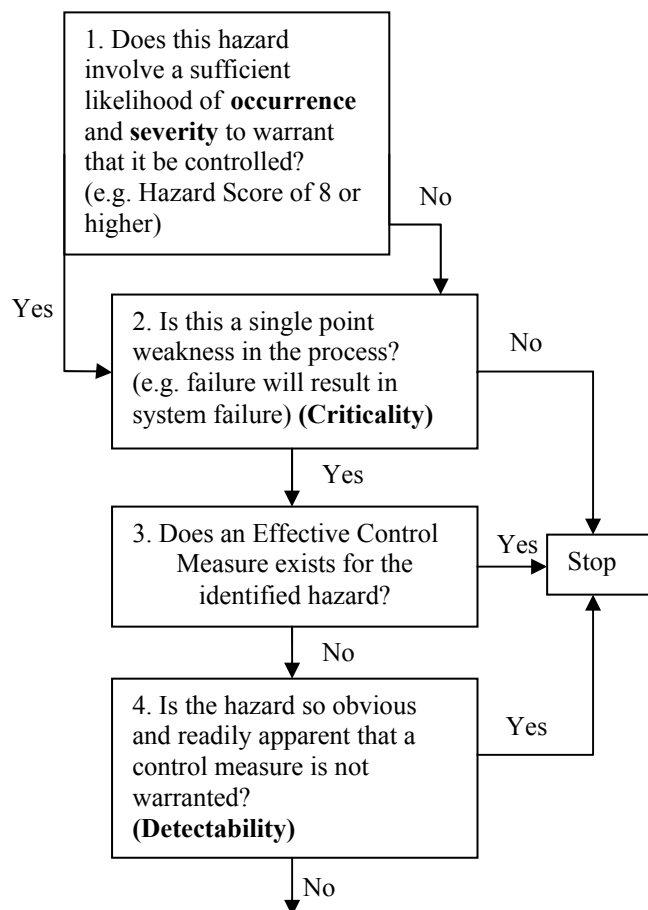
Where:

S = severity of effects rating score

O = frequency of occurrence ranking score

D = probability of detection ranking score.

The tree decision and prioritization flow diagram of the HFMEA is presented in figure 2.



**Figure 2. Tree decision flow**

For kick off the HFMEA session it's used the worksheet presented in fig.3 for purpose and team defining.

During HFMEA session the moderator is guiding the team using the form presented in figure 4.



### Healthcare FMEA Process Steps 1 and 2

**Step 1.** Select the process you want to examine.  
Define the scope (Be specific and include a clear definition of the process or product to be studied).

*This HFMEA™ is focused on* \_\_\_\_\_

**Step 2.** Assemble the Team

HFMEA Number \_\_\_\_\_

Date Started \_\_\_\_\_ Date to be Completed \_\_\_\_\_

Team Members 1. \_\_\_\_\_ 4.

2. \_\_\_\_\_ 5.

3. \_\_\_\_\_ 6.

Team Leader \_\_\_\_\_

Are all affected areas represented? YES NO

Are different levels and types of knowledge represented on the team? YES NO

Who will take minutes and maintain records? \_\_\_\_\_

**Figure 3.** Kick off HFMEA meeting

| HFMEA Subprocess Step Title and Number  |                  |          |             |                   |                        |                            |               |  |  |                                   |                 |                    |                        |
|---|------------------|----------|-------------|-------------------|------------------------|----------------------------|---------------|--|--|-----------------------------------|-----------------|--------------------|------------------------|
| HFMEA Step 3 - Hazard Analysis  |                  |          |             |                   |                        |                            |               | HFMEA Step 4 - Identify Actions and Outcomes |  |                                   |                 |                    |                        |
| Failure Mode: First Evaluate failure mode before determining potential causes | Potential Causes | Scoring  |             |                   | Decision Tree Analysis |                            |               |  | Action Type (Control, Accept, Eliminate) | Actions or Rationale for Stopping | Outcome Measure | Person Responsible | Management Concurrence |
|   |                  | Severity | Probability | Hazard Score (HC) | Single Point Weakness? | Existing Control Measure ? | Detectability | Criticality Index                            |  |                                   |                 |                    |                        |
|   | →                |          |             |                   |                        |                            |               |  |  |                                   |                 |                    |                        |
|   |                  |          |             |                   |                        |                            |               |  |  |                                   |                 |                    |                        |

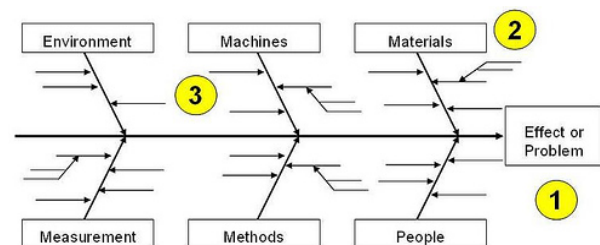
**Figure 4.** HFMEA form

During session it is used the step 3 from the head of figure 4 for decision according to decision flow from fig.2 and step 4 to full in action plan.

After implemented measures counter the criticality index CI (figure 4) is evaluated again by all multidisciplinary team to see if the risk decrease.

To have effectiveness implementation, during HFMEA analyses is important to define the real root causes.

The diagram cause –effect (Ishikawa or fish bon) used by the team can detect all the causes taken in consideration all the process influences according to figure 5.



**Figure 5.** Classical cause –effect diagram



During the analyze it is possible to find out several causes per each bone, which can be more deep analyze in the problem solving meeting using the same diagram according to figure 5.

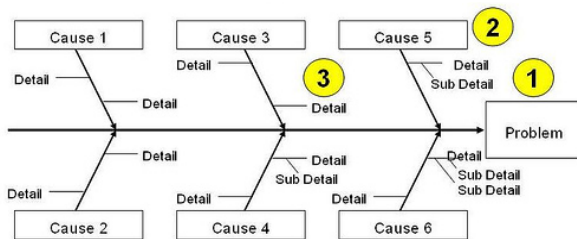


Figure 5. Cause-effect diagram

The HFMEA is treated from design phase until the start of production phase and is continuously updated.

Part of safety management system implementation is the working condition, which means design the right ergonomic workplace to avoid future professional diseases. In production are working different kind of people: man, female, tall, shot, slim, fat etc.

Ergonomics is the study of designing equipment and devices that fit the human body, its movements, and its cognitive abilities.

Ergonomics (or human factors) is the scientific discipline concerned with the understanding of interactions among humans and other elements of a system, and the profession that applies theory, principles, data and methods to design in order to optimize human well-being and overall system performance.

Ergonomics is employed to fulfill the two goals of health and productivity. It is relevant in the design of such things as safe furniture and easy-to-use interfaces to machines. Proper ergonomic design is necessary to prevent repetitive strain injuries, which can develop over time and can lead to long-term disability.

In the next pictures are presented the most often working positions implemented in production area with the right dimension [1]:

- Sitting position is presented in figure 6.

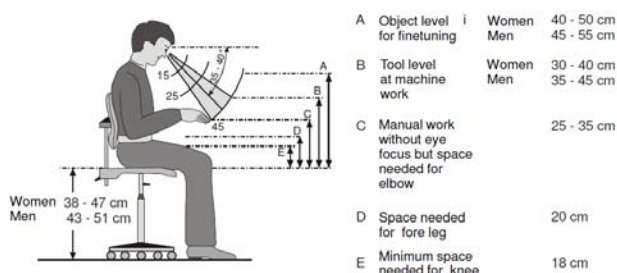


Figure 6. Sitting position dimensions

- Cut through grasping area at the table level is presented in figure 7.

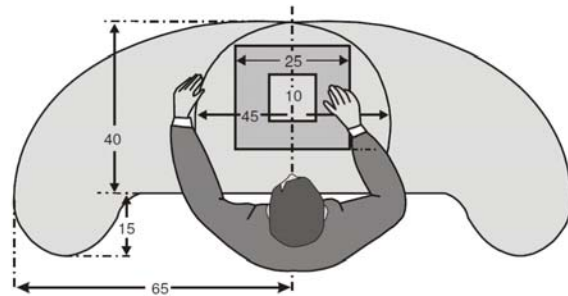


Figure 7. Cut through grasping area at the table level

- Space for leg action is represented in figure 8.

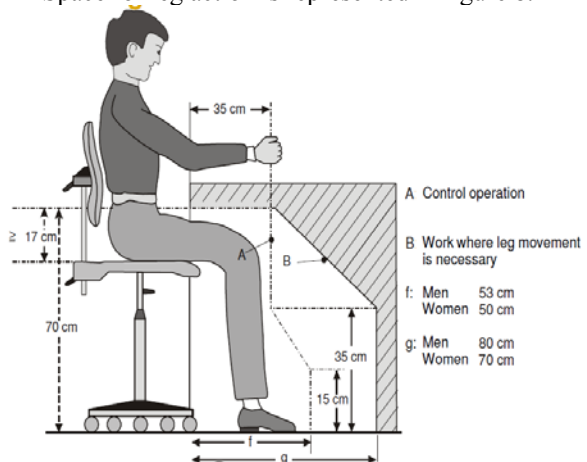


Figure 8. Space length action

- Work level stand up position is presented in fig. 9.

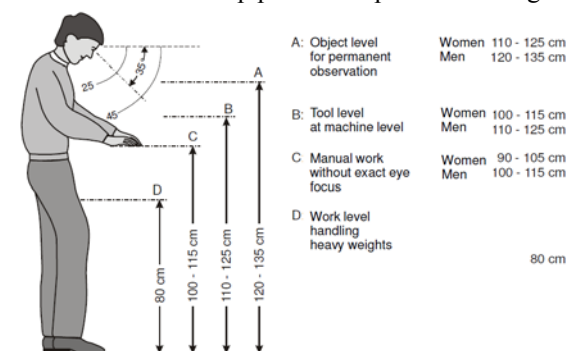


Figure 9. Stand up position work level

- The correct body position – figure 10.

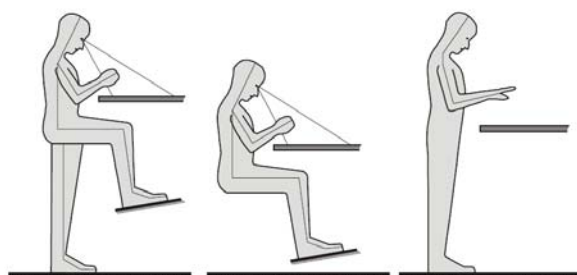


Figure 10. The correct body position

The factors which are important from ergonomics are:

- Force of working,
- Posture of body,
- Frequency of movement.

The ergonomic approach has to be part of healthcare program which have to be done continuous according to the cycle presented in picture 11.



Figure 11. Continuous ergonomic cycle

## CONCLUSION

HFMEA is a systematic method of identifying and preventing injuries before they occur.

It is very important to run HFMEA with a multidisciplinary team to find out the real root causes and to implement efficient the measurements.

Safety and healthcare is a responsibility of all people into the organization and also in the product chain from the customers to the suppliers. The HFMEA have to be kick off from the design phase, so that to take in consideration all the risks and to design the work places in the ergonomic way.

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This work was a guiding line used for cell design of High Frequency Welding.

## BIOGRAPHY

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## PRIMENA SISTEMA UPRAVLJANJA ZA ZDRAV I BEZBEDAN RAD U AUTOMOBILSKOJ INDUSTRIJI

Nicolaie Varzaru, Ion Mitelea

**Rezime:** Ovaj rad se odnosi na redosled koraka pri implementaciji sistema upravljanja za zdrav i bezbedan rad, kojim se obezbeđuje povećanje odgovornosti za radno okruženje, uz učešće zaposlenih, potrošača, vlade, tržišta kapitala i dobavljača. Veliki korak u unapređenju radnog okruženja je sistemski pristup, primenom metode kao što je Zdravstvena analiza načina i efekata otkaza (HFMEA), koja predstavlja alat za anticipaciju i procenu, a kojom se identifikuju, sprečavaju i rešavaju problemi u procesu pre nego što do njih dođe.

**Ključne reči:** HFMEA, rizik, radni uslovi, uzročno-posledični dijagram.

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## REPETITION AS A RISK FACTOR FOR THE DEVELOPMENT OF MUSCULOSKELETAL DISORDERS

**Summary:** *Work-related musculoskeletal disorders (WRMSDs) are becoming a major problem in world economy. There is many and various risk factors that contribute to their development. Repetitive work is one of the most important risk factor. In this paper is described the body's response to repetitive strain, existing methods for evaluation/quantification of repetition as risk factor for musculoskeletal disorders. The author proposes a new multidimensional scale for rating the level of risk of repetitive work, which may be useful in the risk assessment of the workplace.*

**Key words:** ergonomics, work related musculoskeletal disorders, risk assessment.

### INTRODUCTION

The cause of the development of musculoskeletal disorders can be found in the fact that there are many, both professional as well as nonprofessional risk factors. The generally accepted view is that musculoskeletal disorders usually occur after exposure to a combination of risk factors, and the risk increases with increasing exposure. Although there is still no consensus about risk factors themselves, nor about their distribution, generally we can divide risk factors for musculoskeletal disorders to:

- Work risk factors,
- Organizational risk factors,
- Psychosocial risk factors and
- Individual risk factors.

Repetition / repetitive movements are one of the most important risk factors in the group of work risk factors.

Repetition can be defined as cyclical/repetitive work activity that involves repetitive movements of certain body parts. Repetition refers to tasks or series of movements that are executed over and over again with slight variations in the given time. Repetitive work became a hallmark of the industrial revolution, when the management have had the goal to increase production efficiency by eliminating or simplifying workers' movements. Today, this trend continues through the mass use of computers. Physiological problems that result from repetitive work or overuse of certain muscles, tendons and soft tissue are related to muscle fatigue, changes in the density of tissue and tissue exertion, which will be briefly discussed.

