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REVIEW CONCERNING THE CONDITIONING AND RECONDITIONING OF DRILLING SHIPS

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ABSTRACT

The drill bit consists of: heavy rods, drill rods, drive rod, reducers and fittings. After a certain number of operating hours for a subassembly, some parts, more difficult to request, have an advanced state of wear, which makes it impossible to continue functioning of the respective assembly. In the tubular bases, the rods brought from the yard are identified, sorted and pre-directed. If they are clogged, they are cleaned with very long drills. For a good cleaning, the rods are left for a time in a room containing a solution of detergents and caustic soda. Then the rods are washed on the outside and inside, with water jets and rotary plastic fiber brushes. Afterwards, they are dried with hot air. After correcting their rectilinearity, with hydraulic presses, the actual control begins. Measure the length, outer diameter, wall thickness and, using the methods below, detect any operating defects.

KEYWORDS: Drilling gasket, reconditioning, Reconditioning by welding

1. Introduction

The drill bit consists of: heavy rods, drill rods, drive rod, reducers and fittings. The heavy rods are at the bottom of the gaskets, the drilling poles at the middle of them have the longest length, and the drive rod at the top of the gasket.

Drilling rods are tubes of steel, aluminum, or light alloy (titanium). In order to increase the capacity of resistance to joints, their ends are thickened (reinforced). Cutting the thread in this case does not weaken the strength of the rod [1].

2. Reconditioning of used parts

After a certain number of operating hours for a subassembly, some parts, more difficult to request, have an advanced state of wear, which makes it impossible to continue functioning of the respective assembly.

There are also accidental malfunctions due to which the machines may be out of service. Some of these reasons could be: overloads, hits, incorrect mountings, defects of material, etc.

It can be observed that, after disassembly, the WEIGHT DEGREE is established (the analysis of the parts, measurements, comparisons, checks from where the nature and size of the wear results). This degree of wear is the factor that directly influences the cost of reconditioning, it helps us to assess correctly whether or not to resort to reconditioning [2].

3. Reconditioning of parts through machining on machine tools

This process is carried out in an organized framework, after the elaboration of an economic technological process, which is expressed by the technological processing documentation, where all the necessary technological operations are prescribed. The technological process is carried out following the technological sheet and the operations plan [3].

- TECHNICAL DATA SHEET - a standardized form in which we can read all the data of the technological process.

- OPERATION PLAN - establishes the sequence of operations and work phases (each operation on a tab).

The wear can be compensated by the execution and introduction of bushings, with tightening, or fixed by other procedures such as threading, small fixing welds, threaded pins, etc.

Analysing a little the technology of reconditioning the teeth of this wheel (not the whole

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wheel, with radial beats, wear on the hub, etc.) for success we need to do:

- Washing, thickening, measuring.
- Complete removal of the defective part, until the remaining material has no defect.
- Weaving the edges of the rupture, cracks, joints.
- Loading of the used surface by successive deposition of metal layers (electrode chosen according to the chemical composition of the piece material).
- Final mechanical processing, which ensures the dimensions required in the drawing and the quality of the surfaces.

When the parts have high wear (for example a rack) or have been reconditioned several times (for example by welding and then processing), they can be remedied by removing the worn area mechanically (by cutting or heat) and applying instead of an additional part. For example, some racks, from the design, are made of several pieces, being very long. They are worn unevenly, especially on certain portions, so the total replacement is not justified [4].

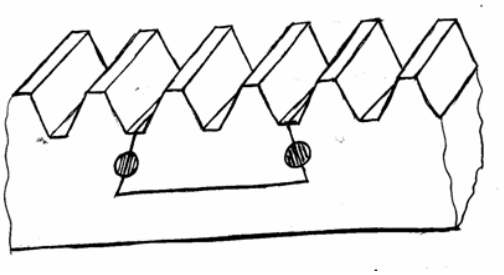

Fig. 1. *Reconditioning of a rack by removing an area and replacing it* [4]

4. Reconditioning by welding

Welding is one of the most used reconditioning procedures. In addition to the fact that we have many welding procedures available, a wide range of repairs can be provided:

- compensation of wear by metal deposits;
- reconditioning of cracks, cracks or breaks;
- combining broken pieces;
- joining component parts to a welded device or construction.

A repair using a specific welding process is indicated to meet the following conditions:

- the resistance of the piece in the welding area to approach that of the base material;
- the addition metal should be as close as chemical composition and mechanical properties to that of the part;
- the layer or the deposited cord will then allow processing by cutting to correct the shape and size [5].

BENEFITS:

- allows the reconditioning of parts that have a lot of workmanship;
- material economy;
- low cost;
- repairs are made that cannot be done by other procedures;
- the equipment used for welding is simple, cheap, with great possibility of diversification;
- welding is easily suitable for machining and automation.

DISADVANTAGES:

- the structure of the joint usually differs from that of the base material;
- remaining tensions that can cause deformations or even breakages in operation [6].

5. Reconditioning of parts by soldering

The method of reconditioning the pieces by soldering is applied in case of breaks, cracks, cracks or it is necessary to replace a part of the used part.

The process is used for joints of parts that are not subjected to high demands. There is a mutual diffusion on the surfaces of the base metal (the soldering parts) and the alloy for soldering, there is an exchange of atoms between the two materials resulting in a bonding alloy in the form of an intermediate layer [7].

It is necessary to prepare the parts before the soldering operation, in order for the jointing place to be well cleaned of fats, dirt, oxides, etc. The main operations that are performed before gluing are:

Mechanical cleaning - (wire brush, grinding, blasting, polishing, scraping, etc.).

Degreasing - (gasoline, petroleum, sodium hydroxide, sodium carbonate, sodium silicate).

Pickling - (sulfuric, hydrochloric or phosphoric acid solutions).

Depending on the melting temperature of the soldering alloys, it is possible to apply soft soldering (with alloys having a melting temperature below 500 ºC), and hard soldering (with alloys having melting

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temperatures above 500 ºC, such as AmSiLp and AmSnLp alloys) [8].

6. Control and conditioning of drilling rigs

In the tubular bases, the rods brought from the yard are identified, sorted and pre-directed. If they are clogged, they are cleaned with very long drills. For good cleaning, the rods are left for a time in a chamber containing a solution of detergents and caustic soda. Then the rods are washed on the outside and inside, with water jets and rotary brushes made of plastic fibers. Afterwards, they are dried with hot air [9].

After correcting the rectilinearity with hydraulic presses, the actual control begins. Measure the length, outer diameter, wall thickness and, using the methods below, detect any operating defects. The area where the pens are fixed is very important. Where the electromagnetic inspection signals an invisible defect through a voltage peak (the defect can be inside the wall), the area is thoroughly cleaned and magnetic particles are used: the method has a much higher resolution. Defects on the inner surface (corrosion attacks or erosion traces) can be located by an optical technique, with reflection mirrors [10].

Rods that are identified as having cracks are removed. Some superficial defects can be identified by simple grinding.

The controlled rods are classified in the classes corresponding to the size of the outer diameter, the thickness of the wall and the relative value of the various defects.

Sometimes rods are tested for traction and internal pressure [11].

7. Conclusions

Heavy rods, reductions and drive rods are generally controlled after one month of work. If one or three cracks are detected at the base of the spirals, the inspection interval is appropriate. If the number of cracks is large, checks should be performed more often.

Modern procedures also take into account the growth rate of fatigue cracks. The calculation shows that the working time of an element from the moment of detection of cracks until its rupture is relatively short.

According to the Romanian norms, the control periods are fixed in rotation hours and vary within the quite wide limits, depending on the importance of the controlled element, the wear class, the control place (probe, base), the complexity of the control and the total duration of use (the intervals decrease in time): 300-2500 h. Of course, a strict record of working time is required for each element in the gasket.

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INFLUENCE OF THERMOMECHANICAL PROCESSING PARAMETERS ON THE MECHANICAL PROPERTIES OF AN ALUMINUM ALLOY USED IN CUTTING-EDGE TECHNIQUE

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ABSTRACT

Special aluminum alloys are mainly used in the aeronautical and machine-building industries, areas of technique where materials must possess superior mechanical properties. These properties are obtained as a result of special methods of elaboration and subsequent processing. The special properties of these alloys are also influenced by the alloying elements present in their chemical composition. In this paper it is studied the way in which the parameters of the thermomechanical treatment process applied to an aluminum alloy influence the mechanical properties of the studied alloys. Thermomechanical processing consists of solution hardening, cold plastic deformation and artificial ageing at different temperatures and various times of maintenance at these temperatures.

KEYWORDS: aluminum alloy, thermomechanical processing, mechanical properties

1. Introduction

In this work it has been experimentally researched the influence of thermomechanical treatments on mechanical properties for an alloy belonging to the Al-Zn-Mg-Cu system. This aluminum alloy belongs to the category of special alloys. Special aluminum alloys (those used in cutting-edge technique) have a design technology with specific peculiarities presented in the field literature [1, 2], which are determined on the one hand by the variation of their physico-mechanical properties and on the other hand by some conditions that they must meet, either in moulded state or in a deformed plastic state.

The elaboration of aluminum alloys in induction electric ovens and vacuum atmosphere has a wide spread worldwide. Vacuum induction melting plants can work both in advanced vacuum conditions, 10^{-4}-10^{-5} Pa and in inert gas atmosphere [3]. Copper concentration in duralumin alloys does not generally exceed 5%. The increase in copper content leads to increased mechanical resistance, but continuously decreases the plasticity and corrosion resistance of the alloy. Plasticity decreases as a result of the fragility of the $CuAl_2$ compound.

Another element of hardening of aluminum alloys by the formation of the Al_2Mg_3 compound is the magnesium that also has the role to increase the corrosion resistance, and in the presence of the silicone forms the Mg_2Si compound. Magnesium concentration in deformable aluminum alloys is limited to 2.5% because over this value the plasticity of alloys decreases greatly. At higher concentrations 0.5...1.2% S, the mechanical properties of alloys do not increase significantly, but plasticity decreases greatly. Zinc is one of the main hardenable elements in special aluminum alloys, with high mechanical strength, by forming the Al_2Zn_3 compound that has a higher hardening effect than other compounds [4].

The fact that they benefit from good corrosion resistance and are easily processed by cutting, the Al-Zn alloys are increasingly used in foundries. Between Al and Zn the solid α solution has a very wide range and therefore, in the structure of industrial alloys do not appear separate phases, rich in zinc. At 382 °C, the solubility of zinc in aluminum is 84% and it decreases with temperature decrease, reaching the value of 2% at ambient temperature. In the limit of concentrations of 31.62...77.72%, a non-scibility domain appears between two solutions, α1 and α2, with different zinc content [5].

Zinc, due to its high solubility, influences in a considerable degree the improvement of mechanical properties. For this reason, the Al-Zn and Al-Zn-Si alloys are characterized by good casting properties, as

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well as appropriate mechanical properties, without the application of heat treatment.

Zinc is added as a basic element for increasing resistance of Al-Zn-Cu alloys, which were used among the first aluminum-based metallic materials, both for casting and for plastic deformation. In these alloys, copper is introduced for hardness, improved casting properties and corrosion resistance under load. The silicon introduced into these alloys increases fluidity and eases casting, but decreases plasticity. Iron, zirconium, nickel, chromium and manganese decrease sensitivity at high temperatures, but the last two elements improve corrosion resistance properties under load [4].

Magnesium increases resistance, but decreases plasticity; the properties of casting and processing by cutting and antifriction are improved by calcium, lead and tin. The structure of the alloys is of solid solution for small quantities of zinc and copper, or the AlCuZn compound is formed which diffuses to the border of the grain. When the copper content exceeds 2% and that of silicon is greater than 0.5%, ternary eutectic Al-Al_2Cu-Si is formed. Iron, silicon and manganese present in these alloys form Fe_2SiAl_8, when they do not contain Mn, and when they also have in composition Mn, they form $FeMn_3Si_2Al_{15}$. Nickel strongly influences the properties in the presence of copper by forming the compound of AlCuNi or $Al_3FeCuNi$. Magnesium forms the Mg_2Si compound and a large amount is dissolved in the solid solution, but by segregation can lead to the occurrence of the Mg_2Zn_{11} compound [5].

Phase transformations in solid state, if allowed in the alloy balance diagram, are an essential condition for carrying out a heat treatment by quenching in solution and artificial ageing on an aluminum alloy. An alloy of this type is the one that can withstand an order-clutter reaction; the hardening process accompanying this process (similar to the hardness by precipitation) is determined by the order-hardening reaction. The conditions for this form of hardening are quite stringent so that the most important methods, often used for alloys, are based on precipitation from a solid oversaturated solution and by eutectoid decomposition [6-8].

