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ȘTIINȚA ȘI INGINERIA MATERIALELOR

## POSSIBLE MATERIALS SELECTION METHOD BASED ON THE "TREE FAULT METHOD"

BY

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**Abstract:** The paper aims to bring in the attention a point of view and an adaptation of a well-known reliability prediction modeling method for use in materials selection. Basically if one can show why a system failure mode can occur, describing the combination of events, by a fault tree, it may be possible to build such a tree, but for obtaining a better choice for a material and thus obtaining a new materials selection or evaluation method. The paper discusses the steps and analogies to be made for adapting the fault tree method for use in materials selection.

**Keywords:** materials selection method; reliability prediction by the fault tree analysis.

### 1. Introduction

Designing of products generally consists in the following steps: general preparation, theoretical preparation, the sketch of the product, elaboration of the technical design, laboratory prototype making, experimenting and testing of laboratory prototype, finishing the design and correcting the errors, zero series manufacturing, in factory tests, conclusions and recommendations (Alexandru *et al.*, 1997).

Materials selection is an important stage in products design and is being done in the early stage of technical design. Nevertheless, materials can be

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changed during the experimenting and testing of laboratory prototype if necessary (Alexandru *et al.*, 1997).

## 2. About the Materials Selection Methods

There are now some efficient materials selection methods.

These methods are very efficient in the early stages of materials choice.

Traditionally there are multiple criteria for materials choice and utilization as follows: purpose, operational requirements, technological possibilities, operational environment, production size, reliability, esthetics, availability and possibility to purchase, cost (Alexandru *et al.*, 1997).

In the last few years some new “environmental friendly criteria” as biodegradability, degree of recovery, degree of using green technologies to obtain the material must be added. Moreover, it is necessary to introduce new criteria regarding the emergent risks in labor safety and health, risks linked with nanotechnologies and nanomaterials in production and in use.

For example, the metallic material choice, *i.e.* let say obtaining a certain carbon steel, for a machine element, the following steps are compulsory: evaluation as exactly as possible of the real working conditions (operational role, type, character and values for mechanical strains, temperature conditions and environment and so on); determination of the priority of main factors in the base of which the material will be chosen; establishing the materials that satisfy the criteria; necessary reasoning of selecting the variant that, in the condition of a good technological solution, possible to apply, determines the lower price in the final stage of operation (Alexandru *et al.*, 1997).

This method needs a lot of experience and the judgment of the engineer remains hidden.

To outcome this last inconvenient a matrix based method has been proposed by Gheorghe Bădăraș *et al.* (2005).

A very efficient early method of materials selection was proposed by Michael F. Ashby (2005).

The method establishes a link between material and function.

“A material has attributes. A design demands a certain profile of these. The materials selection consists in: identifying the desired attribute profile and then comparing it with those of real engineering materials to find the best match” (Michael, 2005).

The Ashby’s method has four major steps: translation, screening, ranking, and supporting information.

“Translation means express the design requirements as function, objectives, constraints and free variable. Screening means eliminate, based on established constraints, the materials that cannot do the job. Ranking means find between the screened materials those which do the job best using the objectives.

Seek supporting information means research the family history of top ranked candidates.

The final choice between competing candidates can depend on local conditions: availability of local suppliers, in-house expertise and equipment and so forth.

The use of the method is based on materials properties charts and the method itself is available as software” (Michael, 2005).

### **3. New Approach in Materials Requirement Definition Based on Block Diagrams and Use of “the Fault Tree Method”**

All these methods work properly if they are being used by an expert but even so, breakdown because of the materials can occur in the laboratory testing stage of the prototype or even worth, in the field.

In that case what can be done more?

Obviously applying again the method will give the same result.

Taking all from the top, rethinking in the first stage of defining material requirements is the solution.

How to do it better?

First of all one have to find out if any fault occurred in identifying the desired attribute profile of the design. This is not easy. In some cases, even just slight misinterpretations or “weighing” can be the cause of the fault and this is even harder to discover.

The proposed approach of the problem is simple and based on analogy using the following “tools”.

First a computer science theorem, called the structure theorem, ensures that a major task can always be divided in an equivalent finite set of subtasks given that the result of solving all the subtasks is equivalent of solving the major one.

Following this idea defining the material requirements for a design means defining sub-requirements and the links between them.

Having in mind that the properties of a material are being defined as responses at various types of requirements one can see a similitude with a system and its way of operation.

The second idea comes from the field of systems reliability, maintainability and risk, namely from reliability prediction.

“Reliability prediction (*i.e.* modeling) is the process of calculating the anticipated system reliability, availability, maintainability and safety-integrity from assumed component failure rates. It provides a quantitative measure of how close a proposed design comes to meeting the design objectives and allows comparisons to be made between different design proposals.”

Finally all these analogies being done we consider that the application of reliability prediction methods in materials choice is doable and can be efficient, of course, by making some adjustments.

For example the block diagrams are being used to describe systems failure modes and Markov analysis to calculate reliability. Smith D.J. describes the method as it follows.

“It is necessary to describe the system as a number of functional blocks which are interconnected according to the effect of each block failure on the overall system reliability.

Fig. 1 is a series diagram representing a system of two blocks such that the failure of either block prevents operation of the system.



Fig.1

Fig. 2 shows the situation where both blocks must fail in order for the system to fail. This is known as a parallel, or redundancy, case.

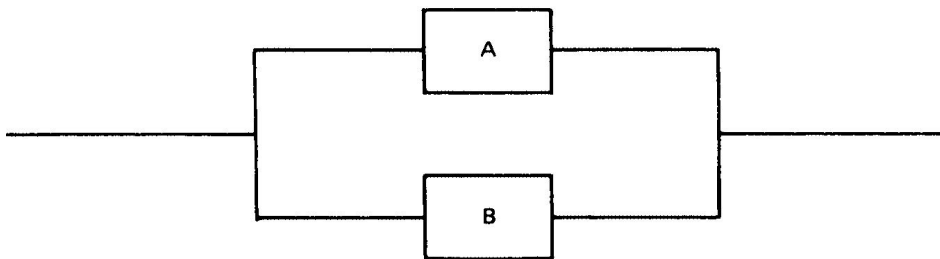


Fig. 2

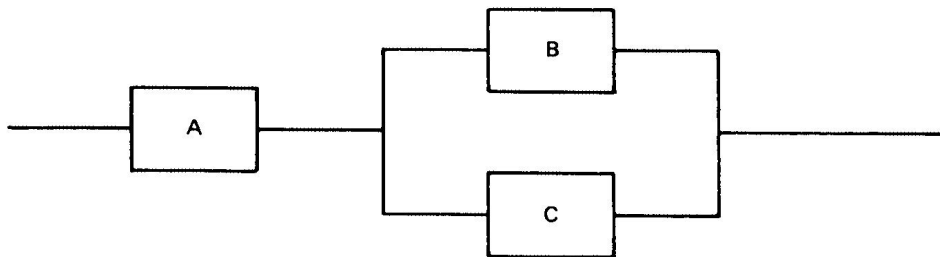


Fig.3



Fig. 3 shows a combination of series and parallel reliability. It represents a system which will fail if block A fails or if both block B and block C fail. The failure of B or C alone is insufficient to cause system failure” (Smith, 2001).

“A number of general rules should be borne in mind when defining the blocks.

1. Each block should represent the maximum number of components in order to simplify the diagram.
2. The function of each block should be easily identified.
3. Blocks should be mutually independent in that failure in one should not affect the probability of failure in another.
4. Blocks should not contain any significant redundancy otherwise the addition of failure rates, within the block, would not be valid.
5. Each replaceable unit should be a whole number of blocks.
6. Each block should contain one technology, that is, electronic or electro-mechanical.
7. There should be only one environment within a block” (Smith, 2001).

The adjustments needed for materials choice method proposed by the authors are as follows:

a) the series diagram Fig. 1 can be used when describing properties without connections, for example, thermal conductivity and cold plastic deformability (for a steel).;

b) the parallel diagram Fig. 2 can be used when describing connected properties, for example, weldability and cold plastic deformability (for a steel).

When defining blocks, (for materials selection this would mean mentioning the properties needed in the material profile), only the first four from the above rules can be used.

Calculation of “system reliability” will be equivalent with materials selection when comparing variants.

Relating the block failure rates to the system reliability is a question of mathematical modeling which is given in literature (Smith, 2001).

Literature also states “in the event that the system reliability prediction fails to meet the objective, then improved failure rate (or down time) objectives must be assigned to each block by means of reliability allocation” (Smith, 2001) and this shows the possibility of improving materials selection, namely finding a better material if it exists or, envisaging the need for another constructive solution.

Authors believe that a proper way to do it is to build and, if it is possible, evaluate “an adapted fault tree.”

In short, the fault tree method is usually applied in the field of prediction reliability and risk. Smith D.J. shows the method as it follows.

“A Fault Tree is a graphical method of describing the combination of events leading to a defined system failure.

In fault tree terminology the system failure mode is known as the top event.

The fault tree involves essentially three logical possibilities and hence two main symbols. These involve gates such that the inputs below gates represent failures. Outputs (at the top) of gates represent a propagation of failure depending on the nature of the gate.

The three types are:

The OR gate whereby any input causes the output to occur;

The AND gate whereby all inputs need to occur for the output to occur;

The voted gate, similar to the AND gate, whereby two or more inputs are needed for the output to occur” (Smith, 2001).

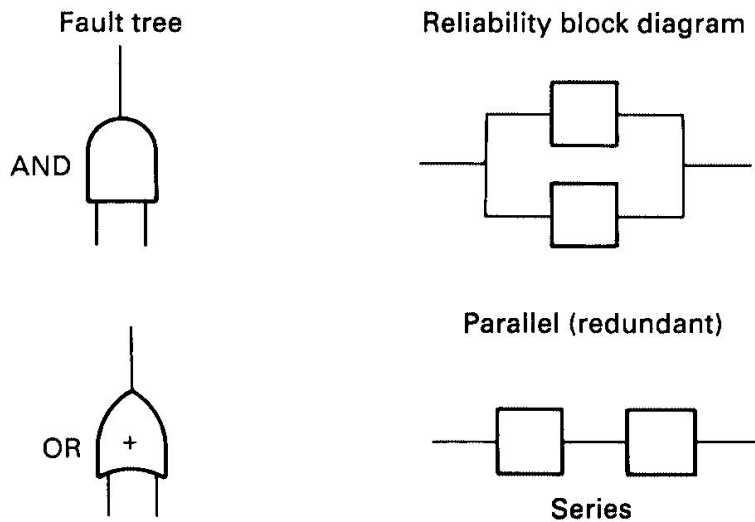


Fig. 4 – Symbols of gates and equivalence with reliability block diagram (Smith, 2001).

For materials selection an “adapted fault tree” would be the describing of the conditions needed for guarantee the success of a design.

From top down, the blocks will have as equivalent:

- first line (level) - the general criteria a material should meet;
- the second level should express the main properties expressing a given criteria;
- in some cases more levels can be also be expressed.

For example if the materials candidates are metallic materials some combinations of properties can be obtained by technological design and control of the micro let's say by heat treating. For example, the supporting features at microstructure level would be: the grain size, the quantitative phase composition and distribution and so on.

#### 4. Comments

The paper presents just a sketch of a proposed method based on the experience of the authors in metallic materials properties and selection and in metallic materials failure diagnosis.

It has to be stated that the possibility of exact evaluation of an “adapted fault tree” remains in discussion. To mention just some reasons to prove it difficult: not all the properties of a material can be express in figures; it is difficult to measure technological issues and differences that can appear when processing quasi similar materials; the costs of economical evaluation of processing and so on.

Also translating the analogy from failure rates, usually obtained from practice, to some values to measure the merits of a certain choice must be stated.

Nevertheless the method enables comparison between material variants and this is why we consider it possible even if some more work must be done.

Moreover the method carries with it “the original features”, namely:

“Reliability prediction is an imprecise calculation, but it is nevertheless a valuable exercise for the following reasons:

a) It provides an early indication of a system’s potential to meet the design reliability requirements.

b) It enables an assessment of life cycle costs to be carried out.

c) It enables one to establish which components, or areas, in a design contribute to the major portion of the unreliability.” (Smith, 2001).

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#### POSSIBILĂ METODĂ DE ALEGERE A MATERIALELOR BAZATĂ PE METODA ARBORELUI DE DEFECTARE

(Rezumat)

Lucrarea are ca scop să aducă în atenție un punct de vedere și o adaptare a binecunoscutei metode de modelare a arborelui de defectare din domeniul prezicerii

fiabilității pentru a fi utilizată în alegerea materialelor. În principiu dacă se poate arăta de ce apare un anumit mod de defectare a unui sistem descriind combinația de evenimente printr-un arbore de defecte, ar putea fi posibil să se construiască un astfel de arbore, dar pentru a obține o alegere mai bună a unui material și astfel, să se obțină o nouă metodă de alegere sau evaluare a alegerii materialelor. Lucrarea discută pașii care trebuie parcurși și analogiile care trebuie făcute pentru a adapta metoda arborelui de defectare pentru a fi utilizată în alegerea materialelor.

**ANTI-OXIDANT RICH DIET, HEALTHY LIFE-STYLE AND A  
RIGOROUS RADIATION EXPOSURE CONTROL PROGRAM  
PROTECT HEALTHCARE EMPLOYEES FROM RADIATION-  
INDUCED OXIDATIVE DAMAGE**

BY  
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**Abstract:** Reactive oxygen species (ROS) are defined as free radicals of oxygen and hydroxyl ions which at higher concentration create oxidative stress and may cause many diseases including cancer. Ionizing radiation (IR) is one of the main sources of ROS generation. This pilot study determined potential health risks associated with oxidative stress due to long-term low-dose IR exposure and analyzed effects of dietary habits and lifestyle in healthcare personnel in a university hospital setting. Participants were chosen from a healthcare workforce occupationally exposed to IR for more than 10 years. Employees in the non-radiation sector were included as study controls. A total of 20 participants were included in the study. Oxidative Stress is directly measured by intracellular ROS level in the blood and indirectly by total antioxidant level in urine samples. Genotoxicity was determined from the buccal smears by micronucleus. No significant differences were observed between experimental and control participants regarding ROS, anti-oxidant levels, and micronucleus. Results indicated that regular consumption of antioxidant rich diet, practicing healthy life-style and implementation of a rigorous radiation exposure control program might protect radiation workers from the harmful effects of ROS following long-term low dose radiation exposure.

**Keywords:** ionizing radiation; reactive oxygen species; oxidative stress.

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## 1. Introduction

ROS are free radicals of oxygen which include oxygen ions and peroxides and can either be organic or inorganic. They are highly reactive due to presence of unpaired valence electrons. ROS is a byproduct of normal metabolism of  $O_2$  and has important roles in cell signaling at low level. Oxidative stress is caused by the imbalance between Reactive Oxygen Species and Antioxidants and is involved in many diseases including cancer. Ionizing radiation (IR) is one of the main sources of Reactive Oxygen Species (ROS). Several studies have indicated that low dose IR causes ROS generation in cancer patients and preclinical animal models. Although there are strict annual exposure limits for occupationally exposed radiation workers in the United States, limited research has been undertaken to evaluate the relationship between long term exposure to low dose IR and oxidative damage in the US radiation workforce. This study has focused on the measurement of reactive oxygen species level in the radiation workers exposed to long-term low dose of IR.

The objective of the study is to establish a correlation between IR and level of oxidative stress among US radiation workers exposed to low doses of IR for a long time. The study also evaluated if there is a preventive advantage over oxidative stress in radiation workers practicing healthy lifestyle and consuming anti-oxidant rich food.

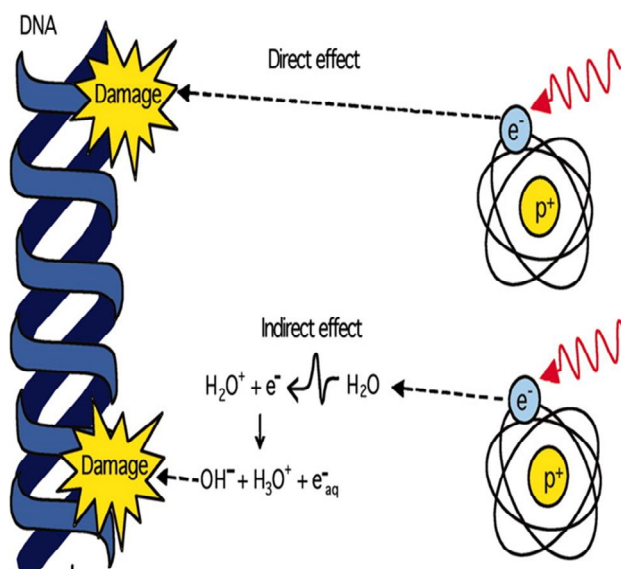


Fig.1 – Direct and Indirect effect of DNA Damage to IR exposure.  
Morgan WF and SOWA MB, PNAS, 2005.

## 2. Methods

This is a Cross Sectional clinical study. Total 20 participants volunteered in the pilot study. Experimental group and control group consisted of 10 people each. Experimental group has been chosen from a Hospital and have been exposed to IR for 10 years or more. Control group has been chosen from non-radiation sector of the same hospital. Institutional Review Board (IRB) approval has been obtained for this study. Detail radiation doses were obtained from the dose badges collected by the Occupational Health and Safety division of the University. Survey questionnaires about food intake and healthy lifestyle were handed out to participants. Intra-cellular ROS levels were determined from erythrocytes. Total Antioxidant levels were determined from urine samples. Buccal swab were analyzed for presence of micronucleus.

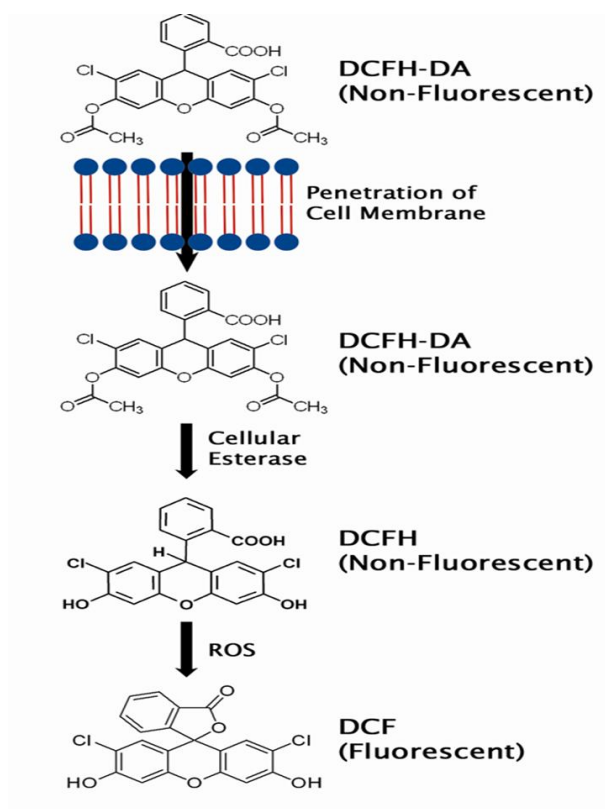


Fig. 2 – Mechanism of DCF assay for Intracellular ROS detection (Cell Biolabs, Inc).

### 3. Conclusion

The study did not find significant oxidative stress in University Hospital employees exposed to low dose IR compared to control participants. This study conclude that hospital employees in a Higher Education University setting are keeping themselves safe by maintaining stringent regulations to IR exposure and practicing healthy lifestyle and anti-oxidant rich food intake. In the future, this study can be expanded to individuals employed in private nuclear industries or rural health clinics to find out oxidative stress in them due to long term IR exposure relative to socioeconomic status and education level.

**Acknowledgements.** This study was supported by Deep South ERC through a Pilot Project Research Training grant (NIOSH 5T42OH008436). Special thanks to Allison Pollard (RN), Deep South Center for Occupational Health and Safety, Dr. Rui Ming Liu, Max Richard, Radiation Safety Dept. and Dept. of Pathology of UAB.

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DIETA BOGATĂ ÎN ANTIOXIDANȚI, STILUL DE VIAȚĂ SĂNĂTOS ȘI UN  
PROGRAM DE CONTROL RIGUROS AL EXPUNERII LA RADIAȚII  
PROTEJEAZĂ SĂNĂTATEA ANGAJAȚILOR DE DAUNE OXIDATIVE INDUSE  
DE RADIAȚIE

(Rezumat)

Speciile de oxigen activ (ROS) sunt definite ca radicali liberi ai oxigenului și ionilor hidroxil care la concentrații mai mari crează solicitări oxidative și pot cauza multe boli inclusive cancer. Radiația ionizantă (IR) este una dintre principalele surse generatoare de ROS. Acest studiu pilot a determinat riscul potențial de îmbolnăvire asociat stresului oxidative datorat expunerii îndelungate la doze reduse de radiație ionizantă și a analizat efectele obiceiurilor alimentare și a stilului de viață asupra sănătății personalului dintr-un spital universitar. Participanții au fost aleși din cadrele medicale de îngrijire expuse la IR pe o durată mai mare de 10 ani. Angajații din sectoarele fără radiații au fost incluse ca lot de control. În studiu au fost incluși un număr total de 20 de participanți. Stresul oxidativ este măsurat direct prin nivelul ROS intracelular din sânge și indirect, prin nivelul total de antioxidanți din probele de urină. Genotoxicitatea a fost determinată prin micronuclei pe frotiuri bucale. Nu au fost observate diferențe semnificative între participații din experiment și lotul de control în ce privește ROS, nivelul de antioxidanți și micronuclei. Rezultatele au indicat că un consum regulat de antioxidanți în dietă, practicarea unui stil de viață sănătos și implementarea unui program de control riguros de expunere la radiații ar putea proteja lucrătorii din zona cu radiații de efectele dăunătoare ale speciilor de oxigen activ în urma expunerii pe termen lung la radiații în doze scăzute.



**COMPARISON OF TOLUENE EFFICIENCY OF FABRICATED  
SINGLE-WALLED CARBON NANOTUBE (SWNT)  
BUCKYPAPER (BP)**

BY

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**Abstract:** Single-walled carbon nanotubes (SWNTs) were fabricated into buckypaper (BP) to be used as sorbent in volatile organic compound (VOC) passive samplers. Three fabrication methods included non-cleaned, acetone-cleaned, and methanol-cleaned, and toluene adsorption efficiency by different fabrication methods was compared. Surface area, pore size, and adsorption capacity were examined as indicators for adsorption efficiency. As a result, BET surface area and pore diameter of non-cleaned BP, acetone-cleaned BP, and methanol-cleaned BP were 45, 217, and 348 m<sup>2</sup>/g, and 15, 9, 8 nm, respectively. Therefore, cleaning process increased surface area and decreased pore diameter. In addition, methanol-cleaned BP had higher adsorption capacity, 770 mg toluene/g BP, compared to acetone-cleaned BP, 618 mg toluene/g BP, as it could be predicted from the surface area measurement (non-cleaned BP data not included). Methanol-cleaned BP was the most adsorptive, hinting for further investigation in photothermal desorption efficiency for the application to VOC passive samplers.

**Keywords:** single-walled carbon nanotube (SWNT); buckypaper (BP); adsorption, desorption, photothermal desorption (PTD); volatile organic compounds (VOCs); toluene.

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## 1. Introduction

Charcoal or activated carbon has been commonly used as a sorbent for sampling volatile organic compounds (VOCs) because of high adsorption capacity and availability. For analysis, VOCs are usually desorbed through chemical or thermal desorption along with gas chromatography (GC). In case of chemical extraction, at least 30 min of desorption in usually a toxic solvent (*e.g.*, carbon disulfide) is required and the desorbed sample is transferred to GC vials for analysis (Fabrizi *et al.*, 2013). Only a tiny portion (*i.e.*, 0.1 %) of the prepared sample is analyzed in GC. On the other hand, thermal extraction traditionally has been one time analysis and there have been reliability issues (*e.g.*, complicated plumbing) (Harper, 2000). Though the thermal desorption system has been improved to overcome those drawbacks, GC system with thermal extraction unit is quite expensive.

Recently, a new analytical technique called photothermal desorption (PTD) has been suggested as an alternative for VOC analysis of passive sampler (Floyd *et al.*, 2014). PTD employs a visible light to thermally desorb an analyte directly from sorbent and thus, it can eliminate such expensive laboratory procedures and shorten exposure assessment time. Moreover, it bridges the sensitivity gap between chemical and thermal desorption. Single-walled carbon nanotubes (SWNTs) have been investigated for the application of PTD as a potential sorbent as SWNTs have large surface area, indicating high adsorption capacity, and can be more porous through further fabrication processes (Bacsa *et al.*, 2000). Especially SWNTs have been shown excellent thermal conductivity (Choi *et al.*, 2005; Berber *et al.*, 2000). In our study, 20 mg SWNT powders were pre-loaded with 435  $\mu\text{g}$  toluene and a light flash (4.77 J) was applied once per minute and repeated 10 times. Recovery rates were 0.87 and 7.7% for the first flash and all ten flashes, respectively. However, only one type of SWNT (chemical vapor deposition, CVD) was examined and it was in powder form.

The purpose of this study was to develop a sorbent which works efficiently with PTD using arc discharge SWNTs. For that, three fabrication methods of SWNTs were investigated in order to make them a self-standing form called buckypaper (BP) since a self-standing form would be handy when building a passive sampler with it. Adsorption efficiencies of the fabricated BPs were examined in terms of surface area, pore size, and toluene adsorption isotherm. Toluene was selected as a representative VOC because of similar physical and chemical properties to benzene but less toxic.

## 2. Methods

Arc discharge SWNT solution suspended in 1% surfactants (*i.e.*, sodium cholate and sodium dodecyl sulfate) was purchased at Nanointegris and

three fabrication methods were designed: non-cleaned, acetone-cleaned, and methanol-cleaned. The typical filtration process is shown in Fig. 1. In the first method (non-cleaned), 50 mg SWNTs were suspended in 400 ml acetone for 15 hours and the solution was filtered through a filtration apparatus in which a PTFE (polytetrafluoroethylene) membrane filter (EMD Millipore, 47 mm, 5  $\mu\text{m}$  pore) was inserted. After the solution was filtered through, CNT cake deposited onto the membrane filter was delaminated to obtain a BP. The second method (acetone-cleaned) was the addition of cleaning process to the first method. 250 ml deionized (DI) water (18.2 M $\Omega$ .cm) and 50 ml acetone were poured into the filtration apparatus after the solution filtered through. The cleaning process with DI water and acetone was repeated. The last method was the same as the second one except methanol was used instead of acetone.

After BPs were fabricated, their adsorption efficiency (*i.e.*, surface area, pore size, and toluene adsorption isotherm) was characterized using Micromeritics® ASAP 2020 Physisorption analyzer. Nitrogen was used as an adsorbate for surface area and pore size analysis and 2 samples per each were used. Before analysis, samples were degassed at 200°C for 60 min. Analysis was performed at 77 K (–196°C) two times. Toluene adsorption isotherm was performed at Micromeritics because of the possible contamination of our equipment. 1 sample per each was sent for analysis and non-cleaned sample was not included because of considerably lower surface area (see result section). Samples were degassed at 300°C for 960 min, and analysis was done at 25°C. After toluene adsorption isotherm, samples were re-analyzed for surface area and pore size since such long period of degassing would have changed the properties of the samples. Analysis was repeated 2 times.

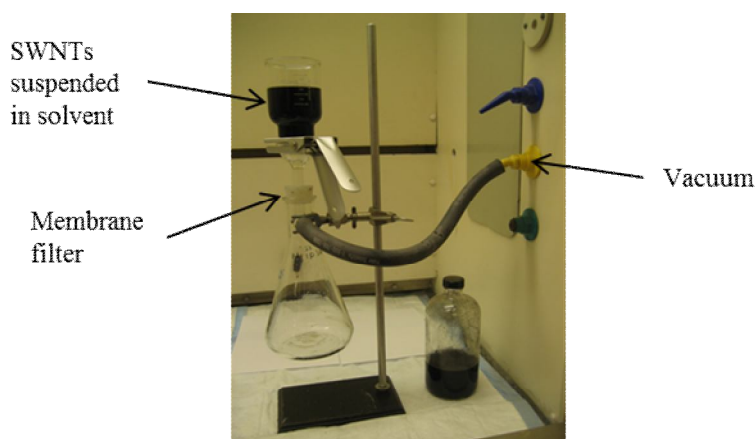


Fig. 1 – Filtration process of SWNTs.

### 3. Results

Three types of BPs were successfully fabricated (Fig. 2). Non-cleaned BPs showed 45 m<sup>2</sup>/g Brunauer, Emmett and Teller (BET) surface area with 15 nm average pore width while acetone-cleaned BPs and methanol-cleaned BPs exhibited 217 and 348 m<sup>2</sup>/g BET surface areas with 9.1 and 8.0 nm average pore widths, respectively (Table 1). The adsorption capacity from toluene adsorption isotherm was 618 and 770 mg toluene/g BP for acetone-cleaned and methanol-cleaned BPs, respectively. Surface area and pore size analysis data after toluene adsorption isotherm are shown in parentheses in Table 1. Acetone-cleaned BP exhibited 349 m<sup>2</sup>/g BET surface area with 9.8 nm pore size whereas methanol-cleaned BP had 421 m<sup>2</sup>/g BET surface areas with 8.6 nm pore size.



Fig. 2 – Buckypapers non-cleaned, acetone-cleaned, and methanol-cleaned from left.

**Table 1**  
*BET Surface Area and Pore Size*

Fabrication method	Non-cleaned BP	Acetone-cleaned BP	Methanol-cleaned BP
Surface area, [m <sup>2</sup> /g]	45±2 - <sup>1</sup>	217±27 (349±10) <sup>2</sup>	348±13 (421±6) <sup>2</sup>
Pore width, [nm]	14.9±0.0 - <sup>1</sup>	9.1±0.4 (9.8±0.1) <sup>2</sup>	8.0±0.1 (8.6±0.1) <sup>2</sup>

<sup>1</sup> not analyzed; <sup>2</sup> re-analyzed after toluene adsorption isotherm

### 4. Conclusion/Discussion

The cleaning process increase surface area and decreased the average pore width, indicating the impurities (*i.e.*, surfactants and solvents) were removed by the cleaning process. Toluene adsorption capacity increased with increasing surface area of BP. Methanol-cleaned BP was the most adsorptive, facilitating PTD investigation. Longer degassing resulted in increased surface area and more examination on other fabrication processes (*e.g.*, annealing) is necessary in order to increase surface area.

Since surfactants in SWNTs seemed to be affecting surface area, a powder form could be an alternative. Other types of SWNTs (*e.g.*, high pressure carbon monoxide) will also have to be examined to find the most appropriate sorbent for PTD application.

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## COMPARAȚIE A EFICIENȚEI ADSORBȚIEI TOLUENULUI PE HÂRTIE SPECIALĂ DIN NANOTUBURI DE CARBON CU UN SINGUR PERETE

(Rezumat)

Nanotuburile de carbon cu un singur perete au fost introduse în fabricarea hârtiei speciale (BP) utilizate în construcția indicatorilor pasivi ca absorbant a compușilor organici volatili. Au fost comparate trei metode de fabricație incluzând nanotuburi necurățate, curățate cu acetonă și curățate cu metanol și a fost comparată eficiența adsorbției toluenului. Au fost examinate ca indicatori ai eficienței adsorbției aria suprafeței, dimensiunea porului și capacitatea de adsorbție. Ca rezultat, aria suprafeței Brunauer, Emmett and Teller (BET) și diametrul porului hârtiei cu nanotuburi necurățate, a celei cu nanotuburi curățate cu acetonă și a celei cu nanotuburi curățate cu metanol au fost 45, 217 și 348 m<sup>2</sup>/g și 15, 9, 8 nm, respective. De aceea, procesul de curățare a mărit aria suprafeței și a micșorat diametrul porului. În plus, hârtia cu nanotuburi curățate cu metanol are o capacitate de adsorbție mai mare a toluenului 770 mg toluen/g, în comparație cu cea cu nanotuburi curățate cu acetonă 618 mg toluene/g după cum s-ar fi putut prevedea din măsurarea ariei suprafeței (datele privind BP cu nanotuburi necurățate nu au fost incluse). Hârtia cu nanotuburi curățate cu metanol a fost cea mai adsorbantă recomandând investigații suplimentare în ce privește eficiența desorbției fototermice pentru aplicații în indicatori pasivi pentru compuși organici volatili.





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## USE OF SCAFFOLD TOOLKIT FOR THE EVALUATION OF HEALTH, SAFETY AT WORK AND ENVIRONMENT PROTECTION FOR THE MANUFACTURING PROCESSES OF PANELS

BY

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RAZVAN-IOAN GRAPINA<sup>2</sup> and COSTEL ȚUGUI<sup>3</sup>

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**Abstract:** The case study of manufacturing processes was conducted in ICECON S.A. - Technological Development Department, that has proper equipment for manufacturing fire-resistant panels containing MNMs -activated bentonite nano-clay and recycled powders from WEEE (Waste Electrical and Electronic Equipment). The case study used as MNMs: bentonite nano-clay from natural sources activated with 5–10% sodium carbonate to improve the ion exchange process and recycled powders from WEEE according to Ursan (2014).

The technological development department of ICECON SA have conducted an extensive analysis for identifying the dangers that can occur during processing, manipulation and instalation of pannels made.

The package “SCAFFOLD” has been used during the study for risk assesment and generation of models of instructions at the working place

The risk evaluated was low in the phase of production but rather big after (cutting and drilling) of pannels. On the basis of recommandations of “SCAFFOLD” package a procedure concerning Health and Safety at work and Emvironment protection has been done.

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On the basis of this study the Company ALL GREEN has developed a new prototype of electromagnetic ecranation systema, containing plaster activated with BENTONITE NANO-CLAY, recycled powders from **WEEE**.

**Keywords:** risk assement; waste electrical and electronic equipment.

## Materials

The generic formula for bentonite is as follows:

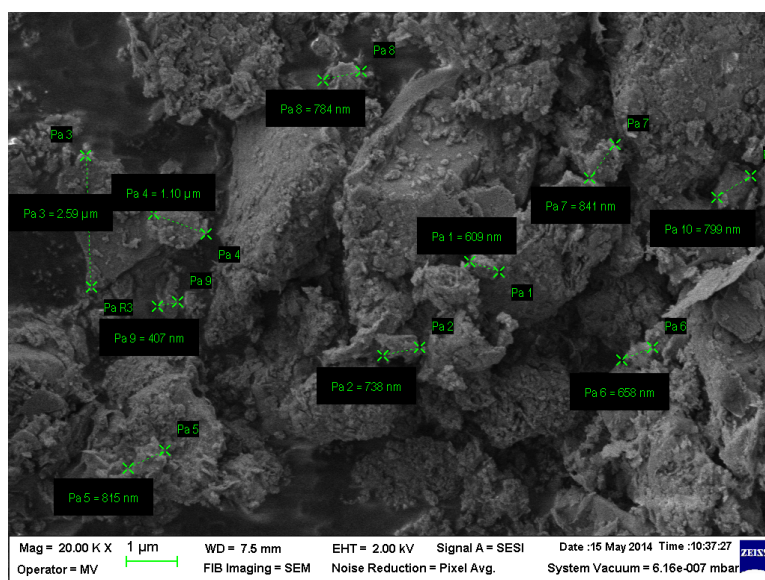
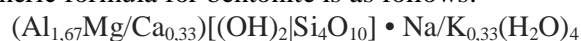


Fig. 1 – Particle dimensions of bentonite nano-clay.



Fig. 2 – Pilot plant for manufacturing of fire-resistant panels.

Pilot plant for manufacturing of fire-resistant panels by use of bentonite nanoclay activated with sodium carbonate and recycled powders from WEEE, consists on basic process of Storage and dimensioning of raw materials, basic process of preparation of compositions (The composition preparation requires: dosage of raw materials and mixing/homogenization of raw materials), manufacture of panels, Storage of panels and ageing – Racks/storage room.

For the implementation and auditing of the body ASOCIACION Espanola in Spain NORMALIZACION Y CERTIFICACION, the Management System for Occupational Health and Safety, of the Department of Technology Development from ICECON SA performed an extended analysis to identify all hazards that may occur in the manufacturing processes, handling and installation of the panels made based on bentonite nano-powder activated with sodium silicate and recycled powders from WEEE. Accordingly, the exposure to bentonite nano-clay can cause:

- a) eye irritation;
- b) unprotected skin irritation – mainly hands;
- c) inhalation of nanoparticles;
- d) ingestion of nanoparticles.