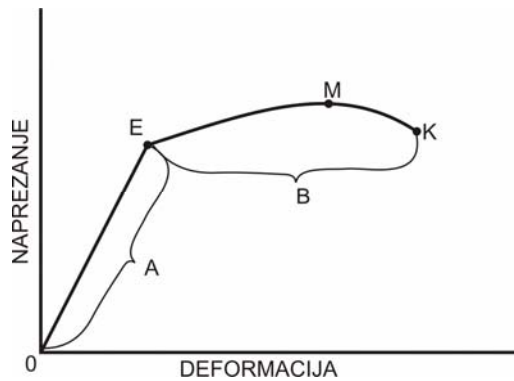
#### 1. Repetition and exertion of the tissues

The exertion of the tissues due to repetitive movements can be explained in relation to the properties of the materials that constitute the tissue. All materials have certain essential characteristics that determine how each material will respond to the external load or force.

Deformations and exertions are terms used to describe changes in the size or shape of the material as a response to the external load.

Material properties determine the extent of deformation. When an external force is applied, elastic materials suddenly warp or change shape, and then just as quickly returned to its original state, when the force is removed. Viscoelastic material is slowly deform when force is applied, and also slowly returns to original shape after removal of the load. The majority of body tissues such as muscles, tendons and ligaments are made of viscoelastic materials (Leveau, 1992)

Relationship between the load (the applied force) and deformation (change in the shape of materials) is described by the Hooke's law, which states that the deformation increases in proportion to the applied load. In other words, the amount of deformation depends on the strength of the external load and the material's ability to resist to the load. For example, steel or bones are very hard materials and are therefore minimally deformed if the external force is acting on them. Wooden twig, on the other hand, is flexes (deforms) under the influence of low intensity force, because itself provides little resistance. Exertion-deformation curve describes the relationship between the total load (y axis) and deformation (x-axis). The curve represents the response of materials to progressively overload. Figure 1 shows that in the early stages of loading, the material returns to its original shape after the load is removed (elastic range). After a certain period of time, the material reaches a certain point where it no longer returns to its original shape (elastic limit) and becomes permanently deformed. After this point, further deformations are occurring even with very small increase in load (plastic range). Maximum durability is presented with the highest point M, and the point of failure is marked with the letter K. To deterioration or material failure may occur due to mechanical fatigue or plastic stretching of material.



**Figure 1.** Exertion-deformation curve

A - elastic range; E - elastic limit; B - plastic range;  
M - maximum durability; K - point of failure

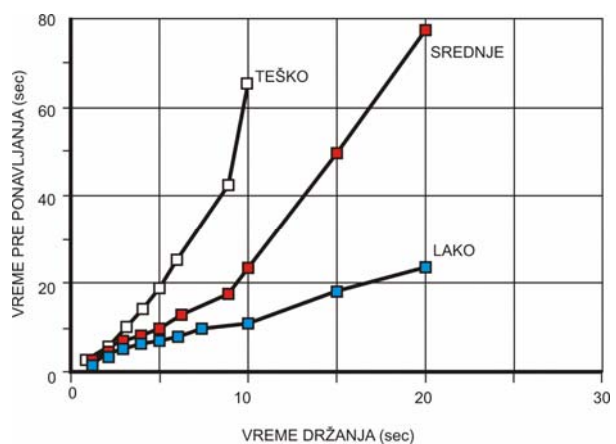
Mechanical fatigue refers to the cyclic load on material against his limit of durability. Plastic stretching of material refers to prolonged or permanent load of material over a maximum limit, which causes an increase of deformation over time.

Although human tissue differs from other material by the ability of self-healing, exertion-deformation model is relevant to the etiology of musculoskeletal disorders associated with repetitive work. External loads applied to the tendons during repetitive work lead to tendons stretching and creating micropitting of the tissue. At the beginning, viscoelastic tendons are recovering and returning to its original length (elastic range). This mechanism allows an employee to work without problems. However, if the external load is applied to the tissue too often or too fast, there is not enough time for full recovery of tissue and the damage to the tendon starts to develop. Over time, the tendon accumulate damage that can weaken, deform (plastic range) or create chronic inflammation. The worker begins to feel pain when performing common tasks. This model may help to explain why is for vulnerable worker harder to cope with repetitive effort, when they return to work after sick leave due to musculoskeletal disorders. For better understand of the relationship between repetitive work and the accumulation of damage in the tissue, Goldstein and his collaborators (1987) are studied the strain in the tendons during repetitive activities of capturing / holding with fingers (similar to pinching) at full load. The researchers exposed the finger flexor tendons to different loads and different work-rest cycles, and then measured the strain accumulated in the tendons. The results showed that work-rest cycles are significantly correlated with exertion in tendon. In the cycle of 2 seconds of work and 9 seconds of rest, there is no change in tendon exertion even after 500 cycles. In the cycle of 8 seconds of work and 2 seconds of rest, the accumulated exertion in the tendon after 500 cycles increased by 80%

Goldstein and colleagues are concluded that the rest time required for tissue repair is the most important indicator of tendon exertion during repetitive work.

## 2. Model of fatigue

It is clear that the duration of rest plays an important role in repetitive work. The concept of the work-rest cycles was presented by Rohmert (1973) and later developed by Rodgers (1987, 1988, 1994) in relation to musculoskeletal disorders in the industry. Rodgers (1987) found that the industry standards for repetitive tasks are based only on the amount of time needed to complete the move, irrespective of the amount of required effort or the time needed for tissue repair. When the worker required to perform physically difficult task as fast as physically easy task, it is clear that he will get tired faster. Rodgers suggested that work cycle in the industry (total time required to complete the task and rest periods from the task) incorporate muscular effort and duration of effort, allowing more recovery time for strenuous physical repetitive work. Rodgers also proposes a model of fatigue, which identifies the interaction between the duration of effort (or time of continuous effort), intensity of effort, the recurrence of certain activities and the overall cycle time.



**Figure 2.** Work-rest cycles for static repetitive work.

Total cycle time (time before repeating, y axis) is a function of the duration of effort (x-axis) and intensity of exertion (shown curves) (Rodgers S., 1987)

Figure 2. showing the duration of exertion (or continuous effort) on the x axis and intensity of exertion (curve) and the total cycle time necessary to perform the task (y-axis). The intensity of exertion corresponded to the percent of MVC (maximal voluntary contraction, the maximum capacity of muscle contraction) of the worker working in a particular position and can be measured as a function of the estimated exertion, and can be easy, moderate and severe exertion, because direct measurements are often not possible.

**Table 1.** *Correlation between the intensity of exertion (expressed as the maximum capacity of muscle contraction, MVC) and the duration of static muscle activity*

| Maximum capacity of muscle contraction (%) | Duration of static muscle or aerobic activity | Duration of aerobic work |
|--|---|--------------------------|
| 100  | 6 s   | 6 min                    |
| 85   | 12 s  | 12 min                   |
| 70   | 20 s  | 20 min                   |
| 50   | 1,0 min                                       | 1 hour                   |
| 40   | 2,5 min                                       | 2 hours                  |
| 33   | 4,0 min                                       | 8 hours                  |
| 15   | 7,5 min                                       | 16 hours                 |

Table 1 shows the relationship between the intensity of exertion for static muscle contraction (% MVC) and the maximum time that muscle group (or person) can be carried out in a static contraction, before fatigue occurs. If the duration of work activities, without adequate rest, exceeds this period of time, cardiovascular and muscular energy decreases, and fatigue develops.

Recovery time can be calculated based on the diagram in Figure 2, subtracting the duration of the effort or time for holding/grasping the objects out of the total cycle time. For example, a task that requires low physical effort, but it is needed to hold/grasp for 10 seconds, will require the cycle time of 12 seconds, allowing 2 seconds for tissue recovery. For the completion of heavy physical task, while holding an object for 10 seconds, length of the cycle time of 65 seconds is required, allowing the muscle recovery period of 55 seconds.

Model of fatigue can be helpful in predicting the occurrence of muscle fatigue, in the evaluation of the physical demands of work, but also in solving problems related to the design of work. For example, using this model can be determined whether the recovery time for a specific effort is sufficient to prevent fatigue or effort should be reduced.

### 3. The link between repetitions and work related musculo-skeletal disorders

So far, scientists have mainly tried to isolate risk factors. However, this is almost impossible, because usually several risk factors are present in the work environment.

Numerous studies have investigated the relationship between repetition and work related musculo-skeletal disorders of the upper limbs, for example, Moore, 1992, Silverstein et al 1987, Osorio et al 1994, Chiang

and colleagues in 1993. Among researchers there is general agreement that it is best to consider repetition as one of exposure factor in association with other risk factors such as force, extreme body position, coldness and rarely with vibration.

Chiang and his colleagues are studied 207 employees in two factories for the production of frozen food. After observing, they divided the tasks into two categories, namely, low repetition of the wrist movements and high repetition of the wrist movements. Tasks are also divided with respect to whether employees are exposed to low temperatures during operation or not. Observed groups of workers were as follows: Group 1 - no coldness, low repetition, group 2 - exposure to coldness or to repetition; Group 3 - exposure to coldness and to high repetition. The existence of carpal tunnel syndrome was present in 3% of group 1, 15% in group 2 and 37% in group 3.

Silverstein and colleagues (1987) have primarily attempted to determine the repetition and force, and later to identify the risk of work related musculo-skeletal disorders from exposure to these risk factors in the workplaces. They examined 652 workers in 39 different jobs, where workers use force and repetition during performing the tasks by hands. All workers were observed, recorded with a video camera, and divided into four groups, based on the exposure to force and to repetition in the workplace. The division into four groups WAs as follows:

1. low intensity force - low repetition,
2. high intensity force - low repetition,
3. low intensity force - high repetition
4. high intensity force - high repetition.

The workers were selected from each of the 39 workplaces, the interviews and medical examinations were conducted, to determine the presence of symptoms associated with work related musculo-skeletal disorders. he results showed that the presence of the work related musculo-skeletal disorders was 5.6% in group 4 "high intensity force-high repetition", and 0.6% in group 1 "low intensity force-low repetition." Group 3 "low intensity force-high repetition" showed a slightly higher risk than group 2 "high intensity force-low repetition", which led to the conclusion that repetition is more important risk factor than force.

Numerous studies have shown that there is a correlation between high repetitive works and the occurrence of work related musculo-skeletal disorders, and also, the association between the occurrence of this disorders and repetition in combination with other risk factors (eg, with high exertions).

If the work tasks or movements repeated frequently (eg, every few seconds) muscles and tendons stress can accumulate, which can lead to permanent tissue damage. The tendons and muscles can often recover from the effects of repetitive stress, if there is enough time to rest between repetitions. Frequent repetition of



certain work activities can also cause effects of unsuitable work postures and intense stress. Table 2 shows examples for the meaning of repetition for different body parts, and the degree of risk, whereby Kilby recommended to define repetition as the cycle time of at least 30 seconds, or when a basic cycle constitutes more than 50% of the whole cycles.

**Table 2.** *Examples of risks associated with repetitive work (Kilby, 1994)*

| Body part       | The number of repetitions per minute | Risk level | Very high risk, if the following is present simultaneously  |
|-----------------|--------------------------------------|------------|---|
| Shoulders       | More than 2,5                        | High       | High external force,<br>High speed,<br>High static effort,<br>Uncomfortable body position,<br>Lack of training,<br>High job demands,<br>Long duration of work |
| Upper arm/elbow | More than 10                         | High       |   |
| Forearm/wrist   | More than 10                         | High       |   |
| Fingers         | More than 200                        | High       |   |

Number of repetitive movements can be reduced or repetition can be eliminated by introducing changes and diversity in the work (by expanding work tasks), shortening the exposure, etc...

#### 4. Assessment / quantification of repetition as a risk factor for work related musculo-skeletal disorders

There are several methods to achieve the desired level of quantification:

- Employee's assessment / ranking
- Expert's assessment / ranking
- Biomechanical analysis, and
- Measuring by instruments

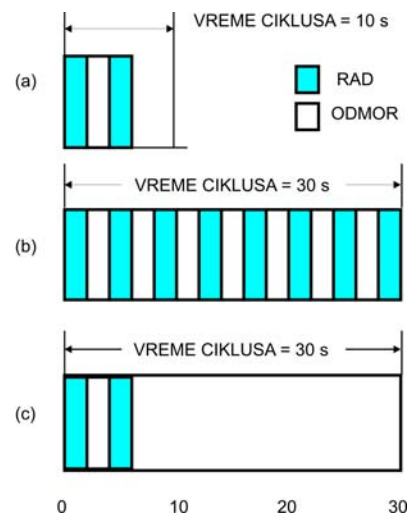
It is generally recognized that **subjective evaluations** are the best way to measure the qualitative data, because they are based on individual impressions and include the evaluation of the subjects that perform specific work, taking into account individual characteristics of the respondents. Robertson and Hendrick (1985) find that the introduction of individual differences is of great importance for obtaining reliable estimate. Other advantages of the method of subjective assessment related to their sensitivity, ease of use, undisturbed performance of basic work tasks and

speed data collection. An example of a linear scale for the subjective assessment is often used Borg's scale (RPE-ratings of perceived exertion) (Borg, 1978).