Heat-treated by hardening and ageing, aluminum alloys acquire a higher mechanical resistance. This is due to interactions between precipitation and matrix dislocations, interactions that decrease the mobility of the deployations. Thus, there are three causes of increased mechanical resistance in alloys hardened by precipitation [8, 9]:

- Hardening by internal tension;
- Chemical hardening (produced when dislocations cross precipitation);
- Dispersion hardening (produced when dislocations bypass precipitation).

The emergence of Guinier-Preston areas or precipitation of compound in the structure of the alloy determines in their vicinity a number of structural, chemical, energy-related discontinuity, etc. [10]. Depending on the nature of the discontinuity, there may be several mechanisms that affect the mobility of these dislocations leading to the production of aluminum alloys hardness [8, 11].

The superficial energy value of the interfaces decides the form of precipitation. Depending on the deformation energy ΔUe for the elastic accommodation of the two networks, the form of precipitation can be spherical or acicular.

The emergence of Guinier-Preston areas and consistent or semi-consistent precipitations create fields of elastic tension surrounding these precipitations. These tensions have the value directly proportional to the concentration of solid C solution and the difference between the network parameters of the matrix and the Guinier-Preston area considered [20].

If the precipitation has spherical shape, the average tension will be [5]:

$$\Delta = 2G \cdot \varepsilon \cdot c \quad (1)$$

where: G = Matrix elasticity module; ε = is a concentration function C.

At the interaction of dislocations with a surge of tensions characterized by a mean internal tension T, occurs the curvature of the deployations whose radius is calculated with the relationship [8, 12]:

$$2R = \frac{G \cdot b}{\sigma} \quad (2)$$

where b is the Burger vector of the dislocation, being the order of the interatomic distance.

2. Experimental conditions

In order to study the influence of thermal and thermomechanical treatments applicable to deformable alloys with aluminum base on physico-mechanical properties, it was necessary to adopt a methodology capable of simultaneously ensuring microstructural changes and the study of the variation of the main mechanical properties, in order to determine the technological variants of optimum thermal and thermomechanical treatments. The alloy studied, due to its chemical composition, allows the phenomenon of structural hardening by heat treatment, because zinc, magnesium and copper, form intermetallic phases with aluminum, phases with variable solubility in solid state ($MgZn_2$, with Al_2Mg_2Si, Al_2MgCu, etc.). Therefore, the work aims

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to investigate the influence of the final thermomechanical treatments on the properties of cold-rolled semi-product aluminum alloys.

The material intended for experimental research is an aluminum alloy from the Al-Zn-Mg-Cu system, with the chemical composition shown in Table 1.

Table 1. *Chemical composition of the research-subject alloy*

Element / The alloy	Zn	Mg	Cu	Cr	Mn	Al
Al6Zn2,5Mg2	6	2.5	0.6	0.2	0.25	rest

Table 2. *Alloy Properties According to EN 485-2-2007* [12]

Property / The alloy	Rm, [Mpa]	$Rp_{0,2}$ [Mpa]	A_5 [%]	HB
AlZn6Mg2,5Cu	540	470	7	161

The mechanical properties of the studied alloy, according to EN 485-2-2007, are shown in Table 2.

These alloys were developed, molded into ingots and homogenized at S.C. ALRO S.A. Slatina.

The manufacture of the test tubes was carried out by cutting from homogenized ingots. The mechanical test tubes were made according to specifications given by SR EN 10 002-1/1995 for traction tests.

Figure 1 shows the geometry of a sample at the end of thermomechanical processing.

The sequence of thermomechanical treatment operations according to the chosen variant is presented in Table 3.

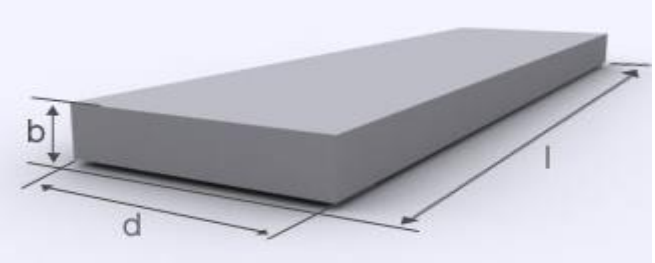

Fig. 1. *The shape and dimensions of a sample at the end of experiments B = 3 mm; D = 60 mm; L = 150 mm*

Table 3. *Experimental variant*

Experimental variant	Description of experimental variant
Chosen variant	1. Homogenization at a temperature of 480 °C for 24 hours of poured bullion; 2. The cooling of the bullion with the furnace; 3. The flow of samples in order to carry out the experiments; 4. Heating up to a temperature of 435 °C for hot lamination; 5. Hot lamination with the degree of plastic deformation: ε = 25%; 6. Cooling in the air up to ambient temperature; 7. Heating for the commissioning of the solution at a temperature of 500 °C for 2 hours; 8. Cooling in water; 9. Artificial ageing at a temperature of 100 °C with a maintenance time of 1 hour; 10. Cold plastic deformation with a deformation degree: ε = 30%; 11. Artificial ageing having several experimental variants in turn.

As shown in Table 3, after quenching in solution, a slight artificial ageing was performed at 100 °C with a maintenance time of one hour. This first artificial ageing achieves structural stability of the material because, in the hardened state, after approximately 3-5 hours, the natural ageing process is

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initiated, which is not an advantage for subsequent deformable alloys. The increase in mechanical characteristics occurs on account of complex interactions between base matrix dislocations and precipitated particles occurring in the structure of alloys following ageing. As a result of the formation of the $CuAl_2$ compound, copper is the main element of hardening of special aluminum alloys.

The cold plastic deformation process, resulting in the final dimensions of the investigated material was made between two artificial ageing processes.

The cold lamination of aluminum alloys resulted in increased density of structural defects and their uniform distribution, which has the effect of intensifying the phenomena of uniform decomposition of the supersaturated solid solution.

The smoother structure, with evenly distributed precipitation obtained in aluminum-based alloys after the application of thermo mechanical treatments leads to an optimum association of properties of resistance and plasticity, the high increase of resilience and elongation at breakage with maintaining at roughly the same level of resistance to breaking the alloy.

3. Experimental results

Putting into practice the technological operations according to the processing variant of the investigated alloy, we obtained a series of values of mechanical properties according to the parameters of thermomechanical processing, shown in Figures 2-5.

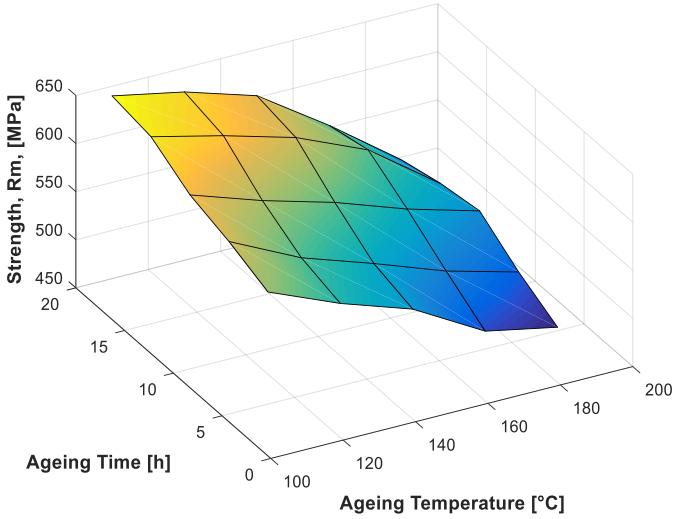

Fig. 2. *Variability in breaking resistance of studied alloy with aging time and temperature for ε = 30%*

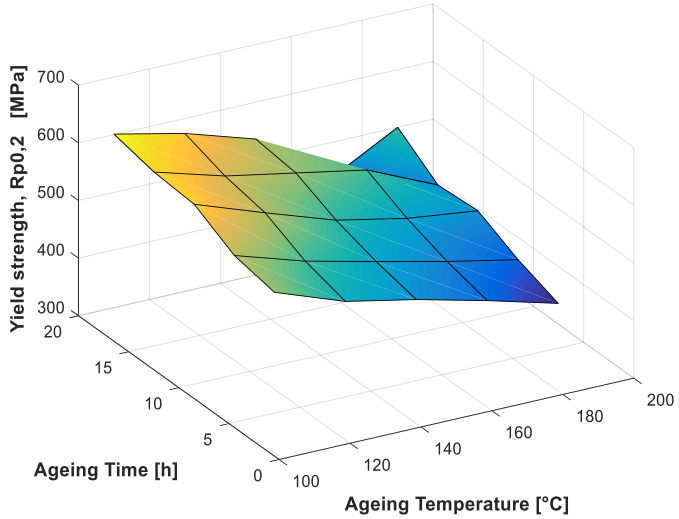

Fig. 3. *Variability in flow resistance of studied alloy with time and temperature of aging for ε = 30%*

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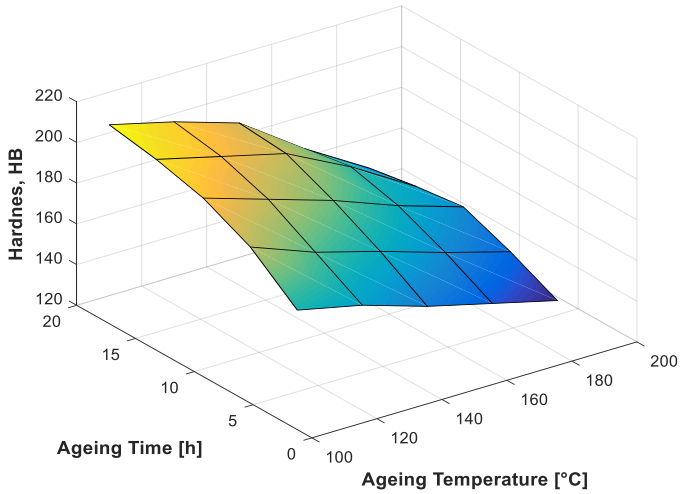

Fig. 4. *The variation of the HB hardness of the studied alloy with aging time and temperature for ε = 30%*

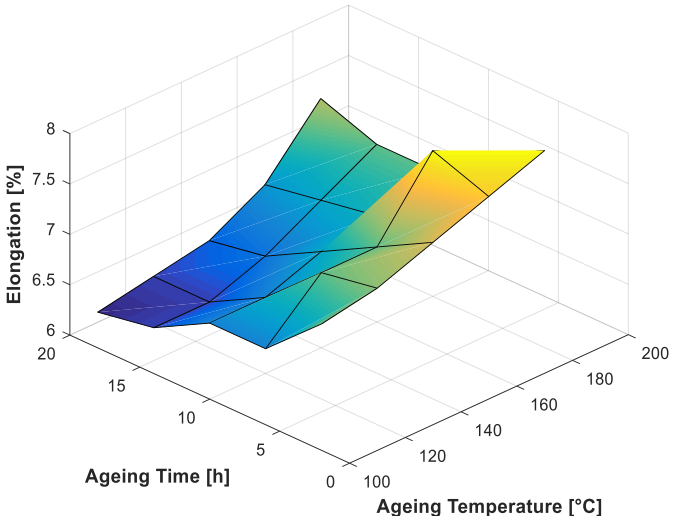

Fig. 5. *Variation of elongation at breaking A_5 of the alloy studied with aging time and temperature for ε = 30%*

4. Conclusions

Analyzing the curves of the variation of properties in the above graphs obtained by statistical processing of experimental data, it can be observed that the mechanical properties of resistance (mechanical strength, flow limit and the hardness of HB) increase with increasing aging time and decrease as the ageing temperature grows.

Elongation at breakage increases as the ageing time increases and decreases as the ageing temperature increases.

The literature offers relatively little information about the combination of thermal treatments and plastic deformation carried out in the order and at the parameters described in this variant, although the results obtained are at a fairly high level, which should give this variant of unconventional treatment an application in practice.

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EVALUATION OF THE POSSIBILITIES OF OCCURRENCE OF HARMFUL EFFECTS CAUSED BY SOME FERROALLOYS USED IN THE METALLURGICAL INDUSTRY ON THE ENVIRONMENT

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ABSTRACT

The raw materials of the metallurgical industry have an important chemical reactivity and when they come in contact with the environment, they can generate effects that in most cases are harmful. Chemical reactions from the solid / liquid interface showed a chemically active environment which caused the formation of reaction products with a certain degree of environmental damage.

The paper aimed to address the interaction between some coarse (0.8 mm) and fine (0.04 mm) ferro-alloys (FeSi with 45% Si) with a physical simulation medium - distilled water for the possible determination of a change of pH. For this purpose, chemical composition determinations were made by the EDX method and the morphological characterization of the surfaces by the SEM electron scanning method. Also, pH measurements were made on different granulations and quantities of FeSi45.