ICECON - ROMANIA

IUC - 2: Manufacture of fire-resistant panels containing MNMs (activated bentonite nano-clay)

## MAIN PROCESSES

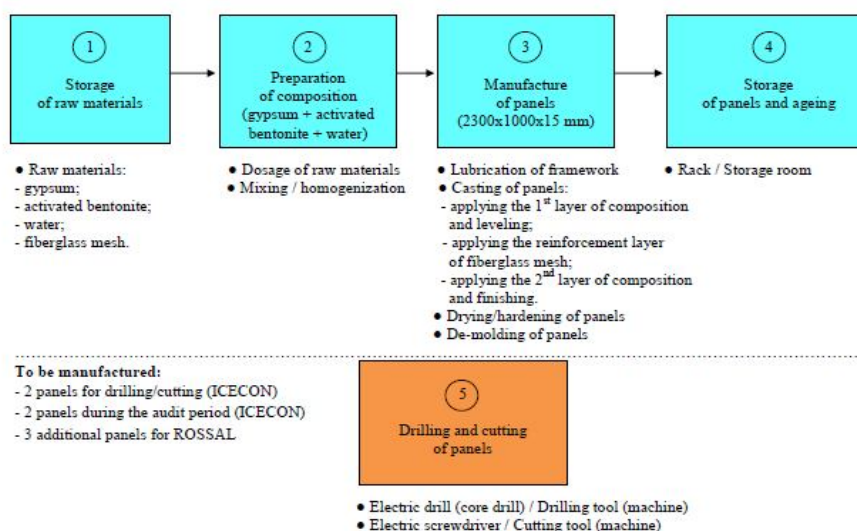


Fig. 3 – Scheme of manufacturing processes of fire-resistant panels.

Calculation of mass concentration of powder nano-clay is according with ISO/PDTS 12901-1 “Nanotechnologies – Guidelines for occupational risk

management applied to engineered nanomaterials – Part 1: Principles and approaches”.

Evaluation of hazard band and emission potential risk is according with ISO/PDTS 12901-2 “Nanotechnologies – Guidelines for occupational risk management applied to engineered nanomaterials – Part 2: The use of the Control Bending approach in occupational risk management”.

Beyond standard protective equipment worn by manufacturing workers, the personnel working with panels containing MNMs – activated bentonite nano-clays and recycled powders from WEEE – shall be required to wear:

1° **Gloves** – nitrilic-glovers FFP3 for processes which require preparation by mixing a composition based on bentonite nano-clays activated with sodium carbonate, plaster and cutting and glass fiber network application;

2° **Gloves** for processes which require preparation by mixing a composition based on bentonite nanoclys, and respectively glass fiber network application/cutting;

3° **Masks** – type FFP1 for processes which require preparation by mixing a composition based on bentonite nanoclys, and respectively glass fiber network application / cutting.

The IUC was deployed under a customized plan, basically consisting in 4 reference steps:

- 1) information and first training;
- 2) diagnosis of the OHSMS;
- 3) implementation, monitoring and internal audit;
- 4) external audit .



Fig. 4 – Workers during quantitative risk assessment.

After carrying out the external audit, the audit team made recommendations on procedure “Health, Safety at work and environment protection for the manufacturing processes of Panels based on bentonite nano-clay and plaster” Cod.: P-SSM-01 Ed. 01 rev.00 valid from 2014-05-01, training of workers on the criteria to be used to evaluate the significance of risk monitor and measure MNMs RMM performance, updating knowledge for identifying and accessing the legal and other requirements applicable to MNMs RMM, and its compliance.

Scaffold Toolkit was one of the main tool used during the IUC. The General Information about the company was generated, see Fig. 5.

General Information

General data

Company name: ICECON SA

Address: Sos. Pantelimon 266

Post code: 021652 City: Bucharest

Province: - Country: Romania

☒ SME

VAT number: 7702002

OK Cancel

Fig. 5 – Toolkit personalisation for ICECON SA / general information.

The process to be done in IUC – FR Panels was introduced (Fig. 6).

Task List

Process: 4. Industrial

Description	NOAAs
4.1. Clearance and demolition	
4.2. Formwork and concrete	
4.3. Foundation laying	
4.4. Insulations and FR panels	
4.5. Iron works - Walls plumbing	
4.6. Finishing paint polish	
4.7. Maintenance	
4.8. Demolition	

Description	NOAAs
4.4.1. Off-site manufacturing	Nanocleys, CellINF
4.4.2. Fitting of the panels and ma...	Nanocleys, CellINF

Fig. 6 – Toolkit personalisation for ICECON process/general information.

In the next steps, the toolkit was used for specific implementation and audit operations (Figs. 7,...,12).

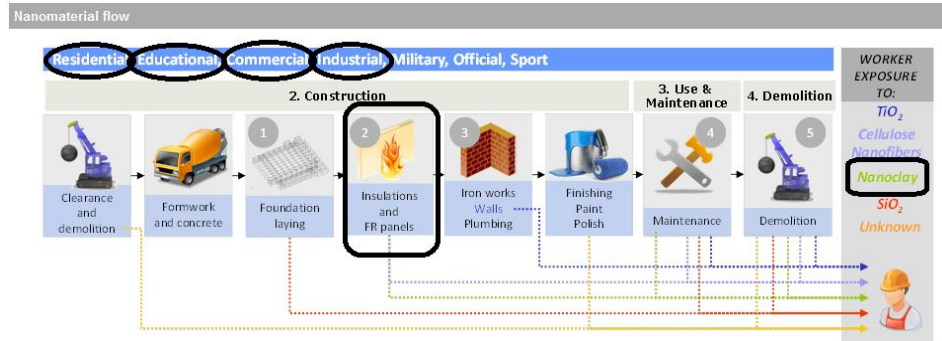


Fig. 7 – Selecting areas of interest.

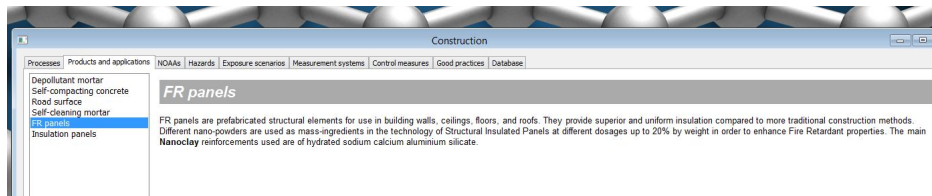


Fig. 8 – Selecting products and possible application.

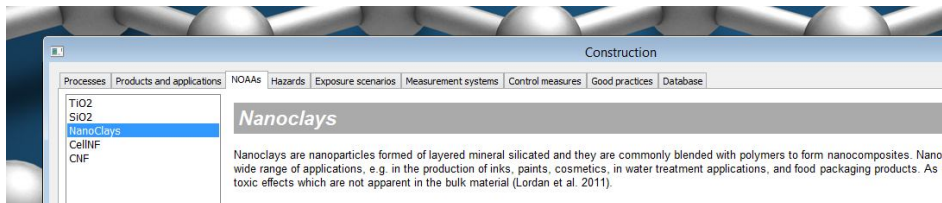


Fig. 9 – Selecting products nanoclays and nanoparticles.

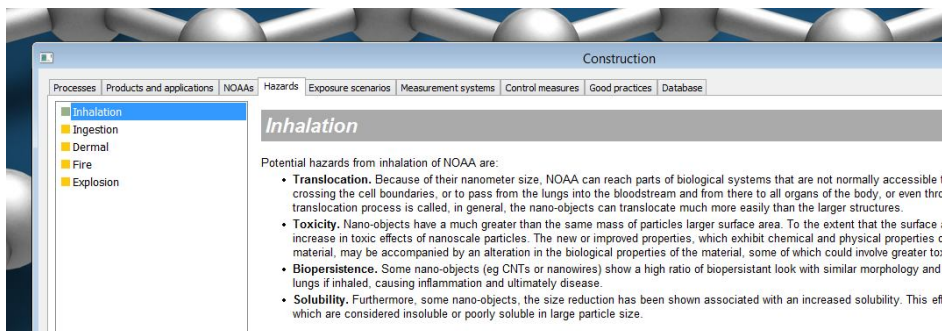


Fig. 10 – Establish the hazards.



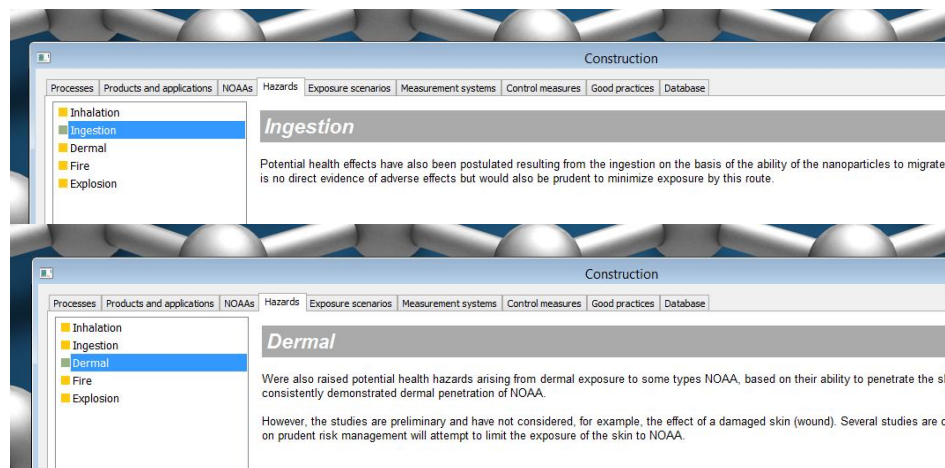


Fig. 10 – Establish of the hazards.

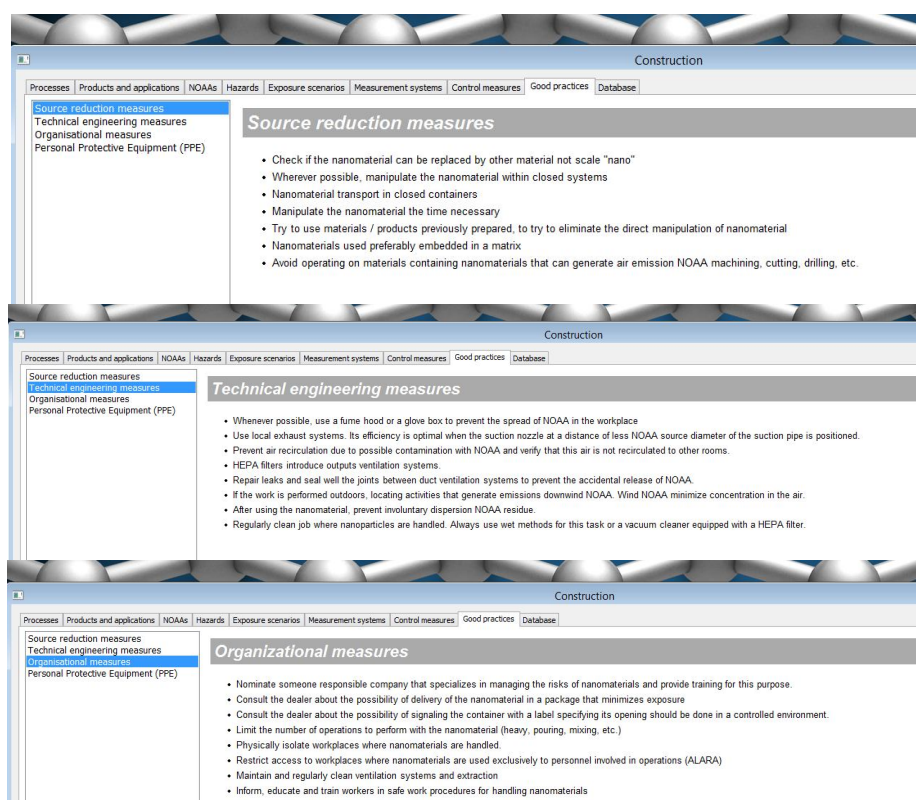


Fig. 11 – Toolkit scenario personalisation – implementation for ICECON SA.

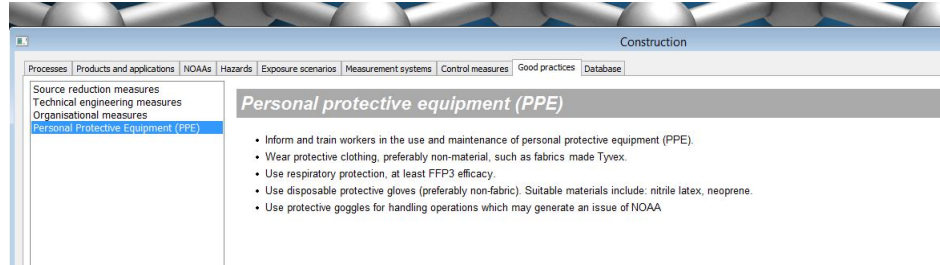


Fig. 11 – Toolkit scenario personalisation – implementation for ICECON SA.

Finally, the Scaffold Toolkit was used during IUC for Risk Management and for generating templates for workplace instructions (Figs. 12 and 14).

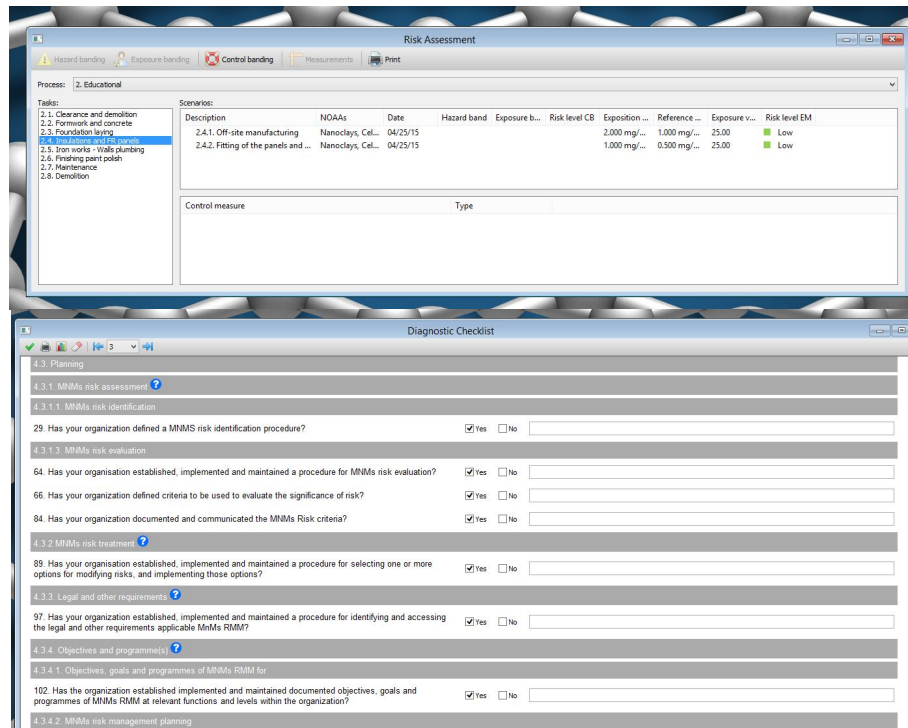


Fig. 12 – Risk assessment – level ‘low’; measures and docs.

The Toolkit Risk Management module was used for qualitative risk assessment. After the specification of the process, task and scenario data, risk assessment module was turned on. With the help of the Hazard and Exposure “Wizards” we integrated questions specified in ISO 12901-2 for determining proper class in order to quickly determine our control category.



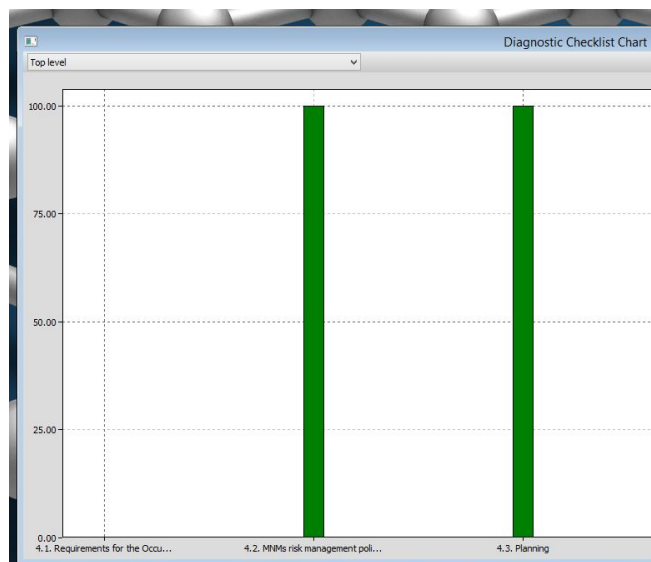


Fig. 13 – Checklist.

The figure shows the 'Risk Assessment' software interface. It includes a 'Process' dropdown set to '2. Educational', a 'Tasks' list on the left, and a 'Scenarios' table. The table has columns for Description, NOAAs, Date, Hazard band, Exposure b..., Risk level CB, Exposure v..., Reference, Exposure v..., and Risk level EM. Two scenarios are listed, both with a 'Low' risk level. Below the table is a section for 'Control measure' and 'Type'.

Description	NOAAs	Date	Hazard band	Exposure b...	Risk level CB	Exposure v...	Reference	Exposure v...	Risk level EM
2.4.1. Off-site manufacturing	Nanoclays, Cel...	04/25/15				2,000 mg/...	1,000 mg/...	25.00	Low
2.4.2. Fitting of the panels and ...	Nanoclays, Cel...	04/25/15				1,000 mg/...	0,500 mg/...	25.00	Low

Fig. 14 – Qualitative risk assessment – implementation for ICECON SA.

The risk was evaluated as low for processing but high for post-processing (cutting & drilling) of panels. Based on the Scaffold toolkit recommendations, a specific procedure was conceived: **PROCEDURE: HEALTH, SAFETY AT WORK AND ENVIRONMENT PROTECTION** - for the manufacturing processes of PANELS BASED ON BENTONITE NANOC-LAY, RECYCLED POWDERS FROM WEEE AND PLASTER. The risk was reduced which means that the introduction of nanomaterials in the development of building materials is beneficial and feasible.

Based on this study **ALL GREEN** Company has developed a new prototype of the electromagnetic insulation system containing plaster activated with BENTONITE NANO-CLAY, recycled powders from **WEEE** (Fig. 15).

Construction															
Processes   Products and applications   NCAs   Hazards   Exposure scenarios   Measurement systems   Control measures   Good practices   Database															
PROCESS						INHALATION								DERMAL	
Nano-Object	Application	Code	Exposure Scenario	Task Description	Engineering Controls	Measurement procedure	Device	Particles	Particles	Particles	Particles	Mass	Mass	Mass	SEM
								Mean (µm)	Max (µm)	Min (µm)		Time	Exposure (mg/m <sup>3</sup> )	Exposure 8 TWA	NOAA
Nano-clay	FR panels	E320	On site assembly/Machining- Control	Machining	Out door	1. Release	ELPI (µm)	5.04E+03	1.05E+04	3.37E+03					
Nano-clay	FR panels	E320	On site assembly/Machining- Material B	Machining	Out door	1. Release	ELPI (µm)	5.90E+03	8.47E+03	3.45E+03					
Nano-clay	FR panels	E320	On site assembly/Machining- Material C	Machining	Out door	1. Release	ELPI (µm)	6.28E+03	7.70E+03	4.79E+03					
Nano-clay	FR panels	E320	Background	Background	Out door	1. Release	ELPI (µm)	6.54E+03	1.50E+04	2.51E+03					
Nano-clay	FR panels	E321	Demolition-Composite (PA- 50% PV) (control)	Shredding	Out door	1. Release	ELPI (µm)	1.91E+05	1.04E+07	4.28E+03					
Nano-clay	FR panels	E321	Demolition-Composite (PA- 40 NPV) (Material B 5 %nanoclay)	Shredding	Out door	1. Release	ELPI (µm)	1.90E+04	1.91E+05	2.02E+03					NO
Nano-clay	FR panels	E321	Demolition-Composite (PA- 30% PV) (Material C 5 %nanoclay)	Shredding	Out door	1. Release	ELPI (µm)	1.55E+04	2.79E+05	1.07E+03					NO
Nano-clay	FR panels	E321	Background	Background	Out door	1. Release	ELPI (µm)	5.96E+03	6.96E+03	4.74E+03					
Nano-clay	FR panels	E322	Accidental Fire: MNMs combustion Material A	Fire											
Nano-clay	FR panels	E322	Accidental Fire: MNMs combustion Material C (1.25 % nano-clay)	Fire											

Fig. 15 – Prototype of the electromagnetic insulation system.

**Acknowledgment.** FP-7 *Scaffold* Project: Operational occupational Risk Management Models and tools for MNMs in the industry, Grant Agreement Nr: NMP4-SL- 2012-280535; **RECEMAT** Project / Operational Program of ANCS under grant ID 1372, SMIS 41074, nr. 460/03.04.2013.

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- \* \* INSHT (2011) MTA/MA – 014/A11 Determination of airborne particles (inhalable, thoracic and respirable fractions) in air (INSHT – Spanish National Institute for Safety and Hygienics).
- \* \* NIOSH 0600 Particulates not otherwise regulated, respirable.

UTILIZAREA PACHETULUI “SCAFFOLD” PENTRU EVALUAREA SĂNĂTĂȚII,  
SECURITĂȚII ÎN MUNCĂ ȘI PROTECȚIEI MEDIULUI PENTRU PROCESELE DE  
PRODUCERE A PANOURILOR PE BAZĂ DE BENTONITĂ, NANOARGILE,  
PULBERI RECICLATE DIN DEEE ȘI GHIPS

(Rezumat)

Studiul de caz referitor la procesele de fabricație a fost realizat în Departamentul de dezvoltare tehnologică al ICECON SA – care are echipamentul adecvat pentru fabricarea de panouri rezistente la foc ce conțin – bentonită activată, nano-argilă și pulberi reciclate din DEEE (Deșeuri de echipamente electrice și electronice). Studiul de caz folosește: bentonită, nano-argilă din surse naturale activate cu carbonat de sodiu 5-10% pentru a îmbunătăți procesul de schimb ionic și pulberi reciclate din DEEE.

Departamentul de dezvoltare tehnologică al ICECON SA a efectuat o analiză extinsă pentru a identifica toate pericolele care pot să apară în procesele de fabricație, manipulare și instalare a panourilor efectuate pe baza de bentonită, nano-argilă activată cu silicat de sodiu și pulberi provenite din reciclarea DEEE.

Pachetul “SCAFFOLD” a fost folosit în timpul studiului pentru gestionarea riscurilor și pentru generarea de modele pentru instrucțiuni la locul de muncă.

Riscul a fost evaluat ca fiind de nivel scăzut în faza de procesare, dar mare pentru post-procesare (debitare și găurire) a panourilor. Pe baza recomandărilor pachetului “SCAFFOLD”, s-a conceput o procedură specifică: PROCEDURA: Sănătate, Securitate în muncă și Protecția mediului - pentru procesele de fabricație a panourilor pe bază de bentonită, nano-argilă, pulberi provenite din reciclarea DEEE și ghips. Riscul a fost redus, ceea ce înseamnă că introducerea nanomaterialelor în dezvoltarea de materiale de construcții este benefică și fezabilă.

Pe baza acestui studiu Compania ALL GREEN a dezvoltat un nou prototip de sistem de ecranare electromagnetică, care conține tencuială activată cu bentonită, nano-argilă, și pulberi din reciclarea DEEE



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ȘTIINȚA ȘI INGINERIA MATERIALELOR

## LABORATORY ESTIMATION OF OCCUPATIONAL EXPOSURES DURING NAIL LACQUER APPLICATIONS IN A NAIL SALON

BY  
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**Abstract:** This study's purpose is to quantify formaldehyde and volatile organic compound (VOC) potential exposures in the process of application of popular nail lacquers using a controlled-airflow chamber. A second goal is to compare quantified sampling results to the Occupational Safety and Health Administration's (OSHA's) permissible exposure limits (PELs), and identify if protective measures are needed during application. Worst Case exposures scenarios were defined as the worker exposure to nail lacquer application to one set of fingernails, simulated by paper plates, every 15 minutes for an 8 hour shift (total nailsets=32) devoid of breaks or other salon procedures. The application time and nail lacquers brands: O.P.I. and China Glaze (2 colors each), and Finger Paints (1 color), were determined based on observations made at a local salon. We collected passive air 8-hour time weighted average (TWA) samples inside a controlled-airflow lab chamber, simulating proximity to the breathing zone of a worker during nail lacquer application. Each of the 5 color shades were sampled 3 times. Samples were sent to Advanced Chemical Sensors for analysis of Formaldehyde (Modified NIOSH 2016) and a full VOC scan (EPA TO-15). Formaldehyde exposures did not exceed 0.35 ppm in any sample. Ethyl acetate exceeded the 400 ppm PEL 8 out of 15 times. Butyl acetate exceeded the 150 ppm PEL 13 out of 15 times. Camphor also exceeded the PEL in one sampled

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exposure. No other sampled exposures exceeded the PELs. For a worst case scenario, formaldehyde exposures were well below the 0.75 ppm PEL. All brands and colors of nail lacquer sampled exceeded the PELs for ethyl and butyl acetate in at least one independent sample. Using this knowledge, future field studies should be conducted to determine true daily exposures.

**Keywords:** formaldehyde; exposure; nail lacquer; VOC.

## 1. Introduction

In 2007, there were over 393,000 registered manicurists (Roelofs, 2007). With the rise in popularity of manicures, the number of registered manicurists has also increased. There have been some studies indicating that nail salon workers are at risk to adverse health effects such as skin, eye, and respiratory irritation, as well as headaches, nausea and reproductive issues (Quach, 2011). Formaldehyde exposures are heavily discussed in current research, therefore knowing that some nail salon products contain formaldehyde, the initial focus of this project was formaldehyde exposure in nail salon workers, particularly considering a worst case scenario. Formaldehyde has been classified by the International Agency for Research on Cancer (IARC) as a human carcinogen (Press Release. 2004). It can also cause eye, nose, skin and throat irritations, as well as wheezing, coughing, and nausea at levels as low as 0.1 ppm (Formaldehyde and Cancer Risk). Additionally, it was found that the main source of formaldehyde in nail salons came from nail lacquer and disinfectant cleaners (Roelofs, 2007). VOCs are also known to induce eye, nose, skin, throat irritation, nausea, headache, and damage to the central nervous system, kidney, and liver (An Introduction to Indoor Air Quality). Therefore, the purpose of this study was to quantify formaldehyde and VOC exposures obtained by the application of popular nail lacquers inside a controlled-airflow chamber; to compare quantified sample results to the Occupational Safety and Health Administration (OSHA) permissible exposure limits (PELs); and to identify possible needs for protective measures, such as gloves, respirators, or localized ventilation, during application.

## 2. Methods

A worst case scenario was identified as an exposure to nail lacquer through the application process conducted 32 times, over an 8 hour time frame. The application time and nail lacquers brands (O.P.I., China Glaze, and Finger Paints) were determined based on observations made at a nail salon. Two paint colors were sampled from the O.P.I. (Big Apple Red and Miami Beet) and China Glaze (Red Pearl and Seduce Me) brands. One paint color was sampled from the Finger Paints brand (Framed in Red). In the Industrial Hygiene lab, we

collected passive air 8-hour time weighted average (TWA) samples using a controlled-airflow lab chamber (Figure 1) set to allow for one air change per hour at 1.908 liters/minute. A fan was placed inside the chamber, connected to and powered by a variable autotransformer to provide air circulation. There were three rounds of sampling, in which each nail lacquer was sampled individually for 8 continuous hours. Nail lacquer was applied to a paper plate, to simulate the act of painting a full set of fingernails, every 15 minutes. There were no allowances for any breaks during the simulated work shift therefore at the end of the sampling period, 32 sets of fingernails have been painted. After each sampled exposure, the chamber was allowed to air out at least overnight, to prevent the contamination of the next sample. A blank sample was also collected in the same manner as the other samples per each round of sampling. At the completion of each cycle, samples were sent to Advanced Chemical Sensors, an American Industrial Hygiene Association (AIHA) accredited laboratory, for analysis of formaldehyde, using the Modified NIOSH 2016 method, and a full VOC scan using the EPA TO-15 method.

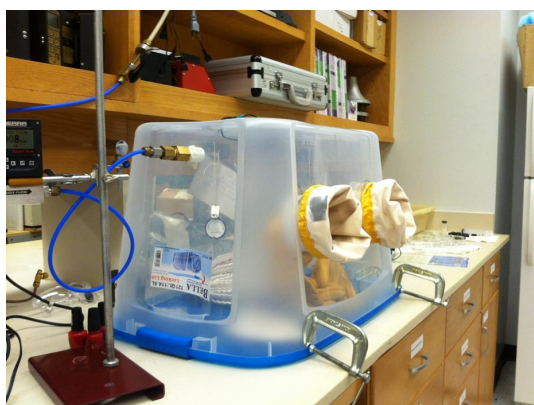


Fig. 1 – Controlled airflow chamber.

### 3. Results

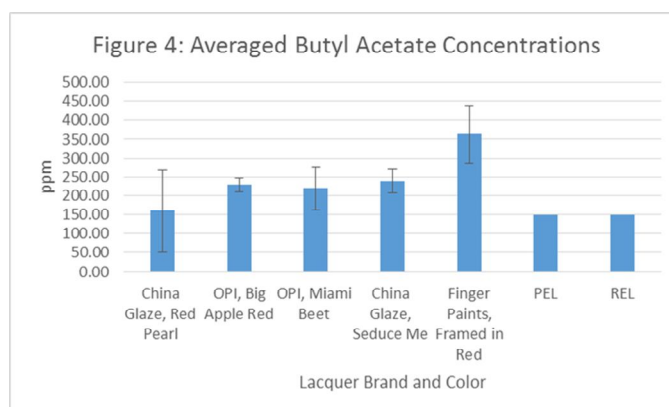
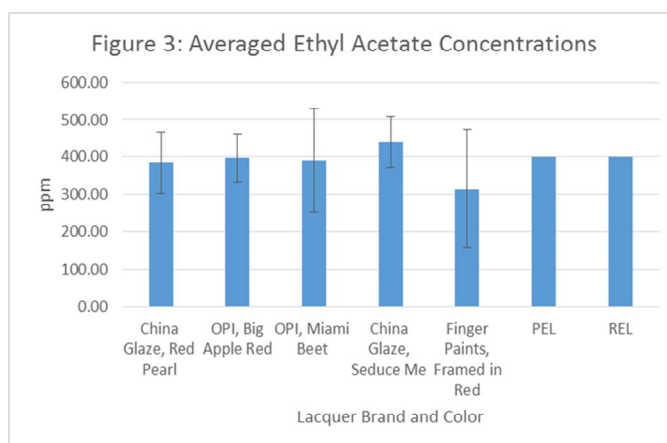
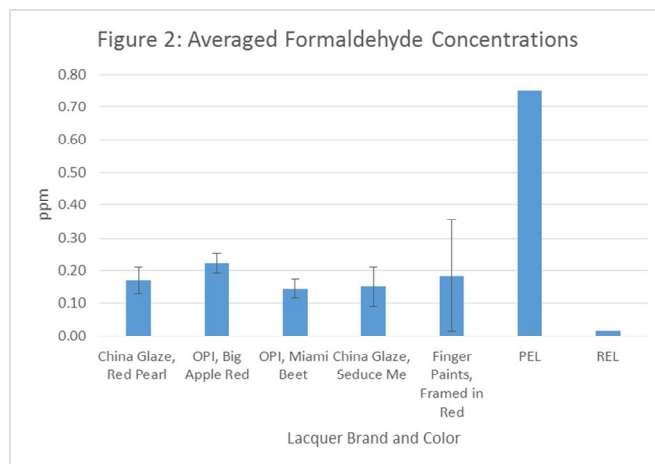
A total of 18 concentration data were collected, including those from the blank samples. For each type of nail lacquer the sampled concentrations were averaged and are shown in Table 1. In the 15 experimental trials, formaldehyde concentrations ranged from <0.01 to 0.35 ppm. The total average formaldehyde concentration was 0.16 ppm, using .01 ppm for the sample that was <.01 ppm. The VOC scan picked up concentrations above the 400 ppm PEL for ethyl acetate in 8 out of the 15 samples, although the total average concentration was 349.44 ppm. Butyl acetate was also found to exceed the PEL of 150 ppm 13 out of 15 times, with a total average concentration of 242.32 ppm. The average formaldehyde, ethyl acetate, and butyl acetate concentrations

are shown for each type of lacquer in Figs. 2,...,4. We found camphor to be over the PEL of 2 mg/m<sup>3</sup>, in the first round of sampling for O.P.I. brand Miami Beet, at 6.65 mg/m<sup>3</sup>. This was the only detectible exposure to camphor, with the exception of the blank in sampling round 3 which captured an exposure of 0.20 ppm.

**Table 1**  
*Average Concentration by Nail Lacquer Type*

	China Glaze, Red Pearl	OPI, Big Apple Red	OPI, Miami Beet	China Glaze, Seduce Me	Finger Paints, Framed in Red	PEL	REL
Formaldehyde (ppm)	0.17 ±.04	0.22 ±.03	0.14 ±.03	0.15 ±.06	0.19 ±.17	0.75	0.016
Ethyl Alcohol (ppm)	4.21 ±1.02	5.44 ±1.18	6.75 ±3.89	4.06 ±.21	10.04 ±3.27	1000	1000
Acetone (ppm)	4.74 ±2.73	0.67 ±.08	0.80 ±.19	0.92 ±.05	0.84 ±.22	1000	250
Isopropyl Alcohol (ppm)	65.99 ±14.27	76.98 ±14.01	70.30 ±25.60	76.26 ±12.59	60.71 ±21.85	400	400
Ethyl Ether (ppm)	0.00 ±0	0.00 ±0	0.01 ±.01	0.00 ±0	0.01 ±.02	400	400
Methyl Acetate (ppm)	0.04 ±.01	0.03 ±.01	0.03 ±.02	0.02 ±.00	0.03 ±.02	200	200
Ethyl Acetate (ppm)	384.90 ±80.84	396.63 ±62.72	390.76 ±138.68	439.63 ±69.13	313.93 ±157.37	400	400
Isopropyl Acetate (ppm)	5.50 ±1.33	5.38 ±1.02	10.80 ±6.28	4.50 ±.83	18.93 ±7.22	250	250
1-Butyl Alcohol (ppm)	2.42 ±.51	2.97 ±.46	4.06 ±1.92	2.23 ±.31	13.38 ±7.32	100	50
Cyclohexane (ppm)	0.00 ±0	0.00 ±0	0.00 ±0	0.00 ±0	0.02 ±.02	300	300
n-Propyl Acetate (ppm)	86.79 ±14.57	85.51 ±7.71	91.06 ±27.81	77.67 ±19.35	29.50 ±41.64	200	200
Butyl formate (ppm)	0.00 ±0	0.00 ±0	0.00 ±0	0.00 ±0	0.03 ±.02	5	5
Isobutyl Acetate (ppm)	0.00 ±0	0.00 ±0	0.00 ±0	0.00 ±0	0.08 ±.06	150	150
Butyl Acetate (ppm)	160.53 ±110.44	228.79 ±19.34	219.76 ±58.49	239.42 ±33.58	363.12 ±75.01	150	150
Methyl Ethyl Ketone (ppm)	0.00 ±0	0.00 ±0	0.01 ±.01	0.01 ±.01	0.00 ±0	200	200
Camphor (mg/m3)	0.00 ±0	0.00 ±0	2.22 ±3.13	0.00 ±0	0.00 ±0	2	2
Toluene (ppm)	0.00 ±0	0.00 ±0	0.00 ±0	0.00 ±0	0.01 ±.02	200	100
Naphthalene (ppm)	<.05	<.05	<.05	<.05	<.05	10	10





#### 4. Discussion

After obtaining the exposure results from the laboratory, we examined the data to detect any pattern across the lacquers of the same brand sampled. We determined that there were a few similar concentrations between the two colors from the China Glaze brand. Formaldehyde concentrations were very comparable. Other concentrations of interest, ethyl acetate and butyl acetate were noticeably different, with a difference of at least 50 ppm. The colors from the O.P.I. brand, however, shared similarities between concentrations for both ethyl and butyl acetates having less than a 10 ppm difference. The averaged formaldehyde concentrations were also only different by 0.08 ppm.