#### Repeated or continuous static exertion

Ponavljajuće ili trajno statičko naprezanje Repeated or continuous static exertion is related to the time pattern of the applied forces and body positions. Time patterns can affect the mechanical and physiological load of the musculoskeletal system. It is often described using a time of exertion, recovery time, cycle time and frequency of exertion. It is believed that only the data about the time cycles, can lead to erroneous conclusions. Job A (Figure 3) includes one effort of 3 s during the cycle of 10 s. Job B includes six efforts of

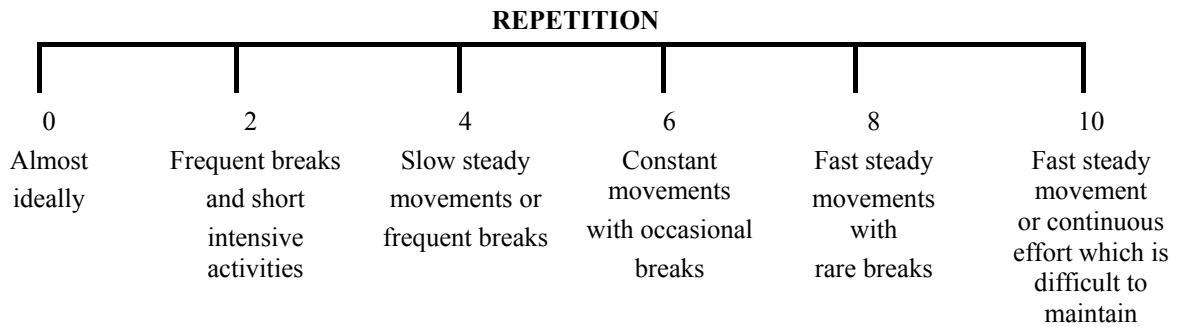
3 s for cycle time of 30 s. If consider only the time of cycle, the impression is that the job B is less stressful of job A, but the incidence of efforts, duration of efforts and recovery time are the same for both jobs. Job C also has a cycle time of 30 seconds, but requires only two efforts of 3 S, because the operator has to wait for the machine to complete its cycle. The operator who performs the job B will pause 40% of the time, while the operator at job C will pause 80% of the time. If everything else is exactly the same, a worker on the job B will be exposed to more stress than the worker on the job C. To be able to calculate the frequency of stress and needed recovery time, it is necessary to know the content of the work.



**Figure 3.** *Activity / repetition of hands for three different jobs*

Repetition can be determined also by observation of work, or by analyzing the video recording of representative work (Latko 1997). Figure 4 shows the scale for evaluation/ranking of repetition.





**Figure 4.** The scale for the risk assessment of the development of work related musculo-skeletal disorders for risk factor REPETITION (Latko et al, 1997)

It would be best if several operators or independent experts ranked a factor or factors, and then, through discussion, to reach consensus. It turned out these estimates are fairly accurate, so, since 2000, the ACGIH (American Conference of Industrial Hygienists) accepted these estimations together with normalized levels of forces, as the basis for the limit values for the monotype work of hands (ACGIH, 2000).

Repetition is measured in several ways. Doctors are mainly focused on the number of similar movements in a given period of time, and engineers are interested in the quantity of work, i.e. time required for completion of the assignment. This would mean that, as the quantity of work is growing, the repetition is growing, too. However, repetition is increased only if all of the movements during performing the tasks involved the same or similar muscle groups. Silverstein and colleagues (1987) have developed a method by which jobs are categorized into two groups, namely low repetitive jobs and high repetitive jobs. This categorization was based on calculated cycle time of the assignment, and on the percentage of time performing the same basic cycle. Cycle time refers to the amount of time required to complete the assignment. Inside the cycle may be a series of steps or movements that are repeated, and these movements or steps are called the basic cycle. According to the method Silverstein and co-workers, jobs are classified as low repetitive, if the cycle time exceeds 30 seconds, and if less than 50% of the cycle time involves performing the same type of basic / primary cycle, i.e. similar movements are repeated less than 50% of the time. Jobs are classified as highly repetitive, if the cycle time is less than 30 seconds, or if more than 50% of the cycle time involves performing the same type of basic cycle.

Different approaches to the measurement of repetition are based on measurement of repetitions, i.e. average number of movements performed in a unit of time, such as the number of movements per shift (Putz-Anderson, 1988), where the number of movements greater than 10,000 and less than 20,000 per work shift falls within the category of high reps. Hammer (1934) measured the repetition as the number of movements per hour

and found that more than 2,000 movements per hour, or 30-40 movements per minute can be considered repetitive work.

Although shown approaches are trying to quantify repetitive work, both consider only the speed at which the worker performs the movement, but not the quality of the movement. Armstrong and Ulin (1995) have recommended a qualitative scale that takes into account the ability of employees to continue with work, so according to them, repetitive work can be divided into:

*Very high:* The body parts of worker are in fast, steady motion; worker has a problem to continue work in same pace.

*High:* The body parts of worker are in constant motion, any difficulty could lead to the delay.

*Moderate:* The body parts of worker are in constant motion, but he is able to continue its work, taking time for a short breaks.

*Low:* There are frequent breaks during work, while waiting on the next job or the machine to complete its cycle.

*Very low:* The worker is idle most of the time, but occasionally uses his hands.

**Instrumental methods** for measuring repetition involve the use of electromyography to record muscle activity of the forearm, and the goniometer to measure the speed and acceleration of the wrist. These methods can examine the duration and frequency of force and motion. There are goniometers which can be fixed to the wrist to provide an electrical signal proportional to the position of the wrist. The signal is recorded in a computer and sums up as a frequency histogram. Position of a particular body part is repeated periodically for the repetitive work, which can be described using a series of sine waves. The velocity and acceleration of the repetitive movement can be presented as the first or second derivative of body part position.

$$\text{Body part position} = \sum \theta_{pi} \sin(2t\pi / T_i + \Phi_i)$$

$$\text{Velocity} = \sum \theta_{pi} (2\pi / T) \cos(2t\pi / T_i + \Phi_i)$$

$$\text{Acceleration} = -\sum \theta_{pi} (2\pi / T)^2 \sin(2t\pi / T_i + \Phi_i)$$

where:

$\theta_{pi}$  - peak amplitudes of movement,

$t$  -time,

$T_i$  – duration of movement,

$\Phi_i$  - phases between repeating movement

The velocity of the repetitive movement is a linear function of frequency and amplitude of motion, while the acceleration is a function of the square of frequency and amplitude. According to Marras and his associates (1993), the risk of work related musculo-skeletal disorders was significantly higher among workers who had average acceleration of the wrist ( during flexion-extension movement) of  $820^\circ / s$ , than in those with a mean acceleration of only  $490^\circ / s$ .

Electromyography and electromechanical goniometers enable the quantitative measurement of efforts and patterns of movement, although it are rarely used as a routine tool for the analysis, except in situations where there is a very defined problem.

## INSTEAD OF A CONCLUSION

Given the complex nature of risk factors, the lack of verified and generally accepted methods of measurement / quantification of some risk factors, as well as limited financial resources to research the causes of musculoskeletal disorders in the workplace in our country, the author advocates the access to a risk assessment based on the development of multidimensional scale for each of the risk factors. Unlike the one-dimensional, multi-dimensional scale can also provide information on the nature of the task, in addition to the usual information about the intensity or degree of difficulty (pain or discomfort).

The criteria for assessing repetition as a risk factor, with numeric and verbal determined levels, are the result of the extensive analysis of various researches and conclusion of the author (Pavlović-Veselinović S., 2008) and are presented in Table 3.

**Table 3.** The proposed multidimensional scale for assessment of REPETITION as a risk factor, for different body parts

| RISK FACTOR       | LEVEL OF RISK                           |  |  |  |  |
|-------------------|---|--|--|--|--|
| REPETITION        | NO RISK<br>0,00-0,20                    | LOW RISK<br>0,21-0,40  | MODERATE RISK<br>0,41-0,60   | HIGH RISK<br>0,61-0,80   | VERY HIGH RISK<br>0,81-1,00  |
| Fingers           | No movement or extremely rare movements | Up to 50 movements per minute  | > 50-150 movement per minute; intensive typing up to a total of 2 hours daily                  | >150-200 movement per minute; intensive typing up to a total of 4 hours daily  | More than 200 movements per minute; intensive typing more than 4h daily  |
| Forearm / wrist   | No movement or extremely rare movements | Up to 5 movements per minute   | 5-10 movements per minute  | More than 10 movements per minute, up to 4h daily  | More than 10 movements per minute, more than 4h daily  |
| Upper arm / elbow | No movement or extremely rare movements | Up to 5 movements per minute   | 5-10 movements per minute  | More than 10 movements per minute, up to 4h daily  | More than 10 movements per minute, more than 4h daily  |
| Shoulder          | No movement or extremely rare movements | 1 movement per minute  | Up to 3 movements per minute   | More than 3 movements per minute, up to 4h daily   | More than 3 movements per minute, more than 4h daily   |
| Knee / ankle      | No movement or extremely rare movements | Rarely kneeling, squatting, climbing / descending a ladder or using the knee as a hammer | Occasionally kneeling, squatting, climbing / descending a ladder or using the knee as a hammer | Often kneeling, squatting, climbing / descending a ladder or using the knee as a hammer more than once per minute, up to 4 hours daily | Often kneeling, squatting, climbing / descending a ladder or using the knee as a hammer more than once per minute, more than 4 hours daily |

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## BIOGRAPHY

**Sonja Pavlovic-Veselinovic, Ph.D.**, was born in Nis, where she graduated at the Faculty of Occupational Safety. She completed master's thesis and doctoral dissertation also at the Faculty of Occupational Safety in Nis, in the field of ergonomics. She is an associate professor at the Faculty of Occupational Safety on the undergraduate, master's and doctoral studies, for the subjects Basic of safety systems, Ergonomics, Ergonomic design, Product ergonomics and Ergonomics of automatised systems. Her main areas of interest in researches are human factors / ergonomics, ergonomic design of work and environment systems, safety and health at work, the work related musculoskeletal disorders, work places risk assessment, especially ergonomic risk assessment. Her work includes more than 40 papers published in international and national conference proceedings as well as in leading national and international scientific journals. Sonja Pavlovic-Veselinovic is the author of the monograph of national importance, called Ergonomic risk. She received The Ronald and Eileen Weiser Center professional development award for 2012, at the University of Michigan.



## PONAVLJANJE KAO FAKTOR RIZIKA ZA NASTANAK MIŠIĆNO-SKELETNIH POREMEĆAJA

**Sonja Pavlović-Veselinović**

**Rezime:** Radom uzrokovani mišićno-skeletni poremećaji su postali veliki problem u privredama širom sveta. Postoje brojni i raznoliki faktori rizika koji doprinose njihovom nastanku. Ponavljanje / ponavljajući pokreti su jedan od najznačajnijih faktora rizika. U radu je prikazan odgovor tela na ponavljajuće naprezanje kao i postojeće metode za procenu / kvantifikaciju ponavljanja kao faktora rizika za nastanak mišićno-skeletnih poremećaja. Predložena je multidimenzionalna skala za rangiranje nivoa rizika od ponavljajućeg rada, koja može biti od koristi pri proceni rizika radnog mesta.

**Ključne reči:** ergonomija, mišićno-skeletni poremećaji uzrokovani radom, procena rizika.

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## FLAMMABLE AND TOXIC MATERIALS WHICH ARE NOT ALLOWED TO GET IN CONTACT WITH WATER - A CALCIUM CARBIDE CASE

**Abstract:** The paper presents materials which in contact with water emit flammable and toxic gases. Their classification according ADR and identification according NFPA 704 standards are presented. The physical-chemical, toxic, flammable and reactive properties of calcium carbide are shown. Also, first aid and fire fighting measures are given. Regular handling of flammable and toxic materials is conditioned by the knowledge of their properties. Regular handling reduces the risk of chemical accident followed by a fire and explosion.

**Key words:** dangerous material, water, toxicity, fire, explosion.

### INTRODUCTION

Production and consumption of hazardous materials is continuously increasing. A large number of organic and inorganic chemical compounds are produced and used in many industries. Many chemical compounds, particularly those in concentrated form, can be dangerous to people. People, who come in contact with chemical substances, often know little or nothing about the hazardous properties of substances and their influence on the human body. This is confirmed by many accidents of dangerous substances, various acute and chronic diseases, disabilities and even deaths. The potential risks of adverse effects of hazardous materials threaten the wider environment.

The world's attention has been focused to potential risks that hazardous materials are carrying. International Programme on Chemical Safety (IPCS) is constantly improving [1]. The main elements of Programme are: evaluation of chemical risks to human health (preparation and publication of chemicals assessments, development of scientific methods for chemicals assessment, evaluating the safety of food components); poisons information, prevention and management; chemicals incidents and emergencies.

Hazardous materials are divided into nine classes on the basis of the specific chemical characteristics which are producing the risk [2]:

- Class 1 - Explosive substances and articles (1.1 - 1.6);
- Class 2 - Gases:  
Class 2.1. - Flammable gas,  
Class 2.2. - Non-flammable, non-toxic gas,  
Class 2.2. - Toxic gas;
- Class 3 - Flammable liquids;
- Class 4 - Flammable solids:  
Class 4.1 - Flammable solids, self reactive substances and solid desensitized explosives,  
Class 4.2 - Substances liable to spontaneous combustion,

Class 4.3 - Substances which, in contact with water, emit flammable gases;

- Class 5 - Oxidising substances:  
Class 5.1 - Oxidizing substances,  
Class 5.2 - Organic peroxides;
- Class 6 - Toxic substances:  
Class 6.1 - Toxic substances,  
Class 6.2 - Infectious substances;
- Class 7 - Radioactive substances;
- Class 8 - Corrosive substances;
- Class 9 - Miscellaneous dangerous substances and articles.

In international classification of hazardous materials there is class of materials which are not allowed to get in touch with water. Solid substances that emit a flammable gas when wet or react violently with water emit flammable gases can form explosive mixture with oxygen from the surrounding air or other oxidizing substances.