KEYWORDS: FeSi with 45% Si, pH, aqueous extract, harmfulness, chemically active surfaces

1. Introduction

In general, the raw materials used in the metallurgical industry due to the quantities used and their intrinsic physico-chemical characteristics can cause harmful effects on the environment. A suggestive example of raw materials with harmful potential used in steelmaking processes can be given by the usual ferroalloys - FeSi45 in this case. They contain in addition to the main chemical elements Fe and Si and traces of other chemical elements such as: Na, K, Al, Ca, Ni, P, S. resulting from the processes of elaboration of ferroalloys. Because the presence of these chemical elements in the industrial processes of obtaining ferroalloys are not specifically mentioned in international standards SR ISO 5445/1995 [1], they nonetheless feel their presence coming from the chemical composition of the raw materials that make them and are confirmed when chemical analysis is performed by EDX method in detail.

The paper aims to show that these chemical elements have direct effects on the environment. The impact on the environment is given by the fact that these raw materials are used in high quantities and their transport is done in bulk. Also, their storage is possible also by placing them directly on the ground in closed or open warehouses. Upon the contact of this with the water from the atmosphere (rain), they are washed and the water infiltrates the soil causing harmful effects on it in the sense of changing the physico-chemical character, in this case, the pH of rain or snow water, etc.

By the appearance of some changes in the pH of a physical simulation environment, that is, an aqueous extract consisting of distilled water and granular particles of FeSi45 with different dimensions, the degree of harmfulness of the chemical elements present on the active chemical surfaces of the ferro-alloy particles. For this purpose, experiments were performed to form an aqueous extract consisting of distilled water (50 mL) with granular particles of FeSi45 ferroalloys with coarse (0.8 mm) and fine (0.04 mm) particle sizes.

2. Materials and methods

The determination of the changes of the chemical character of the environment by physical simulation was made by choosing a common dissolution medium - the fresh distilled water called and demineralized water because the impurities contained by the distillation process which involves

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the boiling (vaporization) were eliminated, and then by the condensation of the vapor obtained into a container followed by pH measurements.

We mention that there may be other methods of obtaining distilled water such as deionization and reverse osmosis [2].

Water, in general, has an amphoteric character that can be highlighted by the auto-protolytic reaction and thus it dissociates into H^+ and OH^- ions [5, 6].

H^+ ions (or H_3O^+ ions) give the aqueous solution an acidic character and OH^- ions give the same aqueous solutions an alkaline character [6].

$$H_2O \leftrightarrows H^+_{(aq)} + OH^-_{(aq)} \quad (1)$$

One way to determine the acid-base character of aqueous solutions is to use the notion of pH [5]. Thus, Sorensen defines pH (hydrogen index) as the decimal logarithm (base 10) with changed sign (cologarithm) of hydrogen ion concentration. When water (H_2O) interacts with other chemical elements, some of the chemical bonds in the water break down and new chemical bonds are formed, at the same time releasing hydrogen and the effect is to change the pH which can increase or decrease.

Literature [4, 7, 8] mention among the first ways to obtain safe hydrogen gas at low temperatures the use of FeSi in the presence of an alkaline NaOH and water environment. This results in the decomposition of water and the release of hydrogen from the liquid state into the gaseous state according to the chemical reaction [9]:

$$Si + 2NaOH + H_2O \leftrightarrows Na_2SiO_3 + 2H_2 \quad (2)$$

It is also possible to ambient temperature and the reaction [10]:

$$Si + 2H_2O \leftrightarrows SiO_2 + 2H_2 \quad (3)$$

The direct effect is the pH shift of distilled water and this can be accounted for by the decomposition reaction of water and the release of H ions.

The second component is given by solid granular particles of FeSi45 with coarse (0.8 mm) and fine (0.04 mm) particle size fractions. For these, the morphology of the surface and the chemical composition were analyzed using the electron scanning electron microscope (SEM) equipped with an electronic probe (EDX) from Fei Quanta 200.

The measurements involved the introduction of granular particles into distilled water followed by mechanical stirring and pH measurements. To determine the pH of the aqueous extract we used a Hach Lange HQ40d multiparameter.

3. Results and discussions

The morphological analysis of the chemically active surface revealed a rough surface, often with defects that further enlarged the surface.

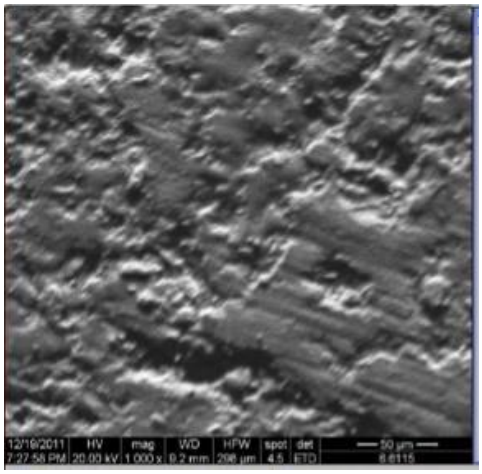

Fig. 1. *Surface morphology of a granular particle of FeSi45 by SEM electron microscopy* [3]

It should also be mentioned that the FeSi45 ferroalloys have a rather high friable character which during the handling creates new active chemical surfaces by mechanical crushing, increasing the harmful effect even more.

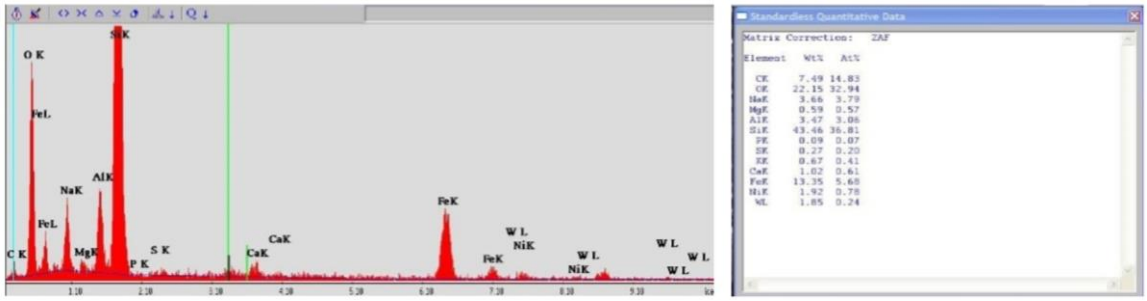

Fig. 2. *Chemical analysis of a granular particle of FeSi45 with the help of the EDX probe*

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The analyzed surface of the sample revealed the presence of active chemical elements in low concentrations of Na, K, Al, Ca, Ni, P, S at the trace level with a possible significant impact on the environment. The identification of these chemical elements suggests that at the contact with an aqueous environment the pH may swerve to the alkaline domain.

The high oxygen concentration can represent for us an indicator of the high reactivity of the surfaces with direct consequence in the formation of oxides.

Table 1. *The values of the measured parameters of the aqueous extract consisting of FeSi45 with particle size 0.8 mm and 0.04 mm*

No	Component		Component			Indicator	
	A	Quantity [ml]	B	Granulation [mm]	Quantity [g]	pH	Temperature [ºC]
A1	Tap water	50	-	-	-	7.71	23
A2	Distilled water	50	-	-	-	6.77	23
A3	Distilled water	50	FeSi 45	0.8	0.5	9.05	23
A4	Distilled water	50	FeSi 45	0.8	5	10.21	23
A5	Distilled water	50	FeSi 45	0.8	50	10.92	23
A6	Distilled water	50	FeSi 45	0.04	0.5	10.6	23
A7	Distilled water	50	FeSi 45	0.04	5	10.85	23
A8	Distilled water	50	FeSi 45	0.04	50	10.92	23

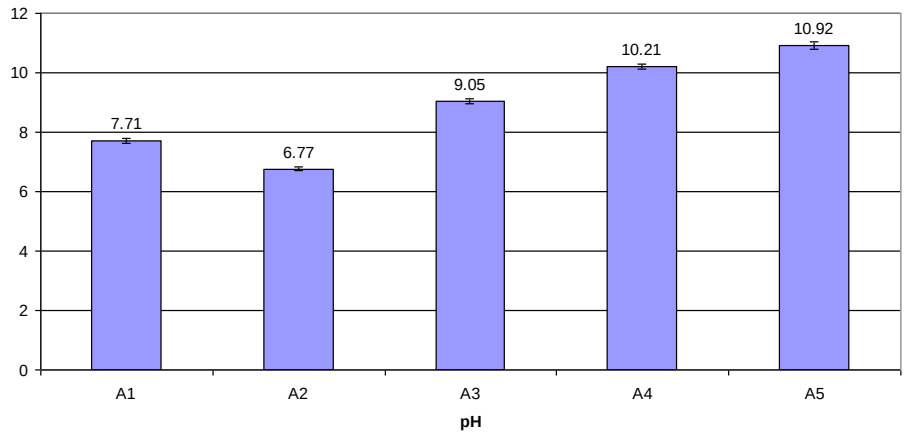

Fig. 3. *pH values for aqueous extract with granular particles of FeSi45 with 0.8 mm*

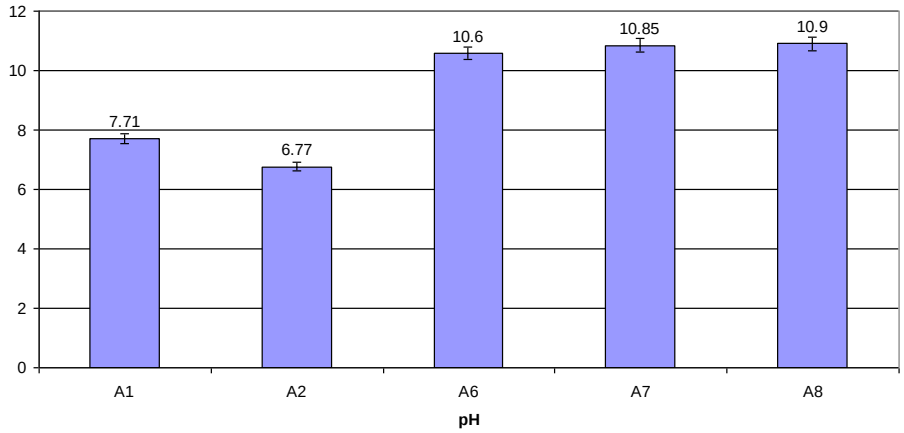

Fig. 4. *pH values for aqueous extract with granular particles of FeSi 45 with 0.04 mm*

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The data shown in Figure 3 show an increase in pH values for the three concentrations (0.5 g, 5 g and 50 g) of FeSi45 introduced into distilled water as a result of their chemical reactivity. An increasing tendency of the pH can be observed suggesting that when the number of particles is higher and the concentration of transferred chemical elements in the distilled water is higher resulting an aqueous extract with pH in the alkaline domain.

In Figure 4 it can be observed an effect on the pH in the alkaline domain when we tested by the introduction of the granular particles of 0.04 mm. It can be observed also, an increasing tendency when was increased the chemically active surface, and this is being able to be accounted by the chemical elements from their surfaces.

The results presented in Figures 3 and 4 show the formation of an aqueous extract with pH in the alkaline domain and thus an anionic rich water that can be used successfully in the industrial environment, a suggestive example being the emulsion of water in oil. The papers [11-13] show that water with pH in the alkaline domain stabilizes the emulsion of water in oil through an electrostatic stabilization mechanism.

4. Conclusions

The chemically active surfaces of the granular particles of FeSi45 with different granulations interacted with distilled water and they performed a chemical transfer of the constituents (Na, K, Al, Ca, Ni, P, S ions) changing the pH by turning it into alkaline domain.

The formation reaction of the aqueous extract took place at ambient temperature and we can suppose that also in the environment it can be favored the increase of the pH.

By correlating the chemical composition with the pH of the aqueous extract we can assume that the conditions for the formation of basic oxides such as NaOH, KOH and others have appeared.

It can be observed an increasing tendency by relating the quantity of granular particles to the amount of distilled water that we can put on account of the available chemically active surface. This can be observed in both situations for 0.8 mm and for 0.04 mm.

Water with a pH in the alkaline domain can be used to stabilize oil emulsions in water.

It is desirable to use these ferroalloys for the purpose for which they were developed for the economic advantages they have.

The raw materials used in the metallurgical industry have a certain reactivity that requires attention because they can influence the quality of the environment.

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THE ASSESSMENT OF RISK FACTORS FOR WORK SAFETY AT THE WORKPLACE FOR DRIVER

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ABSTRACT

In this is paper present the calculation of the overall risk level for workplace - driver. Risk assessment is the first step towards safer and healthier jobs, and it is the way to reduce accidents at work and occupational diseases. The new trends in managing an organization are to consider as performing an organization that is equally concerned with improving the quality of products / services and increasing economic efficiency, as well as providing adequate working conditions for employees and environmental protection environment, by increasing the quality of life in general. All of these components are addressed within integrated management systems, which usually aim to organize the operation of companies. Employee health and safety, protection of neighbouring populations, flora and fauna, water and soil are just as important as the organization's profit. But what does the health and safety component of work in this integrated system involve? The increase in profit results from the reduction of material losses due to accidents and damages, the reduction of absenteeism due to medical leave, the elimination of losses caused by penalties resulting from non-compliance with legal requirements, etc.