Formaldehyde exposures in this study did not exceed 0.35 ppm, which is well below the OSHA PEL of 0.75ppm. However the exposures did exceed the NIOSH REL of 0.016 ppm. Therefore, based on the NIOSH REL standards, it is possible in a worst case scenario for a nail salon worker to experience some adverse health effects do to a chronic exposure to formaldehyde. The first sampling round blank did register formaldehyde exposure at 0.01 ppm, which raises the concern that the first round of sampling may have been influenced by contamination outside of the experiment.

Referring to Figure 3, we notice that only one of the averaged ethyl acetate concentrations exceeded the OSHA PEL and the NIOSH REL. Although the other averages are lower than the exposure limit it should be noted that these averages hover around the 390 ppm mark and that some of the individual concentrations in these averages did exceed the 400 ppm limit.

Considering Figure 4, it can be said that there were obvious exceedances of an OSHA PEL/NIOSH REL found in the experimental worst case scenario. All 5 of the lacquers included in this study exceeded the OSHA PEL/ NIOSH REL of 150 ppm for butyl acetate. The lowest averaged concentration for butyl acetate was 160.53 ppm from the China Glaze, Red Pearl. The highest concentration of 363.12 ppm, more than the limit doubled, was observed in Framed in Red from the Finger Paints brand.

Both ethyl and butyl acetates are known to be skin and respiratory irritants. Our findings reinforce the suggestion that nail salon products can lead to allergic reactions and irritations as suggested in previous research. (Sainio, 1997; Hausen, 1995).

#### 5. Summary and Conclusions

This project sought to quantify formaldehyde and volatile organic compound (VOC) exposures obtained by the application of salon popular nail lacquers inside a controlled-airflow chamber, compare quantified sample results

to OSHA PEL, and identify if protective measures are needed during application.

We determined that concentrations of formaldehyde exceeded the NIOSH REL thus nail salon workers could be potentially at risk to adverse health effects associated with formaldehyde exposure. Concentrations of ethyl acetate hovered around the OSHA PEL. Also, all averaged concentrations of butyl acetate exceeded the OSHA PEL with the lowest concentration at 160.53 ppm observed in the China Glaze, Red Pearl. The highest average concentration of butyl acetate was double the PEL.

Considering that this experiment was conducted on a worst cases scenario basis, no immediate protective measures are recommended to be put into place. Some studies indicate that the use of N95 dust masks with build in organic vapor control would reduce the exposure concentration, but the masks do not properly fit the Asian females that dominate the nail salon business (Roelofs, 2007). However, actions should be taken to limit the nail salon workers exposure to ethyl and butyl acetates, because they are irritants to the skin and respiratory system, through the use of local exhaust ventilation (LEV) at each station in the salon. The installation of LEV systems are recommended to better filter out the VOC concentrations, particularly the ethyl and butyl acetate. The researchers believe that nail worker exposures inside nail salons should be revisited in future work with personal exposure monitoring to better understand the overall exposure risks to all of the nail products in the salon.

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### ESTIMĂRI DE LABORATOR PRIVIND EXPUNEREA OCUPAȚIONALĂ ÎN TIMPUL APLICĂRII LACURILOR DE UNGHII ÎNTR-UN SALON DE MANICHIURĂ

(Rezumat)

Scopul acestui studiu este de a cuantifica potențialul de expunere la formaldehidă și compuși organici volatili în procesul de aplicare a lacurilor de unghii obișnuite utilizând o cameră cu flux de aer controlat. Un al doilea scop este de a compara rezultatele obținute pe mostrele prelevate cu limitele de expunere limită și identificarea măsurilor necesare în timpul aplicării. Au fost definite scenarii de expunere extreme a lucrătorului (cazul cel mai defavorabil) corespunzând unui set de unghii simulate pe discuri de hârtie, la fiecare 15 minute pe un schimb de 8 ore (32 de seturi de unghii) fără pauze sau alte activități specifice salonului. Timpul de aplicare și brandurile de lacuri: P.P.I. și China Glaze (2 culori fiecare) și Finger Paints (1 culoare) au fost determinate prin observare la un salon local.

Am colectat mostre de aer pasiv corespunzător a 8 ore medie ponderată într-o cameră de laborator cu flux de aer controlat, simulând proximitatea zonei de respirație a lucrătorului în timpul operației de aplicare a lacului de unghii. Fiecare dintre cele 5 tonuri de culoare au fost eșantionate de câte 3 ori. Probele au fost trimise la Advanced Chemical Sensors for analysis of Formaldehyde (Modified NIOSH 2016) și a fost realizată o scanare completă privind compușii organici volatili cu (EPA TO-15).

Expunerea la formaldehidă nu a depășit 0,35ppm în nicio probă. Acetatul de etil a depășit valoarea limită admisă de 400 ppm de 8 ori din 15 probe. Butiacetatul a depășit valoarea admisă de 150 ppm de 13 ori din 15 probe. De asemenea a fost depășită valoarea admisă la camfor la una din probe. Niciuna dintre celelalte valori limită de expunere nu a mai fost depășită. Pentru un scenariu de tip "cazul cel mai defavorabil", formaldehida a fost mult sub 0,75 ppm, valoarea limită admisă. Toate brandurile și toate culorile de lacuri au depășit limita admisă la acetat de etil și acetat de butil cel puțin într-o probă independentă. Utilizând aceste cunoștințe vor fi realizate studii de teren viitoare pentru a determina valoarea reală a expunerii zilnice.

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## DEVELOPMENT OF CATWOE METHOD USING FUZZY NUMBERS

BY

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**Abstract:** This paper presents an analyze inside of an automotive company of the most important indicators identified using Catwoe method. Three teams with different number of members are deciding and evaluating the most critical characteristics of each Catwoe indicator, from the point of view of an important and competitive company in the lamps production market.

The present analysis aims to analyze the results of Catwoe method, using mathematic modeling through fuzzy numbers. The study is focused starting with the analysis of all Catwoe indicators with impact in innovation management in the automotive field and it is continuing with identification of specialized items that lead to a detailing of the characteristics analyzed in a company dedicated to the development and production of automotive components.

The study represents a qualitative analysis of three different teams inside of a automotive company based on innovative ideas, specialized indicators, the analysis being done using several methods for obtaining matrix of the consequences and for obtaining ranking of the teams results – several methods are used - method of global utilities, method maxi-max, Wlad’s method and Hurwicz’s method.

**Keywords:** CATWOE method; fuzzy numbers; fuzzy systems; CATWOE indicators; triangular fuzzy numbers.

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## 1. Introduction

CATWOE Technology (Checkland and Scholes Soft Systems Methodology in Action, 1990), requires an analysis of a phenomenon on several levels, which in turn should be investigated and observed, to provide insight as close to employees' needs but also to understand better complementary phenomena. Innovation as a complex process and as a phenomenon concerned by its globalism, the assets and business units defined systems: marketing, product adoption, technology - technology transfer as part and parcel of the innovation is the key to materializing research and development results. This method is applied by using assessment to the three teams - different departments - and facilitates decision making especially in unexpected situations. For successful implementation of the method, it is necessary to consider several developments that could be possible to prepare several action plans for each situation.

In decision making, CATWOE is used by describing actual future scenario, including all relevant information for the decision to be implemented. There are specific situations where this method is very safe, an example would be when decisions are long-term and very long.

As mathematical models used for storing knowledge, but also for their handling include:

- logical proposition ( $A \rightarrow B$ );
- logic predicate;
- fuzzy logic.

The method used by fuzzy systems, *learning through exposure*, directly or indirectly involves the implementation of a set of heuristic rules in a system.

*Learning by analogy* instead, is applied in certain applications, where the system learns how to solve a problem, relying on solving other problems, for which the solution is already known.

Depending on the type of information used as input, the processing can be made with different systems:

		Processing	
		symbolically	numerical
KNOWLEDGE	Structured	Expert systems	Fuzzy systems
	Unstructured		Neuronal systems

For this paper, we used fuzzy systems for evaluating automotive products with the help of six features (CATWOE method) with major influence in the development, production and sale of LED lamps.

Considering the specific problem, we decide to define the triangular fuzzy numbers, according to Gherasim O., who developed the arithmetic of elementary fuzzy numbers. The most important indicators were identified using the CATWOE method, in the light of the three departments (production, technical and management).

These factors were subsequently evaluated with grades from 1 to 5, using automotive product developed in the last 5 years, from the perspective of the risk in the development of the following projects.

For each indicator of the CATWOE, the teams founded three important factors:

**Clients** – Price, quality, innovative aspect

**Actors** – Qualified staff, management result-oriented, engagement

**Transformation** – Production capacity, sales power, flexibility

**World view** – Price policy, company reputation, market share of the company

**Owner** – Financial capacity, experience, managerial capacity of the company

**Environment** – Competition, legislation, innovation

Each CATWOE INDICATOR, with 3 important characteristics, is also evaluated with grades starting with: 1 – less important .. up to 10 – the most important.

There are 3 departments that are making the evaluation, each one having different number of employees, so in order to keep a accurate analysis, I calculated the average of the grades awarded, based on the number of participants in each department.

- ✓ Technical department – 7 engineers;
- ✓ Production department – 10 engineers;
- ✓ Management department – 8 employees.

For each CATWOE indicator, and for each department, we obtain triangular fuzzy numbers, but with different proportions:

#### **C-Price, quality, innovative aspect**

And we proceed in the same way, for the other 5 indicators of CATWOE. According to this kind of situation we have to apply a method that will not avoid certain responses, such as those which are extreme.

Considering previous fuzzy numbers applications, and also considering the specific of the problem, we will select the method to define the triangular fuzzy numbers – according to **Ovidiu Gherasim**, who developed the arithmetic of elementary fuzzy numbers.

We will calculate centers of gravity for the six indicators CATWOE, then we will continue with processing of fuzzy numbers.

$$N_C^{\text{technic}} = (4.3, 4.5, 4.4); \quad N_C^{\text{production}} = (4.0, 4.3, 4.6);$$

$$N_C^{\text{management}} = (4.1, 3.9, 4.2).$$

**Table 1**  
*Table of Results*

CATWOE	Importance proportion	Tehnickal department	Production Department	Management department
C-Price, quality, innovative aspect	9 = 21,5% 0,215	4.3	4	4.1
		4.5	4.3	3.9
		4.4	4.6	4.2
A-Qualified staff, management result-oriented, engagement 7	7 = 16,5% 0,165	3.1	4.1	4.2
		3.3	4.3	3.3
		3.2	4.2	4.1
T Production capacity, sales power, flexibility	8 = 19% 0,19	3.2	3.4	4.4
		3.4	2.8	3
		3.3	4.1	3.7
W- Price policy, company reputation, market share of the company	7 = 16,5% 0,165	3.6	3.3	4.1
		4	4	3.6
		2.8	2.6	2.8
O - Financial capacity, experience, managerial capacity of the company	5 = 12% 0,12	3.8	3.4	2.5
		2.6	2.7	2.9
		4.2	2.5	2.8
E - Competition, legislation, innovation	6 = 14,5% 0,145	3.1	2.9	3.3
		3.5	3.6	2.6
		3.3	2.7	3.4

We start with *Clients* indicator: there are 3 elements of which the first two represent the extremes triangular fuzzy number, and the 3rd center of gravity, calculated as follows:

$$<\tilde{R}_{11}> = \frac{4.3 + 2 \cdot 4.4 + 4.5}{4} = 4.4; \quad <\tilde{R}_{12}> = \frac{4.0 + 2 \cdot 4.3 + 4.6}{2} = 4.3.$$

The operation of normalization of lines (linear interpolation, the range  $[0, 1]$ ), is performed simultaneously for all of the components (real) on each line.

$$R_1^{\min} = \min(4.3; 4.4; 4.5; 4.0; 4.3; 4.6; 3.9; 4.1; 4.2) = 3.9;$$

$$R_1^{\max} = \max(4.3; 4.4; 4.5; 4.0; 4.3; 4.6; 3.9; 4.1; 4.2) = 4.6.$$



**Triangular fuzzy numbers**

The fuzzy number is expressed as a fuzzy set from a fuzzy range, defining a real number from set of real numbers R.

$$\tilde{a} = (a_1, a_2, a_3) \in \mathbf{F}_\Delta \stackrel{\text{def.}}{\leftrightarrow} a_1 \leq a_2 \leq a_3 \quad (1)$$

Center of gravity, basic operations and the order relation with triangular fuzzy numbers are defined by relations:

$\tilde{a}, \tilde{b} \in \mathbf{F}_\Delta \quad \tilde{a} = (a_1, a_2, a_3), \tilde{b} = (b_1, b_2, b_3)$	
the center of gravity (real number associate)	$a_G = \langle \tilde{a} \rangle = \frac{a_1 + 2a_2 + a_3}{4}$
Sign	$\delta_a = \begin{cases} \text{sign } a_G, a_G \neq 0 \\ \text{sign } a_N, a_G = 0 \end{cases}$ where: $\text{sign}(x) = \begin{cases} 1, & x > 0 \\ 0, & x = 0 \\ -1, & x < 0 \end{cases}$
multiplication scalar	$t \cdot \tilde{a} = \begin{cases} (t \cdot a_1, t \cdot a_2, t \cdot a_3), & t \geq 0 \\ (t \cdot a_3, t \cdot a_2, t \cdot a_1), & t < 0 \end{cases}, t \in \mathbf{R}$
Congregation	$\tilde{a} + \tilde{b} = (a_1 + b_1, a_2 + b_2, a_3 + b_3)$
Subtraction	$\tilde{a} - \tilde{b} = (a_1 - b_3, a_2 - b_2, a_3 - b_1)$
Multiplication	$\tilde{a} \cdot \tilde{b} = \frac{\langle \tilde{a} \rangle \cdot \tilde{b} + \tilde{a} \cdot \langle \tilde{b} \rangle}{2}$
Division	$\frac{\tilde{a}}{\tilde{b}} = \frac{\langle \tilde{a} \rangle \cdot \tilde{b} + \tilde{a} \cdot \langle \tilde{b} \rangle}{2 \cdot \langle \tilde{b} \rangle^2}, (\forall) \langle \tilde{b} \rangle \neq 0$
Order relation	$\left\{ \begin{array}{l} a_G < b_G \text{ or} \\ (a_G = b_G \text{ and } a_2 < b_2) \text{ or} \\ (a_G = b_G \text{ and } a_2 = b_2) \text{ și } \delta_a \cdot (a_3 - a_1) < \delta_b \cdot (b_3 - b_1) \end{array} \right\} \Rightarrow \tilde{a} < \tilde{b}$

Methods (4) to prioritize variants of decision and specific indicators:

Method	Specific indicators, $[(\forall)j = \overline{1, n}]$
Global utilities	$\tilde{U}_j = \sum_{i=1}^m \tilde{u}_{ij}$
Maxi-Max	$\tilde{M}_j = \max_{1 \leq i \leq m} \tilde{u}_{ij}$
Wald	$\tilde{W}_j = \min_{1 \leq i \leq m} \tilde{u}_{ij}$
Hurwicz (optimism coefficient $\alpha \in [0, 1]$ )	$\tilde{H}_j = \alpha \cdot \tilde{M}_j + (1 - \alpha) \cdot \tilde{W}_j = (\tilde{M}_j - \tilde{W}_j) \cdot \alpha + \tilde{W}_j$

Matrix of results (initial matrix)

	Level o apreciation	V1 –team1	V2-team2	V3-team3
C1	9	4.3	4	<b>3.9</b>
		4.4	4.3	4.1
		4.5	<b>4.6</b>	4.2
		4.4	4.3	4.075
C2	7	<b>3.1</b>	4.1	3.3
		3.2	4.2	4.1
		3.3	<b>4.3</b>	4.2
		3.2	4.2	3.925
C3	8	3.2	<b>2.8</b>	3
		3.3	3.4	3.7
		3.4	4.1	<b>4.4</b>
		3.3	3.425	3.7
C4	7	2.8	<b>2.6</b>	2.8
		3.6	3.3	3.6
		4	4	<b>4.1</b>
		3.5	3.3	3.525
C5	5	2.6	<b>2.5</b>	<b>2.5</b>
		3.8	2.7	2.8
		<b>4.2</b>	3.4	2.9
		3.6	2.825	2.75
C6	6	3.1	2.7	<b>2.6</b>
		3.3	2.9	3.3
		3.5	<b>3.6</b>	3.4
		3.3	3.025	3.15

In each cell in the tables are four elements of which the first three are components of triangular fuzzy number, and the 4th center of gravity, calculated as follows:

$$<\tilde{R}_{11}> = \frac{4.3 + 2 \cdot 4.4 + 4.5}{4} = 4.4; <\tilde{R}_{12}> = \frac{4.0 + 2 \cdot 4.3 + 4.6}{2} = 4.3; \dots$$

All other centers of gravity are calculated similarly. We note the triangular fuzzy numbers in brackets, with center of gravity as index:

$$\tilde{R}_{11} = (4.3, 4.4, 4.5)_{4.4}$$

Operation of normalization of lines (linear interpolation, the range  $[0, 1]$ ), is performed simultaneously for all of the components (real) on each line.

For the first line:

$$R_1^{\min} = \min(4.3; 4.4; 4.5; 4.0; 4.3; 4.6; 3.9; 4.1; 4.2) = 3.9$$

$$R_1^{\max} = \max(4.3; 4.4; 4.5; 4.0; 4.3; 4.6; 3.9; 4.1; 4.2) = 4.6$$

$$R_{1x} \rightarrow \frac{R_{1x} - R_1^{\min}}{R_1^{\max} - R_1^{\min}} = \frac{R_{1x} - 3.9}{4.6 - 3.9} = \frac{R_{1x} - 3.9}{0.7}, \quad 4.3 \rightarrow \frac{4.3 - 3.9}{0.7} = \frac{0.4}{0.7} \approx 0.571,$$

$$4.4 \rightarrow \frac{4.4 - 3.9}{0.7} = \frac{0.5}{0.7} \approx 0.714, \quad 4.5 \rightarrow \frac{4.5 - 3.9}{0.7} = \frac{0.6}{0.7} \approx 0.857,$$

$$\tilde{u}_{11} = (0.571, 0.714, 0.857)_{0.714} \dots$$

The remaining 5 lines are calculated similarly. Matrix of utilities is as follows:

*Matrix of Utilities*

	K	V1	V2	V3
C1	0.214	0.571	0.143	0
		0.714	0.571	0.286
		0.857	1	0.429
		0.714	0.571	0.25
C2	0.167	0	0.833	0.167
		0.083	0.917	0.833
		0.167	1	0.917
		0.083	0.917	0.688
C3	0.190	0.25	0	0.125
		0.313	0.375	0.563
		0.375	0.813	1
		0.313	0.391	0.563
C4	0.167	0.133	0	0.133
		0.667	0.467	0.667
		0.933	0.933	1
		0.6	0.467	0.617
C5	0.119	0.059	0	0
		0.765	0.118	0.176
		1	0.529	0.235
		0.647	0.191	0.147
C6	0.143	0.5	0.1	0
		0.7	0.3	0.7
		0.9	1	0.8
		0.7	0.425	0.55

The weights  $k_i$  are obtained with calculations bellow – gathering all appreciations levels made from 1 to 10 and calculating the percentage of each one:

$$9 + 7 + 8 + 7 + 5 + 6 = 42$$

$$9 \rightarrow \frac{9}{42} \approx 0.214, \quad \dots, \quad 6 \rightarrow \frac{6}{42} \approx 0.143$$

The utilities are obtained by multiplying the corresponding weights  $k_i$  of each line:

$$\begin{aligned} \tilde{u}_{11} \leftarrow \tilde{u}_{11} &= 0.214 \cdot (0.571, 0.714, 0.857)_{0.714} = \\ &= (0.214 \cdot 0.571, 0.214 \cdot 0.714, 0.214 \cdot 0.857)_{0.214 \cdot 0.714} \approx \\ &\approx (0.122, 0.153, 0.184)_{0.153}, \dots \end{aligned}$$

*Matrix of Utilities with Weights*

	V1	V2	V3
C1	<b>0.122</b>	0.031	0
	<b>0.153</b>	0.122	0.061
	<b>0.184</b>	0.214	0.092
	<b>0.153</b>	0.122	0.054
C2	<b>0</b>	<b>0.139</b>	<b>0.028</b>
	<b>0.014</b>	<b>0.153</b>	<b>0.139</b>
	<b>0.028</b>	<b>0.167</b>	<b>0.153</b>
	<b>0.014</b>	<b>0.153</b>	<b>0.115</b>
C3	0.048	0	0.024
	0.06	0.071	0.107
	0.071	0.155	0.19
	0.06	0.074	0.107
C4	0.022	0	0.022
	0.111	0.078	0.111
	0.156	0.156	0.167
	0.1	0.078	0.103
C5	0.007	<b>0</b>	<b>0</b>
	0.091	<b>0.014</b>	<b>0.021</b>
	0.119	<b>0.063</b>	<b>0.028</b>
	0.077	<b>0.023</b>	<b>0.018</b>
C6	0.071	0.014	0
	0.1	0.043	0.1
	0.129	0.143	0.114
	0.1	0.061	0.079

a) **Method of Global Utilities**

Specific indicator  $U_j, j=\overline{1,3}$  is calculated by summing weighted of utilities, on columns:

$$U_1 = \sum_{i=1}^6 u_{i1} = \tilde{u}_{11} + \tilde{u}_{21} + \tilde{u}_{31} + \tilde{u}_{41} + \tilde{u}_{51} + \tilde{u}_{61} = (0.122, 0.153, 0.184)_{0.153} + \\ + (0, 0.014, 0.028)_{0.014} + (0.048, 0.060, 0.071)_{0.060} + \\ + (0.022, 0.111, 0.156)_{0.100} + (0.007, 0.091, 0.119)_{0.077} + \\ + (0.071, 0.100, 0.129)_{0.100} = (0.270, 0.529, 0.687)_{0.504}.$$

Assembly is done for each component. For example, the first component:

$$0.122 + 0 + 0.048 + 0.022 + 0.007 + 0.071 = 0.270.$$

The three values of the indicator are listed in the following table:

	V <sub>1</sub>	V <sub>2</sub>	V <sub>3</sub>
$\tilde{U}_j$	0.27	0.184	0.074
	0.529	0.481	0.539
	0.687	0.898	0.744
	0.504	0.511	0.474
$\tilde{M}_j$	0.122	0.139	0.028
	0.153	0.153	0.139
	0.184	0.167	0.153
	0.153	0.153	0.115
$\tilde{W}_j$	0	0	0
	0.014	0.014	0.021
	0.028	0.063	0.028
	0.014	0.023	0.018

Down ordering centers of gravity of the specific indicator and concomitantly the variants is obtained the ranking by the method of global of utilities:

$$0.511 > 0.504 > 0.474$$

$$\boxed{V_2 \succ V_1 \succ V_3}$$

b) **Maxi-max Method**

Values of the specific indicator  $\tilde{M}_j, j=\overline{1,3}$  are calculated in this way (maximum fuzzy numebrs are selected from the coloms of the previous table):

$$\tilde{M}_1 = \max_{1 \leq i \leq 6} \tilde{u}_{i1} = \max(\tilde{u}_{11}, \tilde{u}_{21}, \tilde{u}_{31}, \tilde{u}_{41}, \tilde{u}_{51}, \tilde{u}_{61}) = \tilde{u}_{11} = (0.122, 0.153, 0.184)_{0.153}.$$

We selected the fuzzy number  $\tilde{u}_{11}$  because this one it is having the biggest center of gravity

$$\tilde{M}_2 = \max_{1 \leq i \leq 6} \tilde{u}_{i2} = \tilde{u}_{22}, \quad \tilde{M}_3 = \max_{1 \leq i \leq 6} \tilde{u}_{i3} = \tilde{u}_{23}.$$

The three indicator values are entered in the 2nd row of the previous table. Indicator  $\tilde{M}_3$  has the smallest center of gravity,  $\tilde{M}_1$  and  $\tilde{M}_2$  are having centers of gravity and the biggest values – equal:

$$(\tilde{M}_1)_2 = (\tilde{M}_2)_2 = 0.153 \quad \text{and} \quad <\tilde{M}_1> = <\tilde{M}_2> = 0.153.$$

For hierarchisation we can use relation number (3):

$$\delta_a \cdot (a_3 - a_1) < \delta_b \cdot (b_3 - b_1) \Rightarrow \tilde{a} \prec \tilde{b}$$

$$\delta_a = \delta_b = \text{sign}(0.153) = 1$$

$$(\tilde{M}_1)_3 - (\tilde{M}_1)_1 = 0.184 - 0.122 = 0.062$$

$$(\tilde{M}_2)_3 - (\tilde{M}_2)_1 = 0.167 - 0.139 = 0.028$$

$$1 \cdot 0.062 < 1 \cdot 0.028 \Rightarrow \tilde{M}_1 \succ \tilde{M}_2$$

Ordering of specific indicator generates ranking by the method of maximum:

$$\tilde{M}_1 \succ \tilde{M}_2 \succ \tilde{M}_3$$

$$\boxed{\mathbf{V}_1 \prec \mathbf{V}_2 \prec \mathbf{V}_3}$$

### c) Wald's Method

Specific indicator  $\tilde{W}_j, j = \overline{1,3}$  is calculated as follows (minimum fuzzy numbers in columns):

$$\begin{aligned} \tilde{W}_1 &= \min_{1 \leq i \leq 6} \tilde{u}_{i1} = \min(\tilde{u}_{11}, \tilde{u}_{21}, \tilde{u}_{31}, \tilde{u}_{41}, \tilde{u}_{51}, \tilde{u}_{61}) = \tilde{u}_{21} = \\ & \quad (0.000, 0.014, 0.028)_{0.014} \quad \dots \end{aligned}$$

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The three values of the indicator are entered in the 3rd row in the above table. Down ordering centers of gravity of the specific indicator and concomitantly the variants is obtained the ranking by the method of Wald:

$$0.023 > 0.018 > 0.014$$

$$\boxed{\mathbf{V}_2 \succ \mathbf{V}_3 \succ \mathbf{V}_1}$$

d) **Hurwicz's Method** (of the coefficient of optimism  $\alpha \in [0,1]$ )

Specific indicator  $\tilde{H}_j$ ,  $j = \overline{1,3}$  is calculated by the formula:

$$\begin{aligned} \tilde{H}_1(\alpha) &= (\tilde{M}_1 - \tilde{W}_1) \cdot \alpha + \tilde{W}_1 = \\ &= [(0.122, 0.153, 0.184)_{0.153} - (0, 0.014, 0.028)_{0.014}] \cdot \alpha + (0, 0.014, 0.028)_{0.014} = \\ &= (0.122 - 0.028, 0.153 - 0.014, 0.184 - 0)_{0.153-0.014} \cdot \alpha + (0, 0.014, 0.028)_{0.014} = \\ &= [(0.094, 0.139, 0.184)_{0.139} \cdot \alpha + (0, 0.014, 0.028)_{0.014}] = \\ &= (0.094\alpha, 0.139\alpha + 0.014, 0.184\alpha + 0.028)_{0.139\alpha+0.014} \\ &< \tilde{H}_1(\alpha) > = \frac{0.094\alpha + 2 \cdot 0.139\alpha + 2 \cdot 0.014 + 0.184\alpha + 0.028}{4} = \\ &\quad \frac{0.556\alpha + 0.056}{4} = 0.139\alpha + 0.014. \\ \tilde{H}_2(\alpha) &= (\tilde{M}_2 - \tilde{W}_2) \cdot \alpha + \tilde{W}_2 = \\ &= (0.076\alpha, 0.139\alpha + 0.014, 0.167\alpha + 0.063)_{0.130\alpha+0.023} \\ &< \tilde{H}_2(\alpha) > = 0.130\alpha + 0.023 \\ \tilde{H}_3(\alpha) &= (\tilde{M}_3 - \tilde{W}_3) \cdot \alpha + \tilde{W}_3 = \\ &= (0, 0.118\alpha + 0.021, 0.153\alpha + 0.028)_{0.097\alpha+0.018} \\ &< \tilde{H}_3(\alpha) > = 0.097\alpha + 0.018 \end{aligned}$$

The order of the segments  $< \tilde{H}_1(\alpha) >$ ,  $< \tilde{H}_2(\alpha) >$ ,  $< \tilde{H}_3(\alpha) >$  ( $\alpha \in [0,1]$ ) can be changed only in the points where it is intersecting:

$$\begin{aligned} &< \tilde{H}_1(\alpha) > = < \tilde{H}_2(\alpha) > \\ 0.139\alpha + 0.014 &= 0.130\alpha + 0.023 \Leftrightarrow 0.009\alpha = 0.009 \Leftrightarrow \alpha = 1 \\ &< \tilde{H}_1(\alpha) > = < \tilde{H}_3(\alpha) > \end{aligned}$$

$$0.139\alpha + 0.014 = 0.097\alpha + 0.018 \Leftrightarrow 0.042\alpha = 0.004 \Leftrightarrow$$

$$\alpha = \frac{4}{42} \approx 0.095$$

$$\langle \tilde{H}_2(\alpha) \rangle = \langle \tilde{H}_3(\alpha) \rangle$$

$$0.130\alpha + 0.023 = 0.097\alpha + 0.018 \Leftrightarrow 0.033\alpha = -0.005 \Leftrightarrow$$

$$\alpha = -0.15 \notin [0,1]$$

We will have following possibilities:

	value intermediate	$\langle H_1(\alpha) \rangle$	$\langle H_2(\alpha) \rangle$	$\langle H_3(\alpha) \rangle$	
$\alpha = 0$ (Wald)	0	0.014	0.023	0.018	$V_2 \succ V_3 \succ V_1$
$\alpha \in (0, 0.095)$	0.05	0.021	0.030	0.023	$V_2 \succ V_3 \succ V_1$
$\alpha = 0.095$	0.095	0.027205	0.035	0.027215	$V_2 \succ V_3 \succ V_1$
$\alpha \in (0.095, 1)$	0.6	0.097	0.101	0.076	$V_2 \succ V_1 \succ V_3$
$\alpha = 1$ (Maxi-max)	1	0.153	0.153	0.115	$V_1 \prec V_2 \prec V_3$

So, we will obtain:

Prioritization	Coefficient of optimism
$V_2 \succ V_3 \succ V_1$	$\forall \alpha \in [0, 0.095]$
$V_2 \succ V_1 \succ V_3$	$\forall \alpha \in (0.095, 1)$
$V_1 \prec V_2 \prec V_3$	$\alpha = 1$

## 2. Conclusions

Method of global utilities is giving us the results according to the production is more influenced by CATWOE indicators, then the technical department and management.

Maxi-max method offers information's about the hierarchy between departments, technic department, production and management. This method is calculating the indicators using maximum and minimum of the evaluations, so it is influenced by the extreme values of the respondents.

According to Wald's method, the production department is having a bigger influence regarding the analyzed CATWOE indicators.

The last method, Hurwicz's, is giving us an hierarchy that is influenced by the coefficient of optimism.



**Anexe – calcul cu numere fuzzy triunghiulare**

Modelul initial	POND	V1	V2	V3
C 1 - Modelul initial	9	4.3	4	3.9
		4.4	4.3	4.1
		4.5	4.6	4.2
CentG		4.4	4.3	4.075
C 2 - Modelul initial	7	3.1	4.1	3.3
		3.2	4.2	4.1
		3.3	4.3	4.2
CentG		3.2	4.2	3.925
C 3 - Modelul initial	8	3.2	2.8	3
		3.3	3.4	3.7
		3.4	4.1	4.4
CentG		3.3	3.425	3.7
C 4 - Modelul initial	7	2.8	2.6	2.8
		3.6	3.3	3.6
		4	4	4.1
CentG		3.5	3.3	3.525
C 5 - Modelul initial	5	2.6	2.5	2.5
		3.8	2.7	2.8
		4.2	3.4	2.9
CentG		3.6	2.825	2.75
C 6 - Modelul initial	6	3.1	2.7	2.6
		3.3	2.9	3.3
		3.5	3.6	3.4
CentG		3.3	3.025	3.15

Matricea utilitatilor	POND	V1	V2	V3
C 1 - Matricea Utilitatilor	0.214	0.571	0.143	0
	0	0.714	0.571	0.286
	0	0.857	1	0.429
CentG	0	0.714	0.571	0.25
C 2 - Matricea Utilitatilor	0.167	0	0.833	0.167
	0	0.083	0.917	0.833
	0	0.167	1	0.917
CentG	0	0.083	0.917	0.688
C 3 - Matricea Utilitatilor	0.19	0.25	0	0.125
	0	0.313	0.375	0.563
	0	0.375	0.813	1
CentG	0	0.313	0.391	0.563
C 4 - Matricea Utilitatilor	0.167	0.133	0	0.133
	0	0.667	0.467	0.667

	0	0.933	0.933	1
CentG	0	0.6	0.467	0.617
C 5 - Matricea Utilitatilor	0.119	0.059	0	0
	0	0.765	0.118	0.176
	0	1	0.529	0.235
CentG	0	0.647	0.191	0.147
C 6 - Matricea Utilitatilor	0.143	0.5	0.1	0
	0	0.7	0.3	0.7
	0	0.9	1	0.8
CentG	0	0.7	0.425	0.55

Matricea utilitatilor ponderate	V1	V2	V3
C 1 - Utilitati Ponderate	0.122	0.031	0
	0.153	0.122	0.061
	0.184	0.214	0.092
CentG	0.153	0.122	0.054
C 2 - Utilitati Ponderate	0	0.139	0.028
	0.014	0.153	0.139
	0.028	0.167	0.153
CentG	0.014	0.153	0.115
C 3 - Utilitati Ponderate	0.048	0	0.024
	0.06	0.071	0.107
	0.071	0.155	0.19
CentG	0.06	0.074	0.107
C 4 - Utilitati Ponderate	0.022	0	0.022
	0.111	0.078	0.111
	0.156	0.156	0.167
CentG	0.1	0.078	0.103
C 5 - Utilitati Ponderate	0.007	0	0
	0.091	0.014	0.021
	0.119	0.063	0.028
CentG	0.077	0.023	0.018
C 6 - Utilitati Ponderate	0.071	0.014	0
	0.1	0.043	0.1
	0.129	0.143	0.114
CentG	0.1	0.061	0.079

Ord.UG: Indic. Spec.	0.27	0.184	0.074	
Ord.UG: Indic. Spec.	0.529	0.481	0.539	
Ord.UG: Indic. Spec.	0.687	0.898	0.744	
CentG	0.504	0.511	0.474	
Ord.UG: Indic. Spec.	0.184	0.27	0.074	
Ord.UG: Indic. Spec.	0.481	0.529	0.539	
Ord.UG: Indic. Spec.	0.898	0.687	0.744	

CentG	0.511	0.504	0.474	0.511>0.504>0.474
Ord.UG: Ordinea Var.	2	1	3	V2>V1>V3
Ord.SV: Indic. Spec.	0.111	-0.056	0.03	
Ord.SV: Indic. Spec.	0.139	0.077	0.092	
Ord.SV: Indic. Spec.	0.167	0.119	0.184	
CentG	0.139	0.054	0.1	
Ord.SV: Indic. Spec.	-0.056	0.03	0.111	
Ord.SV: Indic. Spec.	0.077	0.092	0.139	
Ord.SV: Indic. Spec.	0.119	0.184	0.167	
CentG	0.054	0.1	0.139	0.054>0.100>0.139
Ord.SV: Ordinea Var.	2	3	1	V2>V3>V1
Ord.MM: Indic. Spec.	0.122	0.139	0.028	
Ord.MM: Indic. Spec.	0.153	0.153	0.139	
Ord.MM: Indic. Spec.	0.184	0.167	0.153	
CentG	0.153	0.153	0.115	
Ord.MM: Indic. Spec.	0.122	0.139	0.028	
Ord.MM: Indic. Spec.	0.153	0.153	0.139	
Ord.MM: Indic. Spec.	0.184	0.167	0.153	
CentG	0.153	0.153	0.115	0.153>0.153>0.115
Ord.MM: Ordinea Var.	1	2	3	V1>V2>V3
Ord.WD: Indic. Spec.	0	0	0	
Ord.WD: Indic. Spec.	0.014	0.014	0.021	
Ord.WD: Indic. Spec.	0.028	0.063	0.028	
CentG	0.014	0.023	0.018	
Ord.WD: Indic. Spec.	0	0	0	
Ord.WD: Indic. Spec.	0.014	0.021	0.014	
Ord.WD: Indic. Spec.	0.063	0.028	0.028	
CentG	0.023	0.018	0.014	0.023>0.018>0.014
Ord.WD: Ordinea Var.	2	3	1	V2>V3>V1
Hurwicz - ALFA	0.094	0.076	0	
Hurwicz - ALFA	0.139	0.139	0.118	
Hurwicz - ALFA	0.184	0.167	0.153	
CentG	0.139	0.13	0.097	
Hurwicz - 1-ALFA	0	0	0	
Hurwicz - 1-ALFA	0.014	0.014	0.021	
Hurwicz - 1-ALFA	0.028	0.063	0.028	
CentG	0.014	0.023	0.018	
Hw: Alfa intermed.baza	0	0.095	1	
Ord.Hw: (0.000, 0.095) 0.0500	0.021	0.03	0.023	
Ord.Hw: Ordinea Var.	1	2	3	
Ord.Hw: (0.000, 0.095) 0.0500	0.03	0.023	0.021	0.030>0.023>0.021
Ord.Hw: Ordinea Var.	2	3	1	V2>V3>V1
Ord.Hw: Alfa=0.095	0.027	0.035	0.027	

Ord.Hw: Ordinea Var.	1	2	3	
Ord.Hw: $\lambda=0.095$	0.035	0.027	0.027	$0.035>0.027>0.027$
Ord.Hw: Ordinea Var.	2	1	3	$V2>V1>V3$
Ord.Hw: (0.095, 1.000) 0.6000	0.097	0.101	0.076	
Ord.Hw: Ordinea Var.	1	2	3	
Ord.Hw: (0.095, 1.000) 0.6000	0.101	0.097	0.076	$0.101>0.097>0.076$
Ord.Hw: Ordinea Var.	2	1	3	$V2>V1>V3$

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## DEZVOLTAREA METODEI CATWOE FOLOSIND NUMERELE FUZZY

(Rezumat)

Este prezentată o analiză realizată în cadrul unei companii de automobile, cu scopul de a identifica și evalua cei mai importanți indicatori cu impact în dezvoltarea și producerea de lămpi auto. Factorii caracteristici sunt identificați folosind metoda Catwoe, apoi evaluați de către trei echipe cu număr diferit de membri, care decid asupra importanței caracteristicilor cele mai critice aferente fiecărui indicator Catwoe.