All chemicals that react violently with water or in contact with water liberate toxic gas are included in the list of substances covered by the majority of the international legislation on major hazards. The toxicity and the effects of water reactive materials on humans and on the environment are highly variable, depending not only on their properties, but also on the properties of their products on reaction with water or the atmosphere or the substrate. This category includes a large number of chemicals that are used widely in the process industries.

Knowledge of the reactivity of any substance with water is especially important when water is present in the spill area or a fire takes place and firefighters do not wish to make the situation worse by applying water to the flames or chemicals.

### MATERIALS WHICH REACT WITH WATER

There are many water reactive chemicals of significance in major hazards. The main ones have

been categorized as follows: inorganic acid halides (such as  $\text{POX}_3$ ,  $\text{SOX}_2$ ,  $\text{SO}_2\text{X}_2$ ); organic halides (such as  $\text{CH}_3\text{COX}$ ,  $\text{CH}_2\text{COX}$ ); sulphonic acids (such as  $\text{HSO}_3\text{X}$ ); halides of non-metals (mainly phosphorus-halogen, silicon-halogen and boron-halogen compounds such as  $\text{PX}_3$ ,  $\text{PX}_5$ ,  $\text{SX}_2$ ,  $\text{SiX}_4$ ); a number of silanes (such as  $\text{HX}_3\text{Si}$ ,  $\text{CH}_3\text{X}_3\text{Si}$ ); non-metal oxides, such  $\text{SO}_3$  and oleum (mainly sulphur and phosphorus oxides); anhydrous metal halides (such as  $\text{AlX}_3$ ,  $\text{TiX}_4$ ,  $\text{ZrX}_4$ ,  $\text{SnX}_4$ ); radioactive materials (such as  $\text{UF}_6$ ) [3].

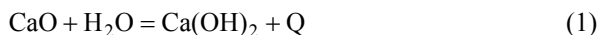
Many materials violently react (burst, explode or ignite) in contact with water. Two categories of these materials exist, as follows:

- Materials which react with water releasing the heat;
- Materials which in contact with water, decompose in flammable gases that are prone to form explosive mixtures with the surrounding air.

Some of the most basic types of exothermic reactions occur when certain materials are dissolved in water.

Such substances have what is called a positive heat of solution. They do not transform to a different material, but simply generate heat while mixing. Some examples are sodium hydroxide (also called caustic soda) and sulfuric acid, which generates considerable heat to the point of causing some degree of "violence" when concentrated or pure materials are spilled into water.

An example is quicklime (calcium oxide -  $\text{CaO}$ ) which exothermically reacts with water while developing a high temperature, as follows:

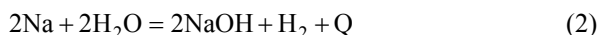


Because of vigorous reaction of quicklime with water, quicklime causes severe irritation when inhaled or placed in contact with moist skin or eyes. Although quicklime is not considered a fire hazard, its reaction with water can release enough heat to ignite combustible materials.

Other materials may ignite, evolve flammable gases, or otherwise react violently when in contact with water.

Materials which in contact with water, decompose in flammable gases that are prone to form explosive mixtures with the surrounding air. This group of materials include alkali metals ( $\text{Na}$ ,  $\text{K}$ ,  $\text{Li}$ ), carbides of calcium and alkali metals, alkali metal chlorides, etc. When these compounds interact with water, they then create flammable gases that are lit at the expense of the heat released during a chemical reaction.

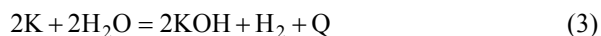
Elementary sodium reacts strongly with water, according to the following reaction mechanism:



A colorless solution is formed, consisting of strongly alkalic sodium hydroxide (caustic soda) and hydrogen gas. Sodium metal is heated and may ignite and burn with a characteristic orange flame. Hydrogen gas released during the burning process reacts strongly with

oxygen in the air. A number of sodium compounds do not react as strongly with water, but are strongly water soluble.

Potassium reacts rapidly and intensely with water, forming a colorless basic potassium hydroxide solution and hydrogen gas, according to the following reaction mechanism:



This is an exothermal reaction and potassium is heated to such an extent that it burns a purple flame. Additionally, hydrogen released during the reaction strongly reacts with oxygen and ignites. Potassium reacts with water more slowly than rubidium, but it reacts with water more rapidly than sodium.

## CLASSIFICATION OF MATERIALS WHICH IN CONTACT WITH WATER EMIT FLAMMABLE AND TOXIC GASES

Given the fact that there are many hazardous materials, their classification has been made in the world. The classification was done according to analogous properties of hazardous materials which enable the use of identical protection measures when handling certain classes.

According to ADR [2], materials which in contact with water emit flammable and toxic gases are classified into class 4.3. of dangerous substances. Those substances are classified, as follows:

- **W** - substances which, in contact with water, emit flammable gases, without subsidiary risk, and articles containing such substances:  
W1 - liquid,  
W2 - solid,  
W3 - articles;
- **WF1** - substances which, in contact with water, emit flammable gases, liquid, flammable;
- **WF1** - substances which, in contact with water, emit flammable gases, solid, flammable;
- **WS** - substances which, in contact with water, emit flammable gases, solid, self-heating;
- **WO** - substances which, in contact with water, emit flammable gases, oxidizing, solid;
- **WT** - substances which, in contact with water, emit flammable gases, toxic:  
WT1 - liquid,  
WT2 - solid;
- **WC** - substances which, in contact with water, emit flammable gases, corrosive:  
WC1 - liquid,  
WC2 - solid;
- **WFC** - substances which, in contact with water, emit flammable gases, flammable, corrosive.

## IDENTIFICATION OF WATER REACTIVE MATERIALS

Water reactive chemicals are generally aggressive materials with complicated properties. The hazardous nature of these substances is recognized in various items of legislation relating to industrial safety. Under the Seveso II EU Directive, all substances that attract the risk phrases R14 "reacts violently with water" (including R14/15 "reacts violently with water liberating highly flammable gases") or R29 "in contact with water, liberates toxic gas" are described as major hazards and are included in the list of chemicals [4].

According to ADR, UN hazard warning diamond of materials which react with water is shown in Figure 1 [2].



Figure 1. UN hazard warning diamond

NFPA 704 [5] presents a system to simplify determining the degree of health, flammability and instability hazards of chemical materials. The objectives of the system are: to provide an appropriate signal or alert and on-the-spot information to safeguard the lives of emergency response personnel (e.g., fire fighters, HAZMAT responders); to assist in planning effective fire and emergency control operations, including clean up; to assist all designated personnel, engineers, plant and safety personnel in evaluating hazards.

The NFPA 704 ratings are displayed in markings that are commonly referred to as the NFPA hazard diamond (Figure 2).

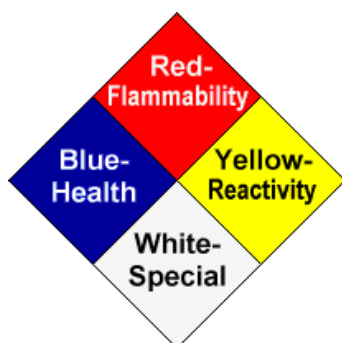


Figure 2. NFPA hazard diamond

The hazard diamond comprises four sections. Each section of the diamond contains a number from 0 (minimal hazard) to 4 (severe hazard) that indicates the relative degree of risk presented by the material.

The red section indicates flammability, or the susceptibility of a material to burning:

- A "0" rating indicates a non-combustible material, or a material that will not burn, such as water;
- A "1" rating indicates that a material must be pre-heated before it will ignite. The flash point or the lowest temperature at which a liquid produces sufficient vapor to form an ignitable mixture with air near the liquid's surface, of a liquid rated "1" is over 93°C;
- A "2" rating indicates that the material must be heated or exposed to relatively high ambient temperature before it will ignite. The flash point of a liquid rated "2" is between 38°C and 93°C;
- A material rated "3" is a liquid or solid that can ignite regardless of ambient temperature. The flash point of a liquid or solid rated "3" is between 23°C and 38°C;
- A material rated "4" is a material that will vaporize at normal temperatures and atmospheric pressure or that will readily disperse in air and burn easily. The flash point of a material rated "4" is below 23°C.

The blue section conveys information on health hazards to people exposed to the material:

- A "0" rating indicates no hazard other than that of a combustible material, such as peanut or vegetable oil;
- A "1" rating indicates potential irritation or minor injury if not treated;
- A "2" indicates temporary incapacity or potential injury. Exposure requires medical treatment;
- A "3" rating indicates that serious temporary or residual injury may occur even with medical treatment;
- A material rated "4" may cause death or major residual injury even with medical treatment.

The yellow section indicates chemical reactivity or stability:

- A material rated "0" is normally stable even when exposed to fire and does not react with water;
- A material rated "1" is normally stable but becomes unstable at high temperature and pressure and will react with water;
- A material rated "2" is normally unstable, will explode when mixed with water, or will undergo violent chemical reactions under elevated temperature and pressure, but will not detonate;
- A material rated "3" may detonate or explode when exposed to an initiating force or when heated, and reacts explosively with water;
- A material rated "4" detonates or explodes readily at normal temperature and pressure.



The white section indicates required protective equipment and other special considerations:

- "W" denotes materials that react with water;
- "OX" denotes materials with oxidizing properties.

These materials may decompose to yield oxygen and may cause fire when exposed to combustible materials.

## A CALCIUM CARBIDE CASE

Pure calcium carbide is a colorless solid with a characteristic garlic-like odour. The pure material is colorless, but most samples have a color ranging from black to grayish-white. Its main use industrially is in the production of acetylene and calcium cyanamid [6].

### Physical and chemical properties

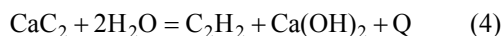
The most important physical and chemical properties of calcium carbide are shown in Table 1.

**Table 1.** Properties of calcium carbide

| Property                 | Value                     |
|--------------------------|---------------------------|
| Chemical formula         | CaC <sub>2</sub>          |
| Molecular weight         | 64.1 (g/mol)              |
| Melting point            | 1700÷2300 (°C)            |
| Density                  | 2.22 (g/cm <sup>3</sup> ) |
| Vapour density (air = 1) | 2.2                       |

### Chemical dangers

Calcium carbide decomposes violently on contact with moisture and water producing highly flammable and explosive acetylene gas and corrosive calcium hydroxide solution, as follows:



Even very small amounts of water will react with calcium carbide developing sufficient heat to make the acetylene gas ignite spontaneously. Simultaneously, very small amounts of poisonous phosphine and hydrogen sulphide gas are set free.

Calcium carbide is a reducing agent. It may react vigorously with oxidizing materials. The powdered mixture of the acetylide and iron oxide and iron chloride burns violently upon ignition, producing molten iron. Calcium carbide incandesces with chlorine, bromine, or iodine at 245, 350, or 305°C, respectively. The carbide burns incandescently when mixed and heated with lead difluoride, magnesium, hydrogen chloride, and tin (II) chlorid. Interaction of calcium carbide with methanol to give calcium methoxide is vigorous, but subject to an induction period of variable length. Once reaction starts, evolution of acetylene gas is very rapid. Mixing calcium carbide with silver nitrate solutions forms silver acetylide, a highly sensitive explosive. Copper salt solutions would behave similarly. The mixture of

calcium carbide and sodium peroxide is explosive, as is calcium carbide and perchloryl fluoride as gases at 100-300°C.

### Calcium carbide identification

Identification of the chemical substance can be made based on relevant numbers. Identification numbers of calcium carbide are shown in Table 2 [1,2,7,8].

According to the standard NFPA 704 hazard diamond of calcium carbide is shown in Figure 3 [5].

**Table 2.** Identification numbers of calcium carbide

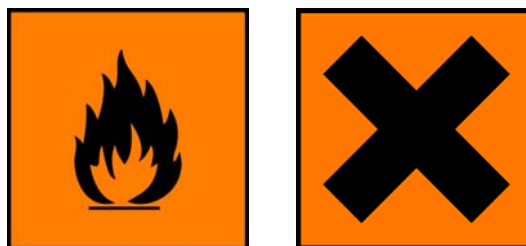
|               |              |
|---------------|--------------|
| CAS number    | 75-20-7      |
| RTECS         | EV9400000    |
| UN number     | 1402         |
| EINECS        | 200-848-3    |
| EC            | 006-004-00-9 |
| Hazard class  | 4.3          |
| Kemler number | X423         |



**Figure 3.** Calcium carbide hazard diamond

A "3" health rating indicates that exposure of calcium carbide may result in serious temporary or residual injury, even with medical treatment. A "3" flammability rating indicates that calcium carbide is material which can ignite regardless of ambient temperature. A calcium carbide reactivity rated with "2" means that it is normally unstable, will explode when mixed with water, or will undergo violent chemical reactions under elevated temperature and pressure, but will not detonate. "W" denotes calcium carbide as material that reacts with water or with it forms explosive mixture. Fire extinguishing of this material should not be used with water.

According to ADR hazard symbols of calcium carbide are shown in Figure 4 [2].



**Figure 4.** Hazard symbols of calcium carbide

Risk phrases of calcium carbide are:

- R15: Contact with water liberates extremely flammable gases.
- R37/38: Irritating to respiratory system and skin.
- R41: Risk of serious damage to eyes.

Safety phrases of calcium carbide are:

- S2: Keep out of the reach of children.
- S8: Keep container dry.
- S24: Avoid contact with skin.
- S26: In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
- S39: Wear eye/face protection.
- S43A: In case of fire, use dry chemical (never use water).

### Toxicity

Toxicity of calcium carbide and its decomposition products during the chemical reaction with water are shown in Table 3 [6].