KEYWORDS: risk factors, work process, risk level, safety

1. Introduction

The optimization of the activity of prevention of accidents at work and occupational diseases in a system, is the risk assessment of the respective system.

Risk assessment involves identifying all the risk factors, from the analysed system, and quantifying their size, based on the combination, between two parameters: the severity and frequency of the maximum possible consequence, on the human body. Thus, partial risk levels are obtained, for each risk factor, respectively global risk levels, for the entire system analysed [1, 5].

The method developed by I.N.C.D.P.M. Bucharest, is part of the analytical, semi-quantitative methods category, and consists, in identifying all the risk factors, in the analysed system, (workplace), with the help of predetermined checklists, and quantifying the size of the risk, for each risk factor in part, based on the combination, between the severity, and the frequency of the maximum foreseeable consequence. The overall risk level, at the workplace, is determined, as a weighted average, of the partial risk levels, so that the compensations are minimal. The level of security results indirectly, being inversely proportional to the level of risk [2].

The application of the method is finalized with two centralizing documents, for each job: the risk assessment sheet, and the proposed measures sheet.

2. Theoretical considerations and method of research

2.1. Work process

The work process consists in carrying out transports of various goods both on national and international routes in accordance with legal requirements to the beneficiaries, as well as carrying out the current maintenance of the means of transport (oil change, antifreeze, brake fluid additions, wheels, tire running, car wash, etc.).

Components of the assessed work system

2.2. Work equipment

Means of transport: heavy goods vehicles for international transport; toolbox; spare tire; reflective

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triangle; medical kit; jack; fire extinguisher; shovel (in winter); rubber chains (in winter); maintenance materials (oil, antifreeze, refill brake fluid, fuses, bulbs, etc.); various merchandise.

2.3. Work task

In order to accomplish the workload, the driver performs mainly the following activities:

- before leaving the race, the company will be presented in a good health condition, resting, prepared for the transport; assist in cargo loading; does not load the vehicle over the transportation capacity; carries out the transport in accordance with the contractual provisions and the instructions received; is responsible for the observance of the health and safety measures of labour and the US provided by the legislation in force, namely: personal documents (auto license, driver attestation, identity card, medical insurance); documents for the vehicle (registration certificate, beaver, technical inspection, tachograph, etc.); prepares supplies with spare parts, materials, tires, fuel; immediately communicate to the transport coordinator any traffic event in which he or the vehicle is involved; upon arrival from the race, hand over all the documents of the race received on departure and those obtained in the course of the course to justify its activity and the vehicle throughout the race; has the obligation to sign at the arrival of the race any reported malfunction or any abnormal operation of any faction; has the obligation, on arrival from the race, to provide details about the technical condition of the truck, the need for spare parts or other operations which it considers necessary for the optimum operation of the truck; assist in making repairs; permanently takes the necessary measures in the optimal conditions of transportation depending on the atmospheric conditions; it is forbidden to comply with any provision made by the transport beneficiary which would lead to the circumvention of the law or the commission of offenses; has the obligation to answer the phone by providing full details of the situations for which it is called; permanently monitors the validity of documents; respects the driver's work and rest regime provided by the legislation in force; it is forbidden for the employee to claim and receive money, gifts or other advantages to act against his obligations.

This is true even when, by receiving undue benefits, society has not been directly damaged; the obligation to observe the provisions of the internal regulations, as well as in the individual labour contract; maintain order and cleanliness at work; not to drink alcohol or to facilitate the practice of doing these things at the workplace; executes according to the requirements, available to the administrator and other stipulated provisions; is responsible for compliance with the road code; is responsible for the maintenance in service of the truck entrusted; announces the administrator in the event of a malfunction of the truck entrusted when he is in the race; participates in regular work safety training and emergency situations; perform regular medical check-ups specific to the job; carry on the routes and routes indicated, eliminating unjustified interruptions; do not run without the tachograph being in operation.

2.4. The work environment

The elements that define the work environment of the performer (driver) are:

- low air temperature in the cool season in the event of air conditioning failure; high air temperature in the warm season for the heating system; airflows in some working areas, due to ventilation, leakage in the cabin, open windows on both sides of the cabin; noise level - discontinuous (below the maximum allowable); low light level at work at night - example when driving at night, is the phenomenon of blindness caused by the incorrect use of lights by other road users; natural calamities - surprise, earthquake; weather - wind surprise, blizzard ground breaks, tree crashes, landslides; pneumoconiogeni powders present in the outer atmosphere of the workplace - example driving the dust by selling etc.

3. Identified risk factors

3.1. Work equipment

Mechanical risk factors:

- moving machine organs: gripping, entrainment of the hand or clothing by transmissions (water pump) or by mechanical transmissions (planetary, cardan) when making interventions on the car; road traffic accident when driving on public roads (hitting the means of transport); hitting the cars when traveling through the beneficiary premises, through the premises of the supplying company, as well as traveling from home to the workplace and vice versa; automatic locking of the steering mechanism or the brake system on the road, as well as stopping the engine operation while the truck is moving, failure of the hydraulic safety system; displacements of trucks under the effect of gravity, due to their non-assurance during stationary (stationary without the introduction of the gearshift lever in a gear and without pulling the handbrake); slipping, rolling or toppling of stored materials without ensuring stability in the receiving company's premises, as well as slipping, rolling, overturning or collapsing materials in the vehicle bin; the free fall of parts to work under the truck in case of interventions; dropping the truck on the jack, the

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press on changing the wheels or during the interventions under the car, the fall of the shuttle from the truck bay to its descending or lifting; dropping the truck from the truck to its normal position, during engine operation, electrical installation, etc., due to the fact that it is not fitted with devices provided for this purpose; knocking with hand tools; liquid oil, fuel, brake fluid leakage; deviation from the normal carriage trajectory (tread depth, trench holes, runway obstacles, tire burst, avoidance of an obstacle, car, pedestrian, etc.) - danger of overturning the car while driving; the design of particles on the windscreen when broken; antifreeze rupture when pressure hoses are broken; airborne rupture at hose breakage to ensure inflation of the tire, including the possibility of hitting the hose connection at the air compressor; contact with dangerous surfaces or contours (bumpy, bumpy, slippery, abrasive etc.) - example when performing maintenance and maintenance operations; pressure vessels - example: fire extinguisher from the machine - explosion hazard; vibrations in the car's cab, caused by inadequate engine operation, running track irregularities, defective damping systems, etc.

Thermal risk factors:

- high temperature of surfaces, accidentally touched by inspections or repairs; lowered temperature of metallic surfaces in cold weather; flame, flame - example: short circuit at the car's electrical system - fire hazard.

Electric risk factors:

- Direct and indirect touching by electric shock and through the emergence of step voltage - possibilities that can occur to the beneficiaries, to the suppliers of materials, when traveling on public roads (road drops of some air conductors that ensure the transport of electricity).

Chemical risk factors:

- working with toxic substances - antifreeze, brake fluid; working with caustic substances - electrolyte batteries - chemical burns; work with or in the vicinity of flammable substances (fuels, oils, greases).

3.2. Work environment

Physical risk factors:

- low air temperature in the cool season in the event of air conditioning failure; high air temperature in the warm season for the heating system; airflows in some working areas, due to ventilation, leakage in the cabin, open windows on both sides of the cabin; noise level - discontinuous (below the maximum allowable); low light level at work at night - example when driving at night, is the phenomenon of blindness caused by the incorrect use of lights by other road users; natural calamities - earthquake; weather - wind surprise, blizzard ground breaks, tree crashes, landslides; pneumoconiogenic powders present in the outer atmosphere of the workplace - example driving the dust by selling etc.

Chemical risk factors:

- toxic gases - example: exhaust gas from the truck - possibility to accumulate in the truck cabin; working in the area with potential fire or explosion hazard - example: within the fuelling stations where the fuel is being fed.

Work task:

Inappropriate content of workload relative to security requirements:

- admission of workers to work, under inappropriate psychological and physiological conditions; tolerance of deviations from work discipline, from observing the rules of work safety; the use as a working method of the open flame to start the engine; the assignment of the driver in order to carry out work tasks with incomplete work in the field of safety and health at work; omissions or errors in the preconditioning of work operations - example: disposition of activities for a driver who does not have the proper qualification for the activity to be carried out, etc.

Physical request:

- dynamic effort in manual handling of masses; forced or vicious jobs - job position predominantly "sitting"; high working pace on some days of service; permanent attention to truck driving on public roads (especially when traveling at night); difficult decisions taken shortly in some situations when driving on public roads; performing short and medium cycle operations; psychological stress related to the danger of a traffic accident when traveling with the means of public transport on public roads, psychological stress related to the danger of being assaulted by unknown persons during the performance of their duties.

3.3. Executor

The wrong actions:

- performing unpredictable operations in the work task or in a different manner than the technical working provisions; execution of manoeuvres not permitted by the legislation (road code) governing the circulation on national and international public roads or technological provisions during the stationary work; not to carry out statutory breaks at the intervals stipulated by the legislation in force, in the case of long-distance journeys; car interventions without

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stopping the engine; the introduction of the upper limbs in the belt area through the belt or in the area of the mechanical transmission when the engine is in running order; the use of an inappropriate technical machine or the periodic checking period, exceeded; the use of inappropriate manual tools during the works; exceeding the maximum number of people admitted in the cab or the maximum permissible load that can be carried by truck; lowering the slopes with the gear lever in the "neutral" position; carrying out the towing operation with supplied means or connecting the trailer with improvised means; inappropriate positioning of the car when performing interventions at or under the car, when changing wheels - example: use of jacks, defective presses, non-use of wheel feathers, non-introduction of the gearshift lever in a gear, non-assurance with handbrake etc.; non-uniform loading of the materials in the bin of the car - danger of overturning while traveling on public roads; loading the car with a mass greater than the maximum authorized weight; inflating tires with higher pressures or using them at lower pressures than the technical book; performing operations on the engine without securing the cab against the closure with the device provided for this purpose; failure to secure the shuttle from the car's bay during its loading / unloading - accidental fall; non-synchronization to teamwork - example: with workers from the trade companies that insure the repair or repair of the car, the workers who load / unload the truck, etc .; displacements, stationary in dangerous areas; falling to the same level: by unbalance, slippage, obstruction; falling from a height: through a hollow, unbalanced, sliding; accidental communications; lightening cigarette lighter in the fuel supply station; at work under the influence of alcohol, in fatigue, under the influence of drugs, etc.;

Omissions:

- omission of performing operations that ensure its own security; misapplication or misuse of E.I.P. and other means of protection.

The overall level of risk in the workplace is:

- organizing the work so as to reduce the noise by limiting the duration and intensity of the exposure and establishing sufficient breaks, during the work program.

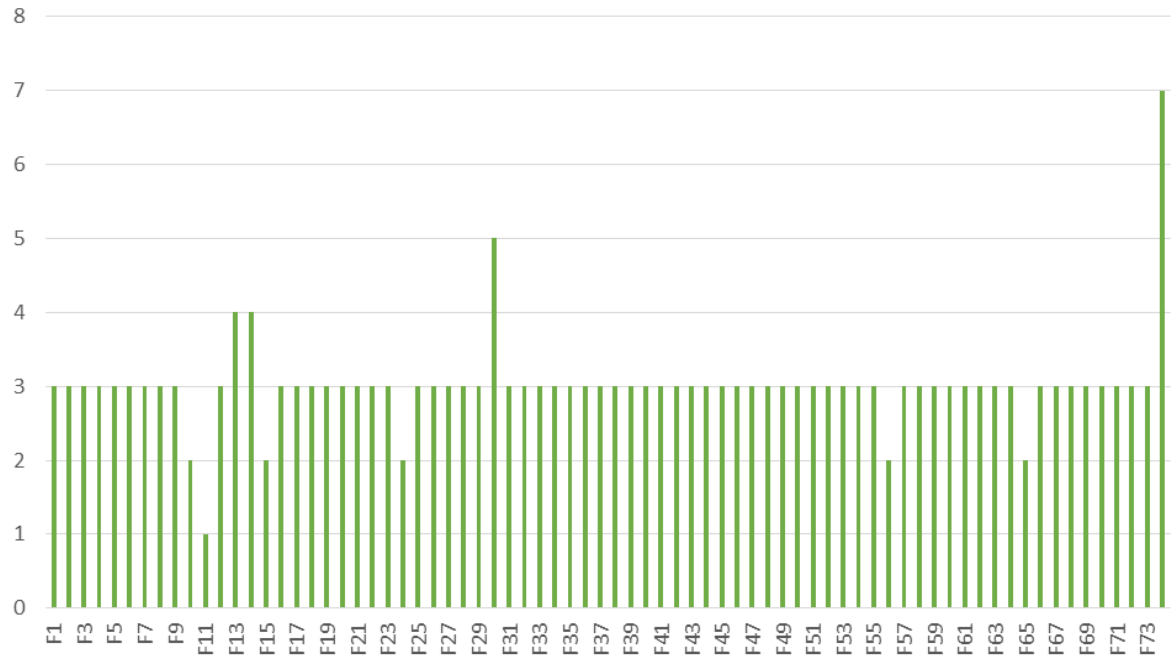

Fig. 1. *Partial risk levels on risk factors*

$$\sum R_i r_i$$

$$N_{rg}\ \frac{i=1}{74} = \frac{1(7x7)+0(6x6)+1(5x5)+2(4x4)+64(3x3)+5(2x2)+1(1x1)}{1x7+0x6+1x5+2x4+64x3+5x2+1x1} = \frac{703}{223} = 3{,}15$$

$$\sum r_i$$

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Table 1. *Proposed measures for workplace – driver*