Prezenta analiză își propune să ierarhizeze rezultatele metodei Catwoe, folosind modelarea matematică prin numere fuzzy triunghiulare. Studiul este realizat începând cu analiza tuturor indicatorilor Catwoe cu impact în managementul inovației în domeniul auto și apoi se continuă cu identificarea elementelor de specialitate care conduc la o detaliere a caracteristicilor analizate într-o companie dedicată dezvoltării și producției de componente și lămpi auto.

Această analiză calitativă a fost realizată cu ajutorul a trei echipe diferite din interiorul unei companii de automobile, echipe ce au definit și evaluat indicatorii de specialitate, analiza ulterioară bazată pe modelare matematică folosind mai multe metode pentru obținerea matricii consecințelor și pentru obținerea unui clasament al rezultatelor echipelor – metoda utilităților globale, metoda maxi-max, metoda lui Wald și metoda Hurwicz.



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## COMPACTED GRAPHITE – GRAPHITE POLYCRYSTALLINE AGGREGATE – FORMED OF MONOCRYSTALS IN THE FORM OF SMALL LEAVES

BY

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**Abstract:** One obtains grey cast iron with compacted graphite by iron inoculating with a mixture formed of FeSiCaMg ferro-alloy and Al. Analysis by the electron microscope shows compacted graphite shape as graphite polycrystalline. This one is formed of monocrystals as small leaves, these having constant thickness, relatively and a very varied surface.

**Keywords:** graphite, monocrystal; inoculating agent; cast iron.

### 1. Production of Grey Cast Iron with Compacted Graphite

Cojocaru-Filipciuc (2014), presented a obtaining method of grey cast iron with compacted graphite by iron inoculation with a mixture formed of FeSiCaMg ferro-alloy and Al. That paper determined obtaining of a grey cast iron whose proportion of nodular graphite was of 5-10% the rest of graphite being compacted.

Introducing method of the inoculating agent into the metallic bath was “sandwich” (for small quantities of iron, this method have not great efficiency because of small yield of inoculating agent distribution into the metallic bath).

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About 6.5 kg of liquid iron were inoculated. The inoculating mechanism was presented by Cojocaru-Filipiuc (2014, 2011).

Explaining of the inoculating mechanism (Cojocaru-Filipiuc, 2011), takes into account graphite monocrystals increasing into the inoculating agent drops. Graphite monocrystals have shape of small leaves, of different sizes and of the same thickness, relatively.

## 2. Experiments

In Fig. 1, the structure of iron which is analyzed is presented.

Sample whose structure is presented in Fig. 1 was analysed at an electron microscope of type Vega Tescan LMH II.

Imagines were obtained by a detector EDS (Energy Dispersive Spectroscopy).

Getting method of the imagines was SE (Secondary Electrons).

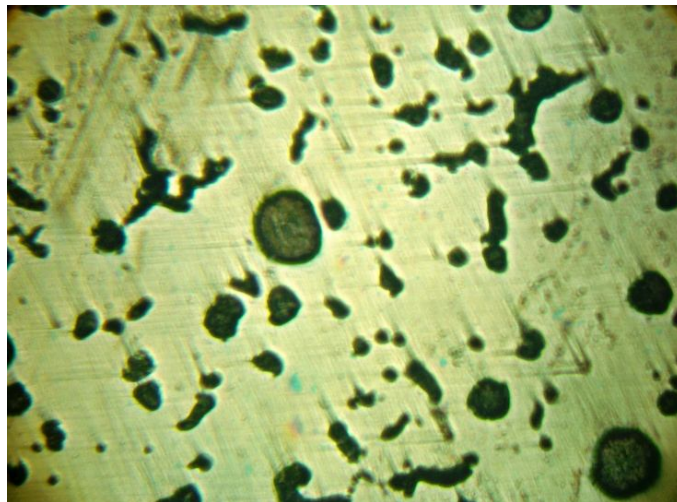


Fig. 1 – Structure of grey cast iron with compacted graphite.  
Aggrandizement 112.

Fig. 2 shows image of some compacted graphite inclusions by the differentiation of the Fe zones in relation to C zones (graphite zones). Buletinul Institutului Politehnic din Iași has not colour printing possibilities, this one generating difficulties for readers of this publication. Thus, in black-white representation, green colour which was chosen for graphite inclusions was transformed in white colour and red colour which was chosen for the metallic matrix was transformed in black colour – Fig. 2. Gray colour from Fig. 2 represents surfaces whose inclinations are steep, almost perpendicular in relation to paper plane.



Fig. 3 represents natural imagine – imagine from Fig. 2.

Fig. 4 shows graphite monocrystals small leaves of compacted graphite presented in Figs. 2 and 3.

To highlight of graphite monocrystals small leaves, another compacted graphite inclusion is presented in Figs. 5,...,7, but, by an aggrandizement of ten times bigger.

Similarly to Figs. 2,...,4 it is presented in Fig. 5 imagine coloured in white (graphite) and black (metallic matrix – iron); gray colour represents planes of the steep rupture, with great inclinations to paper plane.

Fig. 6 represents natural imagine – imagine from Fig. 5.

Fig. 7 shows small leaves of graphite monocrystals of compacted graphite presented in Figs. 5 and 6.

### 3. Discussion and conclusions

Imagines of compacted graphite inclusions confirm small interphase tension between metallic matrix and graphite, expressed by a great surface of graphite: a great interface between metallic matrix and graphite – more than in the case of nodular graphite.

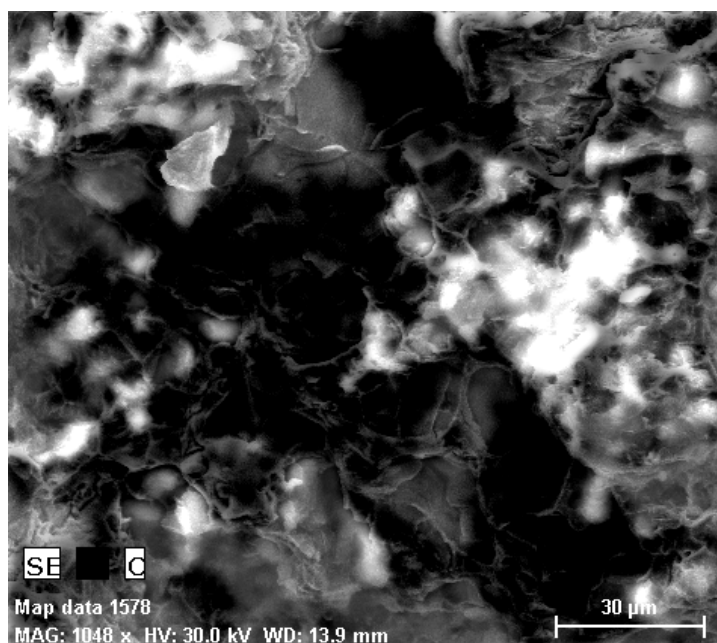


Fig. 2 – Imagine of a compacted graphite inclusion. White colour = compacted graphite. Black colour = metallic matrix. Gray colour = surfaces whose inclinations are great in relation to paper plane (surfaces placed perpendicular on the paper plane, almost).

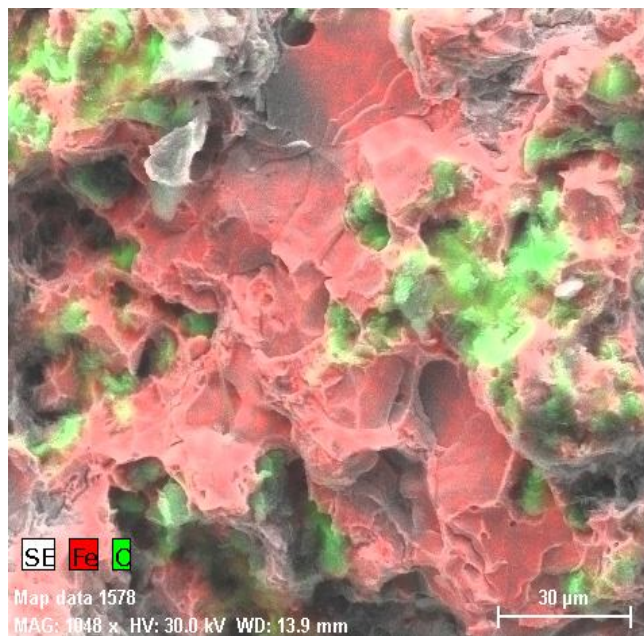


Fig. 3 – Image from Fig. 2, but, with natural black/white colours.

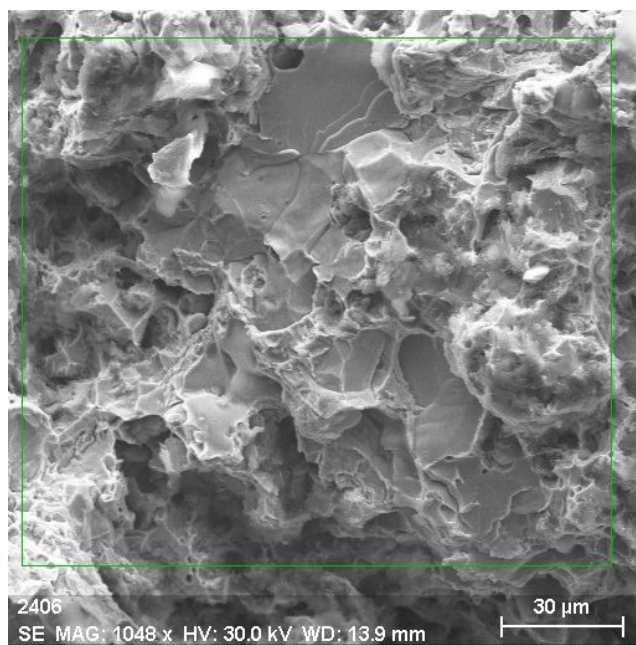


Fig. 4 – Small leaves of graphite monocystals of the compacted graphite inclusions presented in Fig. 2.

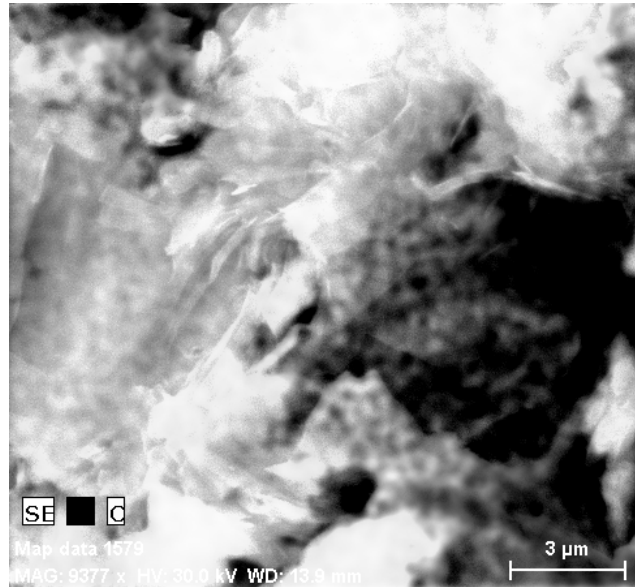


Fig. 5 – Image of a compacted graphite inclusion. White colour = compacted graphite inclusion. Black colour = metallic matrix. Gray colour = surfaces whose inclinations are great in relation to paper plane (surface placed perpendicular on the paper plane, almost).

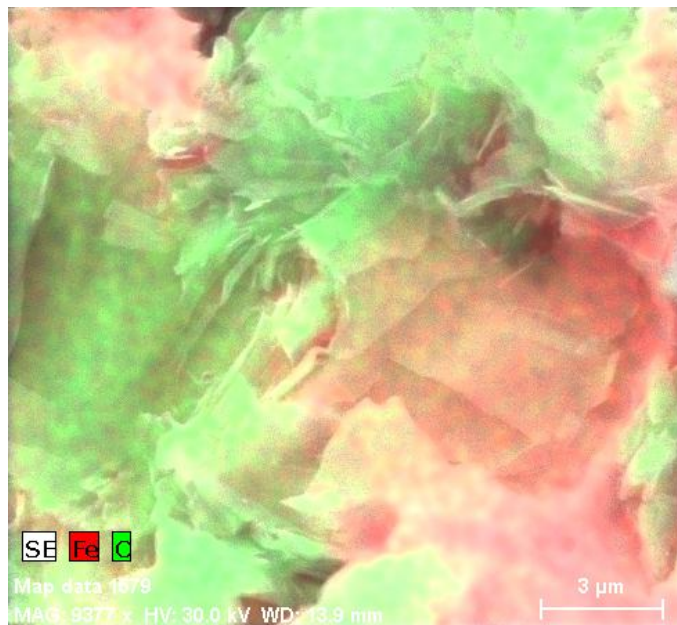


Fig. 6 – Image from Fig. 5, but, with natural black/white colours.

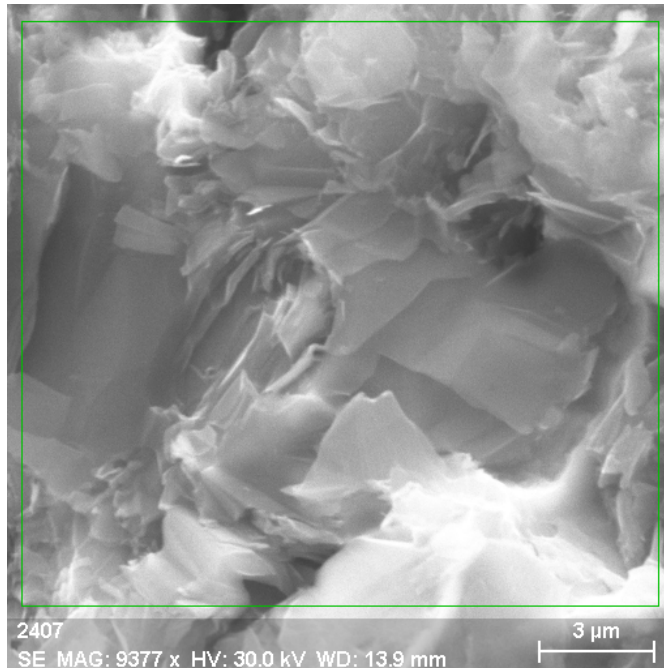


Fig. 7 – Small leaves of graphite monocrystals of the compacted graphite inclusion presented in Fig. 5.

A closer look to compacted graphite is obtained if black ink is introduced into water, at the bottom of a glass, interphase tension water-ink being small.

For a aggrandizement of 9,377, the small leaves of graphite monocrystals are noticed very clearly. One notices that the shape of the small leaves is very varied. This one confirms inoculating mechanism of iron presented by Cojocaru-Filipiuc (2014, 2011). Surface of graphite monocrystals “follows” configuration of the inoculating agent drops which is very varied.

Thus, if the inoculating agent is in liquid state, size of interphase tension “dictates” the shape of graphite obtained by inoculation – nodular, compacted, coral-like and flaky with rounded tops.

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GRAFITUL COMPACTIZAT – AGREGAT POLICRISTALIN DE GRAFIT –  
FORMAT DIN MONOCRISTALE SUB FORMĂ DE FOIȚE

(Rezumat)

Se obține fontă cu grafit compactizat prin modificarea fontei cu un amestec de feroaliaj FeSiCaMg și Al. Analiza la microscopul electronic indică forma grafitului compactizat ca agregat policristalin de grafit format din monocristale de grafit sub formă de foițe, acestea având grosimi relativ constante și suprafața foarte variată.



## INFLUENCE OF THE RAULT'S LAW ON THE INOCULATING PROCESS OF THE ALLOYS

BY

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**Abstract:** Generally, a chemical element from a liquid alloy can cause the formation of a new phase in that alloy if it has a high chemical potential. At the same time, the solution which has this chemical element must have a positive deviation from the Raoult's law. Depending on size of the chemical potential of the chemical element, thermodynamic activity gradient influences obtaining of a new metallic material.

**Keywords:** chemical potential, thermodynamic activity coefficient; partially molar free enthalpy variation.

### 1. Introduction

Fig. 1 shows the drawing of a metallic system made up of phases 1 and 2, where phase 2 is artificially created.

Phase 1, which is in the liquid state, is the predominant phase (Cojocaru-Filipciuc, 2011).

The term impure metallic matrix is synonymous to the term multi-component metallic matrix and also to the term technical metallic matrix or metallic matrix with technical chemical composition.

In practice, specialists have found that the properties of the metallic matrix become unstable in time. The value of these properties changes while the

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metallic matrix is maintained in an isothermal state and it tends to become stable when the isothermal state approaches a critical threshold.

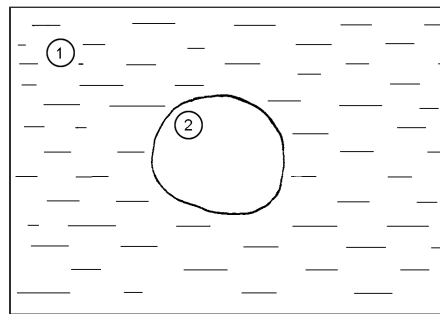


Fig. 1 – Drawing of a metallic system made up of two phases. 1 – liquid metallic matrix; 2 – new phase.

A multi-component metallic matrix determines the occurrence of a liquidus curve in the thermodynamic equilibrium diagram of the metallic matrix. The positioning of the liquidus curve in the equilibrium diagram is easily recognizable if the metallic matrix is with two components, it is relatively easily recognizable if the metallic matrix is has three elements – by sectioning the ternary thermodynamic diagram of the content of a component chemical element – and it is not recognizable at all if the metallic matrix is made up of more than three chemical elements.

When the temperature of the metallic matrix is close to the temperature of the liquidus line (of the liquidus curve), the maintenance time necessary to stabilize the properties may be a few times longer than the usual time required to manufacture the metallic matrix (the alloy, to be precise).

The chemical composition of the metallic matrix is thought to be homogeneous when the properties of the metallic matrix become stable – after the critical period of isothermal maintenance.

In most cases, the properties and structure change so little close to the temperature of the liquidus curve, by isothermal maintenance, that stability is practically impossible. It is only by isothermal maintenance at very high temperatures and by mechanical treatments (stirring), that the properties may be changed and quickly stabilized.

The hysteresis of the properties of the metallic matrix is another piece of evidence of the lack of chemical homogeneity of the metallic matrix. Only the repetition of the test cycle (heating, cooling) leads to result coincidence.

The influence of the microscopic unequilibrium of the metallic matrix on the time variation of its properties is considerable. In concrete terms, some time is needed for the reorganization of the close order after the melting of the metallic matrix components. This microscopic unequilibrium of the metallic matrix is also connected to temperature variation.



A metallic matrix may be approached macroscopically. Thus, macroscopically speaking, a metallic matrix may be defined if its temperature, volume and pressure are known. The exterior properties of the metallic matrix may therefore be described.

A metallic matrix may be defined microscopically if the positions and rates of its particles are known. From the same viewpoint, the metallic matrix may be analyzed either in a state of equilibrium, or in a state of unequilibrium.

A phenomenon of relaxation (*i.e.* of passing from a state of unequilibrium to a state of equilibrium) occurs in a metallic matrix found in a state of unequilibrium.

Macroscopically speaking, a metallic matrix is in a state of equilibrium when it is least ordered.

In principle, the relaxation phenomenon is a sequence of processes occurring at very high rates and of processes occurring at very low rates.

The relaxation phenomenon in a metallic matrix is thought to consist only of quick processes, which means that that metallic matrix can only experience a state of quasiequilibrium.

The metallic matrix is a metastable phase.

The relaxation phenomenon processes, which occur as equilibrium approaches, are very slow since the thermodynamic forces are small. The very slow processes depend on the particle interaction.

The particles in a metallic matrix are not arranged in an orderly manner, and the displacement of a particle changes the positions of the other particles around it.

The particle interaction phenomenon may also lead to the displacement of the atom groups, which takes place in a much shorter time than the displacement of an atom, for instance.

The relaxation phenomenon meant to reach the state of equilibrium may take either tens or even hundreds of years, if the metallic matrix is in the solid state, or determinable periods, if the metallic matrix is in the gaseous state (since in the gaseous state, the equilibrium approaching rate is very high).

When the external conditions change, like temperature, for instance, the close order changes too, both during the heating and the cooling, *i.e.* the interatomic distances, the coordination numbers, the shape of the atomic arrangement, the sizes of the orderly arranged complexes, etc. change. These microscopic properties of the metallic matrix may change at much lower rates than the external condition modification rate. This is the reason why the unequilibrium states of the metallic matrix are very persistent.

The phenomena described above enable one to conclude that one cannot speak of chemical homogeneity as far as an industrially manufactured metallic matrix is concerned.

Clusters of chemical elements (particle agglomerations) may be accepted in the metallic matrix, which complicates the processes occurring there.

## 2. Phase 2 is in Gaseous State

May be it is considered phase 2 in gaseous state.

The metallic matrix – phase 1 – contains the chemical elements  $E_i$  and  $F_j$ , where  $i = 1, 2, 3, \dots$  and  $j = 1$  (the amount of chemical element  $F_j$  is very small or null), while phase 2 contains 100% the chemical element  $F_j$ , where  $j = 1$ .

Here is an analysis of the chemical equilibrium between phases 1 and 2, when phase 1 does not contain the chemical element  $F_j$ , ( $j = 1$ ). The case when phase 1 contains very little chemical element  $F_j$ , ( $j = 1$ ) is actually very similar to the case when the metallic matrix does not contain any chemical element  $F_j$ , ( $j = 1$ ).

Since phase 1 is in the liquid state and phase 2 is in the gaseous state, the diffusion processes occurring in them have very high rates – the distance between particles is big in the metallic matrix and very big in the phase 2 bubbles.

Inequality (1) appears between the metallic matrix and the gas bubbles

$$(\mu_{E_i})_1 > (\mu_{E_i})_2, \quad (1)$$

where:  $(\mu_{E_i})_1$  is the chemical potential of a chemical element  $E_i$  in the metallic matrix – phase 1;  $(\mu_{E_i})_2$  – chemical potential of a chemical element  $E_i$  in phase 2 – in the phase bubble.

Since there are no chemical elements  $E_i$  in phase 2, equations (2) and (3) occur

$$(\mu_{E_i})_2 = 0, \quad (2)$$

$$(a_{E_i})_2 = 0, \quad (3)$$

where:  $(a_{E_i})_2$  – thermodynamic activity of the chemical element  $E_i$ , in phase 2 (in the bubble).

The definition of the thermodynamic activity and inequality (4), which results from relations (2) and (3), determine inequalities (5) and (6)

$$(\mu_{E_i})_1 > 0, \quad (4)$$

$$(a_{E_i})_1 > 0, \quad (5)$$

where:  $(a_{E_i})_1$  – thermodynamic activity of the chemical element  $E_i$  in the metallic matrix (phase 1)

$$(a_{E_i})_1 > (a_{E_i})_2 \quad (6)$$

Generally speaking, for all the cases in the metallic systems, inequality (6) determines the thermodynamic activity gradient of the chemical element  $E_i - \Delta a_{E_i}$  –, relation (7)

$$0 < \Delta a_{E_i} = |(a_{E_i})_1 - (a_{E_i})_2|, \quad (7)$$

where:  $\Delta a_{E_i}$  – thermodynamic activity gradient of the chemical element  $E_i$ .

Considering the particular case dealt with this paper (phase 1 impure and phase 2 pure) and considering relation (3), relation (7) becomes (8).

$$0 < \Delta a_{E_i} = (a_{E_i})_1 \quad (8)$$

In the circumstances described by this paper,  $\Delta a_{E_i}$  has the highest value.

The chemical equilibrium between two phases triggers the diffusion process of the chemical element  $E_i$  from the metallic matrix towards the bubbles of chemical element  $E_j$ .

In addition to relation (8), there is also relation (9)

$$0 < \Delta a_{F_j} = (a_{F_j})_2 \quad (9)$$

where:  $\Delta a_{F_j}$  – thermodynamic activity gradient of the chemical element  $F_j$ ;  $(a_{F_j})_2$  – thermodynamic activity of the chemical element  $F_j$  in the phase 2 bubbles.

Despite the presence of the gradient of the chemical element  $F_j$ , the diffusion of the chemical element  $F_j$  from the bubbles of chemical element  $F_j$  towards the metallic matrix is no longer triggered, as the chemical element  $F_j$  fails to dissolve in the metallic matrix or it dissolves very little.

Since the metallic matrix contains the chemical elements  $E_i$ , all the chemical elements  $E_i$  should theoretically start diffusing towards the bubble of chemical element  $F_j$  ( $i = 1, 2, 3, \dots, n$  and  $j = 1$ ).

It may be generally accepted that the metallic matrix is made up of a basic metal where all the chemical elements accompanying the basic metal dissolve.

Take  $E_1$  as the basic metal in the metallic matrix.

It is not impossible that the metallic matrix be made up of two chemical elements, found in equal amounts, in which case both chemical elements constitute the base.

The metallic matrix is a solution.

A solution contains a solvent and one or several solute elements.

This paper analyzes the metallic matrix where the chemical element  $E_1$

is the solvent and the chemical elements  $E_{i+1}$ , where  $i = 1, 2, 3, \dots, n$ , are the solute chemical elements.

Whatever the case, the phase 2 bubbles will be removed from the metallic matrix, since their density is much lower than the density of the metallic matrix. Bubble density is very low. For instance, magnesium density in the gaseous state, at atmospheric pressure and  $0^\circ\text{C}$ , is  $0.0019 \text{ g/cm}^3$ . It may take longer or shorter periods of time to remove the bubbles from the metallic matrix, as shown by Stokes' basic relation, as other factors, such as the coalescence phenomenon, interfacial surface tension between the metallic matrix and the bubbles, resistance of the metallic matrix, etc. may interfere. From the standpoint of the bubbles present in the metallic matrix, the maintenance of the metallic system with the metallic matrix in the liquid state is nothing but passive to the phenomenon of bubble ascension through the metallic matrix.

Chemical equilibrium may be attained for the chemical element  $E_{i+1}$  easier, which has the highest diffusion coefficient through solvent  $E_1$ . Take the chemical element  $E_2$ , which has the highest diffusion coefficient through solvent  $E_1$ .

Considering the remark in the previous paragraph, inequality (8) becomes inequality (10).

$$0 < \Delta a_{E_2} = (a_{E_2})_1, \quad (10)$$

where:  $\Delta a_{E_2}$  – thermodynamic activity gradient of the chemical element  $E_2$  in the metallic matrix;  $(a_{E_2})_1$  – thermodynamic activity of the chemical element  $E_2$  in the metallic matrix.

In relation to the chemical element  $E_2$ , inequality (6) becomes inequality (11)

$$(a_{E_2})_1 > (a_{E_2})_2, \quad (11)$$

where:  $(a_{E_2})_2$  – thermodynamic activity of the chemical element  $E_2$  in the bubble of chemical element  $F_j$ .

The reality expressed by relations (11) and (10) triggers the diffusion of the particles of chemical element  $E_2$  from the metallic matrix towards the bubbles of chemical element  $F_j$  (Fig. 2).

The particles of chemical element  $E_2$  are usually atoms or ions, yet molecules are not excluded from diffusion.

The diffusion of the particles of chemical element  $E_2$  generates particle agglomerations around the bubbles, like in Fig. 3.

The higher the activity gradient of the chemical element  $E_2$ ,  $\Delta a_{E_2}$ , the

higher the diffusion rate of the particles of chemical element  $E_2$ .

In the circumstances described by this paper, the bubbles are pure (they only contain the chemical element  $F_j$ ). As the bubbles do not contain the chemical element  $E_2$ , this means that, from this viewpoint, the best diffusion conditions are ensured for the chemical element  $E_2$ , since the thermodynamic activity gradient  $\Delta a_{E_2}$  has the highest value.

The highest values of the thermodynamic activity gradient of the chemical element  $E_2$ ,  $\Delta a_{E_2}$ , for a specific temperature and pressure above the metallic matrix, are reached in the following cases:

a) phase 2 – phase 2 bubbles – is pure, *i.e.* it only contains the chemical element  $F_j$ ,  $j = 1$ . In fact, inequality (10) must be fulfilled;

b) the metallic matrix is cooling down, *i.e.* its temperature is decreasing. This condition brings about the increase of the thermodynamic activity coefficient of the chemical element  $E_2 - f_{E_2}$ . It is therefore advisable that the chemical element  $E_2$  should have a very high increase rate of the thermodynamic activity coefficient, while temperature decreases.

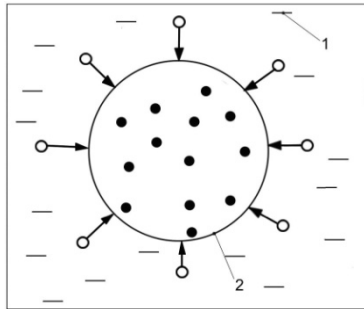


Fig. 2 – Drawing of the diffusion of the particles of chemical element  $E_2$  from the metallic matrix towards the bubble of chemical element  $F_j$ ; ● – particles of chemical element  $F_j$ ; ○ – particles of chemical element  $E_2$ ; 1 – metallic matrix; 2 – bubble of chemical element  $F_j$ .

Regardless of whether the metallic matrix is a solution with positive or negative deviation from Raoult's law, temperature influences thermodynamic activity in a manner that results from the definition of the partially molar free enthalpy variation of the chemical element  $E_2$  – relation (12).

$$\overline{\Delta G}_{E_2}^M = \overline{\Delta H}_{E_2}^M - T \cdot \overline{\Delta S}_{E_2}^M = RT \ln a_{E_2}, \quad (12)$$

where:  $\overline{\Delta G}_{E_2}^M$  – partially molar free enthalpy variation of the chemical element  $E_2$ ;  $\overline{\Delta H}_{E_2}^M$  – partially molar enthalpy variation of the chemical element  $E_2$ ;  $T$  –

temperature;  $\Delta \bar{S}_{E_2}^M$  – partially molar entropy variation of the chemical element  $E_2$ ;  $R$  – universal gas constant.

Relation (12) expresses the thermodynamic activity of the chemical element  $E_2$  and the possible occurrences of the metallic matrix –  $\Delta \bar{H}_{E_2}^M \lesssim 0$  –, as shown hereunder, *i.e.* the occurrences that are not ideal ( $\Delta \bar{H}_{E_2}^M = 0$ ). Temperature decrease increases the thermodynamic activity  $a_{E_2}$  (the variation of factor  $\Delta \bar{S}_{E_2}^M$  depending on temperature may be disregarded in practice).

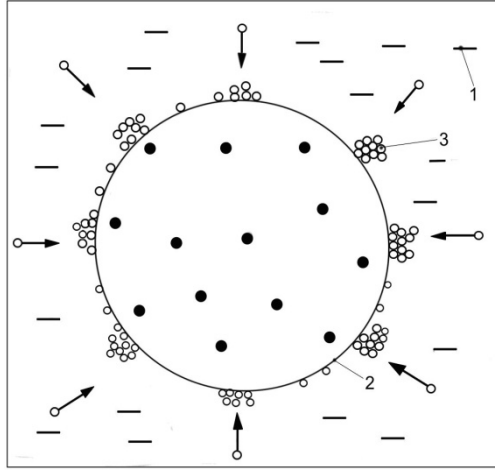


Fig. 3 – Drawing of particle agglomerations of the chemical element  $E_2$  around a bubble of chemical element  $F_j$ . • – particles of chemical element  $F_j$ ; ○ – particles of chemical element  $E_2$ ; 1 – metallic matrix; 2 – bubble of chemical element  $F_j$ ; 3 – agglomeration of particles  $E_2$ .

As shown before, the metallic matrix is not an ideal solution, which means that relation (13) is not compatible with the case analyzed in this paper, when the activity coefficient is 1

$$a_{E_i} = f_{E_i} \cdot X_{E_i}, \quad (13)$$

where:  $a_{E_i}$  – thermodynamic activity of the chemical element  $E_i$ ;  $f_{E_i}$  – thermodynamic activity factor (thermodynamic activity coefficient or, in simpler terms, activity coefficient) of the chemical element  $E_i$ , which may be 1 (ideal solution), below 1 (solution having negative deviation from Raoult's law) and over 1 (solution having positive deviation from Raoult's law);  $X_{E_i}$  – molar fraction of the chemical element  $E_i$ .

The thermodynamic activity factor depends on the following parameters:

- the chemical composition of the metallic matrix;
- the pressure above the metallic matrix;
- the temperature of the metallic matrix.

Fig. 4 shows the thermodynamic activity variation of a chemical element  $E_2$  depending on its molar fraction, when the activity coefficient  $f_{E_2}$  is 1 (dashed curve specific to the ideal solution – the ideal solution is the solution in which the interaction energy between the solvent and the solute chemical element is of the same size grade as the interaction energy between the solvent and solute element particles, for each of these individual components), it is below 1 (the solution has a negative deviation from Raoult's law – curve  $n$ ) or it is over 1 (the solution has a positive deviation from Raoult's law – curve  $p$ ). When the molar fraction of the chemical element  $E_2$  is  $X_{E_2}$ , the activities of the chemical element  $E_2$  have the following values:  $a_{E_{2n}}$  for the solution with negative deviation from Raoult's law,  $a_{E_{2-id}}$  for the ideal solution and  $a_{E_{2p}}$  for the solution with positive deviation from Raoult's law.

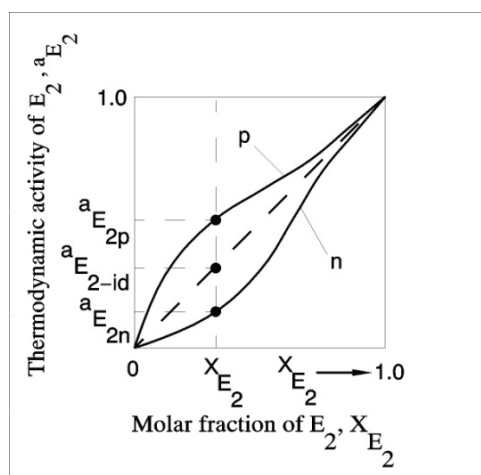


Fig. 4 – Thermodynamic activity variation of a chemical element  $E_2$  in a solution depending on its molar fraction.  $p$  – solution with positive deviation from Raoult's law;  $n$  – solution with negative deviation from Raoult's law;  $X_{E_2}$  – molar fraction of the chemical element  $E_2$ ;  $a_{E_{2n}}$  – thermodynamic activity of the chemical element  $E_2$  in the solution with negative deviation from Raoult's law;  $a_{E_{2-id}}$  – thermodynamic activity of the chemical element  $E_2$  in the ideal solution;  $a_{E_{2p}}$  – thermodynamic activity of the chemical element  $E_2$  in the solution with positive deviation from Raoult's law.