**Table 3.** *Toxity of calcium carbide and its products*

| Chemical name     | Chemical formula              | Max allowable concentration, (mg/m <sup>3</sup> ) | Degree of health hazard |
|-------------------|-------------------------------|---|-------------------------|
| Calcium carbide   | CaC <sub>2</sub>              | -   | 3                       |
| Acetylene         | C <sub>2</sub> H <sub>2</sub> | 2662  | 1                       |
| Calcium hydroxide | Ca(OH) <sub>2</sub>           | 5   | 2                       |

Calcium carbide in contact with eyes causes its severe burns. It may cause blindness and opacity and scarring. In contact with skin it causes irritation and possible burns, especially if the skin is wet or moist. When in contact with moist skin, caustic lime is formed, which can lead to ulceration and scarring. If ingested, it causes gastrointestinal tract burns. During inhalation calcium carbide may cause severe irritation of the upper respiratory tract with pain, burns, and inflammation. It can produce delayed pulmonary edema. During chronic exposure repeated inhalation may cause chronic bronchitis.

Acetylene may cause central nervous system depression with nausea, headache, dizziness, vomiting, and in coordination or difficult breathing. It may cause skin and eye irritation.

Calcium hydroxide is harmful if swallowed or inhaled. It is gastric irritant. Ingestion may be followed by severe pain, vomiting, diarrhea, and collapse. Calcium hydroxide causes irritation of the respiratory tract. Symptoms may include coughing, shortness of breath. It can cause chemical bronchitis. In contact with skin and eyes it is corrosive. It causes burns and blistering of skin. It may produce severe irritation and eyes pain and induce ulcerations of the corneal epithelium.

### Flammability and explosiveness

Dry calcium carbide is not inflammable. Contact with humidity and water liberates acetylene gas which is

highly inflammable and can form explosive mixtures with air.

Acetylene requires very low ignition energy. Its ignition temperature is 305°C. Acetylene explosion limits in the air are 1.5÷82vol%. The gas is lighter than air. Its vapor density is 0.9.

Acetylene may cause flash fire. Its hazardous combustion products are carbon monoxide and carbon dioxide.

Calcium carbide is also flammable in presence of acids. Contact with acid or acid fumes evolves heat and flammable vapors. Some metallic oxides may occur as combustion products of calcium carbide.

### Stability and reactivity

Calcium carbide is stable under normal temperatures and pressures. It reacts vigorously with water to form highly flammable acetylene gas. Lime may also be formed raising the pH of the solution and causing a white precipitate.

It extremely reacts with acids, highly reacts with alkalis and reacts with oxidizing agents.

This material is incompatible with water, moist air or moisture from any source, acids (hydrogen chloride, stannous chloride), oxidizers (sodium peroxide, potassium hydroxide), lead fluoride, magnesium, selenium, sulfur, chlorine and silver nitrate.

### Impact on the environment

Calcium carbide can be found into rivers, lakes, seas, etc. By the reaction with water, the decomposition products of calcium carbide, acetylene and calcium hydroxide are harmful to fish.

Acetylene in quantity of 200 mg/l is lethal for trout fry, and of 400 mg/l is lethal for gold fish within 24 -48 hours. Calcium hydroxide in quantity of 20 mg/l is harmful to fish and 70 mg/l is lethal after 26 minutes

Calcium carbide may affect acidity (pH-factor) in water with risk of harmful effects to aquatic organisms.

### First aid measures

In case of inhalation it is necessary to evacuate the victim to a safe, well ventilated area as soon as possible. Loosen tight clothing such as a collar, tie, belt or waistband. If breathing is difficult, administer oxygen. If the victim is not breathing, perform mouth-to-mouth resuscitation. Seek immediate medical attention.

In a case of ingestion do not induce vomiting. If victim is conscious and alert, give 2-4 cupfuls of milk or water. Never give anything by mouth to an unconscious person. Get medical aid immediately.

If there is contact with eyes, it is necessary immediately to flush eyes with plenty of water for at least 15 minutes, occasionally lifting the upper and lower eyelids. Get medical aid immediately.

After the contact with skin, wash immediately with plenty of water. Gently and thoroughly wash the contaminated skin with running water and non-abrasive

soap. Be particularly careful to clean folds, crevices, creases and groin. Cover the irritated skin with an emollient. If irritation persists, seek medical attention. Wash contaminated clothing before reusing

### Fire fighting measures

Fire of calcium carbide shall not be extinguished with water, foam or halogenated extinguishing agents. Carbon dioxide may be ineffective.

It is necessary to use class D extinguisher or smotherers with soda ash, dry sand, dry clay, dry powdered sodium chloride or dry graphite.

Small fires will be extinguished with dry chemical powder, lime or dry sand. In the case of large fires should withdraw from area and let fire burn.

Firefighters should wear full fire fighting turn-out gear and respiratory protection.

### Accidental release measures

In the case of small spill should use the appropriate tools to put the spilled solid in convenient waste disposal containers. They must not be tightly closed. It should protect the spilled material from contact with water and do not allow it to enter water courses.

In case of large spill should not touch spilled material. It is necessary bulk material cover with dry earth, sand or other non-combustible material and to eliminate all ignition sources. It must be prevented his entry into sewers, basements or confined areas.

## CONCLUSION

Knowledge of potential risks and dangers of hazardous materials is crucial for raising awareness of the necessity of taking certain actions for avoiding the risk of injury, or at least for reducing dangerous and harmful effects to the minimum. The aim of this paper was to highlight the importance of identifying and understanding the nature of hazardous materials.

Based on the categories and the degree of dangerousness, the transportation, storage, ventilation, operating the materials, cleaning of the tanks and equipment containing material, organizational measures of protection, personal protective equipment, procedures in case of emergency at work and in accidents in transport, fire and explosion protection, first aid, decontamination and environmental protection

are determined.

Proper handling of a hazardous material reduces the risk of chemical accidents, fires and explosions. Also, knowledge of the nature of hazardous material is necessary for an adequate response in accident situations.

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## BIOGRAPHY

**Dušica Pešić** was born in Pirot, Serbia, in 1961. She received the diploma in occupational safety engineering and the Ph.D. degree in fire protection from the University of Nis, Faculty of Occupational Safety. Her main areas of research include fire protection, environmental protection, etc.

She is currently working as an associate professor at the Faculty of Occupational Safety in Nis, University of Nis.



## ZAPALJIVI I TOKSIČNI MATERIJALI KOJI NE SMEJU DOĆI U KONTAKT SA VODOM – PRIMER KALCIJUM KARBID

Dušica Pešić, Milan Blagojević, Miloš Milojević, Suad Suljović

*Rezime:* U radu su analizirani materijali koji u kontaktu sa vodom emituju zapaljive i toksične gasove. Prikazana je njihova klasifikacija prema ADR -u i identifikacija prema standardu NFPA 704. Analizirane su fizičko-hemijske, toksične, zapaljive i reaktivne osobine kalcijum karbida. Date su mere prve pomoći i procedure gašenja požara ovog materijala. Pravilno rukovanje toksičnim i zapaljivim materijalima je uslovljeno poznavanjem njihovih osobina. Pravilno rukovanje smanjuje rizik od nastanka hemijskih akcidenata praćenih požarom i eksplozijom.

Ključne reči: opasna materija, voda, toksičnost, požar, eksplozija.

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## **DIJAGNOSTIKA STANJA ROTACIONIH MAŠINA POMOĆU VIBRACIJA**

**Rezime:** Monitoring stanja mašina i opreme predstavlja samo jednu od aktivnosti u okviru tehničkog održavanja za čije se potrebe vrši merenje i analiza vibracija. U principu, upotreba vibracija je zastupljena u realizaciji sedam osnovnih grupa aktivnosti u okviru tehničkog održavanja mašinskih sistema. Svaka grupa aktivnosti poseduje određena ograničenja, kako u pogledu mogućnosti ostvarivanja postavljenih ciljeva i zadataka, tako i u mogućnosti prikazivanja osnovnih karakteristika vibracija kako bi se postigli optimalni rezultati.

**Ključne reči:** vibracije, rotacione mašine, oštećenje, dijagnostika.

### **UVOD**

Monitoring mašina se u današnje vreme razvija u dva osnovna pravca. U okviru jednog od njih, problem smanjivanja broja tačaka za kontrolu vibracija i određivanja vremenskog perioda između merenja rešava se pre svega korišćenjem sistema za kontinualni monitoring. U okviru drugog pravca, vremenski periodi između merenja se maksimalno povećavaju kontrolisanjem vibracija u mnogo tačaka, što podrazumeva merenje vibracija na svakom delu mašine koji može biti izvor vibracija. Povećanje vremenskog perioda omogućava korišćenje pokretne (prenosne) opreme za merenje i analizu vibracija. Efikasnost monitoringa u oba slučaja zavisi od broja raspoloživih (dostupnih) delova za sprovođenje procedure merenja. Taj broj se kod mašina sa rotacionim elementima može povećati sprovođenjem uskopojasne analize, koja se naročito uspešno primenjuje za analizu periodičnih komponenta signala.

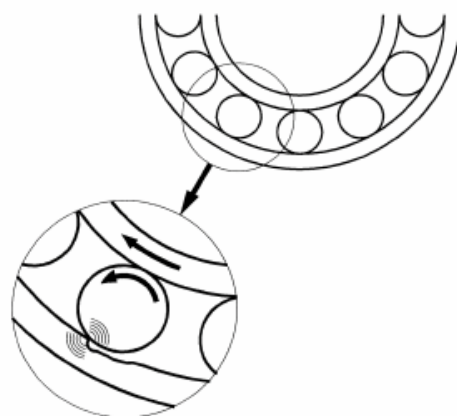
U praktičnoj primeni dijagnostike stanja mašina pomoću vibracija postoje dva osnovna pristupa u rešavanju dijagnostičkih problema.

Prvi pristup podrazumeva sprovođenje postupka dijagnostike samo nakon detekcije promena stanja vibracija mašine posredstvom monitoringa, sa prevashodnim zadatkom tumačenja uočenih promena. Međutim, monitoring se po pravilu sprovodi na niskim i srednjim frekvencijama vibracija koje odgovaraju nastanku razvoja najvećeg broja oštećenja, jer postojanje ozbiljnih oštećenja dovodi do jasno uočljivih i primetnih promena energetske parametara vibracija koje prekoračuju njihove uobičajene fluktuacije uslovljene promenom radnog režima.

Drugi pristup podrazumeva upotrebu metoda i sredstava dijagnostike pomoću kojih je moguće otkriti osnovne tipove oštećenja u njihovoj početnoj fazi, pre nastanka bitnih energetske promena u signalu vibracija mašine. Detekcija oštećenja u fazi njihovog nastanka omogućava posmatranje njihovog razvoja i pravovremeno planiranje aktivnosti (programa) održavanja i potrebnog ljudstva i opreme za popravku mašine. Ovaj pristup se često naziva monitoringom

oštećenja i može se sprovoditi tokom više godina, sve dok kombinacija oštećenja svojim razvojem i brojem ne ukažu na stanje koje se smatra opasnim ili kritičnim. Svakako da je ovakav pristup moguć samo ukoliko je moguće detektovati i identifikovati sva potencijalna oštećenja i nepravilnosti u ranoj fazi njihovog razvoja. Intenzivni razvoj metoda i tehničkih sredstava dijagnostike, a naročito dijagnostike pomoću signala vibracija, učinio je da u današnje vreme široka primena sistema za monitoring oštećenja postane realnost.

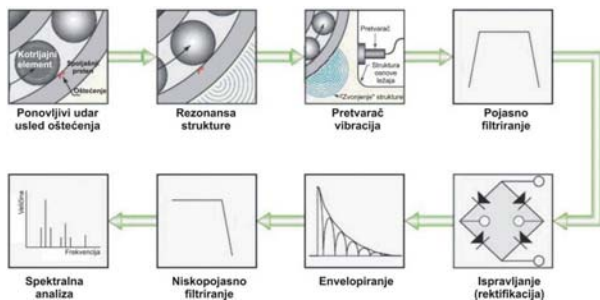
Kod rotacionih delova se za detekciju oštećenja koja su u začetku koriste uobičajeni dijagnostički pokazatelji (simptomi), definisani spektralnom analizom samog signala vibracija ili oscilacijama snage njegovih komponenta, odnosno spektralnom analizom ovojnice signala vibracija (envelope). Na primer, osnovni pokazatelj oštećenja ležaja je promena karakteristika sila trenja i vibracije visokih frekvencija koje se time pobuđuju (sl. 1). Ove promene su posledica bilo pojave mikro-udara ili periodičnih promena koeficijenta trenja na oštećenoj kontaktnoj površini trenja i detektuju se vrlo jednostavno spektralnom analizom envelope signala vibracija visokih frekvencija na kućištu ležaja, pobuđenih silama trenja.



**Sl. 1** Oštećenje spoljnog prstena izaziva udarne impulse koji se prostiru kroz komponente ležaja i mašinsku strukturu [5]



Nakon izvršene detekcije oštećenja i nepravilnosti u radu pojedinih mehaničkih prenosnika, a naročito zupčanika, kaišnika, elastičnih spojnika itd., posebnu pažnju treba obratiti na simptome oštećenja nastalih usled dinamičkih opterećenja koja deluju na transmisione elemente, npr. ležajeve. Ova opterećenja prvo dovode do povećanja određenih komponenata signala vibracija, i drugo, do fluktuacija sila trenja u ležajevima, na osnovu čega dolazi do oscilovanja vrednosti snage vibracionih signala na visokim frekvencijama. Na taj način je kombinacijom rezultata merenja spektra vibracija i spektra envelope moguće detektovati i identifikovati oštećenja mehaničkih prenosnika u početnoj fazi razvoja (sl. 2).