No. crt.	Risk factors	Risk level	Proposed measures
			Nominalization of the measure
0	1	2	3
1.	Incorrect use of protective equipment and other protective equipment	7	Organizational measures: - equipping drivers with protective equipment appropriate to the activity they carry out; - instructing drivers about the consequences of non-compliance with security restrictions.
2.	Low level of nighttime lighting - example: when driving at night, there is a glare caused by the incorrect use of lights by other road users	5	Technical measures: - checking the condition of the lighting installation on the truck before leaving the race and leaving the darkness; Organizational measures: - performing regular medical check-ups at the established deadlines; - the formation of the travel routes according to the driver's fatigue; - transport as much as possible during the day.
3.	Design of particles on the windscreen when it breaks	4	Organizational measures: - observance of the regular distance from the car that is moving forward; - compliance with traffic rules.
4.	Antifreeze flow when the pressure hoses are broken	4	Technical measures: - checking the technical condition of the car at the established deadlines; Organizational measures: - checking the pressure hose condition before starting the machine; - tracking the wear to the hose and immediately replacing those that no longer meet the conditions of use.

Note:
1. The implementation deadlines and the persons responsible for these measures will be established by the worker designated for safety and health at work together with the manager of the work place;
2. The measures proposed to eliminate or mitigate risk factors will be included in the provision and protection plan.

4. Interpretation of workplace evaluation results: driver

The level of global risk calculated for the workplace (driver) is equal to 3.15, the value that is in the category of workplaces with an acceptable level of risk.

The result is supported by the "Evaluation Sheet", which shows that of the total of 74 identified risk factors (Figure 2), only 4 exceeded as a partial risk level the value of 3: one belonging to the category of maximum risk factors (7), one falling under high risk factors (5) and two in the category of medium risk factors (4).

To mitigate or eliminate the four risk factors, the measures outlined in the "Proposed Workplace Bill" are required for the workplace [3, 4].

Regarding the distribution of the risk factors on the generating sources, the situation is as follows (Figure 3):

- 33.78%, factors of the car / work equipment;
- 14.86%, factors of the working environment;
- 17.57%, factors related to the work load;
- 33.78%, contractor's factors.

From the "Evaluation Sheet" analysis, 71.62% of identified risk factors can have irreversible consequences on the performer (DEATH or INVALIDITY).

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Table 2. *The four risk factors that are unacceptable are:*

F74	Misapplication or misuse of E.I.P. and other means of protection	N.V.P.R.	7
F30	Low light level at work at night - example when driving at night, is the phenomenon of blindness caused by the incorrect use of lights by other road users	N.V.P.R.	5
F13	The design of particles on the windscreen when broken;	N.V.P.R.	4
F14	Antifreeze rupture when pressure hoses are broken;	N.V.P.R.	4

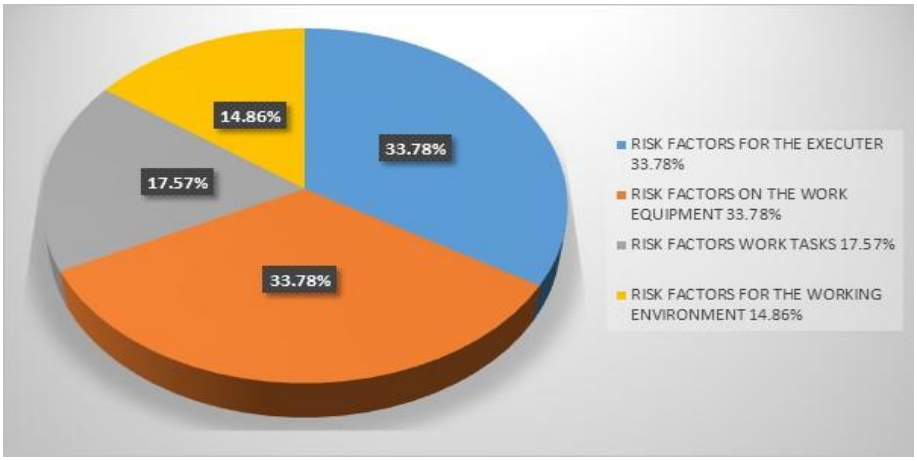

Fig. 2. *Share of risk factors identified by the generating source within the work system*

5. Conclusion

The calculation of the overall risk level resulted in a value of 3.15, which means that driver has an acceptable risk. By analysing the partial risk level of the 74 risk factors, only four of them raised a higher risk, being unacceptable.

From the "Evaluation Sheet" analysis, 71.62% of identified risk factors can have irreversible consequences on the performer (DEATH or INVALIDITY).

Why is workplace safety important? There is more to this question than one think.

Workplace safety is very important for each and every employee in the industry because all the workers desire to work in a safe and protected atmosphere. Health and safety are the key factor for all the industries in order to promote the wellness of both employees and employers. It is a duty and moral responsibility of the company to look after the employee's protection [7, 8].

Each and every person who leaves home for their work in the morning should come back home in good health in evening.

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THE ENVIRONMENT IMPACT OF PHONIC POLLUTION IN AN AREA WITH HYDROCARBS EXPLOITATION ACTIVITIES

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ABSTRACT

The paper presents the obtained results and the conclusions following the measurements regarding the noise pollution, from the analysed area of Galati. Monitoring has been made for as many factors as possible, possible causes of noise pollution, with the purpose of covering the entire area of development and the activity of oil exploitation. The determinations were made at different time intervals, for several working days, and in the end, they were compared with the regulations required by law regarding the exposure limit value for a normal day of 8 hours. Because the activity of exploration and exploitation of hydrocarbons requires the use of many heavy machinery, which pollute, their noise they can have a significant impact on the environment. For the analysis, several work points were monitored with the purpose of providing an overview, regarding the noise pollution, in the Independence oil exploitation area.

KEYWORDS: noise pollution, environment, hydrocarbs exploitation

1. Introduction

The analysed area is located on the territory of Galaţi County, about 22 km away, to the NW, in the vicinity of the localities of Schela and Slobozia Conachi. The acoustic measurements which were made aimed to determine the noise level from the Independența oil area, where a multitude of factors pollute the environment. Noise samples for our analysis were taken from several work points, in order to have a clearer view regarding the noise pollution in the respective area.

The acoustic measurements were made in the Independence oil exploitation area, to determine the noise level in the area. For the analysis, several work points were monitored [1, 3].

The sources of noise pollution monitored are:
- probes with repair and intervention activities;
- wells in production activities;
- reservoir parks;
- combustion plants (boilers);
- traffic;
- deposit (treatment area).

The recorded results were obtained, with the multifunctional digital sound measuring instrument, the PCE - 222 Multiparameter (Fig. 1).

Fig. 1. *PCE-222 sound level meter*

2. Experimental research

2.1. Noise determinations at wells with repair and intervention activities

The probes where intervention or repair activities were carried out are noise generators. The tests were conducted over two working days, divided as follows:

- M 1, day 1 - morning, repair probe; in the afternoon, the intervention probe;
- M 2, day 2 - in the morning, the intervention probe; afternoon, repair probe.

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Although the engines of the work facilities are homologated, it was found that, at times, they exceeded the permissible noise level of 87 dB, admitted by the laws in force. The other equipment set at the location did not exceed the noise level, but when their engines were at full speed, they reached the limit of noise pollution [2, 4] provided by law (see Table 1).

The noise level, resulting from the activity of the two probes, in some cases exceed the threshold imposed by law, but considering that the activity is not carried out near the engines of the installations, the workers are not exposed to the risk of noise pollution.

Table 1. *Noise determination at repair and intervention probes*

Probe	The place where measurements are made	Noise dB- average value	
		M 1	M 2
Capital Repair	The mouth of the probe	65 / 85	63 / 83
	Installation AM 12-40	70 / 90	69 / 88
	Motor pump	63 / 85	61 / 80
	Drive unit	62 / 86	60 / 85
	Outside the square	55 / 65	55 / 64
Intervention	The mouth of the probe	65 / 85	64 / 83
	Installation IC 5-T	70 / 88	70 / 86
	Drive unit	63 / 85	63 / 84
	Outside the square	56 / 68	55 / 67
Exposure limit value (according to GD 493/2006) for a normal working day of 8 hours		87	

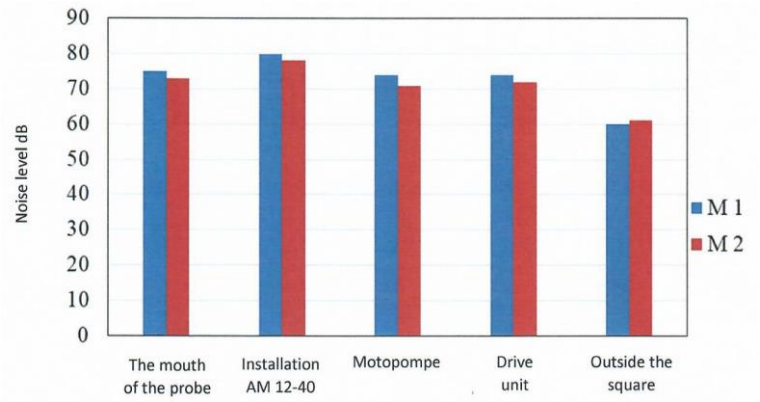

Fig. 2. *Average noise level, produced by machine engines - capital repair probe*

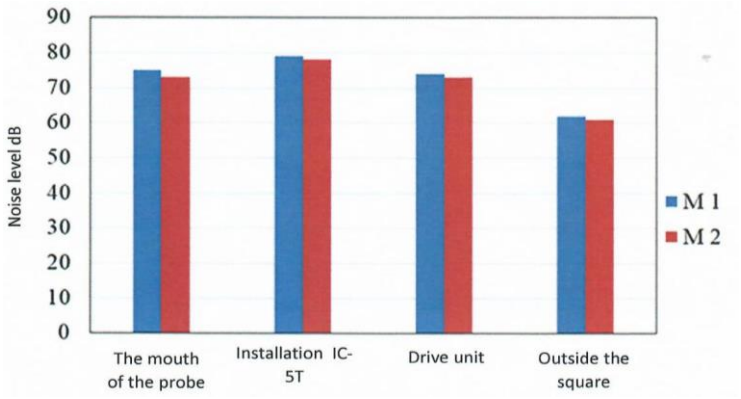

Fig. 3. *The average of the noise level produced by the engines of the machines - the intervention probe*

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We find that there is no exceedance of the threshold of attention, and therefore, the risk of exposure of workers is not a high one.

2.2. Noise determination at production wells

In the exploitation phase of the probes, the potential source of noise is the electric motor. This actuates the rotor, which enters the helical pump, in order to lift the fluids to the surface. Ventilation of the probe (if it contains gases) can be a source of noise. Depending on how they are removed, they can cause noise pollution [5].

The measurements were made near the probe, and on the ring road, near the houses. The monitoring duration was about 30 minutes, for each probe, between 12:00 and 13:00 and the results noted in Table 2 are an average of the noise produced by the drive units at the mouth of the probes.

In order to identify the risk degree of the workers and residents in the vicinity of the monitored objectives, the results were compared with the norms in force regarding the minimum safety and health requirements, regarding the exposure of the workers, the risks generated by the noise, and the permissible limits of noise level, outside the lens and near buildings.