### 3. Discussion and Conclusions

If the metallic matrix is not an ideal solution, it is a solution with either negative or positive deviation from Raoult's law. In practice, there is also the regular solution (where the entropy of mixing – partially molar entropies – is similar with that in the ideal solution).

When the dissolution of the chemical element  $E_2$  is accompanied by heat evolution (negative enthalpy variation;  $\Delta H^M < 0$ , where  $\Delta H^M$  is the enthalpy variation of the mixture;  $M$  actually stands for mixing) and by volume decrease ( $\Delta V^M < 0$ , where  $\Delta V^M$  is the volume variation of the mixture), the interaction energy between the chemical element  $E_2$  and the chemical element  $E_1$  is higher than the interaction energy between the particles of chemical element  $E_1$  or between the particles of chemical element  $E_2$ . In such case, the activity coefficient  $f_{E_2}$  is below 1 and the thermodynamic activity  $a_{E_2}$  is lower than the molar fraction  $X_{E_2}$ . Such a solution does not ensure the highest diffusion rate for the chemical element  $E_2$  since the thermodynamic activity gradient  $\Delta a_{E_2}$  does not have the highest value.

If the dissolution of the chemical element  $E_2$  is accompanied by heat input ( $\Delta H^M > 0$ ) and by volume increase ( $\Delta V^M > 0$ ), the interaction energy between the chemical element  $E_2$  and the chemical element  $E_1$  is lower than the interaction energy between the particles of chemical element  $E_1$  or between the particles of chemical element  $E_2$ . In such case, the activity coefficient  $f_{E_2}$  is over 1 and the thermodynamic activity  $a_{E_2}$  is higher than the molar fraction  $X_{E_2}$ . Such a solution ensures the highest diffusion rate for the chemical element  $E_2$  since the thermodynamic activity gradient  $\Delta a_{E_2}$  has the highest value for a specific temperature of the metallic matrix and for a specific pressure above the metallic matrix.

The diffusion rate of the chemical element  $E_2$  through the metallic matrix is very important, since it is only when it is high or very high that it can determine the chemical equilibrium in the shortest time possible. As shown in Fig. 4, the thermodynamic activity of the chemical element  $E_2$  has the highest value when it forms with solvent  $E_1$  a solution with positive deviation from Raoult's law. According to Fig. 4,  $a_{E_{2p}}$  is much higher than  $a_{E_{2n}}$  – even four times higher, for instance. The conclusion is that the chemical element  $E_2$  has a high diffusion rate only when it forms with the chemical element  $E_1$  a solution with positive deviation from Raoult's law – when its thermodynamic activity is higher than its molar fraction (inequality (14))

$$a_{E_2} > X_{E_2} \cdot \quad (14)$$



The high diffusion rate of the chemical element  $E_2$  through the metallic matrix increases the tendency to chemical equilibrium from phases 1 and 2.

$E_2$  particle agglomerations around the bubbles are a continuous phenomenon due to the high thermodynamic activity gradient of the chemical element  $E_2$ .

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### IMPLICAREA LEGII LUI RAULT ÎN PROCESUL DE MODIFICARE A ALIAJELOR

(Rezumat)

La modul general, un element chimic dintr-un aliaj lichid, poate determina formarea unei faze noi în acel aliaj dacă dispune de potențial chimic mare. În același timp, soluția în care se află acel element chimic trebuie să aibă abatere pozitivă de la legea lui Raoult. În funcție de mărimea potențialului chimic al elementului chimic vizat, gradientul de activitate termodinamică condiționează obținerea unui material metalic nou.



## POSITION OF ALLOYS, WHICH ARE SUBJECT TO INOCULATING, IN EQUILIBRIUM DIAGRAMS

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**Abstract:** A thermodynamic equilibrium diagram, for two chemical elements  $E_1$  and  $E_2$ , is considered. It is analyzed manners of formation of a new phase (3) for hypoeutectic, eutectic and hypereutectic alloys. There is a focus on the uninoculation phenomenon.

**Keywords:** alloys; thermodynamic activity; crystalline boggy.

### 1. Introduction

Here is a concrete example. Take a metallic matrix made up of solvent  $E_1$  and solute element  $E_2$ , when the amounts of the chemical elements  $E_i$ ,  $i = 3, 4, 5, \dots$ , are very small.

Let us suppose that the chemical elements are fully soluble in the liquid state and partially soluble in the solid state, and the equilibrium diagram is as shown in Fig 1 (Borobocev, 1985), eutectic transformation diagram (the diagram refers to the full line curves).

This paper is particularly interested in the transformations that involve the liquid metallic matrix – the processes occurring after the eutectic transformation are in the solid state. Hence, it only focuses on issues related to the chemical equilibrium in the liquid metallic matrix.

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Take  $\alpha$  as the  $E_2$  solid solution in  $E_1$  and  $\beta$  as the  $E_1$  solid solution of in  $E_2$ .

Here are the metallographic constituents of the domains of the diagram in Fig. 10: I – metallic matrix; II – metallic matrix and solid solution of primary  $\alpha$  ( $\alpha'$ ); III – metallic matrix and solid solution of primary  $\beta$  ( $\beta'$ ); IV – solid solution of primary  $\alpha$ ; V – solid solution of primary  $\alpha$  and solid solution of secondary  $\beta$  ( $\beta''$ ); VI – solid solution of primary  $\alpha$  and eutectic; VII – primary  $\beta$  and eutectic; VIII – solid solution of primary  $\beta$  and solid solution of secondary  $\alpha$  ( $\alpha''$ ); IX – solid solution of primary  $\beta$ .

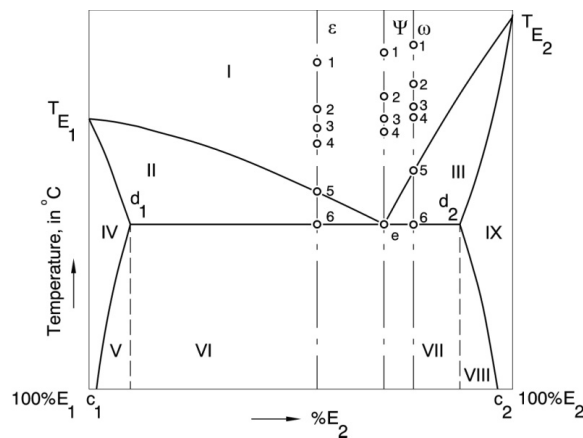


Fig. 1 – Equilibrium diagram of a  $E_1$ - $E_2$  system, where the  $E_1$  and  $E_2$  components are fully soluble in the liquid state and partially soluble in the solid state;  $E_1$  and  $E_2$  – chemical elements of the metallic matrix;  $T_{E_1}$  and  $T_{E_2}$  – melting temperatures of  $E_1$  and  $E_2$ , respectively; I, II, III, IV, V, VI, VII, VIII and IX – distinct structural domains; dotted line curves – imaginary curves separating the structural domains;  $c_1$ ,  $d_1$ ,  $e$ ,  $d_2$  and  $c_2$  – critical points revealing also  $E_2$  concentrations, for instance;  $T_{E_1}$  and  $T_{E_2}$  – melting temperatures of  $E_1$  and  $E_2$ , respectively;  $\varepsilon$ ,  $\Psi$  and  $\omega$  – hypoeutectic, eutectic and hypereutectic alloys, respectively.

Alloys suffer a eutectic transformation between points  $d_1$  and  $d_2$ .

The alloys that contain  $E_2$  with  $d_1$  to  $e$  concentrations are called hypoeutectic alloys, those that contain  $E_2$  with  $e$  concentration are called eutectic alloys, whereas those that contain  $E_2$  with  $e$  to  $d_2$  concentrations are called hypereutectic alloys.

## 2. Analysis of the Inoculating Phenomenon

### 1.1. Hypoeutectic Alloys

Fig. 2 shows the drawing of a metallic system made up of phases 1 and 2, where phase 2 is artificially created.

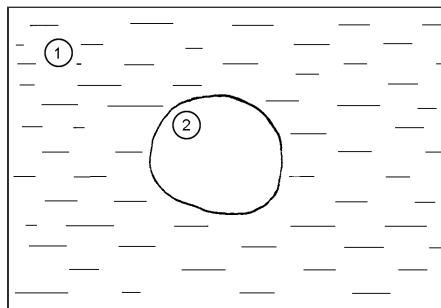


Fig. 2 – Drawing of a metallic system made up of two phases. 1 – liquid metallic matrix; 2 – new phase.

Phase 1, which is in the liquid state, is the predominant phase (Geru, 1981).

The metallic matrix – phase 1 – contains the chemical elements  $E_i$  and  $F_j$ , where  $i = 1, 2, 3, \dots$  and  $j = 1$  (the amount of chemical element  $F_j$  is very small or null), while phase 2 contains 100% the chemical element  $F_j$ , where  $j = 1$ .  $E_1$  represents solvent and  $E_2$  represents solvated.

Take the hypoeutectic alloy  $\varepsilon$ . Its structural transformations are analyzed along the dashed line curve.

The chemical element  $E_j$  is inserted in the metallic matrix when temperature reaches 1. This is the relative temperature of formation of the  $F_j$  bubbles.

The activity increase of the chemical element  $E_2$  and the diffusion of the  $E_2$  particles towards the  $F_j$  bubbles occur during metallic matrix cooling from 1 to 2 (phase 2 is gaseous).

The activity of the chemical element  $E_2$  is 1 in the  $E_2$  particle agglomerations around the  $F_j$  bubbles, when temperature reaches 2 –  $T_2$ .

The  $E_2$  crystalline body is completed in the smallest bubble, when temperature reaches 3 –  $T_3$ , according to inoculating theory.

If the unit weight of the crystalline body of chemical element  $E_2$  is lower than the density of solvent  $E_1$ , the crystalline bodies have a specific ascension rate, *i.e.* they have an ascensional trajectory. Larger amounts of  $E_2$  crystalline bodies would be detected at the metallic matrix surface, if the metallic matrix were hardened from the liquid state, at a hardening temperature of  $T_4$ , for instance. The  $E_2$  crystalline body is completed in the biggest bubble, at the  $T_4$  temperature.

If the unit weight of the crystalline body of chemical element  $E_2$  is higher than the density of the metallic matrix, those crystalline bodies have a specific deposition rate at the bottom of the metallic matrix, which may also be proven by the hardening of the metallic matrix at a maximum hardening temperature of  $T_4$ .

When the temperatures of the metallic matrix are lower than  $T_4$ , the  $E_2$  crystalline body starts dissolving in the metallic matrix, since that crystalline body is outside the thermodynamic equilibrium.

The  $E_2$  crystalline body is outside the thermodynamic equilibrium for the following two reasons:

a) the binary diagram illustrating the thermodynamic equilibrium in Fig. 10 contains only the metallic matrix in its 1<sup>st</sup> domain, meaning that phase contains only liquid. Therefore, the  $E_2$  crystalline body found in the metallic matrix is outside the equilibrium and it tends to dissolve in the metallic matrix;

b) a thermodynamic activity gradient of the chemical element  $E_2$  occurs after the completion of phase 3 ( $E_2$  crystalline body), which is defined by relation (1) and which triggers the tendency towards chemical equilibrium of the chemical element  $E_2$ , between phases 3 and 1 (between the  $E_2$  crystalline body and the metallic matrix).

$$\Delta a_{E_2} = (a_{E_2})_3 - (a_{E_2})_1, \quad (1)$$

where:  $\Delta a_{E_2}$  – activity gradient of the chemical element  $E_2$ ;  $(a_{E_2})_3$  – activity of the chemical element  $E_2$  in the crystalline body of  $E_2$  (in phase 3);  $(a_{E_2})_1$  – activity of the chemical element  $E_2$  in the metallic matrix (in phase 1).

Since the activity of the chemical element  $E_2$  in the crystalline body is equal to the unit ( $(a_{E_2})_3=1$ ), relation (1) turns into relation (2)

$$\Delta a_{E_2} = 1 - (a_{E_2})_1. \quad (2)$$

Take the initial amount of  $E_2$  in the metallic matrix, marked  $\%E_{2i}$ , when the crystalline body of  $E_2$  is completed in the biggest  $F_j$  bubble – at the  $T_4$  temperature.

The  $\%E_{2i}$  value is important for the quality of the metallic material that is manufactured – metallic matrix with crystalline bodies of  $E_2$ . The amount of  $E_2$  in the metallic matrix after the completion of the crystalline bodies of  $E_2$  is very important for the metallic matrix, since the latter solidifies as chemical compositions of some specific amounts of  $E_2$  that are lower or much lower than those of the metallic matrix before the inoculation. The metallic matrix therefore no longer follows the cooling in the liquid state, the solidification and cooling in the solid state, according to the  $\varepsilon$  alloy, but according to an alloy that enjoys an  $E_2$  content even lower than the one in point  $d_1$ .

The metallic matrix with crystalline bodies may be called by different names, depending on the names of the chemical elements  $E_1$  and  $E_2$ , such as, for instance, nickel with nodular graphite, cobalt with nodular graphite, platinum with nodular graphite, rhodium with nodular graphite, uranium with nodular

graphite, cast iron with nodular graphite, etc. (Borobocev, 1895; Mihailov *et al.*, 1985; Sofroni & Ștefănescu, 1974; Cojocaru-Filipiuc, 1988).

The space occupied by the crystalline bodies of  $E_2$  is in close connection with the amount of  $F_j$  bubbles – *i.e.* with the space occupied by the  $F_j$  bubbles – and with the initial amount of chemical element  $E_2$  in the metallic matrix.

While the metallic system made up of phases 1 and 3 (crystalline body of  $E_2$ ) cools down below the  $T_4$  temperature, the  $E_2$  particles start diffusing from phase 3 towards the metallic matrix, according to the inequality  $(a_{E_2})_3 > (a_{E_2})_1$ , due to the tendency towards chemical equilibrium of the chemical element  $E_2$ , which thus returns to the metallic matrix.

As there is little activity of the  $E_2$  element in the metallic matrix  $(a_{E_2})_1$ , the activity gradient of the  $E_2$  element ( $\Delta a_{E_2}$  in relation (2)) is, at  $T_4$  temperature, much higher than the activity gradient of the  $E_2$  element before the inoculation. Therefore, the significant dissolution of the crystalline bodies of  $E_2$  occurs at high rate. Consequently, the  $F_j$  particles should be adsorbed on the crystalline bodies of  $E_2$ , thus delaying their dissolution in the liquid metallic matrix (in the  $E_1$  solvent). Phase 3 more rarely dissolves in the  $E_1$  solvent until the  $E_1$  solvent has fully solidified according to curve  $(T_{E_1}d_1)$  and mainly, according to curve  $d_1e$ .

If the new metallic material cools continuously until it drops below the point 4 temperature (Fig. 1), the activity of the chemical element  $E_2$  increases continuously in the metallic matrix, depending on case, which actually means the decrease of the activity gradient of the  $E_2$  element, according to relation (2) and, hence, the weaker dissolution of phase 3 in the  $E_1$  solvent.

To conclude with, if the new metallic material is maintained in the liquid state at a temperature within the  $[T_4 - T_{(T_{E_1}e)}]$  range for a period of time longer than the critical one, phase 3 fully dissolves in the metallic matrix. Considering that the chemical element  $F_j$  is called inoculating agent and the operation is called inoculation, the inoculating effect is canceled, ( $T_{(T_{E_1}e)}$  is the temperature of a point on the  $T_{E_1}e$  curve).

The new metallic material is also maintained in the liquid state in the thermal axis, at a temperature within the  $[T_4 - T_{(T_{E_1}e)}]$  range, when the casting walls are thick – *i.e.* when the casting wall thickness exceeds the critical thickness. Reference *Pièces épaisses en fonte...* (1977), even states that if the casting walls are thicker than 100 mm, the structure of the nodular graphite cast iron is no longer guaranteed. Consequently, the critical wall thickness starting from which phase 3 no longer occurs in a cast iron where  $E_1$  is iron and  $E_2$  is

carbon is 100 mm. In other words, phase 3 may disappear in the thermal axis of very thick walls.

The chemical elements  $E_i$  (where  $i = 1, 3, 4, 5, \dots$ ) may be absorbed in the crystalline body of  $E_2$ , under the chemical equilibrium influence – *i.e.* under the influence of the tendency to chemical equilibrium of the chemical elements  $E_i$ ,  $i = 1, 3, 4, 5, \dots$ , between phases 1 and 3 – in the  $[T_4 - T_{(E_1e)}]$  temperature range,

*i.e.* during the eutectic transformation, when the amount of  $E_2$  in the metallic matrix, at the  $T_4$  temperature, is larger than the concentration corresponding to point ( $d_1$ ). Since the thermodynamic activities of the chemical elements  $E_i$ ,  $i = 1, 3, 4, 5, \dots$ , are zero in phase 3 and they have definite values in the metallic matrix, which is the cause of the fact that, during the cooling of the new material, the activity of the chemical elements  $E_i$ ,  $i = 1, 3, 4, 5, \dots$ , increases with temperature decrease, the activity gradients of the chemical elements  $E_i$ ,  $i = 1, 3, 4, 5, \dots$ , increase, which encourages diffusion rate increase. One or several chemical elements  $E_i$ ,  $i = 1, 3, 4, 5, \dots$ , will penetrate the crystalline bodies of  $E_2$ , at various depths, depending on the diffusion laws, on the size of the interstices between the phase 3 single crystals, on the size of the particles of  $E_i$ ,  $i = 1, 3, 4, 5, \dots$ , or on the amounts of  $E_i$ ,  $i = 1, 3, 4, 5, \dots$ . This is supported by references (Sofroni, 1975; Sofroni *et al.*, 1985; Cojocaru-Filipiuc, 1990; Ripoșan & Sofroni, 1984) for nodular graphite cast iron and for compacted/vermicular graphite cast iron. The more chemical elements are included in the metallic matrix, the more chemical elements diffuse in the crystalline bodies.

The eutectic transformation may be complex, depending on the type of equilibrium diagram.

Small amounts of  $E_2$  may cause the thermodynamic activity of the chemical element  $E_2$  to be lower, which would lead to a low diffusion rate of the chemical element  $E_2$  through the metallic matrix, whereas the  $E_2$  particle agglomerations around the  $F_j$  bubbles would not manage to make the activity of the chemical element  $E_2$  to reach 1, hence preventing  $E_2$  nuclei formation. If such is the case, the  $F_j$  bubbles will be released from the metallic matrix. Very small amounts of  $F_j$  particles may be found as isolated single crystals in the solid metallic matrix, at room temperature.

Crystalline body dissolution in the metallic matrix consists mainly of the particles of  $E_2$  element that are released by the small leaves or other forms of  $E_2$  single crystals at the crystalline body surface and that diffuse in the metallic matrix. The temperature of the metallic matrix is relatively similar to that of the crystalline bodies throughout the crystalline body dissolution process, which means that the thermal equilibrium is reached. The mechanical equilibrium is also reached in that metallic system during the crystalline body dissolution process occurring in the metallic matrix, which means that the system has the same pressure throughout. On the other hand, there is no thermal



equilibrium in the thermal axis of thick walls, since there are temperature gradients in the metallic matrix in the thermal axis. Thus, the crust is formed close to the mould wall, the solidifying metallic matrix is close to the crust, whereas the new metallic material in the liquid state is close to the metallic matrix. Relation (3) thus expresses the temperature gradient

$$\Delta T = T_{\text{therm.ax}} - T_{\text{solidif.crust}}, \quad (3)$$

where:  $\Delta T$  – the temperature gradient of the new metallic material in the liquid state;  $T_{\text{therm.ax}}$  – the temperature of the new metallic material in the thermal axis;  $T_{\text{solidif.crust}}$  – the temperature of the new metallic material in the crust, at the interface with the solidifying area.

Other chemical elements  $E_i$ ,  $i = 3, 4, 5, \dots$ , are found in an engineering alloy in addition to the main chemical elements  $E_1$  and  $E_2$ , which makes the engineering metallic alloy even more chemically heterogeneous. Therefore, the  $E_2$  single crystals have different sizes.

Consequently, (considering the spherical shape of the  $F_j$  bubbles, etc.), the final shape of a crystalline body – its real shape – may be very varied, like, for instance, in Fig. 3 a).

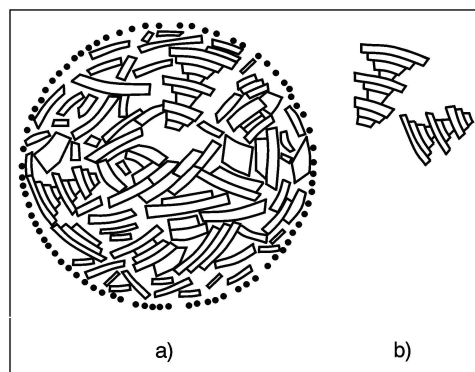


Fig. 3 – Schematic representation of a crystalline body of  $E_2$ , a), and schematic representation of two formations of  $E_2$  crystals detached from the crystalline body of  $E_2$  by the convection currents in the thermal axis of thick walls, b); • – inoculating agent atoms.

If the castings have thick walls, that leaves us with two distinct cases to analyze, as follows:

- alloy inoculation is done in the pouring ladle;
- alloy inoculation is done in the mould.

If the inoculation occurs in the pouring ladle, the crystalline body dissolution process starts in the pouring ladle. The height of the metallic bath in

the pouring ladle is big, varying, for instance, from 500 mm to 2,000 mm or even more. The pressure applied on a crystalline body differs depending on its height in the metallic matrix, on the pressure above the metallic bath and also on the interfacial surface tension between the metallic matrix and air. Metallostatic pressure has a significant influence. Thus, the crystalline bodies found towards the surface of the metallic bath are subjected to a lower metallostatic pressure. The spherical shape and integrity of the crystalline body are also ensured by the metallostatic pressure applied to it. The metallostatic pressure applied on the crystalline bodies found towards the bottom of the metallic bath is high, which means that their disintegration is difficult. All the crystalline bodies undergo a dissolution process, regardless of whether they are at the surface or at the bottom of the metallic bath. The crystalline bodies are solid bodies. The temperature of the metallic bath in the pouring ladle is relative homogeneous. Once the temperature of the metallic bath decreases, the crystalline bodies start contracting. If the decrease of the temperature of the metallic bath is significant, so is the decrease of the crystalline body temperature, which leads to contraction tensions in the crystalline bodies. The slow decrease of the temperature of the metallic bath releases the tension on the crystalline bodies, which means that their integrity is preserved. The high contraction tensions would lead to the occurrence of fissures and cracks in the crystalline bodies, and hence to their disintegration. Crystalline body disintegration in the metallic bath is mainly prevented by the metallostatic pressure and by the slow cooling of the metallic bath. As long as the new metallic material is present in the pouring ladle, the crystalline bodies will have either an ascension rate, if their unit weight is lower than that of the metallic matrix, or a deposition rate, if their unit weight is higher than that of the metallic matrix. On the other hand, if the new metallic material in the liquid state is kept in the pouring ladle for a long time, it causes the crystalline bodies to shrink and hence it decreases either the ascension or the deposition rate of the crystalline bodies. Moreover, this would also lead to crystalline body shape degeneration, as the shape would be far from spherical.

A crystalline body in the metallic matrix is also under the influence of the atmospheric pressure – *i.e.* the pressure above the metallic bath. If the atmospheric pressure is increased by overpressure, this increases crystalline body integrity, while decreasing any disintegration risk altogether. If depression is subtracted from the atmospheric pressure, crystalline body integrity is decreased. The crystalline bodies may disintegrate at the surface of the metallic bath in the pouring ladle, under the depressed atmosphere influence, causing crystal formations, which are smaller than the crystalline bodies and have different compactness degrees. Such crystal formations follow the same cooling process as the crystalline bodies, finally leading, after solidification and cooling in the solid state, to non-spherical angular crystal formations, which are smaller than the crystalline bodies and cause tension in the castings, which significantly

decreases the mechanical resistance properties of the new metallic material. Let us also bear in mind that the castings that will be formed using the new metallic material at the surface of the metallic bath in the pouring ladle have poor mechanical resistance properties. The pouring conditions of the new metallic material in the moulds – *i.e.* the ratio between the capacity of the pouring ladle and the size of the mould cavity – are also important. Thus, if the mould cavity is small, the new metallic material is kept in the pouring ladle for a longer time, which means that the inoculation effect is reduced. Hence, if the weight of the castings that have to be manufactured using the new metallic material is low or, in other words, if the cavity of a mould is small, the inoculation of the metallic matrix should occur in low capacity pouring ladles or inoculation equipment.

If the inoculation of the metallic matrix is done in a mould, the inoculation conditions are different than the pouring ladle inoculation conditions.

Mould inoculation actually means the significant decrease of the time devoted to new metallic material maintenance in the liquid state, at temperatures lower than  $T_4$ . Therefore, crystalline body dissolution in the metallic matrix is considerably diminished, if not inhibited altogether.

The height of the metallic matrix in a mould is much smaller than the height of the metallic matrix in a pouring ladle, the former currently varying between 100-200 mm and 500 mm, while the latter is 1,500-2,000 mm. This means that the metallostatic pressure is much lower in the mould than in the pouring ladle, and this pressure acts both on the initial  $F_j$  bubble and on the crystalline body. Therefore, the ascension of the  $F_j$  bubbles is short, as the bubbles cannot grow while the metallostatic pressure diminishes. Consequently, if the inoculation occurs in a mould, the  $F_j$  bubbles are smaller, while the crystalline bodies resulted from the former are also smaller. As the crystalline bodies are smaller, the tension on the castings manufactured is lower, which means that the mechanical resistance properties of the castings thus manufactured are superior to those achieved when the inoculation occurs in a pouring ladle.

The crystalline body size is more even if the inoculation is done in a mould than if it occurs in a pouring ladle, due to the small height of the casting walls. The positioning of a casting wall during the pouring process has little importance, due to the short time of cooling in the liquid state and to the short time of solidification of the new metallic material.

However, the metallostatic pressure acting on the crystalline bodies in the thick casting wall is much lower than that in the metallic bath in the pouring ladle. Therefore, the thermal axis of the thick walls has crystalline body disintegration conditions.

The crystalline body disintegration phenomenon is very strong if the position of the thick wall is horizontal as compared to the position of the mould during the solidification of the new metallic material. If the position of the thick

wall is vertical during the solidification of the new metallic material, the disintegration phenomenon is considerably diminished due the metallostatic pressure increase at the foot of the wall.

If the thick wall is vertical, yet short, the disintegration phenomenon is of the same size grade as the phenomenon affecting horizontal thick walls.

The low metallostatic pressure and high contraction tensions occurring in the thermal axis area are accompanied by low intensity convection currents with circular shapes, which are caused by the high temperature gradient between the thermal axis and the surface of the solidification front, which gradient may exceed even 250°C. The convection currents enhance the disintegration of the crystalline bodies of  $E_2$  into formations of  $E_2$  crystals – *i.e.* into blocks of  $E_2$  crystals.

Fig. 3 shows the detachment of two formations of  $E_2$  crystals, the shape of which in nodular graphite cast iron is considered to be, by Ripoşan & Sofroni, (1984), a degenerate shape of nodular graphite (chunky graphite) – more details on chunky graphite formation will be provided in this paper. The formations of  $E_2$  crystals will finally be caught in the solidification front and they will be visible in the metallographic structure of the castings, in the thermal axis of thick walls.

If the crystalline bodies are small, the probability of occurrence of formations of  $E_2$  crystals is lower, as the tension level is lower. This usually occurs when an alloy is inoculated in a mould, where the small height of the metallic matrix results into small  $F_j$  bubbles (Cojocaru-Filipiuc, 2005).



Fig. 4 – Drawing of a crystalline body at the beginning of the solidification range, when there is less remanent  $F_j$ ; • – inoculating agent atoms.

As shown above, the crystalline body dissolution process starts at temperatures lower than  $T_4$  and, consequently, at solidification onset temperatures, the surface of the crystalline body is no longer smooth, but bumpy, as shown by Fig. 4. Such shapes of the crystalline bodies of  $E_2$  are caused by the small amount of  $F_j$ , due to which it is not adsorbed on the entire surface of the crystalline body of  $E_2$ . Therefore, when subjected to a metallographic analysis and  $\times 1000$  magnified, a crystalline body appears as shown in Fig. 5.

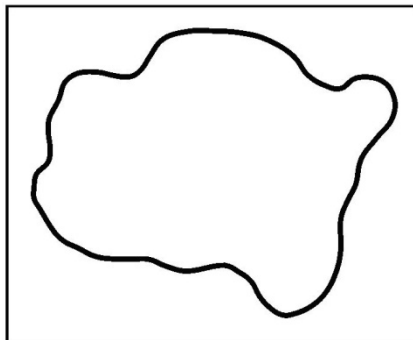


Fig. 5 – A  $\times 1,000$  magnified crystalline body, at the solidification onset temperature.

If the walls are very thick, the disintegration phenomenon is more likely to occur in the horizontal walls, and it causes crystal formations that are carried along by the solidification front at the border of the  $\alpha$  primary solid solution separations. If the solid solution has a dendritic shape, the formations of  $E_2$  crystals will have an interdendritic distribution, as shown in Fig. 6.

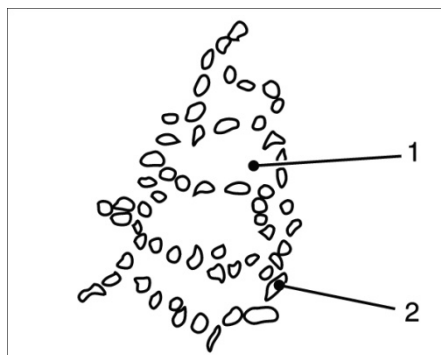


Fig. 6 – Interdendritic distribution of the blocks (formations) of  $E_2$  crystals, in the thermal axis of thick walls. 1 –  $\alpha$  primary solid solution dendrite; 2 – blocks of  $E_2$  crystals.

In thick horizontal walls, the blocks of small  $E_2$  crystals resulted from disintegration have the time they need to dissolve in the metallic matrix. If this is the case, the eutectic transformation occurs in point 6 of the thermal axis, as morphological transformation, due to the fact that the new metallic material in the liquid state is kept in the pouring ladle for a long time, and also due to the fact that it is maintained in the liquid state in the very thick walls of the castings, regardless of the position of the walls during the solidification of the new metallic material.

### 1.2. Eutectic Alloys

$\psi$  is the alloy with eutectic composition shown in Fig. 1.

The amount of  $E_2$  present in the  $\psi$  alloy is larger than the amount of the same element present in the  $\varepsilon$  hypoeutectic alloy. Consequently, the activity of  $E_2$  in the former alloy is stronger than its activity in hypoeutectic alloys. Concretely speaking, the solution must be an either positive or negative deviation from Raoult's law, for both categories of alloys.

The formation mechanism of crystalline bodies of  $E_2$  is identical to the one described in paragraph 2.1.

As the activity of  $E_2$  is stronger in the  $\psi$  than in the  $\varepsilon$  alloy, the temperatures  $T_1$ ,  $T_2$ ,  $T_3$  and  $T_4$  corresponding to the  $\psi$  alloy are higher than the temperatures  $T_1$ ,  $T_2$ ,  $T_3$  and  $T_4$  corresponding to the  $\varepsilon$  alloy. Therefore, crystalline bodies of  $E_2$  are formed in eutectic alloys at higher metallic matrix temperatures.

If the atmosphere above the metallic matrix is depressed, points 1, 2, 3 and 4 have higher temperatures due to an enhanced activity of the chemical element  $E_2$ .

### 1.3. Hypereutectic Alloys

The activity of the chemical element  $E_2$  is stronger in hypereutectic alloys than in hypoeutectic and eutectic alloys. Consequently, points 1, 2, 3 and 4 of the  $\omega$  hypereutectic alloy have higher temperatures than the same points of the hypoeutectic and eutectic alloys.

Further to the analysis of the particular diagram in Fig. 1, please note the ascending slope of the equilibrium curve ( $e T_{E_2}$ ), which requires high temperatures for a significant superheating. Under these circumstances, when high-melting alloys are concerned, special refractory materials are required, which are expensive and thus increase the cost of the new metallic material. Therefore, hypereutectic alloys with low hypereutecticity degrees are subjected to inoculation.

The conclusions to be drawn as concerns hypereutectic alloys are different, depending on the type of  $E_1$ – $E_2$  alloy and on its chemical composition – *i.e.* the amounts of  $E_i$ ,  $i = 3, 4, 5, \dots$ , in the metallic matrix.

## 2. Conclusions

Thanks to overheating possibility, in liquid state, better, in practice one recommends eutectic alloys for inoculating.

Hypereutectic alloys are able to inoculate best thanks to the higher thermodynamic activity of the chemical element  $E_2$  (that which the new phase 3).

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### POZIȚIA ALIAJELOR, CE SE SUPUN MODIFICĂRII, ÎN DIAGrameLE DE ECHILIBRU

(Rezumat)

Se consideră o diagramă de echilibru termodinamic pentru elementele chimice  $E_1$  și  $E_2$  și sunt analizate particularități de formare a unei faze noi (3) pentru variantele de aliaje hipoeutectice, eutectice și hipereutectice. Se pune accent pe fenomenul de demodificare.





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## MORPHOLOGICAL CHARACTERISTICS OF COATINGS OBTAINED BY ATMOSPHERIC PLASMA SPRAYING

BY

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**Abstract:** The atmospheric plasma spraying method is one of the processes of achieving coatings used successfully to increase the life of various parts in operation. The spraying process is characterized by a series of very important parameters that affects both the coating quality and the substrate layer. When the sprayed particles impact the substrate, a series of events occur, that may result in a combined thermal and mechanical stress. Thus there is a structure transformation on a depth of a few microns, which becomes quasicrystalline or amorphous. In the present study were conducted a series of observations on two types of coatings deposited using the atmospheric plasma spraying method in two different systems: WC-Cr si Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>.

**Keywords:** surface coatings; atmospheric plasma spraying; SE images.

### 1. General Considerations

The deposition methods of thermal spray coatings are becoming increasingly used because they enable the obtaining of active coatings characterized by hardness, excellent adhesion to the substrate, resistance to corrosion and wear (Davis, 2004; Qiao *et al.*, 2000) The layer thickness can vary from a few microns to several millimeters, depending on the desired behavior. The types of materials that can be deposited cover almost all

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categories: metals, cermet, ceramic and plastic. For this reason, thermal spraying can be considered even a type of surface modifying treatment because it can only provide layers in some areas to meet operational needs. The substrate can be designed for a certain strength and resilience while deposited layer to be responsible for resistance to corrosion, heat and wear ([www.sulzermetco.com](http://www.sulzermetco.com)). Thus, thermal spraying is used to produce parts used in almost all branches of industry.

One of the thermal spraying methods, which is very versatile in terms of materials that can be deposited and regarding the possibilities of coatings quality variation by varying the deposition parameters (power, spray distance, etc.) is the atmospheric plasma spraying method.

The atmospheric plasma spraying method was originally developed in order to achieve coatings from ceramic materials, and is still being the most important method of achieving these layers. With this method may be also sprayed metallic and plastic materials, provided they are in powder form and can be melted or become plastic during the spraying process. Propulsion velocities of the particles are much larger than in electric arc or flame spraying, resulting in more dense layers characterized by a low surface roughness (Surface and coatings technology; *Chicet et al.*, 2011; *Janisson et al.*, 1999).

In Fig. 1 is presented a schematic section through the gun used for atmospheric plasma spraying method. It consists of a copper anode and a tungsten cathode, both water cooled. The gases used for plasma are: primary gases (argon, nitrogen) and secondary gases (hydrogen, helium), that flow around the cathode and through the anode, which has the shape of a nozzle.

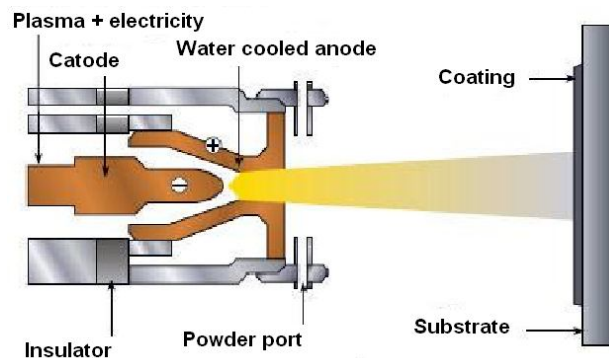


Fig. 1 – Schematic section through plasma spraying gun ([www.sulzermetco.com](http://www.sulzermetco.com)).

Plasma is initiated by a high-voltage discharge which causes a local ionization and a conductive path for an electric current to form an arc between cathode and anode. Heat caused by the arc causes the gas to reach very high temperatures, to dissociate and to ionize to form plasma (Davis, 2004).