Sl. 2 Postupak envelopiranja signala vibracija [9]

Osnovni dijagnostički simptomi oštećenja protočnih elemenata rotacionih mašina, poput radnih kola centrifugalnih pumpi i kompresora, kao i lopatičnih kola turbina, veoma su slični simptomima oštećenja mehaničkih prenosnika i ležajeva, a posledica su promena karakteristika turbulentnog strujanja u oblasti razvodnika i radnog kola. Pulsacije pritiska koje nastaju na tim mestima prvenstveno pobuđuju vibracije visokih frekvencija i potom stvaraju dinamička opterećenja koja deluju na ležajeve, tako da se oštećenja nastala protokom fluida mogu detektovati paralelnom analizom spektra mašinskih vibracija i spektra envelope vibracija visokih frekvencija na kućištima radnih kola i ležajeva. Sile trenja u ležajevima i pulsacije pritiska pri proticanju gasova i tečnosti, usled postojanja mnoštva oštećenja i nepravilnosti, znatno menjaju radne karakteristike mašina i pojedinih elemenata. Međutim, sva oštećenja ne moraju da potiču neposredno od rotacionih mašina. Tako, na primer, pojedina oštećenja električnih mašina utiču na promene parametara magnetnog polja, usled čega dolazi do dejstva dodatnih sila i promenljivih momenata na rotor mašine. Budući da u električnim mašinama bez oštećenja ne postoje pulsacioni momenti, pomoću pulsacionih momenata i vibracija koje oni pobuđuju moguće je vrlo efikasno detektovati oštećenja električnih mašina u ranoj fazi nastanka. Spektralna analiza vibracija električnih mašina na niskim i srednjim frekvencijama, izmerenih u različitim pravcima, omogućava identifikaciju skoro svih oštećenja magnetnih uređaja elektronskih mašina, osim slabljenja i propadanja izolacije, sve do trenutka probijanja izolacije magnetnog polja i time nastalih promena vibracija mašine.

Jedna od karakteristika vibracija je mogućnost njihovog korišćenja za detekciju oštećenja rotora, naročito kod rotacionih mašina koje rade na velikim brzinama i koje su osetljive na promene vrednosti i strukture centrifugalnih sila. U zavisnosti od vrste oštećenja dolazi do povećanja vibracija na niskim frekvencijama i promene spektralnog sadržaja. Ova osobina vibracija se koristi za identifikaciju vrste oštećenja ili nepravilnosti.

Prema tome, signali vibracija omogućavaju detekciju praktično svih tipova oštećenja rotacionih mašina u ranoj fazi njihovog nastanka, bez potrebe za drugim fizičkim postupcima dijagnostike (pomoću pritiska, temperature, ...), što znači da se za održavanje i popravku opreme u realnim uslovima mogu koristiti prenosni sistemi za dijagnostiku stanja pomoću vibracija koji u postupku održavanja ne zahtevaju postojanje stalno postavljenih (fiksiranih) pretvarača na mašinama ili njihovim delovima.

## VIBRODIJAGNOSTIKA ROTACIONIH MAŠINA

Monitoring stanja mašina primenom vibrodijagnostike omogućava praćenje promena u radu mašine na dva načina:

1. Merenjem nivoa ukupnih (opštih) vibracija mašine, praćenjem njegove promene i trenda rasta tokom vremena, imajući pritom u vidu dozvoljene vrednosti nivoa opštih vibracija za datu grupu i vrstu mašina predviđene odgovarajućim standardom, i
2. Vršanjem frekvencijske analize na fiksni mernim tačkama na mašini i upoređivanjem dobijenog individualnog spektra sa referentnim spektrom, zabeleženim kada je mašina bila u dobrom stanju. Promene nivoa komponenata spektra na pojedinim frekvencijama mogu biti pokazatelj poremećenog stanja određenih delova mašine.

U tom smislu, svrha merenja vibracija nije određivanje nivoa vibracija koji neki deo sistema može da izdrži pre nego što otkaze, već predstavlja mogućnost da se postigne odgovarajuća opomena u pogledu postojanja određenih smetnji i nepravilnosti koji se mogu eliminisati pre nastanka otkaza. Utvrđivanje apsolutnih tolerancija vibracija za mašinu, ili graničnih vrednosti vibracija za bilo koji njen deo je praktično nemoguće s obzirom na priličnu složenost analize neispravnosti i otkaza, pri čemu prethodna iskustvena saznanja mogu da pomognu samo u dobijanju izvesnih realnih smernica. Prilikom utvrđivanja prihvatljivih nivoa vibracija potrebno je razmotriti iskustvene podatke i činioce kao što su: bezbednost radnika, troškovi otklanjanja neispravnosti, troškovi usled zastoja u proizvodnji, važnost sistema u tehnološkom lancu proizvodnje i dr.

Objekte dijagnostike predstavljaju iste mašine i oprema čije se stanje prati i ispituje sistemima za monitoring stanja pomoću vibracija. Dijagnostika stanja pomoću

vibracija se vrlo često koristi kako za kontrolu kvaliteta procesa proizvodnje ili remonta, tako i za kontrolu kvaliteta mašinskih sklopova – detekciju oštećenja novih (ili remontovanih) mašinskih delova, ili za detekciju i praćenje razvoja oštećenja i defekata na njima u toku eksploatacije. Za svaki od navedenih slučajeva mogu se koristiti različite dijagnostičke metode. U poslednjem slučaju se dijagnostička merenja mogu izvoditi bez bilo kakvih izmena radnih uslova (režima rada) objekta dijagnostike.

Suprotno monitoringu, dijagnostika stanja mašinske opreme pomoću vibracija nije namenjena za detekciju promena stanja vibracija, već za detekciju promena stanja i predviđanje (predikciju) stanja mašine, kao i svakog njenog elementa koji ima realnu verovatnoću otkaza u periodu između dva postupka održavanja. Iz tog razloga je, pored merenja vibracija na niskim i srednjim frekvencijama, potrebno vršiti i merenja vibracija na visokim frekvencijama, pa je time i postupak analize vibracija, koji omogućava dobijanje svih neophodnih dijagnostičkih informacija, daleko složeniji od samog postupka monitoringa. Vibracije se mere na svakom elementu čije stanje treba utvrditi, ili bar u tačkama na kojima se vibracije visokih frekvencija, koje potiču od elementa čije stanje treba utvrditi, prepoznaju na drugim elementima koji su pristupačni za merenje vibracija. Uređaji za merenje i analizu vibracija mogu biti jednokanalni.

Dugi niz godina su se metode za kontrolu i dijagnostiku mašina pri upotrebi bilo kojeg dijagnostičkog signala zasnivale na upoređivanju veličine (amplitude) izmerenog signala ili njegovih komponenta sa nivoima koji označavaju loše i dobro stanje mašine. Sistemi za kontrolu i dijagnostiku stanja mašina konstruisani na bazi takvih metoda vrše izbor pojedinih informacija od značaja iz merenog signala i određuju vreme kada će oni prekoračiti unapred utvrđene nivoe. Svako prekoračenje unapred utvrđenih nivoe se registrovalo kao nepravilnost. Tipovi nepravilnosti su definisani na osnovu sadržaja komponenta spektra koje su premašile određene nivoe. Savremeni sistemi za monitoring stanja vode poreklo od sistema za kontrolu i do skora su bili zasnovani na tim načelima, dok danas neki od njih omogućavaju ne samo kontrolu amplitude parametara, već takođe i analizu trendova tih parametara, pa čak i predviđanje datuma kada će ti parametri prekoračiti nivoe neispravnosti. Pri tome, zadatak korisnika sistema za monitoring stanja je tumačenje nastalih promena u stanju mašine, detektovanih i predviđenih pomoću tog sistema.

Pokušaj stroge podele sistema na sisteme za monitoring stanja i sisteme za dijagnostiku stanja mašina može biti izveden prema osnovnoj razlici u mogućnosti sistema da izvrši podelu svih promena stanja mašine u dve grupe:

1. Povratne promene stanja, koje nastaju usled promene radnog režima mašine i radnih uslova, i
2. Nepovratne promene stanja, koje nastaju usled oštećenja.

Nažalost, većina sistema za monitoring stanja ne omogućava potpuno rešenje ovog problema, zbog čega za podelu promena stanja na povratne i nepovratne promene pre treba koristiti sisteme za dijagnostiku stanja nego sisteme za monitoring stanja. U tom pogledu, stepen integracije dijagnostičkih sistema u sisteme za monitoring stanja treba smatrati jednom od glavnih karakteristika dijagnostičkih sistema.

Nivo potrebne obuke dijagnostičkih operatera predstavlja drugo veoma bitno svojstvo sistema za dijagnostiku stanja. Uzimajući nivo obuke operatera kao kriterijum, dijagnostički sistemi se mogu podeliti u tri grupe:

1. Profesionalne dijagnostičke sisteme, u kojima operateri biraju dijagnostičke tehnike i mernu opremu. Iskustvo i znanje operatera u potpunosti određuju dubinu (detaljnost) i preciznost (tačnost) dijagnostike stanja i predikcije.
2. Ekspertske dijagnostičke sisteme, koji pružaju odgovore na karakteristična pitanja operatera, tj. pomažu mu u nalaženju rešenja u konkretnim situacijama. Ekspertske sisteme mogu koristiti operateri sa posebnom obukom, bez ekspertskog znanja i iskustva.
3. Automatske dijagnostičke sisteme, zasnovane na metodama koje omogućuju automatsku (samostalnu) dijagnostiku. Ovakvi sistemi definišu operateru mernu putanju i ne zahtevaju neku posebnu dijagnostičku obuku. Naime, da bi radio sa automatskim dijagnostičkim sistemima, operateru sa osnovnim poznavanjem rada na računaru je sasvim dovoljno dva do tri dana obuke.

Dakle, metode dijagnostike stanja pomoću vibracija treba klasifikovati u metode za monitoring stanja u skladu sa tehničkim zahtevima za njihovom integracijom i problemima korisnika dijagnostičkih sistema na koje nailazi u radu. Ništa manje bitni su zahtevi za obradu dijagnostičkih merenja i dubinu (detaljnost) dijagnostifikovanja stanja mašina.

Uzimajući u obzir navedene zahteve, postojeće dijagnostičke metode se mogu podeliti u sledeće grupe:

- Dijagnostike montaže (sklapanja i instaliranja) mašina,
- Dijagnostike stanja pomoću monitoringa,
- Metode spojene (združene) dijagnostike i monitoringa stanja,
- Dijagnostičke i predikcione metode pomoću periodičnih merenja vibracija, i
- Dijagnostika stanja i predikcija na osnovu samo jednog merenja vibracija.

Dijagnostika montaže mašina se primenjuje u toku sklapanja i neposredno nakon instaliranja mašine i puštanja u rad, a naročito tokom balansiranja mašina u pogonskim uslovima. Ove metode dijagnostike ne zahtevaju bilo kakve podatke od sistema za monitoring stanja i korišćene su u prenosivim dijagnostičkim sistemima ili u pultovima za kontrolu proizvoda.



Karakteristika ovih metoda je mogućnost delimičnog korišćenja test-dijagnostičkih metoda kao vrlo podesnih. Na primer, dodatne centrifugalne sile, koje nastaju nakon montaže probnih tegova i uravnotežavajućih masa u odgovarajuću ravan mašine u toku postupka uravnotežavanja, mogu biti smatrane test-signalima. Dinamičke sile promenljivih frekvencija, koje nastaju u toku rada neispravnih mašina, takođe mogu biti smatrane test-signalima.

Od tehničkih podataka koji su neophodni u razmatranim dijagnostičkim metodama, neophodno je istaći početnu fazu. Podaci o početnoj fazi se po pravilu obezbeđuju iz spektra i njegove envelope.

Zadatak dijagnostičkih sistema koji koriste navedenu tehniku je pre svega detekcija različitih tipova nesaosnosti vratila. Drugi zadatak je pronalaženje mogućih uzroka umanjivanja efikasnosti uravnotežavanja mašine. Na primer, ukoliko na mašini postoje neke nepravilnosti, može biti više od deset razloga za pojavu vibracija na frekvenciji rotacije mašine koji će ometati uravnotežavanje. Takođe, potrebno je pronaći i ostale nepravilnosti koje su nastale usled grešaka u proizvodnji i montaži različitih delova i sklopova.

Zadatak razvoja automatskih dijagnostičkih sistema za montažu mašina se obično ne poverava programerima. Uravnotežavanje mašina uobičajeno rade obučeni profesionalci koji uz to mogu biti u stanju i da izvrše dijagnozu mašine upotrebom ekspertske tehnike.

Metode za dijagnostiku stanja na osnovu rezultata monitoringa su zasnovane na informacionim tehnikama koje su korišćene za kontrolu stanja vibracija na ograničenom broju kontrolnih tačaka i po pravilu se izrađuju u formi profesionalnih ili ekspertske sistema. Dijagnostički rezultati dobijeni ovim metodama nisu vrlo detaljni, odnosno ne podrazumevaju sprovođenje dubinske dijagnostike i obično se primenjuju za definisanje programa daljeg, naprednijeg i opširnijeg proučavanja identifikacije detektovanih promena stanja vibracija.

Metode spojene (združene) dijagnostike i monitoringa stanja se široko primenjuju u sistemima za kontinualni monitoring i dijagnostiku, imajući u vidu da obezbeđuju višu preciznost (klasu tačnosti) dijagnostičkih rezultata u odnosu na prethodne metode. Veća pouzdanost rezultata je postignuta povećanjem broja mernih tačaka.