Table 2. *Noise determination at production wells*

Object	**Noise level - dB**		
	Near the engine	**At the edge of the square**	**Near the houses**
Sample 1	85	60	33
Sample 2	80	57	31
GD 493/2006, a nominal day of 8 hours Stas 10009-88, outside of the objective Stas 10009 - 88, near buildings (day / night)	87	65	50/40

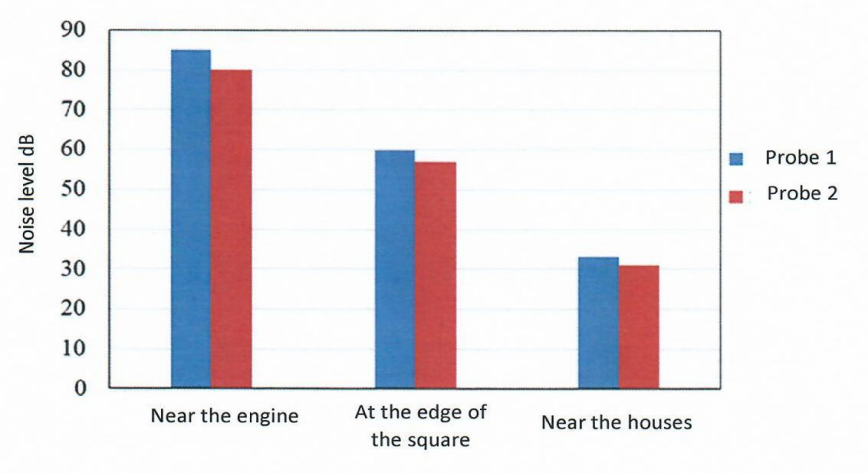

Fig. 4. *Average of sound pressure, at the wells in production*

Following the measurements made, it was found that the analysed objectives do not exceed, on any of the three points, the noise level required by law. Most of the wells in the vicinity of the dwellings are equipped with sound-absorbing cabins, which have the role of optimizing the noise produced by electric motors.

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Fig. 5. *Illustrative view, at the probes, at the outskirts of the town of Schela, which have sound-absorbing cabs, against the noises*

2.3. Research on noise pollution, in reservoir parks

Although modernized for their most part, the reservoir parks are still noise generators, through the thermal power plant, the injection pump, the air compressor, the gas manifold, etc.

Two parks, which require personnel, were chosen, in order to track how they were exposed to noise pollution. Some parks are fully automated, and no longer require permanent staff. The operators and maintenance teams go through them periodically, and check the proper functioning of the equipment.

Table 3. *Noise level determination, in Park no. 3, Independence*

The place where measurements are made		**Noise - dB**	
		M 1	**M 2**
Park nr. 3	The manifold of the gas	55	65
	The boiler	79	80
	Injection pump	80	80
	Air compressor	84	85
	Access alleys	60	62
Exposure limit value (according to GD 493/2006) for a normal working day of 8 hours		87	

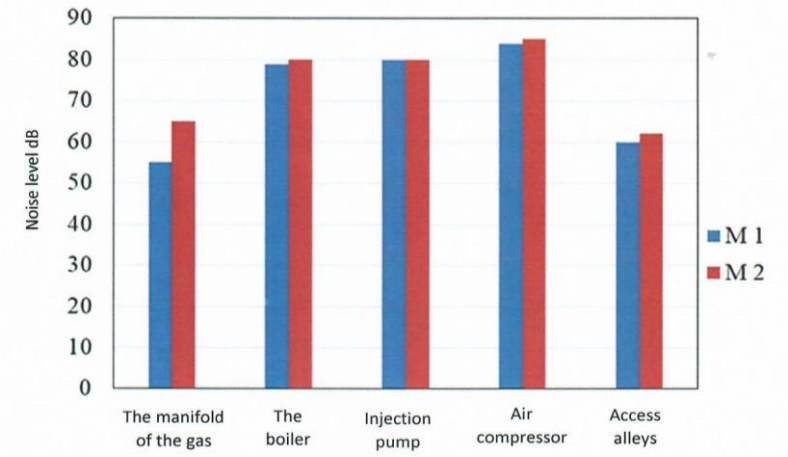

Fig. 6. *Results of sound pressure, recorded in Independence Park 3*

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The research regarding the noise level in Park No. 3, Independența highlights the fact that although modern, the equipment produces enough noise. The periodic monitoring of the noise pollution is necessary.

The measurements showed that the noise produced by the equipment is generally the same, in both situations; a difference exists only in the case of the gas manifold, which has the role of directing the gases to the waste basket in order to be eliminated.

Table 4. *Noise level determination, in Park no. 11, Independența*

The place where measurements are made		**Noise - dB**	
		M 1	**M 2**
Park nr.11	The manifold of the gas	70	58
	The boiler	75	75
	Injection pump	73	74
	Air compressor	84	84
	Access alleys	60	59
Exposure limit value (according to GD 493/2006) for a normal working day of 8 hours		87	

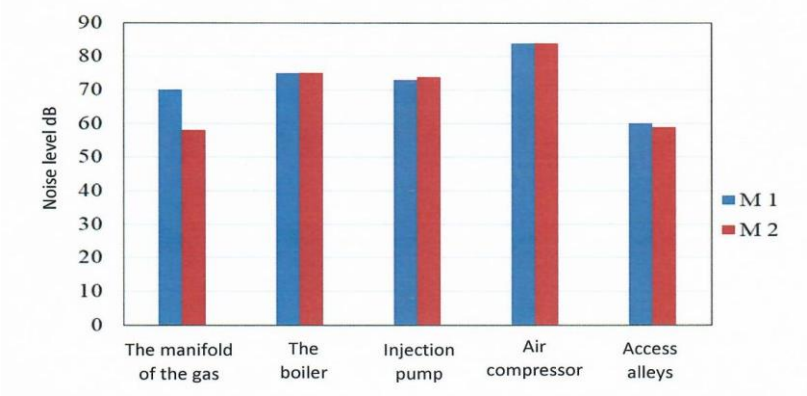

Fig. 7. *Noise level determination, in Park no. 11, Independence*

2.4. Noise analysis in the battery with boilers

The battery with boilers plays an important role in the treatment process, as it provides the hot water necessary for the fluidization of the oil. The two functional boilers produce sufficient noise, which determines a permanent supervision, by the employer, regarding the degree of noise pollution.

The result recorded after the monitoring, showed that the noise level was quite high, sometimes exceeding the alert threshold of 87 dB, provided by the regulations regarding the exposure limit for a nominal day of 8 hours.

Table 5. *Noise analysis in the battery with boilers*

The place where measurements are made	**Noise - dB**	
	M 1	**M 2**
Boiler no. 2	86	87
Boiler no. 3	84	84
Exposure limit value (according to GD 493/2006) for a normal working day of 8 hours	87	

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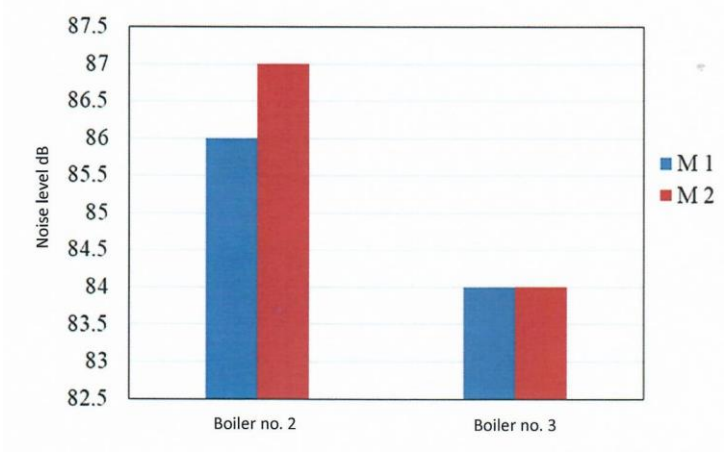

Fig. 8. *Noise analysis in the battery with boilers*

2.5. The measurement of noise due to traffic on the area

The traffic on the ring road was chosen, off the town of Schela was a paved road between two exploitation parks, and a paved road between the wells. The measurements were made over a period of two days, for each day, approximately 30 minutes for each road. During the 30 minutes, as long as the monitoring lasted, an average of the recorded results was made, both during the traffic and in its absence. For comparison, we scored M 1 with the average of the noise level during the traffic and M 2 with the average of its lack.

Table 6. *The measurement of noise due to traffic on the area*

The place where measurements are made	**Noise - dB**	
	M 1	**M 2**
The ring road of Schela commune	72	33
Gravel road, between wells	75	35
Paved road between parks	73	36
Stas 10009 - 88, Acoustics in construction; Urban acoustics – limits allowable at the noise level	65	

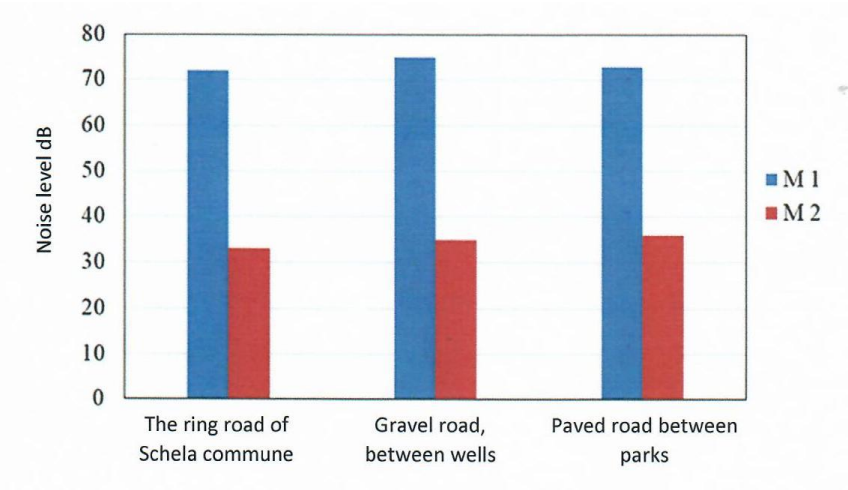

Fig. 9. *The measurement of noise due to traffic on the area*

As can be seen, the noise level produced by the road traffic exceeds the allowable limit value of 65 dB, outside the objective, provided by the law on construction acoustics and urban acoustics.

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2.6. Determinations of noise at the central warehouse (treatment area)

All the fluids extracted from the wells (crude oil and reservoir water) arrive through the parks, which pump the fluids through the pipes in the central warehouse (treatment area). Here, the fluids are first collected in the tanks, where the decanting process takes place, then, after the water has been removed, the remaining oil is subjected to the treatment process. For all these processes (treatment, directing of oil and reservoir water), pumps eliminating the fluids must be used.

Table 7. *Determinations of noise at the central warehouse (treatment area)*

The place where measurements are made		Noise - dB	
		M 1	M 2
Inside deposit	Near decanter	74	73
	At the heaters	73	73
	Between tanks	73	73
	At the skid	74	73
	Access alleys	73	72
Injection pump chamber		91	90
Recirculation pump room		81	81
Oil pump room		83	83
Exposure limit value (according to GD 493/2006) for a nominal day of 8 hour		87	

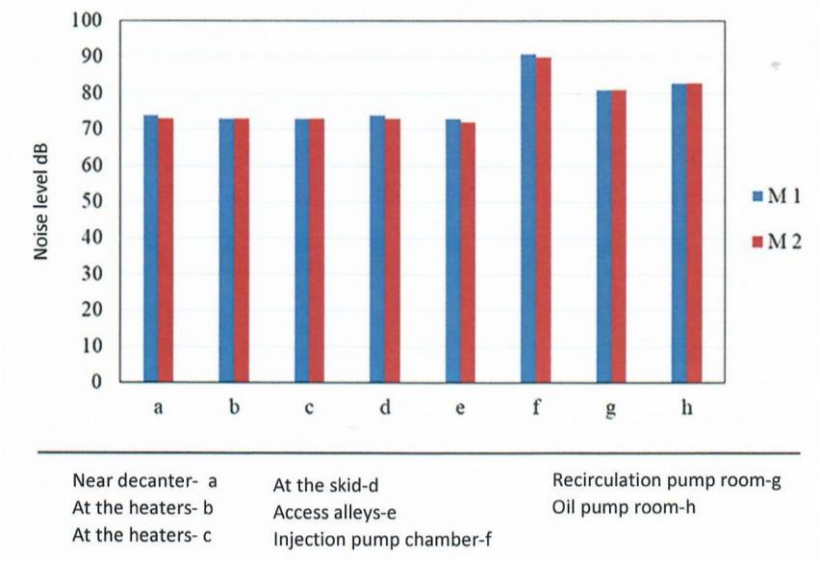

Fig. 10. *Determinations of noise at the central warehouse (treatment area)*

As a result of the noise monitoring process, the injection pumps, which operated at full capacity were observed to produce a high-level noise of 87 dB, during the 8 working hours, which was above the limit imposed by the regulation. For this reason, the employer provided the workers with noise protection equipment (antiphons).

3. Conclusions

The results obtained following the monitoring of the six objectives were compared with the Laws in force regarding the noise pollution: Decision no. 493 of 12.04.2006 [6] and the norms of Standard 10009 – 88 [7], respectively.

Based on the data regarding the acoustics of the noises, machines and means of transport, under normal operating conditions, the noise level relative to the nearest receiver (human settlements) is below the permissible noise values of 50 dB, according to the regulations in force.

Although there have been exceedances of the noise level in several analysed objectives, the risk of the workers' exposure is not high, because, the

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activity does not require permanent supervision. Hearing protection is used when necessary.