Plasma exits through the nozzle anode as neutral plasma (not carrying electricity), a phenomenon that is very different from the electric arc spraying technology (a process where the arc extends to the surface to be covered).

In Fig. 2 is presented the particles distribution in the plasma jet and the different paths they follow, depending on the powder injection angle.

Each trajectory represents a form of particle heating, which affects their overall condition at the impact with the substrate (solid, solid + liquid). Note that the optimal diameter particles end up in the center of the jet and melt completely, while the particles with small diameters don't have enough momentum to penetrate the hottest part of the jet and remain at the edge.

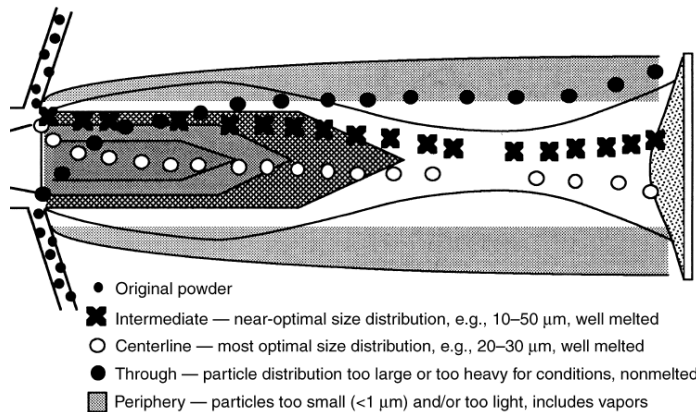


Fig. 2 – Schematic presentation of particles distribution in the plasma jet (Davis, 2004)

Nor particles too large or that have greater weight will not melt because the great speed of the carrier gases can force the large particles to follow a path that crosses the plasma jet.

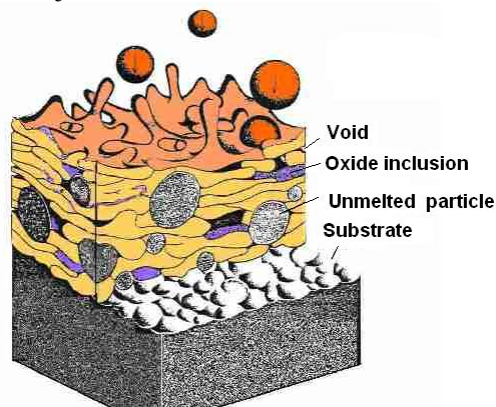


Fig. 3 – Schematic representation of coating obtained after plasma spraying (Davis, 2004).

Thus, in the moment when the molten or semi-molten particles in the plasma jet hit the substrate, they flatten and solidify rapidly, forming the desired coating. In Fig. 3 is schematically presented such a layer. It highlights the lenticular grain structure, and also the presence of not melted particles, oxides or goals.

## 2. Materials and Methods

To obtain the studied coatings were used powders from two different systems:

a) A powder from tungsten carbide system with nominal composition **WC10Co4Cr**. These materials are used in special applications where both wear resistance (abrasion, erosion, fretting) (Wielage *et al.*, 1997) and corrosion are required, supporting a working temperature up to 500°C. Particle sizes range from 45 to 11 microns and were obtained by agglomeration and sintering (Fig. 4).

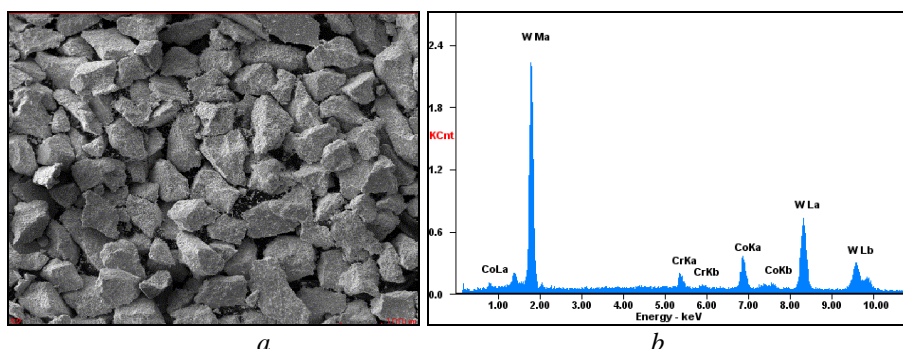


Fig. 4 – WC10Co4Cr powder: *a* – secondary electrons image;  
*b* – chemical elemental analysis EDS.

b) A powder from ceramics – aluminum oxide system mixed with titanium oxide with nominal composition **Al<sub>2</sub>O<sub>3</sub> – 13 TiO<sub>2</sub>**. These materials are used for various parts subject to abrasive and sliding wear, presents resistance to oxidation at working temperatures around 550°C and have good behavior in alkaline or acidic environments (Fig. 5) (Żórawski *et al.*, 2008; Zois *et al.*, 2008; Lima *et al.*, 2006).

Powder morphology was investigated by scanning electron microscopy with microscope Quanta 200 3D, and the chemical elemental analysis by EDS analysis module.

As coating support were used alloyed with Cr rings for bearings, brand 100Cr6 with the following chemical composition according to ISO 683-17: 0.93–1.05%C, 0.15–0.35%Si, 0.25–0.45%Mn, 1.35–1.6%Cr, max. 0.10Mo, max. 0.025%P, max. 0.015%S.

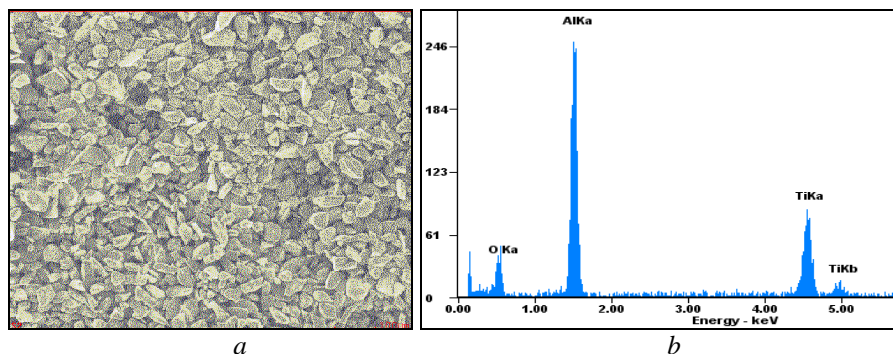


Fig. 5 –  $\text{Al}_2\text{O}_3 - 13 \text{TiO}_2$  powder: *a* – secondary electrons image; *b* – chemical elemental analysis EDS.

To increase the coating adhesion to the substrate was sprayed also an intermediate coating, using Ni-Al-Mo powder.

The coating was performed using an atmospheric plasma spraying system type 9MCE with 9MBM type spray gun. In the Table 1 are synthesized the working parameters of plasma jet deposition used to obtain those coatings.

**Table 1**  
*Working Parameters*

Powder	WC10Co4Cr	$\text{Al}_2\text{O}_3 - 13 \text{TiO}_2$
Ar flow (l/min)	46	46
H <sub>2</sub> flow (l/min)	13.5	13.5
Ar flow (carrier gas) (l/min)	45	45
Working tension (V)	60	60
Working current (A)	600	600
Spraying distance (mm)	120	120

The first stage of coatings realization was the rings surface preparation by sandblasting with corundum type F20, so that later they can be cleaned using an ultrasonic bath and trichloroethylene degreaser solution.

### 3. Results and Discussion

The following images present the morphological appearance of the two coatings obtained after spraying the WC10Co4Cr and  $\text{Al}_2\text{O}_3 - 13 \text{TiO}_2$  powders. In Fig. 6 *a, b* is presented the general appearance of the coated rings.

Using electron microscopy (Quanta 200 3D – FEI Company, Holland), coatings measurements were conducted, layer thicknesses being determined with values between 50 to 90 microns.

It can be noticed in both cases the specific lamellar layered aspect of the studied coatings, according to the results presented in the literature. There are

yet some differences caused by the way the splat crystallization occurs, specific for each material.

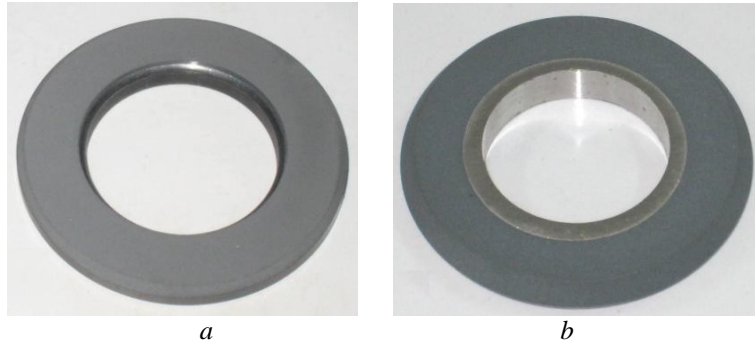


Fig. 6 – General appearance of the coated rings:  
a – WC10Co4Cr; b – Al<sub>2</sub>O<sub>3</sub>-13 TiO<sub>2</sub>.

In Figs. 7 and 9 are presented cross sections of the samples, which highlight the appearance and thickness of the coating.

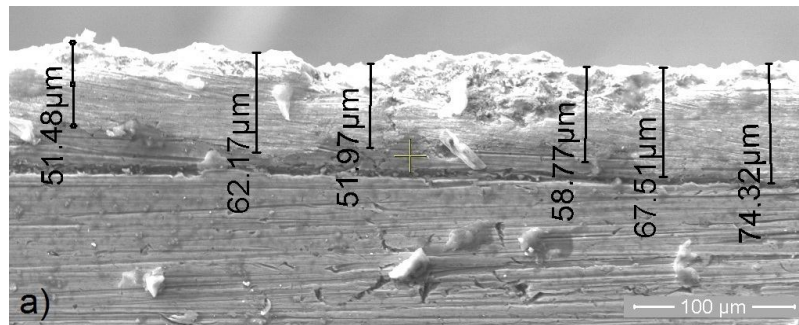


Fig. 7 – Cross section of the sample coated with WC10Co4Cr (Secondary Electrons Image).

In case of WC10Co4Cr sprayed coating is observed the crystallization mode: there are no visible lenticular well defined splats, because they have much smaller dimensions and polygonal geometry. It is obvious the good cohesion between splats, not observable blanks so that obtained layer has superior properties, especially resistance to mechanical stress (see Fig. 8).

In Fig. 10 is presented the appearance in fracture of Al<sub>2</sub>O<sub>3</sub> – 13 TiO<sub>2</sub> coating. The layer is also characterized by lenticular structure specific to coatings deposited by atmospheric plasma spraying. It is shown that splats present a smaller structure in terms of dimension compared to WC10Co4Cr coating structure. In contrast, even if the splats are well defined after fracture, it can't be observed any areas with lack of adhesion between them, the coating being compact and homogeneous.



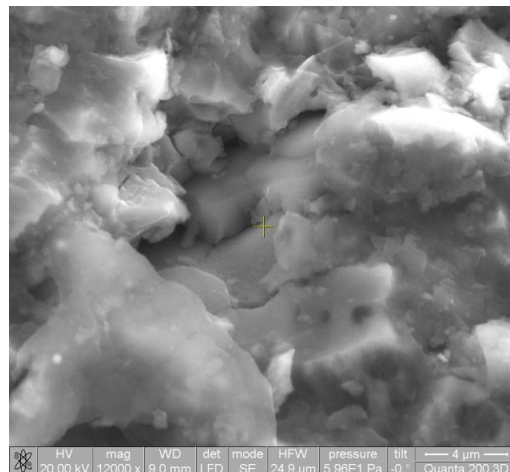
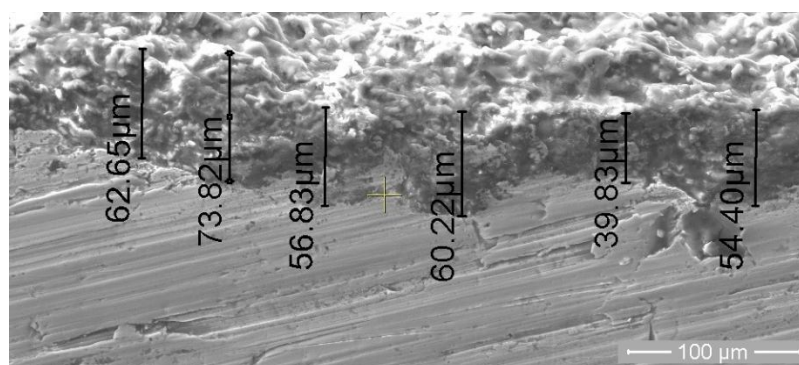
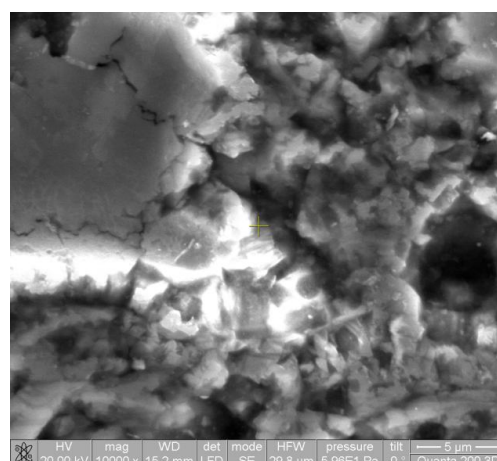


Fig. 8 – Details of WC10Co4Cr coating (SEI, 12000x).

Fig. 9 – Cross section of the sample coated with  $\text{Al}_2\text{O}_3 - 13 \text{ TiO}_2$  (SEI).Fig. 10 – Details of  $\text{Al}_2\text{O}_3 - 13 \text{ TiO}_2$  coating (SEI, 12,000x) .

## 6. Conclusions

Atmospheric plasma spray is a complex process that develops very high temperatures, allowing deposition of a very large range of powders. The systems central element is the spray gun. At this level is produced the gas mixture and is generated the plasma jet that develops temperatures between 6,000°C – 15,000°C in which is injected the powder. This is totally or partially melted instantly and then accelerated towards the substrate.

Layer characteristics can be varied by changing the process elements (gas type, powder type, injection angle in the plasma jet) and process parameters (spraying distance, working atmosphere, the powder injection flow, substrate temperature, the travel speed of the gun towards surface, etc.).

In the secondary electron images was highlighted the lamellar structure of coatings, which may adversely affect coating cohesion and mechanical stress behavior.

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CARACTERISTICI MORFOLOGICE ALE ACOPERIRI OBȚINUTE PRIN  
PULVERIZAREA ÎN JET DE PLASMĂ

(Rezumat)

Metoda de pulverizare în plasmă este unul dintre procesele de realizarea a acoperirilor utilizată cu succes la creșterea duratei de utilizare a diferitelor organe de mașini. Procesul de pulverizare în jet de plasmă este caracterizat de o serie de parametri foarte importanți care afectează atât calitatea acoperirii cât și a substratului. Atunci când particulele pulverizate lovesc substratul apar o serie de evenimente care pot duce la o combinație de eforturi termice și mecanice. Astfel există o transformare a structurii pe o adâncime de câțiva microni, care devine quasi cristalină sau amorfă. În prezentul studiu au fost făcute o serie de observații pe două tipuri de acoperiri utilizând metoda de pulverizare în jet de plasmă în două sisteme diferite: WC-Cr și  $\text{Al}_2\text{O}_3\text{-TiO}_2$ .



## EXPERIMENTAL ANALYSIS OF THE STRESS AND STRAINS OF THE FOREARM BONES

BY

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**Abstract:** In this work we performed an experimental analysis of the state of tension of deformation of bones in the forearm. The complexity of the geometric shape of a cross section of the bone has led to the division of the area in multiple elementary surfaces, which can be approximated by regular contours of straight or curved, quantifiable by measurement. Because only one ulna was available, non-destructive methods were used. For the determination of stress, geometric characteristics of the section were subjected to the experimental measurements, using both practical method to find the complex shape of the ulna, the cross sectional area, and analytical method, when calculating the geometrical of inertia of the geometric elementary surfaces, where the split section was examined.

**Keywords:** experimental analysis; forearm; strain; cross section geometry; biomechanica system.

### 1. Introduction

Experimental analysis of a biomechanical system provides information which may lead to validating or correcting theoretical, analytical or virtual model of that system. The experimental determination "in vitro" of a state of stress and strain of a bone, under precise mechanical loading, allow the necessary corrections on the mechanical characteristics attributed to the material, where the virtual model is correct from a geometrical point of view.

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Experimental determination of stresses and strains can be accomplished by using various methods, including the electro-resistive transducers (TER), commonly known by the name of strain gauges. Using this method provides only information on the stresses and deformations of a given section, chosen by the experimenter. Choosing a section located in a critical area where tension and deformation values are at the maximum, can shape an experiment on the behaviour of real bone, under known mechanical loading.

Using TER method involves the following stages:

- a) determining geometrical properties of the measuring section of stresses and deformations;
- b) determining the geometric moments of inertia of the chosen section;
- c) realization of experimental stand and chain measurements;
- d) calibration of strain gauge bridge;
- e) conduct and interpretation of experimental measurements.

The complexity of the geometric shape of a cross section of the bone has led to the division of the area in multiple elementary surfaces, which can be approximated by regular contours of straight or curved, quantifiable by measurement. At the same time, by making these geometric features and virtual bone model and comparing the values with those obtained by direct measurement, accuracy could be verified of the three-dimensional geometric model.

## **2. Experimental Considerations on the Geometrical Characteristics of Ulna Section**

For determining the characteristics of geometrical section of bone (ulna) subjected to experimental testing, a cross-section was chosen as close to an experimental device that locks the elbow joint as possible. A narrow-mindedness adopted embedment section of the recess due to the fact that the mechanical, axial and bending is at maximum, as it can be observed from the table of mechanical stress in Fig. 1.

Experimental geometric measurements could be made either directly on a cross-section of the bone, and this requires a destructive way of that section of bone, or by using a mold, a negative of the bone, the method of keeping the bone intact. Because we had one ulna available, I used the non-destructive method.

Geometrical cross section of the ulna involved the following steps:

1. application of bone around the affected area, an easily molded material (plaster, clay, resin) which subsequently strengthened and "registered" sectional shape;
2. severing the strengthened "sleeve" and restoring it through bonding, after appropriate removal of the bone;
3. smoothing the collar "sleeve" to present a flat surface and contouring it with black ink (Fig. 2);

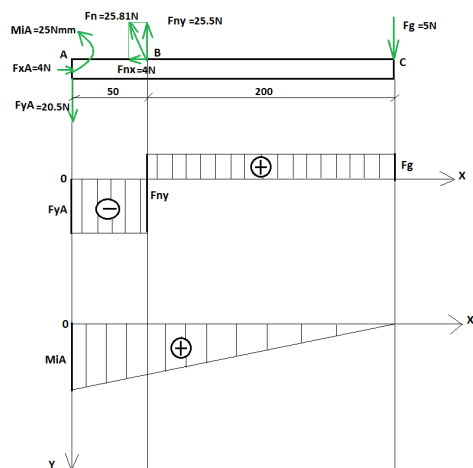


Fig. 1 – Diagrams of requests axial and bending bone embedded in A.

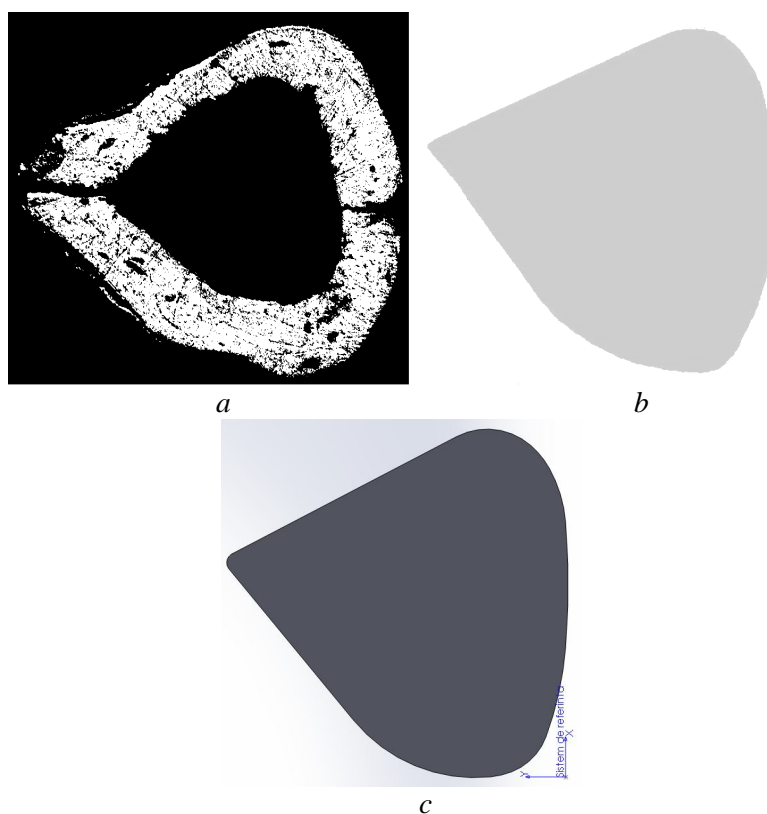


Fig. 2 – *a* – "Sleeve" image of the ulna cross-section, *b* – cross-section processed with Paint and *c* – processed section in a CAD program.

- The section we obtained has been divided into 14 elementary geometric shapes, as shown in Fig. 3 *a*, and the size of the elementary surfaces, obtained by scaling, are shown in Fig. 3 *b*. Using the dimensions of the triangles and sectors of a circle, these surfaces were calculated elementary areas, data shown in Table 1.

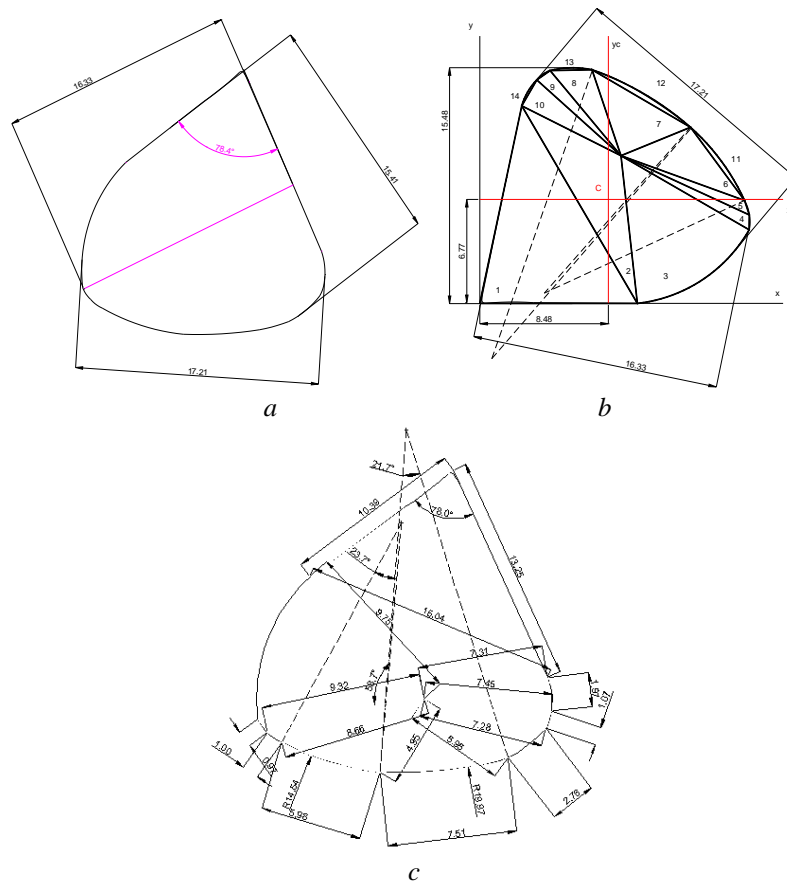


Fig. 3 – *a* – The overall dimensions of the cross section, *b* – elementary geometric surfaces (14 numbers) and *c* – the scale of elementary geometric figures.

Table 1 shows the areas of the elementary surfaces identified and measured in Fig. 3 *b* and 3 *c*.

**Table 1**  
*Elementary Surface Areas*

Geometrical figure number	Area mm <sup>2</sup>	<i>R</i> mm	$\varphi$ rad
1	67.3272	—	—
2	29.9097	—	—
3	44.57481	9.75	0.4689
4	4.14375	—	—
5	3.4018	—	—
6	14.3323	—	—
7	14.68205	—	—
8	7.826	—	—
9	3.874	—	—
10	7.1638	—	—
11	1.243017	14.54	0.2072
12	1.787798	19.97	0.1892
13	0.284079	6.28	0.2218
14	0.163103	3.97	0.2505
Total = 200.7134		—	—

Based on splitting cross section of the ulna in elementary surfaces with regular geometry, it was able to determine the inertial characteristics of the section needed to determine the mechanical stresses.

### 3. Conclusions

Experimental determination of stresses and strains that occur in the ulna was performed using an experimental stand measurement using electro-resistive transducers (TER); stand reproduce the conditions of virtual model analysis and enables voltage measurement and deformation three points of a section under the elbow joint.

Determine the voltage the geometric characteristics of the section were subjected to the experimental measurements, using both practical method to find the complex shape of the ulna, the cross sectional area, and analytical method, when calculating the geometrical of inertia of the surfaces geometrical basic, where the analysis section was decomposed.

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#### ANALIZA EXPERIMENTALĂ A STĂRII DE TENSIUNI ȘI DEFORMĂȚII ALE OASELOR ANTEBRAȚULUI

(Rezumat)

Se realizează o analiză experimentală a stării de tensiune de deformare a oaselor în anteb. Complexitatea formei geometrice a unei secțiuni transversale a osului a dus la divizarea zonei în mai multe suprafețe elementare, care poate fi aproximată prin contururi neregulate de drepte sau curbe, cuantificabile prin măsurare. Pentru că numai un cubitus a fost disponibil, s-au folosit metode non-distructive. Pentru determinarea tensiunii, caracteristicile geometrice ale secțiunii au fost supuse măsurătorile experimentale, utilizând atât metoda practica pentru a găsi forma complexă a ulnei, zona secțiunii transversale, și metoda analitică, atunci când se calculează geometrice ale inerției al elementare geometrice suprafețe, în cazul în care a fost examinat în partea split.



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ȘTIINȚA ȘI INGINERIA MATERIALELOR

## **SPECIFIC RISK ASSESSMENT FOR THE ACTIVITIES OF USE OF PYROTECHNIC ARTICLES CATEGORY 4**

BY

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**Abstract:** The paper presents a theoretical and practical approach to the concept of the risk assessment specific to the activity of use of pyrotechnic articles Category 4, in terms of ensuring secure premises from the effect resulting after execution of fireworks fires with these types of pyrotechnic products.

**Keywords:** risk assessment; pyrotechnic article; safety and health at work; residual risk; safety requirement.

### **1. Introduction**

The legislative framework obliges employers to take all measures to ensure that workers are not exposed to risks that could cause accidents or illnesses. The national methodological norms for applying Law 319 of 14 July 2006 on security and health at work regulates the mechanism by which the employer must do to eliminate or reduce these risks.

Even if the products used are of adequate quality confirmed by assessment documents and certification, at their use there are a number of objective and subjective factors that can lead at the dangerous situations and unwanted events.

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In the systems work, the general obligation of the employer is to ensure state security and health of employees, occupational risk assessment process, allowing to establish appropriate measures of prevention, protection and insurance with reference to the risks of accidents and professional diseases, training and information to employees and to implement an effective occupational safety management.

From the structural point of view, the main stages of occupational risk assessment are:

- Identify the hazards of accidents and occupational disease;
- Identifying people who may be exposed to these hazards;
- Estimation and assessment of occupational risks;
- Study of the potential to eliminate occupational hazards;
- Analysis the appropriateness and necessity of stopping additional measures to reduce (decrease) / control or eliminate risks.

Occupational risk assessment methodology is based on two essential requirements in this area:

- The assessment procedure must include an analysis of all the dangers of accidents and occupational disease, whatever their mode of manifestation (obvious hazards or potential);
- Elimination, if possible, to all the dangers of accidents and occupational diseases identified in the evaluation process.

Risk assessment represents an ongoing concern of the leaders working process from the design stage of the processes, continuing with the preparatory work, the demolition work effectively and monitor the effects on human health and safety, integrity of material goods and the environment.

## 2. Mathematical Model

If the assessed risks which are located at the risk of unacceptable, is applying the procedure of analysis and reducing thereof by applying an appropriate preventive and protective measures of a technical and organizational, to prevent and combat the causes of production of undesirable events (accidents at work and occupational diseases).

In this regard, it is used for " the Risk Analyser " (whose matrix is shown in Fig. 1), which was built based on scales related classes corresponding values of two parameters, the probability of occurrence of an event unwanted peak P and the seriousness of the consequences of predictability G.

It shows further corresponding grid of the professional risk parameters (R)/occupational safety (S), and the scale of the risk attitude and risk matrix analyzer.

*Grid for assessing the level of professional risk*

Levels of Risk Professional / Occupational Safety	Professional risk estimation values R	Level of professional risk assessment	Appreciation of occupational safety level
1 / 7	1 ÷ 8	Minimal risk	Maximum security
2 / 6	9 ÷ 14	Very small risk	High security
3 / 5	15 ÷ 23	Low risk	High security
4 / 4	24 ÷ 32	Medium risk	Medium security
5 / 3	33 ÷ 39	High risk	Small security
6 / 2	40 ÷ 44	Very high risk	Security very small
7 / 1	45 ÷ 49	Maximum risk	Minimum security

Legend:

			Represents the domain of acceptable risk
			Represents the domain of unacceptable risk

*Scale of attitude towards the professional risk*

Level s of risk	Level of professional risk appreciation	Attitude to the professional risk
1	Minimal risk	No special action is taken
2	Very small risk	
3	Low risk	
4	Medium risk	It makes monitoring dangerous situations, control event risk factors additional corrective measures can be applied taking into account cost-effectiveness
5	High risk	Efforts will be made to reduce the level, but the costs of prevention should be carefully measured. Measures to reduce the risk level is implemented in strictly determined period of time. Where high risk is associated with serious consequences, should be set exactly the probability of manifestation of responsible risk factors, and measures will be taken to diminish them.
6	Very high risk	Activities can not continue until the risk is not reduced! Resources should be assigned to reduce the risk. On the occurrence of other risks in the labor action is taken immediately..
7	Maximum risk	Activities can not start until the risk level is not reduced! If it is not possible the immediately reducing of the level of risk, work in these circumstances IS PROHIBITED!

If following the risk assessment for Occupational Safety and Health identify a risk level located in the unacceptable it will highlight the risk index fiches, after which the full form of analysis and risk reduction and diagram will

be constructed to reduce this level on prevention and protection measures that must be taken.

			CLASS OF PROBABILITY "P"					
			1 ↓	2 ↓	3 ↓	4 ↓	5 ↓	6 ↓
			EXTREMELY RARE	RARELY	RARE	LESS FREQUENTLY	FREQUENTLY	VERY FREQUENTLY
CLASS OF CONSEQUENCES "G"	CONSEQUENCES		P > 10 years	5 years < P < 10 years	2 years < P < 5 years	1 year < P < 2 years	1 month < P < 1 year	P < 1 month
7 →	MAXIMUS	DEATH	21	29	35	39	41	42
6 →	VERY SERIOUS	DISABILITY GR. I	20	28	34	37	38	40
5 →	SERIOUS	DISABILITY GR. II	19	26	27	32	33	36
4 →	HIGH	DISABILITY GR. III	13	18	24	25	30	31
3 →	AVERAGE	ITM 45 – 180 DAYS	11	12	16	17	22	23
2 →	SMALL	ITM 3 – 45 DAYS	7	8	9	10	14	15
1 →	NEGLECTIBLE		1	2	3	4	5	6

Fig. 1– Matrix of the professional risk analyzer.

## 2.1. Assessing the Specific Risks of Use of Pyrotechnic Articles Category 4

### 2.1.1. Identification of Specific Risks of Use of Pyrotechnic Articles Category 4

The main risks arising at the use of pyrotechnic articles Category 4 can be grouped, as a source of production into two categories:

- Risks from preparatory work (storage, handling, transportation and installation);
- Risks arising from operation of pyrotechnic articles Category 4 and any misfires

#### *Specific risks of the preparatory work*

The main risks arising at the conducting the preparatory work are:

- lack of assurance of the security personnel and the delimitation of the safety zone;
- inadequate condition of the access routes at the test site of pyrotechnic articles in Category 4;
- obstacles present on the access routes / evacuation;

- the wrong choice of place of firing comply with the distances to the objectives from nearby;
- wrong choice of place of firing regarding the compliance with safety distances from spectators and buildings in close correlation with the type and size of fireworks;
- wrong choice of place of firing when using electric igniters regarding the distances from power lines;
- the environment with extreme temperatures or variable (storm, blizzard, atmospheric electrical discharges);
- inadequate lighting and poor visibility etc.

Concrete analysis and preliminary assessment of the risks outlined above, it allows the establishment of practical measures to eliminate or at least reduce their level.

*Specific risks to the functioning of pyrotechnic articles Category 4 and their potential misfires*

The main risks arising at the conducting the preparatory work are:

- improper placement at the site of the firing of pyrotechnic articles in Category 4 and devices for firing (Mortars, supports, cables, control panel) after downloading from the transport vehicle;
- the lack or shortage (less than 2 extinguishers) elements specific to PSI;
- improper mounting of supports and launching mortars vertical and inclined;
- loading the launching mortars vertical and inclined with nonspecific pyrotechnics from category 4;
- improper mounting of electric igniters;
- improper mounting of pyrotechnic articles from Category 4 which does not charge in mortars;
- prepare several bombs, at a time, before being loaded;
- wrong preparation of firing circuits linking the wires of igniters and control panel through the connecting cables (wrong link, faulty cables, etc.);
- incorrect continuity check of firing circuit with improper gauges (not intended and approved for this purpose where the current test is less than 25 mA);
- lack of supervision of installation activity of pyrotechnic articles in of category 4 by authorized personnel as pyrotechnist;
- lack of supervision pyrotechnic articles of category 4 when installed by authorized personnel as pyrotechnist or staff trained in this regard;
- the wrong choice of area for firing fireworks, so this may be influenced by the effects of pyrotechnic articles Category 4;
- lack of verification of entry of foreigners (Spectators) within the safety zone before an ignition;

- failure to comply with the command of the organizer of the fireworks or poor communication with it;
- wrong connection of the control panel at power source;
- inadequate lighting or other vision problems;
- triggering pyrotechnic articles Category 4 on the storm time, snowstorm or atmospheric electrical discharges;
- absence of performing the control at the ignition place by authorized personnel as pyrotechnist or making the control at less than 20 minutes;
- remnants of products unsupervised which would trigger a fire or products from misfires;
- illegal entry into possession by unauthorized persons of products from misfires.

Concrete analysis and preliminary assessment of the risks outlined above, it allows the establishment of practical measures to eliminate or at least reduce their level.

The risk assessment for worker safety and health activities in the field of use of pyrotechnic articles in Category 4 it was made based on identifying and analyzing specific risks and those related of preparatory work and functioning, highlighted in the risk index sheets (1) partial results and overall assessment it is recorded in the form of analysis and professional risk reduction (2) which includes the diagram to reduce this level based on preventive and protective measures that need to be taken.