Najčešće primenjivane metode ovog tipa imaju potpuno odvojene funkcije monitoringa stanja i dijagnostike stanja, pa se i sistemi koji su zasnovani na ovim metodama sastoje od dva odvojena dela. Prvi deo, sa stacionarno (trajno) postavljenim pretvaračima vibracija na mašini, obezbeđuje kontinualni monitoring stanja kojim se detektuju promene u stanju vibracija mašine i među njima pronalaze one koje ukazuju na nepovratne (trajne) promene stanja mašine i, ukoliko je potrebno, vrši predikciju njihovog razvoja. Nakon toga, ukoliko se donese odluka o produžetku rada mašine, na scenu stupa i startuje drugi deo sistema monitoringa i dijagnostike stanja, kojim se rešava zadatak

identifikacije detektovanih nepovratnih promena i, ukoliko je moguće, predikcije razvoja nepravilnosti i oštećenja. Drugi deo sistema može raditi off-line zbog činjenice da je ponekad za identifikaciju neispravnosti potrebno izvršiti dodatna merenja vibracija na mestima gde se očekuje da bi neispravnost mogla proizvesti najveće posledice.

Savremeni sistemi za monitoring stanja mogu takođe da koriste dijagnostičke metode za identifikaciju neispravnosti pri promenljivim režimima rada mašine. Takva kombinacija monitoringa i dijagnostike stanja povećava višestruko kvalitet rezultata dijagnostike, budući da promene režima rada vrlo često utiču na promene većine dijagnostičkih simptoma (pokazatelja) neispravnosti. Istovremeno, dijagnostički postupak je komplikovaniji i zahteva visoku obučenosť eksperata ili više sofisticiranih sistema za automatsku dijagnostiku mašina. Ovakav način su izabrale i podržavaju vodeće svetske kompanije u proizvodnji sistema za automatski monitoring i dijagnostiku (sl. 3).



SL3 Brüel&Kjær Data Collector 2526 [10]

Sofistikacija metoda za monitoring i dijagnostiku stanja vodi ka povećanju broja mernih tačaka i time do povećanja cene sistema. Sa ekonomskog gledišta, optimalni sistem za kontinualni monitoring i dijagnostiku stanja mora imati mogućnost istovremenog (paralelnog) i sinhronizovanog (usaglašenog) sprovođenja zasebnih funkcija monitoringa i dijagnostike. Granični broj kontrolnih tačaka za monitoring i dijagnostiku stanja nekog elementa ili mašine može biti izabran na način da to nisu obavezno najsnažniji izvori vibracija na mašini, ali da to budu u svakom slučaju tačke koje će verodostojno i pouzdano reprezentovati trenutno stanje mašine i pomoću kojih se može odrediti njen životni ciklus (preostali radni vek). Najčešće su to tačke na kućištima ležajeva. U slučaju mašina koje rade sa velikim brojem obrtaja, kod kojih su ležajevi glavni izvori vibracija, dodatno se mogu koristiti dve do tri kontrolne tačke na kućištu mašine, koje su dosta udaljene od sekcije ležaja. Zadatak monitoringa stanja je uvek detekcija promena stanja vibracija mašine i njenih delova pomoću merenja koja se često ponavljaju. Pri detekciji i najmanjih promena, sistem za dijagnostiku stanja startuje i počinje da vrši potpuna dijagnostička merenja pomoću stacionarnih (fiksno postavljenih) pretvarača vibracija. Samo u slučaju kada podaci dobijeni monitoringom i dijagnostički podaci nisu dovoljni za

identifikaciju uzroka detektovanih promena, rešenje se postiže vršenjem dodatnih merenja posredstvom off-line instrumenata koji su obuhvaćeni kombinovanim (združenim) sistemom za monitoring i dijagnostiku stanja.

Dijagnostičke i predikcione metode pomoću periodičnih merenja vibracija. Većina nepravilnosti (oštećenja) koje se javljaju i razvijaju u mašinskim delovima počinju da utiču na opštu sliku (sastav) vibracija mašine nekoliko meseci pre nastupanja situacije u kojoj može doći do otkaza mašine praćenim ozbiljnim oštećenjima i havarijama. Izuzetak su pojedine neispravnosti usred neadekvatnog sklapanja (montaže) ili neispravnosti usled nepoštovanja uputstava za rad i upotrebu mašine. One se mogu pojaviti u bilo kojoj fazi životnog ciklusa mašine i razvijati vrlo brzo, sve do nastanka samog otkaza mašine i mogućih pratećih opasnih situacija. Ukoliko se ove neispravnosti izostave ili ih jednostavno nema, tada nije potrebno vršiti vrlo česta merenja, čime se stvara mogućnost i povoljna prilika za primenu off-line sistema za mašinsku dijagnostiku. Ovi sistemi zahtevaju periodična (povremena) merenja u intervalima od nekoliko sedmica ili čak i više meseci. Kao i kod metoda monitoringa stanja, metode dijagnostike i predikcije stanja se zasnivaju na različitim kombinacijama dijagnostičkih tehnika i obično su namenjene iskusnim, kvalifikovanim i stručnim analitičarima. Najbolji rezultati se postižu metodama koje se zasnivaju na kombinaciji (spoju) tehnika analize spektra i njegove obvojnice (envelope).

Za razmatranje problema ovom grupom dijagnostičkih metoda potrebno je detaljno poznavanje procesa razvoja neispravnosti i njihovog uticaja na parametre vibracija svih tipova mašina čija se dijagnostika sprovodi. Kako su ove metode zasnovane na uporednoj analizi rezultata merenja koja se vrše u različitim trenucima vremena (vremenskim razmacima), one zahtevaju merenja vibracija izuzetno visokog kvaliteta koja mogu obavljati samo vrlo iskusni tehničari, što sa druge strane ograničava dijagnostičke mogućnosti i njenu efikasnost. Poseban problem predstavlja zadržavanje istog režima rada mašine tokom sprovođenja dijagnostike, jer u suprotnom nije moguće efikasno detektovati promene stanja mašina. Razvoj metoda za dijagnostiku i predikciju stanja u automatsku dijagnostiku i predikciju stanja na osnovu periodičnih merenja vibracija suočen je sa istim problemima kao i u slučaju metoda koje zahtevaju donošenje odluka od strane operatora. Najveći problem je izbor merenja sa zadovoljavajućom preciznošću, naročito ako se ona razlikuje u odnosu na prethodna merenja. Izbor će tim pre biti teži ukoliko se uzme u obzir da za promenu stanja (oblika) vibracija mašine može postojati više razloga, koji ne moraju biti obavezno razvoj nepravilnosti (oštećenja), već to mogu da budu i promene radnog režima mašine, greške operatera u izboru položaja merne tačke, ili pogrešno pričvršćivanje pretvarača. Pritom, kod najvećeg broja mašina je skoro nemoguće zadržati i obezbediti isto

opterećenje, brzinu obrtanja i spoljašnje uslove od merenja do merenja, posebno ako se merenja vrše (ponavljaju) nakon dužih vremenskih intervala, npr. nakon više nedelja ili meseci. Uprkos navedenim teškoćama, metode automatske dijagnostike mašinske opreme na osnovu periodičnih/povremenih merenja vibracija su razvijane u mnogo zemalja, tako da danas postoji veliki broj dijagnostičkih sistema koji efikasno koriste ove metode.

Metode dijagnostike i predikcije stanja na osnovu samo jednog merenja vibracija su vrlo popularne, ali i komplikovane metode, zasnovane na različitim kombinacijama dijagnostičkih tehnika i u većini slučajeva ih mogu koristiti samo iskusni eksperti. Osobenost ovih metoda je da se dijagnostika mašine vrši pomoću dijagnostike delova (sklopova) mašine ili njenih pojedinih delova ukoliko su oni izvori vibracija. Najveća efikasnost se postiže maksimalnom upotrebom tehnika analize spektra i envelope od strane eksperata. Svaka dijagnostička metoda na osnovu samo jednog merenja vibracija zahteva od eksperta vrlo detaljno, dubinsko poznavanje osobenosti razvoja neispravnosti i napredovanja oštećenja, kao i njihovog uticaja na vibracije objekta čija se dijagnostika vrši. Neophodno je poznavati sve postojeće dijagnostičke simptome i nivoe za određene vrste i tipove mašina, što se može rešiti postojanjem eksperata za određenu vrstu mašina ili dijagnostičkim metodama koje se razvijaju za određenu vrstu mašinskih sklopova ili mašinskih elemenata.

U poslednje vreme se naročita pažnja poklanja specijalizovanim dijagnostičkim metodama, sposobnim za automatsko (samostalno) vršenje dijagnostike stanja mašine i njenih delova. Prva od automatizovanih metoda bila je namenjena dijagnostici kotrljajnih ležajeva pomoću envelope spektra visokofrekvencijskih vibracija koje su pobuđene silama trenja unutar sklopa čija se dijagnostika vrši. Danas postoje konstrukcije sistema za automatsku dijagnostiku zupčastih mehanizama, naročito menjača, koje se baziraju na samo jednom merenju vibracija. Ove metode čine osnovu za stvaranje sličnih dijagnostičkih sistema za dijagnostiku radnih kola pumpi i turbina. Svaka od njih je zasnovana na tehnici envelope dopunjenoj spektralnim tehnikama. U najskorije vreme se očekuju i sistemi za dijagnostiku na osnovu samo jednog merenja kod električnih mašina koje rade sa naizmeničnom strujom.

Metode detaljne dijagnostike na osnovu samo jednog merenja vibracija još uvek ne dozvoljavaju rešavanje problema dijagnostike i dugoročne predikcije stanja za sve delove mašine, pa na taj način i mašine kao celine. Izuzetak su delovi koji se najčešće kvare i otkazuju, a naročito kotrljajni elementi ležajeva, za koje su sistemi dijagnostike i predikcije stanja planirani i uspešno se koriste više godina, a zasnovani su na metodama detaljne dijagnostike stanja na osnovu jednog merenja vibracija. Ove metode se mogu koristiti u sistemima za monitoring stanja i predstavljati osnovu sistema koji vrše identifikaciju uzroka detektovanih promena.

Naime, ovim metodama je na osnovu stanja (oblika) vibracija moguće izvršiti razdvajanje povratnih od nepovratnih promena, kao što je npr. razdvajanje promene u režimu rada od trajnih oštećenja i neispravnosti, i na taj način smanjiti broj lažnih alarma koje stvara sistem za monitoring stanja.

## ZAKLJUČAK

Celokupan dijagnostički pristup polazi od činjenice da svaki poremećajni uzročnik generiše vibracije tačno određenog karaktera, prepoznatljive pre svega po frekvenciji kao ključnom parametru. Pri tome se identifikacija dominantnih parcijalnih komponenata, registrovanih u području vremenskog ili frekvencijskog domena, zasniva na korišćenju asimiliranog znanja i iskustva o specifičnim karakteristikama potencijalne slike oscilovanja pokretnih, najčešće rotirajućih mašinskih delova. Za mnoštvo vitalnih rotirajućih mašinskih delova, pored osnovne frekvencije i njenih viših harmonika, egzaktnim matematičkim putem definisan je niz prinudnih i sopstvenih frekvencija kojima mogu odgovarati i dominantne komponente u snimljenim spektrima. Kada se radi o održavanju mašinskih sistema, ključna je činjenica da brojna vrednost nivoa vibracija u suštini nije odlučujuća, već vibracioni trend kao saznanje kako se menja stanje mašine, odnosno kako se sa vremenom menjaju unutrašnje sile u konstrukciji, pospešujući oštećenja pojedinih delova mašinskih sklopova. Promena intenziteta unutrašnjih sila može biti izazvana direktnim promenama u procesu rada ili promenama osobina delova mašina. Njihovo najbolje uočavanje se postiže upravo frekvencijskom analizom.

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## BIOGRAFIJA

**Darko Mihajlov** je rođen 1969. god. u Nišu. Diplomirao je na Mašinskom fakultetu u Nišu, na smeru Hidroenergetika. Magistrirao je na Fakultetu zaštite na radu u Nišu na temu primene vibrodijagnostike u preventivnom održavanju rotacionih mašina. Pored toga, profesionalno se bavi i problemima buke u radnoj i životnoj sredini u okviru delatnosti Laboratorije za buku i vibracije Fakulteta zaštite na radu u Nišu. Trenutno je angažovan u delu realizacije nastave iz više predmeta na osnovnim i master studijama Fakulteta zaštite na radu u Nišu. Autor je i koautor više od 50 naučnih i stručnih radova koji su objavljeni u naučnim i stručnim časopisima i saopšteni na naučnim skupovima.

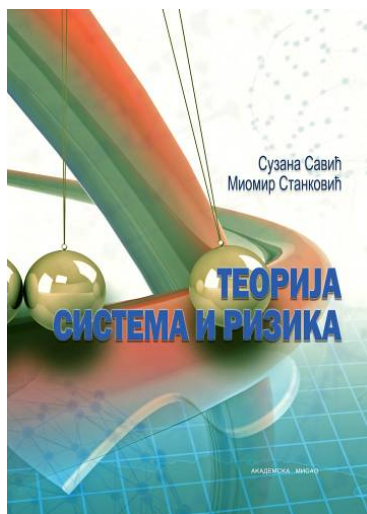


## ROTATING MACHINERY DIAGNOSTICS THROUGH VIBRATIONS

**Darko Mihajlov, Momir Prašćević, Dragan Cvetković**

**Abstract:** *Monitoring of the condition of machines and equipment is just one of the activities under technical maintenance for which the measurement and analysis of vibration is being done. In general, the use of vibrations is present in the realization of seven main groups of activities within the technical maintenance of mechanical systems. Each activity has certain limitations, both in terms of achieving set goals and tasks, as well as in terms of presenting the main characteristic features of vibrations in order to achieve optimal results.*

**Key words:** vibration, rotating machinery, fault, diagnostic.

**BOOK REVIEW / PRIKAZ KNJIGE****TEORIJA SISTEMA I RIZIKA**

*Suzana Savić, Miodir Stanković*

Udžbenik „Teorija sistema i rizika“ autora dr Suzane Savić i dr Miodira Stankovića ima pet poglavlja. Svako poglavlje sadrži rezime (na srpskom i engleskom jeziku), cilj, podpoglavljja, pitanja za proveru znanja i literaturu.