Under these conditions, a series of measures were taken, to limit to the impact caused by the noise pollution. These will decrease the degree of exposure of the workers. The residents are not exposed, because most of the wells, and absolutely all of the parks are located in the outskirts of the town, and the noises produced do not represent any threat to their health.

The level of exposure at workers is 87 dB for a period of 8 hours. If the exposure level exceeds the exposure limit value of 87 dB, the employer will have to ensure:

- individual means of hearing protection;
- technical means for noise reduction;
- the organization of the work so as to reduce the noise by limiting the duration and intensity of the exposure and to establish sufficient breaks during the work program.

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STUDY ON THE PERFORMANCE OF [PAC/PSf]-MIXED MATRIX MEMBRANE USED IN WATER FILTRATION

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ABSTRACT

The polysulfone used in membrane manufacturing showed low performances in wastewater treatment when compared with other special polymers. Researchers worldwide are trying to improve membrane performances through different techniques, such as: blending, grafting and surface chemical reaction, etc. [1]. Blending is an efficient technique with great performance and relative low cost compared with other means of membrane enhancement. All membranes were manufactured by phase inversion and the composite membrane solution was mixed with powdered activated carbon (AC). The activated carbon is used on a large scale in conventional wastewater treatment systems, having good antibacterial properties and high absorption degree of contaminants. The studied membranes were characterized as follows: flux, permeability, retention of Naphthol Green B (NGB) dye, contact angle and SEM microscopy. The permeability results of the composite membranes blended with activate carbon particles showed better performance than the neat membrane, with an increase of 15.384%. Contact angle increased after powdered activated carbon blending in membrane matrix.

KEYWORDS: Polysulfone, Activated Carbon, Membrane, Retention, Flux, Permeability

1. Introduction

Water pollution is one of the major environmental problems in the world. Many techniques methods are used for the treatment of polluted water, such as precipitation by chemical agent, adsorption on activated carbon, membrane processes (microfiltration, ultrafiltration, nanofiltration, reverse osmosis), etc. [1, 2].

Separation based membranes are suitable in many industries, such as the chemical [3], food and pharmaceutical industries [4], possessing important advantages, such as no by-product production, low temperature process and an exceptional cost/ efficiency ratio [5, 6].

Research in this area is increasing in order to continually optimize membrane performance [7, 8]. Increasing separation yield [7] and membrane flux [8] have been the target of many of these investigations [9]. A favourable scenario would be the possibility of increasing the membrane flux and its altogether separation [10].

Composite membranes have gained interest in research because of their combining at the same time properties of both polymer and filler.

Activated carbon (AC) is considered an important material, which is commonly used in water treatment activities.

The groups of organics that are generally adsorbed onto the activated carbon include pesticides, herbicides, aromatic solvents, polynuclear aromatics, chlorinated aromatics, soluble organic dyes, among more others [11]. Similar with nanoparticles, active carbon exhibits an extended surface area with a high degree of porosity [12]. AC is understood as a type of processed carbon particles with nano-micro volumes, meaning a high porosity, that results in a very high surface area (e.g. 500 m^2). For the activation of carbon particles, chemical treatments are often required for their good adsorption properties [13].

Activated carbon-blended membranes used for the experiments described in this article attest an enhancement in terms of permeability and retention.

As far as the authors knowledge is concerned, the attempt to blend activated carbon particles

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directly into the polymer matrix of a membrane has not been approached in literature.

2. Materials and methods

2.1. Materials

The polymer is polysulfone (PSf, average Mw~35000), the solvent is n-methylpyrrolidone (NMP, C_5H_9NO, 99%), both chemicals being purchased from Sigma-Aldrich.

Purchased from local provider, the activated carbon (AC) was in initial form of granules (GAC), with an average granule size of 1.948 mm, requiring a decrease in size so that it could be mixed in the polymer solution.

2.2. Powdered activated carbon (PAC) preparation

Due to their very large granular size, as shown in Figure 1.a, the GAC particles were being continuously ground (for 3 h) to decrease the size of the particles (Figure 1.b), and then they were mesh sieved, in order to eliminate the particles larger than 100 µm.

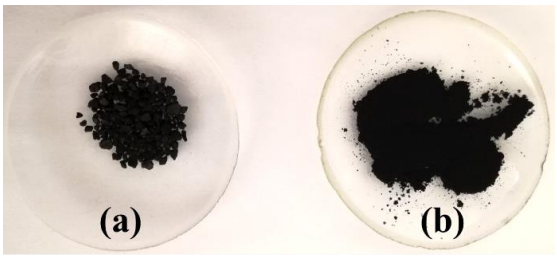

Fig. 1. *Activated carbon in form of: a) granules (GAC) and b) powder (PAC)*

The particle morphology and absorption capacity of NGB dye differences between GAC and PAC particles will be discussed.

2.3. Membrane preparation

The membranes referred to in this study were obtained by phase inversion, the immersion precipitation method.

The neat membrane casting solution was prepared by mixing the PSf polymer (25 wt%) with an NMP solvent solution at a constant temperature and under continuous stirring. For a homogeneous casting solution (Figure 2.a), stirring was being made for at least 24 h.

The AC blended membranes were prepared by adding 0.1 wt% of powdered activated carbon (PAC) in the corresponding volume of NMP for 1 h through continuous stirring at room temperature. The polymer was then added to the solution and stirring was made for at least 24 h (Figure 2.b).

After 24 h, the polymer solution was cast with 250 µm thickness using a film applicator (Automatic Film Applicator PA-2101, BYC-Gardner GmbH) on a very porous polyester as support layer. The casted solution was immersed in a distilled water bath in order to start the phase inversion process.

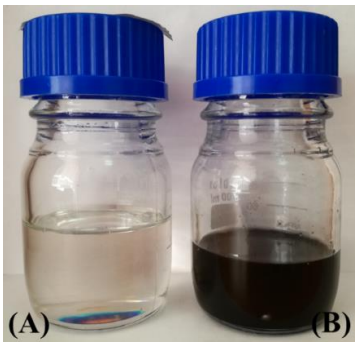

Fig. 2. *Membrane solution after 24 h of continuous stirring for (A) neat PSf and (B) PSf blended with 0.1 wt% PAC*

Table 1. *Membrane characterization by concentrations*

Membrane	*PSf concentration [wt%]*	*PAC concentration [wt%]*
Neat_PSf	25	-
PSf_0.1_AC	25	0.1

The resulting membranes (Table 1) were washed with distilled water and stored wet, until they were used as samples for characterization.

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3. Characterization methods for membranes and activated carbon powder

3.1. SEM analysis

Sample surface and particle morphologies were investigated using the FEI Quanta 200 Scanning Electron Microscope, after coating with gold by sputtering.

3.2. Characterization of GAC and PAC particles

The size and distribution of activated carbon particles (GAC and PAC) were estimated from SEM images using ImageJ software (https://imagej.nih.gov/ij/). An example of ImageJ software particle analysis is shown in Figure 3.

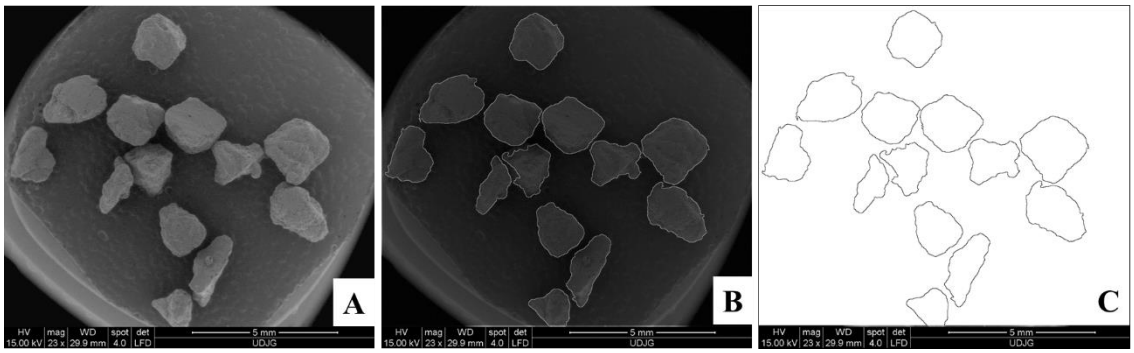

Fig. 3. *Steps in identifying and analysing particles using ImageJ software: (A) SEM image as-received uploaded in the software; (B) Particle identification; (C) Background subtraction for a clearer understanding of particle form*

For a precise determination of activated carbon particle size, a number of 500 particles (for PAC) and 100 particles (for GAC) were measured in terms of circularity, with the Heywood diameter and Feret's diameter (Table 2).

The size of GAC and PAC particles were determined through two widely used methods: the first method was by assuming that the AC particles were perfect spheres, method known as the Heywood diameter, thus finding the diameter with the following equation [14-17]:

$$A = \pi r^2 \quad (1)$$

where A is the particle area, the number π is a mathematical constant and r is the radius of the theoretic-spherical particle.

The Feret's diameter was used as a second measuring method, defined as the distance between two opposite parallel tangents of a particle image, as presented in Figure 4 [14, 16, 17].

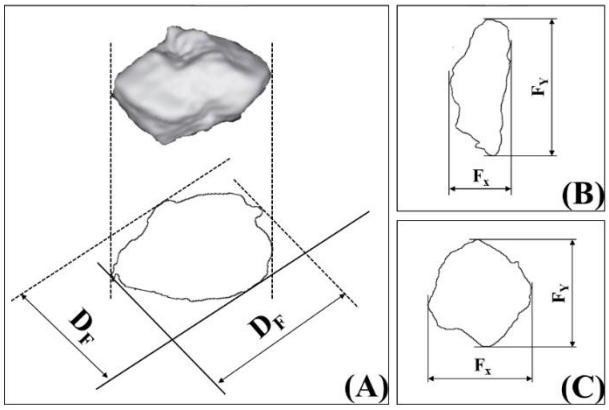

Fig. 4. *Example of particle size analysis with Feret's diameter: (A) 3D projection of a particle; (B) illustration of horizontal (Fx) and (C) vertical (Fy) Feret's diameters of a particle*

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The projection from 3D object on a 2D plane is often used as a measuring technique in particle size analysis [15, 16].

3.2. Contact angle measurements

The hydrophilicity/hydrophobicity property of the samples was evaluated using a goniometer (OCA 15EC, DataPhysics), consisting in the measurements of contact angle between a water drop and the studied membrane surface.

3.3. Permeation tests

All permeation tests (pure water flux, permeability, retention, relative flux and relative flux reduction) were conducted in a dead-end stirred cell (Sterlitech HP4750) with 300 mL total volume and membrane surface area of 14.6 cm^2. The cell is connected to a nitrogen tank in order to create pressure for the liquid to be forced through the membrane.

Pure water flux J_0 (L/m^2 h) was measured using the gravimetric method and was determined by:

$$J_0 = \frac{V}{A \cdot t} \quad (2)$$

where V is the volume of the permeate water (L), A is membrane effective area (m^2) and t is permeation time (h).

Water permeability experiments were carried out with pure water at operating pressures ranging between 6 and 12 bar at room temperature (approx. 25 °C).

The slope of the linear regression of J_0 on Δp was determined as the pure water permeability P_w (L/m^2 h bar), which was calculated using the following expression:

$$P_w = \frac{J_0}{\Delta p} \quad (3)$$

where Δp is the operating pressure (bar).

3.4. Retention tests

The dye of choice is NGB. It is a green nitroso dye used for industry purposes, such as staining wool, nylon, paper, anoxidized aluminum and soap manufacturing [18]. The molecular weight of NGB dye is 878.45 g/mol.

The NGB dye rejection ratio was calculated by the following equation:

$$Retention\ [\%] = \left(1 - \frac{C_f}{C_0}\right) \times 100 \quad (4)$$

where C0 represents dye concentrations in feed solution (100 ppm) and C_f is the permeate concentration. Concentrations were determined spectroscopically using HACH DR 5000 UV-Vis Spectrophotometer (Hach, Germany) device.

3.5. Relative flux

Fouling is evaluated with a relationship of relative flux, which is the ratio of retention flux of NGB dye at any time during the fouling test to the initial flux, calculated with the following equation:

$$RF = \frac{J_r}{J_0} \quad (5)$$

The retention flux J_r [L/m^2 h] is similar with the pure water flux, except that feed subjected to filtering is NGB dye solution of 100 ppm.

In literature, in order for a membrane to have high anti-fouling properties, the relative flux must tend to value 1. If the relative flux tends more towards the value 0, the membrane is rapidly fouling, thus decreasing the production filtered water [19-22].

3.6. Relative flux reduction

The Relative flux reduction, RFR, is calculated as follows:

$$RFR = \left(1 - \frac{Jr}{Jw}\right) \times 100 \quad (6)$$

In simple terms, the RFR method shows how much fouling occurred at the end of filtration.