Risk index sheets (1)

No. doc	Description of identified risk factor (concrete form of manifestation)	Workplace (subsystem)
A.	Specific risks of preparatory work at the use of pyrotechnic articles Category 4.	The area of firing of pyrotechnic articles
B.	Specific risks to the functioning of pyrotechnic articles Category 4 and their potential misfires	

Form of analysis and professional risk reduction (2)

ANALYSIS AND SPECIFIC RISK REDUCTION AT ACTIVITIES OF USE OF PYROTECHNIC ARTICLES CATEGORY 4				
Job (subsystem): the firing area of pyrotechnic articles				
A. Specific risks of preparatory work at the use of pyrotechnic articles Category 4.				
Doc no. 1	Risk: Medium		Level: 4	
Occupational hazard determined - Injury and / or illness of personnel at the carry out preparatory work for the use of pyrotechnic articles Category 4	P	G	Estimation / assessment risk R	
	5	3	22	Me

<b>Identification of potential risk factors:</b> $R_{ig}(p_i, g_i) = (\sum r_i R_i) / \sum r_i \rightarrow R_{ig}(5, 3) = 22$ (In terms of value $\square r_i \square = \square R_i \square, i=1...7$ ). - lack of assurance of the security personnel and the delimitation of the safety zone: $R_1(p_1, g_1) \rightarrow R_1(5, 5) = 33$ . - inadequate condition of the access routes at the test site of pyrotechnic articles in Category 4: $R_2(p_2, g_2) \rightarrow R_2(2, 7) = 29$ . - obstacles present on the access routes / evacuation $R_3(p_3, g_3) \rightarrow R_3(6, 3) = 23$ . - the wrong choice of place of firing comply with the distances to the objectives from nearby: $R_4(p_4, g_4) \rightarrow R_4(1, 7) = 21$ . - wrong choice of place of firing regarding the compliance with safety distances from spectators and buildings in close correlation with the type and size of fireworks: $R_5(p_5, g_5) \rightarrow R_5(1, 7) = 21$ . - wrong choice of place of firing when using electric igniters regarding the distances from power lines: $R_6(p_6, g_6) \rightarrow R_6(5, 3) = 22$ . - the environment with extreme temperatures or variable (storm, blizzard, atmospheric electrical discharges): $R_7(p_7, g_7) \rightarrow R_7(5, 3) = 22$ . - inadequate lighting and poor visibility: $R_8(p_8, g_8) \rightarrow R_8(4, 2) = 10$ .  <b>Description of the risk factors identified concrete form of manifestation:</b> - Wrong ensuring of the safety zone and facilitating entry of unauthorized personnel in the area. - Impairment of stability and of the access routes. - Blocking escape routes of staff. - increasing Insecurity at the use of pyrotechnic articles Category 4 (Category 4 pyrotechnic articles operation could harm the objectives of the neighbourhood). - unexpected initiation due to the electromagnetic field generated by high voltage power lines. - Unstable weather with storm and thunder. - daylighting limited and insufficient. <b>Causes:</b> - Conducting preparatory work for Category 4 use of pyrotechnic articles.  <b>Dysfunctions:</b> - Favouring the phenomenon of accidents and/or occupational disease due to exposure to the risks identified.			
<b>Technical and organizational measures:</b> <b>technical measures</b> - Establish and appropriate choice of the working area. - Use of of pyrotechnic articles Category 4 and firing devices (mortars, supports, cables, control panels) adequate. - Providing of two extinguishers appropriate for intervention if necessary. - Compliance with safety distances according to current regulations. - Proper equipment with PPE. <b>Organisational measures:</b> - Ensure the security and adequate demarcation of the perimeter work. - Appropriate training of personnel involved in the use of pyrotechnic articles Category 4. - The procedure for working mode. - Coordination and appropriate deployment of staff at the jobs / workstations related of the firing area.		<b>References:</b> - Law 319/2006 on safety and health at work and rules for the application of it with subsequent amendments. - Law 126/1995 republished and Technical rules for applying. - OSH instructions. - The technical specification of the product.	
<b>Residual Risk identification:</b> -Type Pyrotechnic articles (category 4) and related working environment.		<b>P</b> 4	<b>G</b> 3
<b>Residual risk:</b> - Execution of preparatory work for the use of pyrotechnic articles Category 4, respecting the technical and organizational measures outlined above.		<b>Estimate/ risk assessment R</b> 17	
		<b>Actions:</b> -Reduced Risk of value 22 (medium risk) to the value of 17 (low risk) by technical and organizational measures.	

Chart risk mitigation professional at the carry out of preparatory work.

Doc no. 2	Risk: High	Level: 5
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**Identification of potential risk factors:  $R_{ig}(p_i, g_i) = (\sum r_i R_i) / \sum r_i \rightarrow R_{ig}(6,4) = 31$  (In terms of value  $\square r_i \square = \square R_i \square, i=1...22$ )**

- improper placement at the site of the firing of pyrotechnic articles in Category 4 and devices for firing (mortars, supports, cables, control panel) after downloading from the transport vehicle:  $R_1(p_1, g_1) \rightarrow R_1(3,7) = 35$
- the lack or shortage (less than 2 extinguishers) elements specific to PSI:  $R_2(p_2, g_2) \rightarrow R_2(3,7) = 35$
- improper mounting of supports and launching mortars vertical and inclined:  $R_3(p_3, g_3) \rightarrow R_3(2,7) = 29$
- loading the launching mortars vertical and inclined with nonspecific pyrotechnics from category 4:  $R_4(p_4, g_4) \rightarrow R_4(2,7) = 29$
- improper mounting of electric igniters:  $R_5(p_5, g_5) \rightarrow R_5(2,7) = 29$
- improper mounting of pyrotechnic articles from Category 4 which does not charge in mortars:  $R_6(p_6, g_6) \rightarrow R_6(3,6) = 34$
- prepare of several bombs, at a time, before being loaded:  $R_7(p_7, g_7) \rightarrow R_7(2,7) = 29$
- wrong preparation of firing circuits linking the wires of igniters and control panel through the connecting cables (wrong link, faulty cables, etc.):  $R_8(p_8, g_8) \rightarrow R_8(5,4) = 30$
- incorrect continuity check of firing circuit with improper gauges (not intended and approved for this purpose where the current test is less than 25 mA):  $R_9(p_9, g_9) \rightarrow R_9(2,7) = 29$
- lack of supervision of installation activity of pyrotechnic articles in of category 4 by authorized personnel as pyrotechnist  $R_{10}(p_{10}, g_{10}) \rightarrow R_{12}(2,7) = 29$
- lack of supervision pyrotechnic articles of category 4 when installed by authorized personnel as pyrotechnist or staff trained in this regard;  $R_{11}(p_{11}, g_{11}) \rightarrow R_{11}(2,7) = 29$
- the wrong choice of area for firing fireworks, so this may be influenced by the effects of pyrotechnic articles Category 4:  $R_{12}(p_{12}, g_{12}) \rightarrow R_{12}(2,7) = 29$
- lack of verification of entry of foreigners (Spectators) within the safety zone before an ignition  $R_{13}(p_{13}, g_{13}) \rightarrow R_{13}(2,7) = 29$
- failure to comply with the command of the organizer of the fireworks or poor communication with it:  $R_{14}(p_{14}, g_{14}) \rightarrow R_{14}(2,7) = 29$
- wrong connection of the control panel at power source:  $R_{15}(p_{15}, g_{15}) \rightarrow R_{15}(5,7) = 29$



- inadequate lighting or other vision problems:  $R_{16}(p_{16}, g_{16}) \rightarrow R_{16}(5,7)=29$
- triggering pyrotechnic articles Category 4 on the storm time, snowstorm or atmospheric electrical discharges:  $R_{17}(p_{17}, g_{17}) \rightarrow R_{17}(3,7)=35$
- noise emitted after performing the operation:  $R_{18}(p_{18}, g_{18}) \rightarrow R_{18}(5,7)=29$
- the emergence of misfires and eliminating them:  $R_{19}(p_{19}, g_{19}) \rightarrow R_{19}(3,7)=35$
- absence of performing the control at the ignition place by authorized personnel as pyrotechnist or making the control at less than 20 minutes:  $R_{20}(p_{20}, g_{20}) \rightarrow R_{20}(5,4)=30$
- remnants of products unsupervised which would trigger a fire or products from misfires:  $R_{21}(p_{21}, g_{21}) \rightarrow R_{21}(5,4)=30$
- illegal entry into possession by unauthorized persons of products from misfires:  $R_{22}(p_{22}, g_{22}) \rightarrow R_{22}(5,4)=30$

**Description of the risk factors identified concrete form of manifestation:**

- Blocking the access ways for place of firing and unnecessary agglomeration of the area concerned when downloading and improper arrangement of pyrotechnic articles Category 4 and firing devices
- Impossibility of intervention or improper intervention in case of fire
- Dangerous operation of pyrotechnic articles Category 4 as a result of the improper installation of supports and launching mortars vertical and inclined
- Wrong operation of pyrotechnic articles Category 4 due to nonspecific loading of pyrotechnic products in the launching mortars
- Improper installation of electric igniters
- Improper installation of pyrotechnics category 4 which does not charge mortars
- Failure to follow instructions for preparing bombs
- Making the wrong firing circuits or wires are defects in these circuits
- The use of improper equipment (mistaken or unauthorized purpose) to verify the continuity of firing circuits
- vulnerability of mounting activity as a result of non-supervision by authorized personnel as pyrotechnist or its staff trained in this regard
- Area site related of initiation of the fireworks predisposed to the effects of pyrotechnic articles Category 4
- The possibility of entering before an ignition of foreigners (the spectators) within the safety zone
- Improper communication with the fireworks organizer (authorized person as pyrotechnist)
- Non-achieving of ignition pyrotechnic articles Category 4 as a result of incorrect connection to the power supply of control panel
- Difficult conditions of visibility or improper lighting
- Conducting activities of initiation of pyrotechnic articles Category 4 during storms, blizzard or atmospheric electrical discharges
- Great noise emitted into the environment from the operation of pyrotechnic articles Category 4
- Possible failures of pyrotechnic articles Category 4, been rendered unusable
- Failure to observe instructions when carry out the control of the place of firing
- The existence of debris products that could lead to fire or products from misfires
- The possibility of entry into the illicit possession of unauthorized products from misfires

**Causes:**

- Operation pyrotechnic articles Category 4 under evaluation

**Dysfunctions:**

- Favouring the phenomenon of accidents and / or occupational disease due to exposure to the risks identified.

**Technical and organizational measures:**

- Technical measures
- The use of pyrotechnic articles of category 4 and appropriate firing devices
  - Following instructions mounting devices for firing
  - Following instructions for charging launching mortars vertical and inclined
  - Carrying out instructions for preparing bombs
  - The use of appropriate measuring equipment, realization of circuits firing and initiate the ignition of pyrotechnical products of category 4
  - The OSH working instructions to the use of pyrotechnic articles

**References:**

- Law 319/2006 on safety and health at work and rules for the application of it with subsequent amendments.
- Law 126/1995 republished and Technical rules for applying.
- OSH instructions.
- The technical specification of the product.

of category 4 - Monitoring the effects due to the operation of pyrotechnic articles of category 4 Organisational measures - Appropriate training of personnel involved in the use of pyrotechnic articles of category 4 - The procedure for working mode - Coordination and appropriate deployment of personnel at the workplace / workstations associated area site					
<b>Residual Risk identification:</b> - Type of pyrotechnic articles (of category 4) and related working environment.		<b>P</b>	<b>G</b>	Estimate / risk assessment R	
		5	3	22	Me
<b>Residual risk:</b> - Control of the area after the operation of the pyrotechnic articles of category 4.		<b>Actions:</b> Reducing the risk to the value of 31 (high risk) to the value 22 (medium risk) by technical and organizational measures			

	1 ↓	2 ↓	3 ↓	4 ↓	5 ↓	6 ↓
Classes of gravity "G"	Probability classes "P"					
7 →	21	29	35	39	41	42
6 →	20	28	34	37	38	40
5 →	19	26	27	32	33	36
4 →	13	18	24	25	← 30	← 31
3 →	11	12	16	17	↓ 22	23
2 →	7	8	9	10	14	15
1 →	1	2	3	4	5	6

Chart to reduce the occupational risk.

### 3. Conclusion

The main aim of occupational risk assessment at using of the pyrotechnic articles of category 4, is to prevent and combat the causes that can cause accidents and/or occupational diseases while performing operations preparatory and securing the effects arising from the operation of these types of pyrotechnics.

Estimation and risk assessment for the use of pyrotechnic articles of category 4 were developed, both graphic-analytical instruments for quantification of risk parameters, represented by "Analyser of professional risk"

and “Diagram of professional risk reduction”, and also “The form of professional analysis and risk reduction”.

The results of the risk assessment obtained in the study ,it provides relevant data and information on the security status and health at work specific to the activity of use of pyrotechnic articles of category 4, in order to improve and dynamize the process of substantiating of policies in preventing and combating the causes that can cause accidents and/or occupational diseases.

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### EVALUAREA RISCURILOR SPECIFICE ACTIVITĂȚII DE UTILIZARE A ARTICOLELOR PIROTEHNICE CATEGORIA 4

(Rezumat)

Se prezintă o abordare teoretică și practică a conceptului de evaluare a riscului specific activității de utilizare a articolelor pirotehnice categoria 4, din perspectiva asigurării premizelor de securizare a efectelor generate în urma executării focurilor de artificii cu aceste tipuri de produse pirotehnice.

Executarea de focuri de artificii cu articole pirotehnice categoria 4 presupune stabilirea de măsuri de securitate precise care să elimine riscurile de accidentare respectiv de afectare a securității clădirilor, infrastructurii sau a mediului.

Spectaculozitatea unor astfel de lucrări de declanșare de articole pirotehnice atrage în cele ai multe situații un public numeros care se situează în zona adiacentă lansării efectelor.

Față de lucrările de împușcare cu explozivi de uz civil unde tot personalul este special instruit pentru a aplica măsurile de protecție referitor la operația de împușcare, la declanșarea încărcăturilor explozive care se încadrează în categoria 4 din articolele pirotehnice, nu se poate realiza retragerea tuturor persoanelor la distanțe considerabile față de locul de declanșare întrucât astfel de evenimente implică prezența publicului într-o zonă de securitate prestabilită de unde să poată urmări efectele.

Față de măsurile educaționale și de disciplină care sunt aplicabile personalului care execută lucrările, pentru publicul care asistă la efectuarea de focuri de artificii toată răspunderea revine firmei executante care trebuie să pună în practică un sistem de securitate foarte eficient.



## BURNOUT SINDROME AND EMOTIONAL INTELLIGENCE

BY

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**Abstract:** In Europe, stress associated with work is the second frequently reported problem, among work associated health problems. Long-term involvement in stressful professional situations can lead to burnout, respectively to a state of physical, emotional and mental exhaustion.

Health experts estimate that, worldwide, there are millions of people suffering from burn-out, considering that this is a phenomenon of modern society. According to estimates, burnout syndrome manifestations are found in more than half of the planet's working population.

Effective management of stress at work can be hampered by insufficient development of a person in terms of emotional intelligence, namely in terms of self-knowledge, self-regulation, self-motivation, awareness and social skills.

The current paper aims to present the theoretical framework and results of several scientific researches that highlight the link between emotion, emotional intelligence and prevention or relief of symptoms and negative conditions associated with burnout syndrome.

**Keywords:** burnout; emotional intelligence; stress; emotions; work.

### 1. Introduction

In Europe, stress associated with work is the second frequently reported problem among work-related health problems. A quarter of European employees believe that they face stress during almost their entire work program

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and still a quarter of them say that work negatively affects their health. Almost half of European employees believe that stress is not managed in an effective manner at their working places. This is because, despite the fact that about 80% of managers are concerned with work-related stress issues, less than a third of companies have implemented specific procedures related to stress (Eurofound and EU-OSHA, 2014).

The figures for Romania show that half of Romanian employees consider cases of work-related stress to be common in their work, while less of the other half considers that such cases are rare (European Opinion Poll ..., 2013).

Long-term involvement in stressful work situation can lead to installation of burnout syndrome, respectively a state of physical, emotional and mental exhaustion. Health experts consider that, worldwide, there are millions of people suffering from burnout, considering that this is a phenomenon of modern society. According to estimates, burnout syndrome symptoms are found in over half of the planet's working population.

## **2. Stress and Burnout**

The term burnout was first used in the 70s by American psychologist Herbert Freudenberger referring to reactions that people showed to interpersonal stress at work. Later, the concept was copied by other psychologists, including Christina Maslach who, besides broadening it, has developed a tool for measuring burnout. This tool, developed in collaboration with Susan Jackson, is a questionnaire containing 25 questions divided into three dimensions: emotional exhaustion (9 items), depersonalization (6 items), personal achievement (10 items) and is, at present, used at large scale.

Although not registered as a distinct disorder in the latest edition of Diagnostic and Statistical Manual of Mental Disorders, burnout is included in the International Classification of Diseases (ICD-10), a tabular list of diseases put together by WHO. In order to be diagnosed as suffering from burnout, according to ICD-10, an individual must display the following symptoms:

- a) at least two of the following symptoms: muscle pain, dizziness, headaches, tension, sleep disorders, inability to relax or irritability;
- b) the patient is unable to recover only through rest, relaxation or entertainment;
- c) the duration of the disorder is at least three months, and criteria for any another specific disorder do not apply.

Burnout syndrome is a state of emotional, mental and physical exhaustion, depersonalization and reduced personal accomplishment caused by workplace related chronic stress (excessive and lengthy) that has not been successfully managed.

Emotional exhaustion occurs due to emotional demands placed on the individual, when there is an inadequacy of emotional feelings to current situation, being manifested by indifference, apathy, decreased emotional tonus.

Depersonalization refers to impaired relationships with others, manifested by cynicism, impatience, negative and critical attitudes or contrary by dependence of others.

Reduced personal achievements relate to loss of confidence in one's own effectiveness, in one's ability to carry out work tasks and to limitation of one's possibilities.

In addition to excessive stress, burnout etiology comprises a complex interaction of social and individual, biochemical and biological factors, <sup>[2]</sup> shown in Table 1.

**Table 1**  
*Burnout Etiology*

Social factors	System of social support, lack of time, assuming too many responsibilities (family, leisure activities etc.), role conflict and role ambiguity
Personal factors	Low tolerance to stress, lack of personal resources, ineffective coping strategies, personality structure, low self esteem, unrealistic expectations, negative experiences, lifestyle etc.
Biochemical and biological factors	Hormonal changes, particularly increasing cortisol levels and imbalances in hypothalamic –pituitary -adrenal control system
Factors related to work environment	Lack of control, stressful work environment, very demanding tasks, high responsibility, unrealistic expectations, monotonous activities, chaotic environment, job uncertainty, increased labor complexity etc.

The way that burnout installs is a stage process and despite the fact that different authors identify different stages, main aspects of the process can be illustrated in Fig. 1 (Korunka *et al.*, 2011).

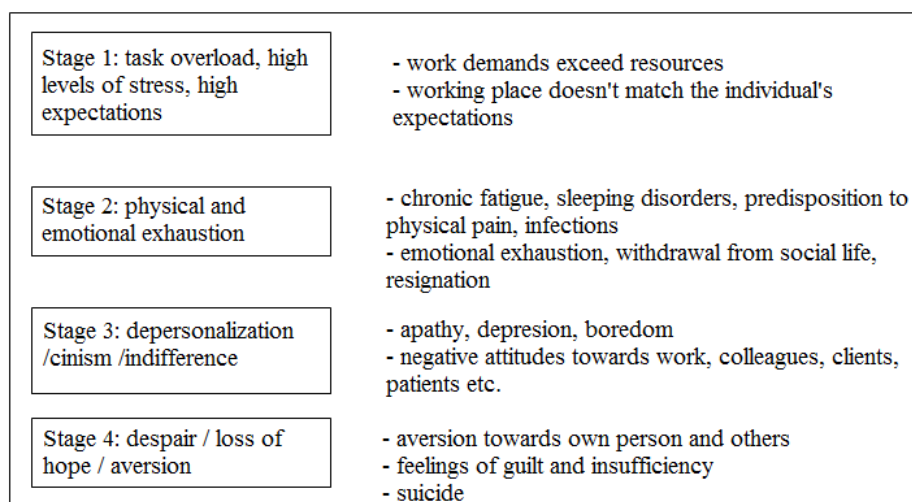


Fig. 1 – Burnout stages.

Although the trigger point for burnout is excessive and prolonged stress, burnout should not be confused with stress. Employees may experience situations where they have to work many overtime hours, where the workload is overloaded without developing burnout.

Significant differences between stress and burnout are summarized in Table 2.

**Table 2**  
*Differences Between Stress and Burnout Syndrome*

Stress	Burnout syndrome
<ul style="list-style-type: none"> <li>-Most symptoms are physical</li> <li>-Produces pressure, urgency and hyperactivity</li> <li>-Loss of energy</li> <li>-Over involvement in activity</li> <li>-Leads to anxiety disorders</li> <li>-Hyperactivity</li> <li>-May lead to premature death</li> </ul>	<ul style="list-style-type: none"> <li>-Most symptoms are emotional</li> <li>-Produces helplessness and despair</li> <li>-Loss of motivation/ideals/hope</li> <li>-Under involvement in activity</li> <li>-Withdrawal from social life</li> <li>-Depression and detachment</li> <li>-Leads to suicidal thoughts</li> </ul>

### 3. Emotional Intelligence and Burnout

The growing importance that organizations and professionals in the field of psychology attach to emotional experiences in the context of work activities is justified by the wide range of behavioral manifestations which are influenced in a direct or indirect manner by experimentation of different emotional experiences by employees.

Interest of researchers and general public regarding emotional intelligence has led to countless studies and research that investigates how the degree of development of emotional intelligence various components (emotional self-control, social awareness, self-knowledge, interpersonal relationship management) influence the life and professional activity of the individual.

There are numerous definitions of emotional intelligence (EI), proposed by various psychology researchers and specialists. According to Mayer and Salovey (1997), who took into account both emotion and cognition in defining emotional intelligence, this doesn't represent a singular skill, but rather a complex of emotional and rational abilities. Thus IE involves:

- The ability to correctly perceive, assess and express emotions;
- The ability to access and/or generate feelings when they facilitate thought;
- The ability to understand emotions and emotional knowledge;
- The ability to regulate emotions in order to promote emotional and intellectual growth.



Numerous studies reveal that emotional intelligence is a good predictor of group performance, individual performance, relationships, and that it is related to stress management, burnout syndrome and job satisfaction.

Employee's emotional intelligence was positively correlated with behavior at work, team behavior and negatively correlated with occupational stress (Chaudhry & Usman, 2011). Employees who possess well-developed emotional intelligence will better handle stress in the work environment, in that they more easily identify, understand and more successfully adjust negative emotions (such as frustration, stress etc.) (Gangai & Agrawal, 2013).

Developing certain components of emotional intelligence, such as social consciousness (especially empathy) and emotional self regulation helps employees to better manage emotions, which directly leads to lower stress levels and indirectly leads to protection of their physical and mental health. Thus, enriching employees' personal resources, respectively developing their emotional intelligence, might be a way to reduce stress level at work (Oginska-Bulik, 2005). Similar results were reported by Shahu and Gole who found that individuals with high personal resources (related to emotional intelligence) will perceive the workplace as less stressful and will experience fewer adverse health effects (Shahu & Gole, 2008). Emotional intelligence, as a personal resource of the individual, also facilitates self efficacy perception and self assessment in work.

Importance of "self-regulation" component of emotional intelligence has also been highlighted in the study by Mikolajczak *et al.* (2006), as they obtained data indicating that the predictive power of emotional intelligence in terms of occupational stress is due mostly to the mentioned component. Thus, self-regulation explains most of the variation of physical and psychological symptoms of stress, regardless of the individual's general health. Individuals who perceive themselves as being able to cope with stressful situations will report fewer mental and physical symptoms in such situations (Mikolajczak *et al.*, 2006).

Vice versa is also available, so that low levels of emotional intelligence, particularly the component of emotional self regulation, were associated with higher levels of perceived stress, by participants in a study carried out by Pau and Croucher (2003). The authors propose that, in order to better adapt to professional requirements, individuals develop coping mechanisms and skills associated with emotional intelligence (Pau & Croucher, 2003).

Many other studies highlight the important role that emotional intelligence plays in the prevention of occupational stress. A well developed emotional intelligence was correlated with lower levels of burnout syndrome and somatic symptoms for teachers in primary and university professors (Vaezi & Fallah, 2011; Adilogullari *et al.*, 2014), nurses (Guleryuz *et al.*, 2008), mental health professionals (Duran *et al.*, 2004), lawyers (Platsidou & Salman, 1997),

services workers (Oginska- Bulik, 2005), students in dentistry (Pau & Croucher, 2003) etc.

#### 4. Conclusion

Long-term involvement in stressful work situation can lead to installation of burnout syndrome, respectively a state of physical, emotional and mental exhaustion.

The influence that emotional intelligence has on general human behavior and, in particular, on behavior at work is demonstrated by numerous studies and research. The fact that emotional experiences influence employees' levels of job satisfaction, perceived stress and thus their physical and mental health brings emphasis on the importance of personal emotion management and development of personal competences for emotional management. These elements are components of emotional intelligence, whose role in moderating the effects of occupational stress and burnout syndrome installation is demonstrated by research of an increasing number of specialists.

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## SINDROMUL BURNOUT ȘI INTELIGENȚA EMOTIIONALĂ

(Rezumat)

În Europa, stresul asociat cu munca este a doua problemă ca frecvență a raportării, printre problemele de sănătate asociate cu munca. Implicarea pe termen lung în situații profesionale stresante poate conduce la instalarea sindromului burnout, respectiv la o stare de epuizare fizică, emoțională și mentală.

Expertii din domeniul sănătății apreciază că, la nivel mondial, sunt milioane de oameni care suferă de burnout, considerându-se că acesta este un fenomen al societății moderne. Conform estimărilor, manifestările sindromului burnout se regăsesc la peste jumătate din populația activă a planetei.

Gestionarea eficientă a stresului la locul de muncă poate fi împiedicată de insuficienta dezvoltare a unei persoane din punct de vedere al inteligenței emoționale, respectiv din punct de vedere al auto-cunoașterii, auto-reglării, auto-motivării, conștiinței și abilităților sociale.

Prezenta lucrare urmărește să prezinte cadrul teoretic și o serie de rezultate ale unor cercetări științifice care evidențiază legătura dintre emoție, inteligența emoțională și prevenirea sau ameliorarea simptomelor și stărilor negative asociate sindromului burnout.



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## THE ELEMENTS OF EXPLOSION RISK ASSESSMENT AT WORKPLACES WITH SUBSTANCES THAT MAY GENERATE EXPLOSIVE ATMOSPHERES

BY

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**Abstract:** The main goal of a risk assessment is to set out the precautions required in order to mitigate risk to an acceptable level.

If flammable materials that could generate explosive atmospheres are involved it will not be dealing with zero risk but with an acceptable level of risk, as provided by norms. This is the reason why one can say that, through abiding by the norms, the presumption of providing an acceptable risk level is ensured. This level evolves in time in the sense of a lower risk along with the technical and scientific development.

The explosion safety risk is determined both by technical measures adopted (the type of installations/equipment employed in potentially explosive atmosphere) and by organizational decisions adopted in order to ensure proper assembling, repairing, maintenance and inspection (drawing up work instructions, personnel training/competency, the Work Permit system, organizing inspections, maintenances and verifications of installations, marking of Ex dangerous areas). Setting out responsibilities has a particular importance for the purpose of ensuring safety against explosions.

There is no recognized method of assessing the explosion risk but regardless of the applied method, the likelihood of an explosive atmosphere occurrence has to be determined, together with the occurrence of an efficient ignition source and the magnitude of foreseeable consequences.

**Keywords:** risk assessment; explosions; equipment/installation; training/competency-responsibilities.

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## 1. Introduction

### Terms and definitions

The **explosion hazard** is related to the materials and substances processed, used or released by equipment, protective systems, and components and materials used to construct equipment, protective systems, and components.

**Ignition risk:** related to equipment / installation that may generate ignition sources. SR EN 15198 defines the *ignition risk*: probability of occurrence of an ignition source that is capable of igniting an explosive atmosphere

**Explosion risk:** probability of occurrence of an explosive atmosphere simultaneously with occurrence of an efficient potential ignition source and the effects induced by it.

## 2. Risk Assessment

Objective / aim: Risk level assessment aiming to set out the protective measures imposed in order to lower the risk at acceptable levels.

If flammable materials that could generate explosive atmospheres are involved, it will not be dealing with zero risk but with an acceptable level of risk, as provided by norms. This is the reason why one can say that, through abiding by the norms, the presumptions of providing an acceptable risk level is ensured. This level evolves in time in the sense of a lower risk along with the technical and scientific development.

The level of explosion safety is determined both by technical measures adopted and the organizational measures.

The risk assessment shall be performed for each specific situation and it will comprise:

- a) identify the explosion hazards and determination of likelihood of occurrence of dangerous explosive atmospheres;
- b) identify the ignition risks and determination of likelihood of occurrence of potential ignition sources;
- c) determine the possible effects of an explosion;
- d) evaluate the risk and if the intended level of protection had been achieved;  
NOTE - The intended level of protection is defined by at least legal requirements and, if necessary, additional requirements specified by the user
- e) consider measures for the minimization of risks.

As provided in the European Directive 1999/92/EC transposed in the Government Decision no. 1058/2005, the employers (users of installations) have responsibility for the following:

- Classification of dangerous areas in Zones;

- Adequate selection of equipment;
- Explosion protection document drawing up;
- Global explosion risk assessment at workplace.

Assuring an adequate assembling, repairing, maintenance and inspections falls into user's responsibility/task. The user shall adopt organizational measures for drawing up work instructions, personnel training, applying the work permit system, organizational the inspections, maintenance and verification of installation, as well as for making of Ex dangerous areas. The user is responsible for competency of personnel employed for assembling, inspection and maintenance works or repair works, regardless if they are part of the company personnel or external personnel. The proofs of specific training, competency and responsibility of the personnel are of a special importance.

Assessment of explosion risks initially focuses on:

- the likelihood that an explosive atmosphere will occur and subsequently on
- the likelihood that sources of ignition will be present and become effective.

Consideration of the effects is of secondary importance in the assessment process, since explosions can always be expected to do a great deal of harm, ranging from major material damage to injury and death. Quantitative approaches to risk in explosion protection are secondary to the avoidance of hazardous explosive atmospheres. The assessment procedure must be carried out for every work or production process and for every operational status and change of status of a plant.

### **3. Hazard Identification**

All possible hazards that may occur shall be identified. The aim is to determine if a potential ignition source may be present and to identify if an explosive atmosphere is present. The assessment begins usually by analyzing the equipment during normal operation, then is extended to take into consideration the foreseeable and rare malfunctions, in order to establish the level of explosion safety. An assessment of the likelihood of occurrence of an ignition source and its efficiency in igniting the explosive atmosphere; this requires detailed information on the flammability and explosion characteristics of the explosive atmosphere.

Practically, first the areas where the explosive atmosphere may occur shall be defined, as well as the likelihood of its occurrence by applying a "Zoning" method; then the possible ignition sources shall be identified, taking into account normal operation conditions and the foreseeable and rare malfunctions. The standard EN 1127-1 presents thirteen types of ignition sources as shown in the Table 1.

**Table 1**

<b>Ignition sources</b>		
<b>Possible</b>	<b>Relevant (Yes/No)</b>	<b>Significant (reason)</b>
Hot surfaces		
Flames and hot gases (including hot particles)		
Mechanically generated sparks		
Electrical apparatus		
Stray electric currents, cathodic corrosion protection		
Static electricity: Spark discharges; Corona discharges; Brush discharges; Propagating brush discharges; Cone discharges		
Lightning		
Electromagnetic fields in the frequency range from $10^4$ Hz to $3 \times 10^{12}$ Hz		
Electromagnetic radiation, frequency range from $3 \times 10^{11}$ Hz to $3 \times 10^{15}$ Hz		
Ionizing radiation		
Ultrasonics		
Adiabatic compression and shock waves, gas flows		
Chemical reactions - Exothermic reactions, including self-ignition of dusts		
Ex Classification: Zone 1 and Zone 2		
The equivalent level of protection corresponds to the zone where the potential ignition source is identified.		

In regard of equipment, protective systems and components in installation under the ATEX Directive's scope, the problem is sort of solved already, since these, before being placed on the market, had already been assessed by the manufacturer and are guaranteed for certain fields of use (the intended use), and the users have only to classify their dangerous areas and then adequately choose the equipment, according to the Table 2.

**Table 2**

<b>ZONE</b>	<b>Presence of an explosive atmosphere</b>	<b>Ignition sources avoidance</b>	<b>Level of protection required</b>	<b>Group II category</b>
<b>2</b>	Infrequent or only on a short period of time	during normal operation	NORMAL	3
<b>1</b>	Likely to occur	also during foreseeable malfunctions (one defect)	HIGH	2
<b>0</b>	Continuously, for long periods of time or frequently	also during foreseeable malfunctions (two independent defects)	VERY HIGH	1
<b>USERS</b> European Directive 1999/92/EC		<b>MANUFACTURERS</b> European Directive 94/9/EC		



Following, the installation as a whole shall be assessed in regard to possible ignition sources.

The extent of protective measures depends on the likelihood that hazardous *explosive atmospheres* will arise (zoning) and should therefore be determined in accordance with Table 3 for all types of *ignition sources*.

**Table 3**

Zoning	Ignition sources to be reliably avoided
0 or 20	<ul style="list-style-type: none"> <li>• in normal operation (no malfunction)</li> <li>• in foreseeable cases of malfunction and</li> <li>• in the event of rare malfunctions</li> </ul>
1 or 21	<ul style="list-style-type: none"> <li>• in normal operation (no malfunction)</li> <li>• in foreseeable cases of malfunction and</li> </ul>
2 or 22	<ul style="list-style-type: none"> <li>• in normal operation (no malfunction)</li> </ul>

If, for example, the ignition risk by electrostatic discharges is addressed, an assessment of hazard of explosion shall take into account the likelihood of electric charges building up and discharging, both on equipment and on products (Fig. 1).

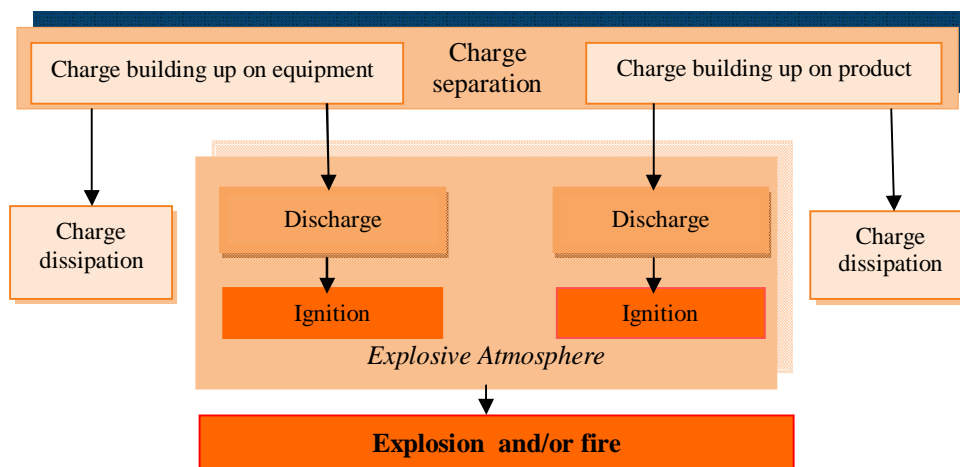
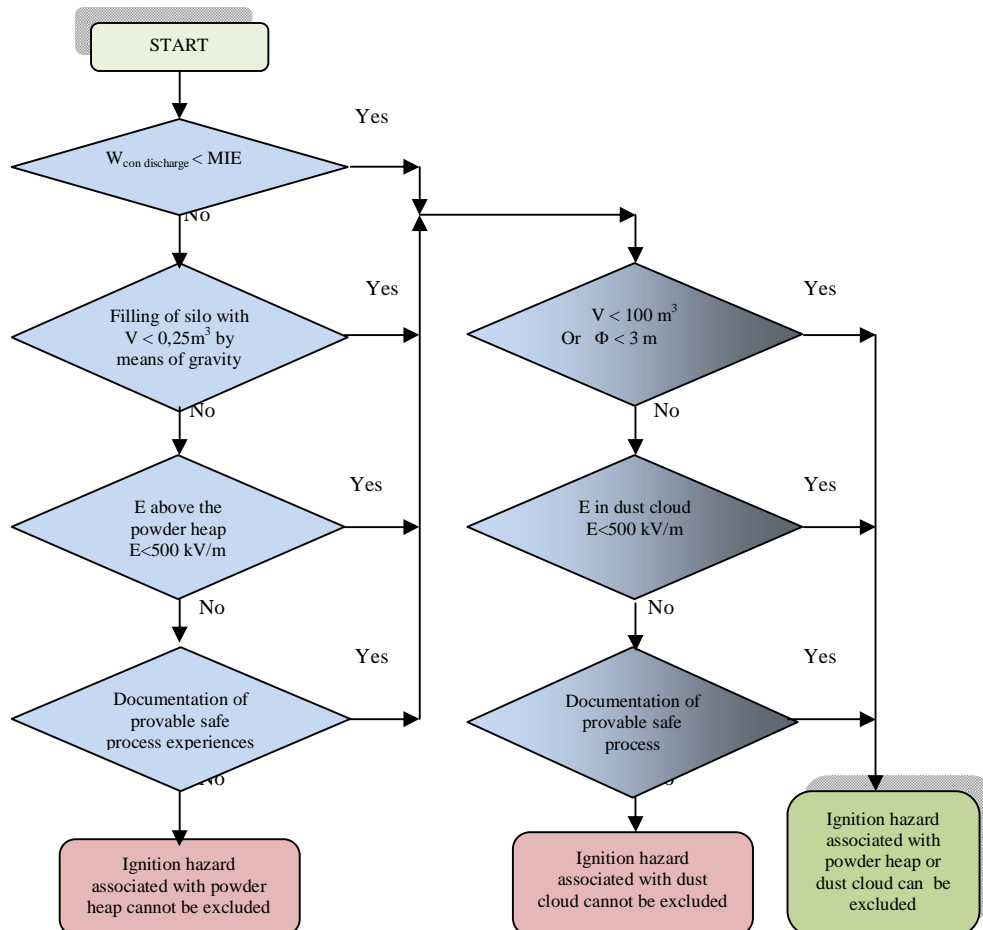


Fig. 1

If for example there is a combustible dust with a resistivity  $\rho > 10 \text{ G}\Omega\text{m}$ , then the assessment shall comprise following steps.