U prvom poglavlju, „**Osnovi teorije sistema**“, date su karakteristike, zakonitosti i zadaci opšte teorije sistema, kao i osnovne odlike sistemskog pristupa, sistemskog mišljenja i systemske analize. Definisani su opšti systemski pojmovi, zatim kvalitet, nivoi i atributi kvaliteta i životni ciklus sistema.

U drugom poglavlju pod nazivom „**Istraživanje sistema**“ analizirane su faze i funkcije systemske analize, kao i algoritam postupka istraživanja sistema. Prezentovane su matrice transformacije sistema, matrice za prikazivanje statičkih i dinamičkih odnosa elemenata sistema i matrice veza elemenata i sistema. Posebna pažnja je posvećena modelima sistema. Analizirani su matematički modeli (model u obliku diferencijalnih jednačina, model u obliku prostora stanja i model u obliku funkcije prenosa) i analogije u matematičkom modeliranju, zatim grafički modeli (blok-dijagrami, grafovi toka signala, bond-grafovi i Petri mreže) i logički modeli.

„**Upravljanje sistemom**“ je naziv trećeg poglavlja. U njemu su prikazani tipovi, elementi i karakteristike sistema upravljanja. ... Prikazane su i analogije u ponašanju različitih tipova sistema: električnih, pneumatskih, ekonomskih, hemijskih, bioloških. S obzirom na značaj odlučivanja u upravljačkom procesu, deo ovog poglavlja je posvećen karakteristikama, fazama, nivoima i vrstama odlučivanja.

Četvrto poglavlje rukopisa, koje nosi naziv „**Osnovi teorija rizika**“, sadrži definicije rizika, suštinu, prirodu i karakteristike rizika, zatim osnovne i izvedene pokazatelje rizika, metode za kvantifikaciju rizika (metod verovatnoće, metod ekspertnih ocena i matrični metodi), kao i mogućnosti i ograničenja primene pojedinih metoda. Posebno su analizirani individualni, socijalni, tehnički, ekološki i ekonomski rizici. Na kraju su razmatrane i vanredne situacije, kao poseban vid rizika.

U petom poglavlju, „**Upravljanje rizikom**“, date su karakteristike, pristupi, elementi i faze upravljanja rizikom, kao i neki od načina strukturiranja procesa upravljanja rizikom. Analizirane su karakteristike i specifičnosti sistema za upravljanje rizikom, a zatim prikazani programi i mere za prevenciju i eliminisanje uzroka i posledica rizičnih događaja. Na kraju poglavlja je prikazan hibridni model upravljanja rizikom kompleksnih sistema, koji obezbeđuje dinamičku integraciju različitih tehnika modeliranja i predstavlja osnov za realnu analizu i upravljanje rizikom kompleksnih sistema.

Udžbenik „Teorija sistema i rizika“ je po sadržaju usklađen sa istoimenim predmetom na studijskom programu osnovnih akademskih studija „Zaštita radne i životne sredine“. U rukopisu se na pregledan, pristupačan i konzistentan način izlažu, objašnjavaju i ilustruju osnovne pojamovne kategorije teorije sistema i teorije rizika, a kroz primere razvija veština primene sistemskog pristupa u analizi i rešavanju multidisciplinarnih problema upravljanja rizikom radne i životne sredine.

Publikaciju mogu koristiti i studenti drugih fakulteta radi sticanja osnovnih ili dopunskih znanja iz oblasti teorije sistema i rizika, kao i sva lica koja se u svom stručnom i profesionalnom radu susreću sa problemima upravljanja rizikom.

*Dr Mirjana Vidanović, vanr. prof.  
Fakulteta zaštite na radu u Nišu*



**BOOK REVIEW / PRIKAZ KNJIGE****BUKA U ŽIVOTNOJ SREDINI**

*Momir Prašević, Dragana Cvetković*

Udžbenik "Buka u životnoj sredini" autora dr Momira Praševića i dr Dragana Cvetkovića predstavlja kombinaciju teorijske analize zvučnih oscilacija (buke) i praktične realizacije znanja kroz rešavanje formulisanih konkretnih problema.

U prvoj glavi "**Fizički koncept zvuka (buke)**" se ukratko opisuju fizičke osobine zvuka i buke kao neželjenog zvuka. Opisuje se emisija buke i njeno prostiranje u elastičnoj sredini s osvrtom na tipove izvora buke, osnovne veličine zvučnog talasa, atmosferski i Doplerov efekat i uticaj apsorpcije, refleksije i difrakcije.

Osnovna teorija se proširuje diskusijom matematičkog alata za izvođenje i rešavanje talasne jednačine. Matematička izvođenja za ravne i sferne talase su prikazana bez korišćenja vektorske algebre. Posebno se razmatra tačkasti izvor kao najčešće korišćena aproksimacija za realne izvore buke. Date su osnovne jednačine za zvučni pritisak i intenzitet zvuka u zavisnosti od rastojanja do izvora.

U drugoj glavi "**Fiziološki koncept zvuka (buke)**" se razmatra psihofiziološki aspekt buke, počev od mehanizma sluha do frekvencijsko-dinamičkog opsega čujnosti ljudskog uha. U drugom delu se uvode osnovne veličine i jedinice za opisivanje buke. Zbog velikog dinamičkog opsega buke tipičnih izvora, za opisivanje buke se objašnjava korišćenje decibela umesto apsolutnih jedinica. Zatim se razmatraju subjektivni efekti buke i definišu najopštije korišćene veličine i jedinice uz objašnjenje njihovog nastanka i oblasti primene. Uvode se ekvivalentni nivo buke i nivo izloženosti buci kao veličina za opisivanje i ocenu vremenski promenljive buke.

Treća glava "**Merenje buke**" opisuje instrumente za merenje buke i opšte tehnike za merenje i analizu, počev od jednostavnih mernih sistema sa filtarskim jedinicama (oktavnim, tercnim i uskopojasnim), pa do složenijih instrumenata i sistema za analizu. Opisani su osnovni elementi mernog sistema sa njihovim glavnim osobinama. Naglašena je neophodnost pažljive kalibracije i u kratkim crtama su opisane procedure koje dovode do najpreciznijih mernih rezultata. Takođe je prikazana tehnika merenja intenziteta zvuka, ukazujući na njene prednosti kroz primere primene. Na kraju je objašnjena primena modularnog preciznog analizatora buke.

U četvrtoj glavi "**Buka u zatvorenom prostoru**" se objašnjava ponašanje zvuka u prostorijama korišćenjem talasne i statističke teorije. Prikazana analiza zvuka u prostorijama ne uključuje samo objašnjenja reflektovanja zvuka u prostoriji, već i kakav efekat imaju različiti materijali pri apsorpciji i kontroli buke u prostoriji. Pažnja čitaoca se usmerava ka prenošenju buke iz jedne u drugu prostoriju i zvučno-izolacionim osobinama građevinskih elemenata. Kao metode za kontrolu buke, posebno se naglašavaju akustička obrada prostorija i zvučna izolacija.

Diskusija u petoj glavi "**Komunalna buka**" ograničena je na prostiranje buke od izvora do prijemnika na otvorenom prostoru kroz atmosferu. Turbulencija, gradijent temperature i vetra, viskozna i molekularna apsorpcija, lišće, barijere, refleksije od podloge i zgrada, utiču na nivo buke i izazivaju promene u buci na mestu prijemnika. Svi navedeni fenomeni su detaljno objašnjeni. Takođe, razmotreni su glavni izvori buke na otvorenom prostoru, uključujući putnički, železnički i avionski saobraćaj, industriju, građevinske i javne radove i buku koja potiče iz susedstva.

U drugom delu se razmatra osnovna filozofija mapiranja buke u životnoj sredini, kao jednog od tri ključna elementa direktive o menadžmentu bukom u životnoj sredini. U kratkim crtama su opsane procedure koje omogućuju najbolju prognozu i mapiranje buke. Nakon toga su definisani indikatori buke koji se koriste za mapiranje. Data je i procedura za izračunavanje merodavnog nivoa buke.

Predstavljani su takođe osnovni principi u oblasti kontrole buke kao i nove tehnologije i tehnike. Predstavljani su osnovni principi kontrole buke na samom izvoru buke, na pravcima prostiranja buke i na mestu prijemnika.

*dr Dragan Veličković, red. prof. u penziji  
dr Nikola Lilić, red. prof.*



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Bilsom antifoni i Howard Leight čepovi za uši su sinonim za tehnološke inovacije, fleksibilnost i nenadmašnu udobnost uz maksimalnu zaštitu.



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Bacou, vodeća kompanija u razvoju jedinstvenih i inovativnih koncepata, nudi širok izbor ultra udobne obuće prilagođene delatnostima i inspirisane poslednjim modnim trendovima uz kombinaciju bezbednosti, udobnosti i stila.



### Miller kao sinonim za bezbednost

Kao globalni lider na polju opreme za zaštitu od pada, Bacou-Daloz već više od pedeset godina razvija rešenja kako bi učinio bezbednijim rad na visini.

Miller, kao najinovativnije priznato svetsko ime u zaštiti od pada, nudi širok izbor proizvoda koji poboljšavaju zaštitu, udobnost i performanse korisnika, i ohrabruju ga da koristi opremu 100% vremena u toku rada.



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Instrumenti za termovizijsku dijagnostiku



Termovizijska dijagnostika se koristi u tehničke i medicinske svrhe, a posebno je našla primenu u zaštiti i bezbednosnim sistemima. Termovizijske kamere omogućavaju da ljudsko oko sagleda ono što ne može da vidi. Svako telo emituje određenu količinu energije koja može da se registruje kamerom za termoviziju.

Na osnovu rezultata snimanja ili posmatranja kroz objektiv kamere, registruje se infracrveno ili toplotno zračenje i najnižeg stepena, a omogućava se izuzetno precizno merenje temperature bez ikakvog kontakta sa objektom čije se fizičke karakteristike mere. Na osnovu rezultata dobijenih testiranjem moguće je napraviti preciznu evaluaciju mehaničkih, termičkih, električnih i bioloških procesa. Informacije o struji, voltaži, otporu i energiji su dragoceni za adekvatno postavljanje električnih instalacija i njihovo puštanje u rad.

Kineska kompanija Wuhan Guide Infrared, koju na našem tržištu zastupa "Aleksandar Inženjering", godinama unapređuje tehnologiju registrovanja termalne, odnosno infracrvene energije. Termovizijske kamere "Wuhan Guide Infrared" su tehnološki superiorni proizvodi, visokih performansi i za životnu sredinu neškodljivi.

#### Za industriju TP8 serija



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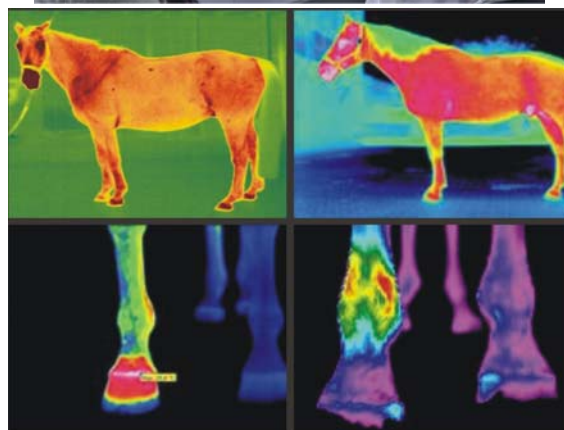
EasiR Serija je nova infracrvena kamera proizvođača Guide, koja pomera granice infracrvenog snimanja svojim odličnim karakteristikama i niskom cenom. Dizajnirana je za rad pod teškim radnim uslovima i za korisnike, koji ne moraju biti visoko obučeni, EasiR Serija je otporna na udarce i robusna i pod najtežim radnim uslovima.



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Termovizijske kamere vrlo lako i precizno detektuju detektuju temperature razlike pojedinih delova površine tela čoveka i životinja i mogu se koristiti u mnogim medicinskim

granama kao u epidemiologiji, virusologiji, reumatologiji, hirurgiji, dijagnostici kancera, metaboličkih bolesti, vaskularnih promena, stomatologiji, kao i za otkrivanje različitih bolesti i pre nego što su doživeli punu kliničku sliku pa je značajna njena uloga u ranom otkrivanju i prevenciji.



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Napredna tehnologija infracrvenog merenja temperature vam pomaže da odredite tačan izvor vatre, a time da donesete tačnu i blagovremenu odluku, koja neće biti ugrožena od strane nepreciznosti merenja detektora. Na raspolaganju je i bežični prenos video informacija, kojim se može ostvariti slanje žive slike iz prve ruke u komandni centar, gde se onda mogu doneti brze i precizne odluke.

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Obim rukopisa je ograničen na osam dvokolonskih stranica formata A4.

Templejt za pisanje radova se nalazi na sajtu časopisa:

**[www.safety.ni.ac.rs](http://www.safety.ni.ac.rs)**

Radove pripremljene prema uputstvu za štampanje slati na adresu:

Časopis Safety Engineering  
Čarnojevića 10 a, 18000 Niš  
ili elektronskim putem na e-mail adresu:

**[casopis@znrfak.ni.ac.rs](mailto:casopis@znrfak.ni.ac.rs)**

Za sva dodatna pitanja obratiti se na telefon:

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