If the ignition hazard is excluded based on the decision step “Documentation of provable safe process experiences”, the explosion hazards should have been analysed in detail and the relevant justification should be explained in explosion protection document.



In many cases, it is not possible to avoid explosive atmospheres and sources of ignition with a sufficient degree of certainty. Measures must then be taken to limit the effects of an *explosion* to an acceptable extent. Such measures are

- explosion-resistant design;
- explosion relief;
- explosion suppression;
- prevention of flame and explosion propagation.

The explosion protection measures so far described can be kept operational, monitored or triggered by safety, controlling and regulating devices (hereafter referred to as process control engineering – PCE). Generally, PCE devices can be used to prevent the occurrence of *hazardous explosive atmospheres*, *ignition sources* or to mitigate the harmful effects of an explosion.

The degree of reliability required of PCE devices depends on the assessment of the explosion risks. Reliability of the safety function of PCE devices and their components is achieved by fault avoidance and fault control (having regard to all operating conditions and the planned servicing and/or maintenance arrangements).

#### **4. Competency of Personnel Involved in Explosion Risk Assessment**

Explosion risk assessment shall be performed by competent persons. These persons shall have specific knowledge regarding:

- explosion protection and prevention
  - general understanding of relevant electrical engineering and ability to read and assess engineering drawings
  - understanding of the general principles of explosion protection , of the general principles of types of protection and marking
  - understanding of those aspects of equipment design which affect the protection concept;
  - working knowledge and understanding of relevant standards in explosion protection, particularly SR EN 60079-10, SR EN 60079-17, SR EN 60079-14 , SR EN 60079-19
  - understanding of the additional importance of Permit to Work systems and safe isolation in relation to Explosion Protection;
  - understanding of certification and its relevant parts concerning selection of the equipment, protective systems and safety control devices.
- risk assessment methods
- basic knowledge of quality assurance, including the principles of auditing, documentation traceability of measurement and instrument calibration

#### **3. Conclusion**

Starting from the classic definition of risk, as a combination between injury severity and the likelihood a hazard would induce an injury, it results that risk assessment presume determination of the likelihood of occurrence of an explosion and its severity, respectively assessing explosion effects.

However, as presented in the paperwork, consideration of the effects is of secondary importance in the assessment process, since explosions can always be expected to do a great deal of harm, ranging from major material damage to injury and death.

Assessment of explosion risks initially focuses on:

- the likelihood that an explosive atmosphere will occur and subsequently on
- the likelihood that sources of ignition will be present and become effective.

The explosion risk assessment methods have to start by classifying the Ex dangerous areas, then verifying the appropriate selection of equipment and protective systems, followed by an analysis of the installation as a whole, from the possible ignition sources standpoint. Risk/safety level assessment shall relate to the safety requirements provided in the norms and standards in the field, whilst the presumption of ensuring a low risk level, acceptable through conforming to the norms, exists.

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- \* \* \* *Methodology for the Risk Assessment of Non-Electrical Equipment and Components for Intended Use in Potentially Explosive Atmospheres.* SR EN 15198: 2008.
- \* \* \* *Explosive Atmospheres. Part 32-1: Electrostatic Hazards, Guidance.* IEC 60079-32-1.
- \* \* \* *Methodology for the Risk Assessment of Unit Operations and Equipment for Use in Potentially Explosive Atmospheres.* EU Project No: SMT4-CT97-2169
- \* \* \* HOTARÂRE nr. 1058 din 9 august 2006 sets out the minimum requirements for improving the health and safety protection of workers potentially at risk from explosive atmospheres (Directiva 1999/92/CE)
- \* \* \* Non-binding guide to good practice for implementing Directive 1999/92/EC "ATEX" (explosive atmospheres).

## ELEMENTELE EVALUĂRII RISCULUI DE EXPLOZII LA LOCURILE DE MUNCĂ UNDE EXISTĂ SUBSTANȚE CARE POT GENERA O ATMOSFERĂ EXPLOZIVĂ

(Rezumat)

Scopul principal al evaluării nivelului de risc este stabilirea măsurilor de protecție ce se impun pentru reducerea riscului la nivele acceptabile.

Atunci când sunt implicate materiale inflamabile care pot genera o atmosferă explozivă nu se poate vorbi de risc zero ci despre un nivel de risc acceptabil care este stabilit prin norme. De aceea se poate spune că prin respectarea normelor există prezumția asigurării unui nivel de risc acceptabil. Acest nivel evoluează în timp în sensul scăderii riscului odată cu dezvoltarea tehnico-științifică.

Nivelul de securitate la explozie este determinat atât de măsurile tehnice luate (de tipul instalațiilor/echipamentelor folosite în atmosfere potențial explozive inclusiv ale echipamentelor mobile/portabile, de tipul echipamentelor individuale de protecție) cât și de măsurile organizatorice luate pentru asigurarea montării corecte, a reparațiilor, mentenanței și inspecțiilor adecvate (elaborare instrucțiuni de lucru, instruirea /competența personalului, sistemul de permis de lucru, organizarea inspecției,

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întreținerii și verificării instalațiilor, marcarea ariilor periculoase Ex). Stabilirea responsabilităților este deosebit de importantă pentru asigurarea securității antiexplozive.

Nu există o metodă recunoscută pentru evaluarea riscului de explozii, însă orice metodă s-ar aplica trebuie să se determine probabilitatea apariției atmosferei explozive concomitent cu apariția unei surse de aprindere eficiente și magnitudinea consecințelor previzibile.



## ROLE OF THE DIRECT LEADER OF THE WORKPLACE IN THE STRESS MANAGEMENT WORK

BY

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**Abstract:** In this paper the authors identify the role of leader of the workplace in the stress management in a company given its place in the functional structure of the company, namely, its double status, both as leader of the workplace and subordinate – at the same time.

**Keywords:** management; stress; prevention.

### 1. Introduction

Any analysis of a problem starts from its definition. Therefore, what is stress? Stress at the workplace is defined as the process in which environmental requirements compromise or exceed the capacity of adjustment of an organism, causing biological and psychological changes that can classify the person in question (the worker) among those with risk of illness or accident.

Lately stress manifests itself as a phenomenon, which seems to have, following the analyses made, serious consequences for workers and for to entities such as: family, enterprise, national economy and society in general.

Another aspect that must be mentioned is that stress appears as an emerging risk, because the traditional risks associated/related to safety, hygiene and traditional ergonomics are declining owing to the adoption and compliance with more stringent security requirements, to the implementation of technical progress and of better work methods. The new workplaces require less and less physical skills and more cognitive skills (processing a large amount of

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increasingly complex information, necessity of decision-making, assuming some uncertainties etc.), organizational skills (time management, resources management, etc.) and relational skills (teamwork, more responsibilities, work with the clients, etc.) which are potential sources of stress.

Stress factors may be related to workload and/or workers' features.

European Framework Directive (D89/391) on Safety and Health at Work assigns the responsibility for conducting the preventive action (including in the field combating stress) to the employer, represented by the superior manager. Therefore, the responsibility for conducting the actions and obligations of an enterprise company lies with the person who has the most decision-making power – the superior manager, however, in the decision-making in respect of health and safety at work the direct leader of the workplace **must** also be involved, namely the person right near the base of the hierarchical pyramid where the employee-performer is situated.

Therefore, which is direct role of the leader of the workplace in relation to the problem addressed, respectively, reducing stress?

## 2. Business Management

The management of an enterprise means the process of achieving efficiently and effectively, through planning, organization, coordination and control, certain things through and with other persons, in order to achieve the objectives of the enterprise.

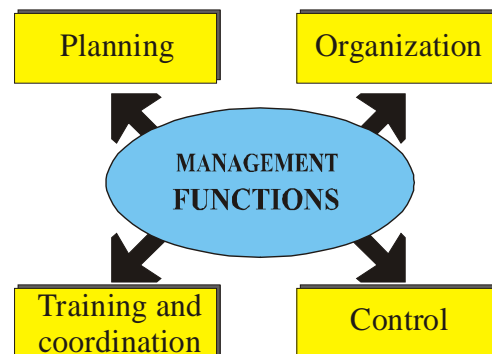


Fig. 1 – Management functions.

The managers, as people entrusted with authority and with decision-making responsibilities regarding the efficient use of the key resources of the organization (persons, machinery and equipment, materials, money, time), exercise powers of planning, organization, coordination-training and control, being placed on different levels the hierarchical pyramid.



Taking into account the general features of their responsibilities, the managers can be divided into three categories:

- superior managers (top-manager, senior manager, chairman, manager, director general, director);
- middle managers (assistant director, chief engineer, production line manager, factory manager, head of department, workshop foreman);
- first line managers (foreman, division manager, team leader).

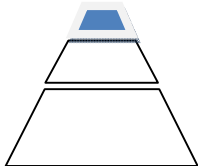
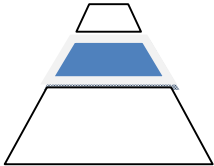
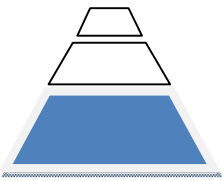
Categories of managers	Funcții și abilități esențiale
<p>Superior managers</p> 	<p>I. Functions: Director general, manager II. Essential skills: Conceptual, strategic orientation of the enterprise. Ability to solve problems from the viewpoint of the entire enterprise, designed as a system.</p>
<p>Middle managers</p> 	<p>I. Functions: Manager, chief engineer, factory manager, head of department II. Essential skills: Ability to develop human relations. Ability to ensure the efficiency of activities, to coordinate and develop harmonious inter-personal relationships.</p>
<p>First line managers</p> 	<p>I. Functions: foreman, division manager, team leader II. Essential skills: Professional knowledge. Ability to use tools and methods, to apply in a coherent manner the specific knowledge and to conduct work processes.</p>

Fig. 2 – Categories of managers and their functions.

An approach to the human factor within the hierarchy of a company may be carried out based on the pattern of middle manager and of the first line manager, which we will be referred to as the “direct leader of the workplace”, a character present in most small and medium-sized enterprises.

The main argument is his double status to the subordination relationship, as chief of the workplace and as subordinate - at the same time. He

is the pin of a network of connections designed to provide to the management system, in addition to stability and performance, the safety and health of workers as well.

The direct leader of the workplace is the one that conveys a great deal of the "pressure" of the workplace (performance indicators, job duties, work content, employment relations, terms of the employment contract etc.) from the top manager towards the employees, but he is also the "channel" through which the problems and concerns of the workers can be sent to the superior manager. Likewise, at his level there may be solved some of the problems concerning the work environment and inter-personal relationships, these being some of the most relevant risk factors in terms of work-related stress.

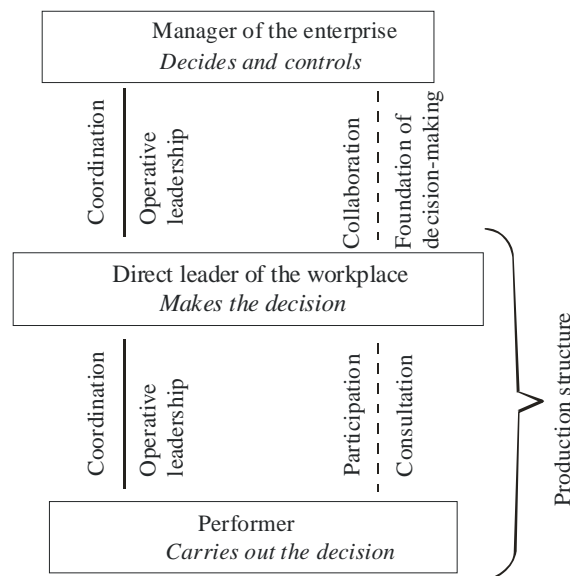


Fig. 3 – Functions of the elements of the organizational structure of the enterprise and the relationship between them.

### 3. Concrete Actions of the Leader of the Workplace in Order to Reduce Stress

Given the position occupied by the direct leader of the workplace into the organizational structure of a company, in order to reduce stress, he could act as follows:

- to be aware that stress is a risk factor that can have negative effects on him, on the workers subordinated to him, the enterprise where he works and so on
- to know and to implement the moral standards of the company (if elaborated).

- to participate in all activities organized on stress (courses, trainings, etc.) and self-training on the subject.
- to transfer, as far as possible, the knowledge (corporate culture, prevention measures etc.) to the workers in his subordination.
- to provide training of workers (especially of the unskilled ones, if applicable) on stress in order to better meet the requirements of the workplace.
- to provide for the medical surveillance of workers.
- to establish for workers precise duties and roles in order to avoid conflicting situations.
- if requested, to bring his contribution to the establishing of a code of conduct specifying what behaviours are rejected within the company and which are the penalties for this sort of misbehaviour.
- to contribute to the achievement of an adequate communication between the manager and workers.
- to analyse and define clearly the subordinated positions.
- not to make often and major changes in the work instructions and procedures, if it is decision to make.
- not to request from the employees to work overtime and/or not to impose a working pace too intense.
- to comply with work breaks and weekly rest.
- to rotate the employees who are performing routine tasks.
- to avoid criticism when the subordinates are mistaken/fail
- to appreciate the employees who are goods workers.
- to carefully consider the subordinate workplaces in terms of stress (the analysis can be made during the risk assessment, compliance with legal requirements, methods and best practices).
- to be aware that he must have skills to identify and manage, resolve conflicts constructively.
- to collaborate with the administrator, with the labour medicine physician, with the designated work/prevention services and, if available, with the company's psychology therapist for stress-related matters.
- to organize the work of the subordinates as good as possible with a right level of tasks that do not turn into overload, or into the use of some workers below their potential (under-loads), in order to remove ambiguities. This can be achieved upon the elaboration of the job descriptions.
- to contribute to the establishment of proper interpersonal relationships and their integration within groups of workers.
- to define and ensure the maintenance of the work environment.
- to encourage the workers to express their proposals for improving the work environment.
- as far as this depends on him, to ensure correct payment of work and performance, for example, through proper record-keeping of working hours.

- to propose instruction plans, training sessions, guidelines which include, depending on the risks identified, measures to reduce bullying, discrimination, violence etc.
- to use the delegation of tasks which involves: clear stating of job duties, deadlines for assessment of their achievement, control over their activities and, if the their activity allows it, to provide freedom of discretion in carrying out the job duties.
- to carefully observe the events occurring at work and to detect the first symptoms of stress at work.
- to notify upper management in case of absenteeism but also in case of "presenteism" phenomena, if any - manifested by the attendance of some workers at the workplace despite despite a poor health condition.
- to ensure and to develop social support among workers at their workplace.
- in collaboration with the specialized services to implement and develop relaxation techniques at work.
- to listen to the employee who complains about the stress at work, to identify the source of stress and try to assist him, including to communicate these concerns to the senior management of the company.
- ensure communication at the workplace by creating a climate favourable to cooperation, cohesion and communication.
- to ensure proper repair and maintenance of work equipment.
- to provide instruction for workers in the introduction of new work equipment and/or technologies.
- to solve the problems on the spot or as soon as possible.
- to have a proper behaviour at work, also by keeping his word. In practice his actions influence more the workers than his words.
- to assure the employee on the confidentiality of some information, where appropriate.

#### **4. Conclusions**

Pressure is generated in general from the level of the senior management but the phenomenon of accidents at work and occupational diseases occurs at the workplace, namely, at the level of the production structure itself, therefore, it logically follows that stress prevention should be carried out more effectively at this level.

However stress does not have a single cause and prevention can not be carried out by adopting a single solution, but, we think that one of the keys to ensuring safety at work is awareness of stress by the leader of the work place, followed by the his active management due to his involvement and also the involvement of employees for changing and/or reducing this risk factor.

We remain convinced that stress prevention must be individualized for each enterprise, by conducting a correct preventive management, that seeks balance between the working conditions and the human factor, in order to avoid any negative consequences both on the health of the employee as and on the enterprise.

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### ROLUL CONDUCĂTORULUI DIRECT AL LOCULUI DE MUNCĂ ÎN MANAGEMENTUL STRESULUI LA SERVICIU

(Rezumat)

În această lucrare autorii identifică rolul conducătorului locului de muncă în managementul stresului având în vedere locul său în structura funcțională a companiei și anume, dublul său statut de lider al locului de muncă și de subordonat în același timp.



## APTITUDE ET INAPTITUDE MEDICALE AU POSTE DE TRAVAIL, EN FRANCE

PAR

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**Résumé.** La question de l'aptitude ou de l'inaptitude médicale des salariés au poste de travail est **au carrefour de multiples préoccupations et enjeux**. Elle mobilise l'inspection du travail, la médecine du travail, les juges administratifs et judiciaires, les médecins traitants et ceux de l'assurance maladie et sollicite les organismes de prévention et les services d'appui au maintien dans l'emploi. Non définie par le code du travail, **l'aptitude médicale au poste de travail** s'appréhende, par la négative de la notion **d'inaptitude**. Seul **le médecin du travail** peut se prononcer sur l'aptitude médicale au poste de travail du salarié. La notion d'aptitude est également contextuelle et est à distinguer de l'« *insuffisance professionnelle* ».

**L'aptitude.** L'article R.4624-47 du code du travail prévoit la délivrance d'une fiche d'aptitude à l'issue des examens médicaux d'embauche, périodiques, de reprise, à la demande du salarié ou de l'employeur ou pour effectuer des travaux spécifiques.

**L'inaptitude** n'est acquise qu'au terme de deux visites médicales espacées de deux semaines. En cas de danger immédiat pour la santé ou la sécurité du salarié ou lorsqu'un examen de pré-reprise a eu lieu dans un délai de 30 jours au plus, elle peut être prononcée dès la première visite.

**L'inaptitude temporaire** peut être prononcée, pour une durée déterminée, par le médecin du travail.

**L'invalidité** se distingue de **l'inaptitude** et s'apprécie par rapport à la capacité de travail restante et à l'ensemble des possibilités d'emploi existant pour le salarié.

**L'aptitude médicale avec réserves.** Un certain nombre de restriction peuvent accompagner un avis médical d'aptitude ce qui ne constitue pas, pour

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autant, une déclaration d'inaptitude. Associée à des préconisations d'aménagement du poste, elle s'inscrit dans une logique de **réintégration** alors que l'inaptitude au poste renvoie à celle de **reclassement**.

**L'aptitude, même assortie de nombreuses réserves, n'équivaut pas à une inaptitude**, qui, seule, déclenche le processus obligatoire de recherche de reclassement sur d'autres postes.

**La visite médicale de pré-reprise** est **obligatoire** dès lors que l'arrêt de travail est d'une durée de **plus de 3 mois**. Le code du travail n'interdit toutefois pas son organisation pour les arrêts plus courts. **Sauf opposition du salarié**, le médecin du travail informe l'employeur et le médecin conseil de ses recommandations afin que toutes les mesures soient mises en œuvre en vue de favoriser le maintien dans l'emploi du salarié. La visite de pré-reprise ne dispense pas de la visite de reprise.

**La visite médicale de reprise**. Tout salarié bénéficie obligatoirement, après certaines absences, d'un examen médical de reprise. Cet examen médical a pour objet de délivrer un avis d'aptitude du salarié à reprendre son poste; de préconiser l'aménagement, l'adaptation du poste ou le reclassement du salarié. Cet examen met fin à la suspension du contrat du travail. L'organisation de cet examen relève de l'initiative et de la responsabilité de l'employeur.

En cas de **difficulté ou de désaccord sur l'avis du médecin du travail**, l'employeur et le salarié peuvent contester l'avis du médecin du travail devant l'inspecteur du travail. La contestation peut viser aussi bien l'avis d'aptitude ou d'inaptitude que les mesures individuelles proposées par le médecin, les recommandations destinées à orienter l'employeur dans sa recherche de poste de reclassement. **L'avis qui n'est pas contesté s'impose à tous**. Le recours doit être exercé dans les deux mois. La décision de l'inspecteur du travail se substitue à l'avis du médecin du travail qui se trouve alors privé de tout effet juridique. La décision de l'inspecteur du travail peut faire l'objet, dans les 2 mois, d'un recours gracieux (devant l'inspecteur lui-même), d'un recours hiérarchique devant le ministre ou/et d'un recours contentieux devant le tribunal administratif. Lorsque l'inspecteur du travail décide de ne pas reconnaître l'inaptitude ou que, sur recours contentieux, sa décision est annulée, si le licenciement est intervenu, le salarié a droit à une **indemnité** qui ne peut être inférieure aux salaires des 6 derniers mois ou à 12 mois si l'inaptitude est d'origine professionnelle. Si le salarié n'est pas encore licencié ou a été **reclassé** dans un autre emploi, il doit être réintégré dans ses précédentes fonctions. Les recours dans le cas particulier du licenciement d'un représentant du personnel reconnu inapte résulte de la combinaison des dispositions relatives à la contestation de l'avis du médecin du travail et celles relatives à la protection des représentants du personnel. En cas de difficultés, l'employeur saisit à nouveau le médecin du travail d'une demande d'avis.

**Mots clefs:** aptitude; inaptitude; licenciement; reclassement; visite médicale; médecin du travail.



## APTITUDEA ȘI INAPTITUDINEA MEDICALĂ LA POSTUL DE MUNCĂ, ÎN FRANȚA

(Rezumat)

Problema aptitudinii ori a inaptitudinii pentru un loc de muncă se află la răscrucea unor multiple preocupări și provocări. Ea mobilizează diverse instituții cum sunt inspecția muncii, medicina muncii, judecători administrativi și juridici, medici curanți și medici de la casa de asigurări, dar solicită și organisme de prevenție precum și servicii care se ocupă de menținerea salariaților în câmpul muncii. Nedefinită în codul muncii, aptitudinea medicală pentru un loc de muncă este abordată prin negarea noțiunii de inaptitudine. Doar medicul de medicina muncii se poate pronunța cu privire la aptitudinea medicală pentru postul de muncă ocupat de salariat. Noțiunea de aptitudine este de asemenea contextulă și este diferită de « insuficiența profesională ».



## L'OBLIGATION DE RECLASSEMENT DU SALARIE DECLARE INAPTE, EN FRANCE

PAR

CRISTINA CODREANU\* et ARMELLE ARSALONI

SMIS, SAUMUR Franța

Reçu le 19 novembre 2015

Acceptée pour publication le 14 décembre 2015

**Résumé.** Le licenciement pour inaptitude médicale n'est fondé que si l'employeur a effectué des **recherches de reclassement** actives, personnalisées et loyales, en collaboration avec le médecin du travail. Si le médecin du travail n'effectue aucune proposition de reclassement, l'employeur doit solliciter son avis. Cette recherche de reclassement doit être faite **dans l'ensemble des établissements de l'entreprise ou dans le groupe** auquel celle-ci appartient, y compris à l'étranger, parmi toutes les entreprises du groupe, même si ce nombre est très important. Le télétravail (travail à domicile) peut faire partie des solutions de reclassement et il doit l'être en priorité si le médecin le précise. Sont également visées, les entreprises avec lesquelles l'employeur entretient des relations de partenariat offrant des possibilités de permutation du personnel. Si l'entreprise est franchisée, la recherche est étendue à l'ensemble des entreprises sous la même enseigne commerciale. **Le reclassement d'un salarié inapte à son poste est prioritaire au recrutement externe.** L'employeur doit prioritairement rechercher un emploi disponible aussi comparable que possible à l'emploi précédent et si ce n'est pas possible, il peut proposer un poste temporairement vacant. L'employeur ne peut pas se séparer du salarié qui éprouve des difficultés dans son nouvel emploi en lui reprochant son « *insuffisance professionnelle* ». L'échec d'une tentative de reclassement ne dispense pas l'employeur de nouvelles recherches de réaffectation. Si l'employeur a connaissance que l'inaptitude de son salarié a, au moins partiellement, une origine professionnelle l'employeur consulte les DP (délégués du personnel).

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Il faut distinguer le « **délai de reclassement** » d'un mois, et la « **période de recherche de reclassement** », dont la durée n'est pas définie par la loi, ni précisée par la jurisprudence. **Il n'y a pas de délai maximal** mais n'est certainement pas infini. Le **licenciement pour faute grave** ne peut pas se déduire du seul refus de reclassement. Il appartient à l'employeur, soit de solliciter à nouveau l'avis du médecin du travail et, après réponse de celui-ci, de formuler de nouvelles propositions de reclassement soit de procéder à un licenciement **fondé sur l'inaptitude du salarié et l'impossibilité de reclassement**. Le caractère abusif du refus a pour conséquences de faire perdre au salarié l'indemnité compensatrice de préavis et l'indemnité spéciale de licenciement.

Les **travailleurs handicapés reconnus inaptes** doivent bénéficier d'un réentrainement au travail et une rééducation professionnelle avant tout licenciement, indépendamment de l'obligation de reclassement. Le **CRPE** (contrat de rééducation professionnelle en entreprise) contrat pour favoriser la réinsertion de travailleurs grâce à une formation pratique en entreprise peut être aussi mis en place à l'issue d'une reprise du travail à temps partiel dans un but thérapeutique avec différents acteurs intéressés: salarié, médecin du travail, employeur, organisme de protection sociale, conseiller Insertion Professionnelle de la Caisse Primaire d'Assurance Maladie.

**Inaptitude et harcèlement.** L'employeur ne peut pas se prévaloir d'une inaptitude médicale déclarée par le médecin du travail pour licencier un salarié, quand l'inaptitude médicale est la conséquence directe d'un harcèlement sexuel ou un harcèlement moral (par exemple brimades, dénigrement ayant gravement altéré la santé du salarié et à l'origine de nombreux arrêts de travail). Un tel licenciement est juridiquement nul. Le fait, pour l'employeur, de méconnaître les prescriptions médicales et de **persister à proposer un reclassement au salarié au lieu de le réintégrer dans son emploi peut, sous certaines conditions, constituer un harcèlement moral.**

**Cas particulier des représentants du personnel.** Aux termes de deux décisions rendus en novembre 2013, du Conseil d'Etat et de la Cour de cassation, l'indemnisation de la perte d'emploi pour les salariés protégés licenciés pour une inaptitude liée à un harcèlement moral, est dorénavant possible. La gravité de la situation au regard de la santé et de la sécurité du salarié, pouvait bien souvent conduire l'inspecteur du travail à autoriser le licenciement, pour faire cesser l'exposition au harcèlement. Il est désormais possible au juge judiciaire d'accorder à un salarié protégé licencié pour inaptitude dans un contexte de harcèlement moral, une indemnisation du préjudice lié au harcèlement et une indemnisation pour la perte d'emploi et ainsi réparer l'ensemble des préjudices. Le salarié protégé dont le licenciement a été autorisé par l'inspecteur du travail, peut faire valoir devant le conseil des prud'hommes, en cas de harcèlement moral, tous les droits qui découlent de la nullité de son licenciement, y compris une éventuelle réintégration.

**Mots clefs:** inaptitude ; reclassement; licenciement; harcèlement.

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## OBLIGAȚIA DE RECLASARE A SALARIATULUI DECLARAT INAPT, ÎN FRANȚA

(Rezumat)

**Licențierea pentru motiv de inaptitudine** medicală nu se poate realiza decât dacă angajatorul a efectuat **cercetări de reclasare** active, personalizate și loiale, în colaborare cu medicul de medicina muncii. Dacă medicul de medicina muncii nu face nici o propunere de reclasare, angajatorul trebuie să solicite avizul acestuia. Această cercetare de reclasare trebuie făcută în cadrul ansamblului de instituții din care face parte întreprinderea ori a grupului de întreprinderi căruia îi aparține, inclusiv cele din străinătate precum și în toate întreprinderile grupului chiar dacă numărul acestuia este foarte mare. Munca la distanță (precum munca la domiciliu) poate fi o soluție de reclasare și constituie o prioritate dacă medicul de medicina muncii precizează acest lucru. Sunt vizate și întreprinderile cu care angajatorul întreține relații de parteneriat oferind astfel posibilități de permutări de personal. Dacă întreprinderea este în franciză, căutarea se extinde la ansamblul de întreprinderi cu același îndrumator comercial. Reclasarea unui salariat inapt pentru postul pe care îl ocupă este prioritară față de o recrutare externă. Angajatorul trebuie să caute cu prioritate o muncă comparabilă cu munca precedentă și poate propune chiar un post vacant temporar. Angajatorul nu poate concedia un salariat care prezintă dificultăți în noua sa muncă reproșându-i « *insuficiența profesională* ». Eșecul unei tentative de reclasare nu scutește angajatorul de a căuta noi căi de realocare. Dacă angajatorul știe că inaptitudinea salariatului său are, cel puțin parțial, o origine profesională, el trebuie să consulte delegatul personalului.



## VIRTUAL MODELING AND FINITE ELEMENTS ANALYSIS OF THE ELBOW JOINT

BY

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**Abstract:** Virtual modeling of a biomechanical system has the advantage of the possibility of simulation of normal or critical situations regarding mechanical loading system elements and highlights the limits between normal and traumatic by the state of stress and strain that is produced in the components of that system. Using these forces allowed the determination of the state of stress and strain on the bones of the elbow joint, the forearm, using the finite element method. Mechanical stresses determined are compared with the allowable values, so that it can be measured at all times during the medical rehabilitation sessions, the mechanical strength of bone.

**Keywords:** elbow joint; FEM; simulation.

### 1. Introduction

Virtual modeling a biomechanical system has the advantage of possibility simulation of normal and critical situations regarding mechanical loading system elements and highlights the limits between normal and traumatic by the state of stress and strain that are produced in the components of that system.

Computed tomography of single-photon emission is able to highlight, in like the CT, the presence or absence of blood in the investigated structure on the basis of the measurement of gamma ray emission from the anatomical structure.

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Virtual modeling system anatomical humerus-the ulna - radius was made based on CT images in succession and involved the following general steps from two-dimensional images of the imaging planes creek section.

Tomography image processing is performed using Mimics software package and MedCad, this being the technical interface between medical imaging and CAD design system. Each tomography image is processed with Mimics module, so all anatomical images components consist of elementary triangles. In this way, the anatomical components begin to be differentiated between them, distinguishing specialized program each component as a single object, without discontinuities associated neighboring triangles. Data files are processed in DICOM format, which is read in successive groups of three images corresponding to the three anatomical planes (frontal, sagittal and transverse) for each section investigated. Segmentation of the image provides the ability to extract the contour of each component in the context of the image, by following two distinct phases, namely: detection and delineation contour - are identified all areas with sudden changes in the edges so that by uniting these areas, defined geometric contour of the object will be analyzed and detection of homogeneous regions - in this respect, those areas of the image are identified with uniform properties and taken to the portion of the image that will define the object of interest.

## 2. Forces for Rehabilitation

Rehabilitation elbow after an immobilization period involves carrying out controlled movement of the forearm exercises in order to restore elasticity to all soft tissues, joint capsule and associated forces regain normal muscle contraction to groups that provide forearm movement. The main movement of the forearm used in physical therapy, is the flexion-extension, high amplitude, so that the hypothesis was adopted of an immobilized arm and a forearm found in flexion angles, from horizontal position,  $0^\circ$ ,  $50^\circ$  and  $120^\circ$ . In Fig. 1 it is noted that on the forearm, in order to ensure movement, it was established that the force of the biceps muscles take action,  $F_m$ , and for an active rehabilitation it was considered a force of gravity,  $F_g$ , with values between 5 N, 50 N.

If it is assumed that the forearm acts only under these two forces applied, the equilibrium equation of the moment written to the elbow joint can be determined by computing the expression of muscle power; equilibrium equation and the ultimate expression are:

$$F_m L_{OD} - F_g L_{OB_0} = 0, \quad (1)$$

where:

$$F_m = \frac{F_g L_{OB_0}}{L_{OD}}. \quad (2)$$




$$\operatorname{tg} \beta = \frac{A_0 C}{A_0 A}, \quad (3)$$

where:  $A_O C = L_b - L_{OA_O}$ ,  $A_O A = L_A \cos \alpha_{ab}$ ,  $L_{OA_O} = L_A \sin \alpha_{ab}$ ,  $L_A$  – the distance between the geometric center of the elbow joint (O) and the point of entering the biceps muscle of the forearm.

Equation (3) can be rewritten as:

$$\operatorname{tg} \beta = \frac{L_b - L_A \sin \alpha_{ab}}{L_A \cos \alpha_{ab}}, \quad (4)$$

where it can calculate the angle of muscle strength, any time of forearm flexion. Based on geometric considerations relations can be written:

$$L_{OB_0} = L_{ab} \cos \alpha_{ab}, \quad (5)$$

$$L_{OD} = \frac{L_b L_A \cos \alpha_{ab}}{L_b - L_A \sin \alpha_{ab}} \sin \beta, \quad (6)$$

where:  $L_b$ ,  $L_{ab}$  is the length of the arm, respectively, of the forearm.

Using relations (5) and (6), muscle strength,  $F_m$ , in relation (2) is written as:

$$F_m = F_g \frac{L_{ab} \cos \alpha_{ab} (L_b - L_A \sin \alpha_{ab})}{L_b L_A \cos \alpha_{ab} \sin \beta}. \quad (7)$$

The graphical representation of the change in muscle strength,  $F_m$ , according to the gravity force used in medical rehabilitation,  $F_g$ , according to the eq. (7), several angles of flexion of the forearm ( $0^\circ$ ,  $50^\circ$ ,  $120^\circ$ ) and a patient height 1.71 m is shown in Fig. 3.

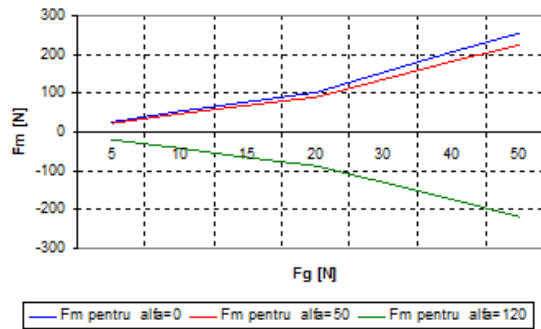


Fig. 3 – Changes in muscle strength.

Negative values of muscle force, which are shown in Fig. 5 indicate the direction of force, as opposed to the positive values, respectively.

Table 1 shows the values of angle data calculated by the relation (4) for a patient with a height of 1.71 m, where:

$$L_b = 0.188H = 0.321 \text{ m},$$

$$L_{ab} = 0.145H = 0.145 \times 1.71 = 0.247 \text{ m},$$

$$L_A = 0.2L_{ab} = 0.049 \text{ m}.$$

**Table 1**  
*The Angle of Muscle Strength*

$\alpha_{ab}$ , [°]	$\beta$ , [°]
0	81.32091
50	83.65969
120	-84.9737

### 3. Conclusions

Using these forces allowed the determination of the state of stress and strain on the bones of the elbow joint, the forearm, using the finite element method. Mechanical stresses determined are compared with the allowable values, so that the mechanical strength of bone can be measured at all times during the medical rehabilitation sessions.

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### MODELAREA VIRTUALĂ ȘI ANALIZA CU ELEMENTE FINITE A ARTICULAȚIEI COTULUI

(Rezumat)

Modelarea virtuală a unui sistem biomecanic are avantajul de posibilitatea de a simulare de situații normale sau critice în ceea ce privește elementele sistemului de încărcare mecanică și subliniază limitele între normal și traumatic de către stat de stres și tulpina, care este produsă în componentele acestui sistem. Folosind aceste forțe au permis determinarea stării de stres și tulpina pe oasele articulației cotului, antebratului, folosind metoda elementului finit. Solicitări mecanice determinate sunt comparate cu valorile admisibile, astfel încât să poată fi măsurat în orice moment în timpul sesiunilor de reabilitare medicală, rezistența mecanică a osului.