4. Results and discussions

4.1. Morphology of GAC and PAC particles and NGB dye absorption capacity

The Electron microscopy is a direct method described in the standards approved by ISO [23] and recognized by Health Agencies to perform size measurements and particle size distribution [17].

As shown in Figure 5.a, the GAC particles are of different sizes and irregular shapes, with an average circularity of less than 0.8 (Table 2).

After grinding the GAC particles, the size is reduced considerably, obtaining fine and very fine particles of activated carbon (Figure 5.b and 5.c).

Figure 6 represents the particle size distribution for GAC and PAC particles.

The size distribution of GAC particles (Figure 6.A) is in the range of 1000-3000 μm, with an

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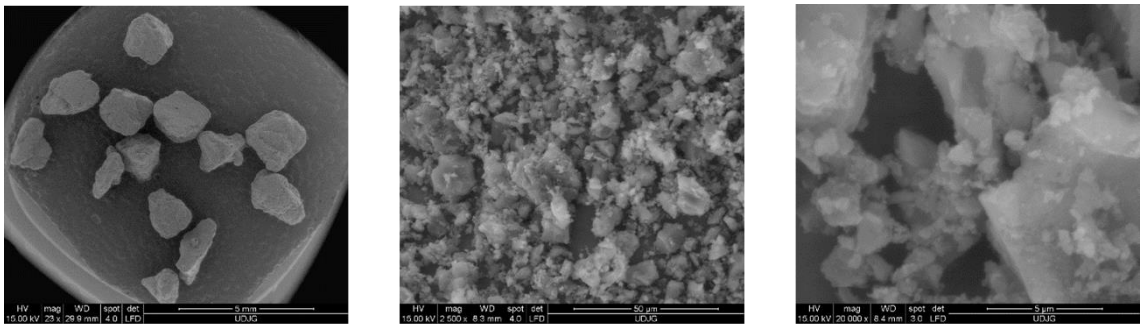
average Feret's diameter of 1948.585 µm (1.948 mm).

When analysing the size distribution of PAC particles, Figure 6.B, it can be seen that most counts were in the 0-20 µm interval, with over 400 counts out of 500. Magnifying the graph to the 0-10 µm interval, 56% of the total numbered particles are less than 2 µm in size, meaning that the grinding process was effective, as it can be seen in Figure 5.b and Figure 5.c.



(a) **(b)** **(c)**

Fig. 5. *SEM image for: (a) GAC particles, magnification 23X and PAC particles at two magnifications, (b) 2500X and (c)20000X*

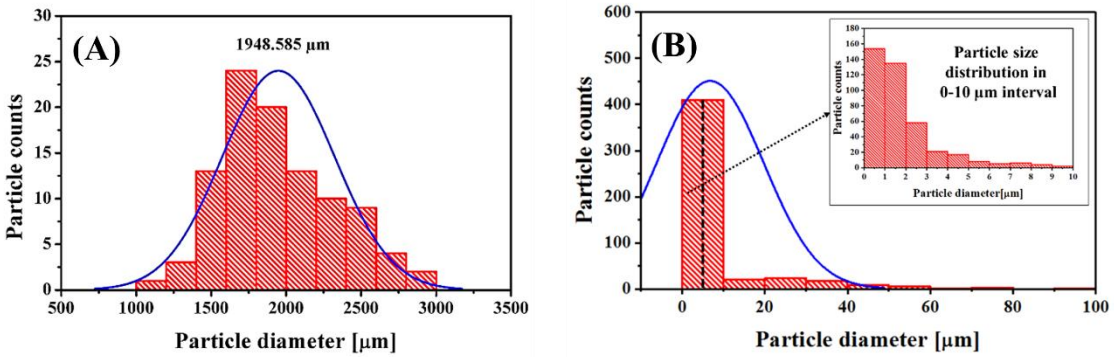


Fig. 6. *Particle size distribution for (A) GAC particle and (B) PAC particles*

Table 2. *Total particle counts, sizes and circularity for GAC and PAC particles*

Activated carbon form	Total particle counts	Heywood diameter [µm]	Feret's diameter [µm]	Circularity
GAC	100	1566.274	1948.585	0.798
PAC	500	6.661	8.565	0.784

According to the American Society for Testing and Materials (ASTM D5158), particle sizes of 0.177 mm (177 µm) and smaller are classified as powdered activated carbon with the acronym PAC [24].

Both the GAC and PAC particles maintain the same form, approved by the average circularity of both types (Table 2).

The size reduction of GAC particles after grinding was approximately equal for the two methods of diameter measuring, of approximately 99.5%, from 1948.585 µm to 8.565 µm, for Feret's diameter method, and from 1566.274 µm to 6.661 µm, for the Heywood diameter method, respectively. The PAC/GAC ratios were similar for the Heywood diameter and Feret's diameter, at a value of 0.004.

Grinding the active carbon granules in order to reduce it to an acceptable size to be mixed in the polymer solution improved the performance of the active carbon in terms of NGB dye absorption. 0.1 g of both activated carbon forms were immersed in a 100 ppm dye solution for one day.

After one day it was observed that the activated carbon powder had absorbed 100 % of the dye solution, while the granulated activated carbon had absorbed only 67% (Figure 7), because of the low surface area which came in contact with the dye solution.

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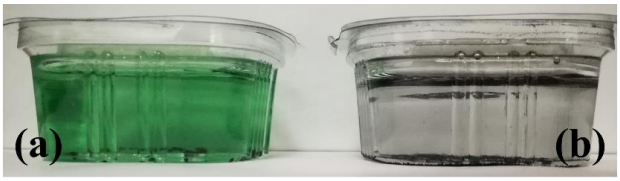
In general, decreasing the particle size leads to an increase in active surface area (m^2/g) [25, 26]. Higher surface area of the activated carbon increases the absorption capacity of dyes, evidenced by Figure 7. It is of great interest that the size of particles to be as small as possible.

Reducing the activated carbon particle size will lead to improved membrane performance.



NGB absorbed: 67% **NGB absorbed: 100%**

Fig. 7. *Absorption of NGB dye after one day for: a) 0.1 g of activated carbon granules; b) 0.1 g of activated carbon powder*

4.2. Membrane characterization with SEM observations

Figure 8 shows the influence of the activated carbon on the membrane surface morphology. Regarding the pore size, the neat membrane shows larger, irregular shaped pores leading to low permeability and flux. Consequently, the decrease in pore size, due to activated carbon addition, the composite membrane will show a better retention of NGB.

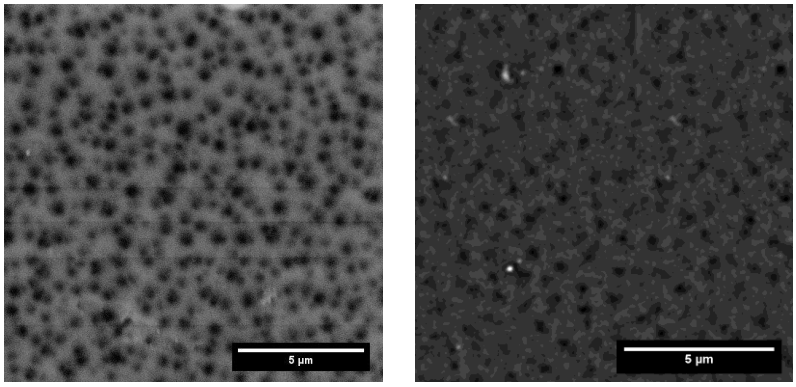


Fig. 8. *Top-view SEM images of neat PSf membrane (left) and activated carbon-blended membrane (right)*

4.3. Contact angle

The contact angle data of PSf-activated carbon membrane is shown in Table 3. The contact angle of the neat PSf membrane surface was lower compared to the AC-blended membrane. However, AC-blended membrane showed a higher water contact angle of 77.637°, which indicated that the activated carbon is hydrophobic, suggesting that the PAC particles changed the polarity of membrane surface from hydrophilicity to hydrophobicity. The hydrophobicity of the activated carbon is reported by other authors, also [27, 28].

Table 3. *Contact angle, permeability, dye retention and relative flux reduction measurements of the studied membranes*

Membrane	Contact angle [°]	Permeability [L/m^{2}h bar]	NGB dye retention [%]	RFR [%]
Neat_PSf	71.4	14.9	47.8	27.4
PSf_0.1_AC	77.6	15.5	56.8	22.2

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Also, the contact angle measurement is a good criterion in approving the presence of activated carbon particles at membrane surface.

4.4. Permeation tests

Distilled water flux was determined by timing from 5 to 5 mL the filtered solution. Values are displayed in Figure 9 in order to study the membrane stability. The neat membrane shows an average flux of 149 L/m^2 h.

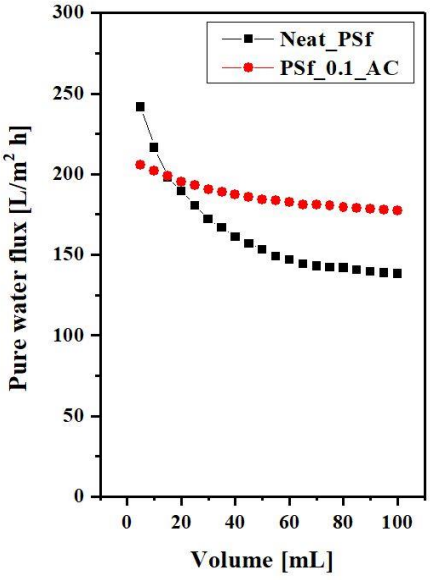

Fig. 9. *Pure water flux for neat membrane and activated carbon blended membrane*

Adding 0.1 wt% activated carbon powder in the membrane matrix increases the flux with 19%. Correlating the lower flux value with the top-view SEM images of the neat membrane, it appears that the irregularity in pore size distribution creates membrane instability over time. In terms of flux stability, the composite membrane displays a better result. Also, the composite membrane shows a 20.8% higher permeability than the neat membrane (Table 3). The retention is proportional with permeability, with an increase of 20.4% (Table 3).

The relative flux is usually used for the comparison of relative membrane antifouling performance [29, 30]. A high relative flux results in higher antifouling ability [31]. Low values (below 0.75) of relative flux indicated that neat polysulfone membranes have poor antifouling ability when comparing with the composite membrane (with a 0.78 relative flux value).

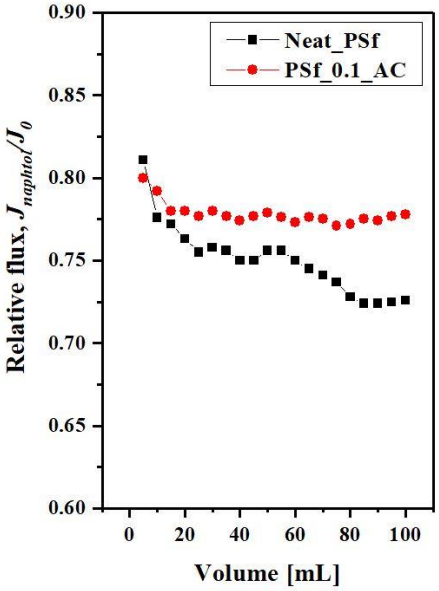

Fig. 10. *Relative flux of pristine membrane and activated carbon composite membrane*

The changing trends in the relative flux of membranes are shown in Figure 10 which demonstrates that the fouling resistance of modified membranes increases, when activated carbon is incorporated in the membrane. An explanation is the fact that the dye deposition on the membrane surface is lower because of the activated carbon ability to absorb dyes, thus cleaning the membrane's surface during the filtration process.

4.5. Relative flux reduction

Table 3 shows the relative flux reduction of the membranes, also. The relative flux reduction is an important membrane investigation tool for the finding of the membrane with the lowest value, meaning that the respective membrane has the highest antifouling ability.

As expected, the neat PSf membrane shows the highest fouling with 27.4%, while the activated carbon blended membranes show a relative flux reduction of 22.2%.

5. Conclusions

The results of this research show that activated carbon particles at low concentration have a positive influence on the PSf membranes. The composite membrane exhibits better properties in terms of flux stability and flux (20.805 % increase), permeability (15.384% increase) and retention (20.408% increase). The presence of activated carbon in the membrane matrix increase the contact angle with 8.45%.

Although the relative flux reduction difference between the neat and composite membrane is low (5%), it is an acceptable proof that the activated carbon powder enhances membrane performances, even with its relatively larger size particles when compared with state-of-the-art nanoparticle blended membranes. Further research is required to determine the optimal concentration of activated carbon addition, but also a study on the influence of the activated carbon particle size in the polymeric membranes.

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DIELECTRIC CHARACTERIZATION OF S_iO_2-PMMA ORGANIC – INORGANIC HYBRID THIN FILMS

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ABSTRACT

For the research presented in this paper, hybrid organic-inorganic materials were prepared using a modified sol-gel reaction.

Hybrid organic-inorganic compounds were synthesized in ethanol using methylmethacrylate (MMA), SiO_2 nanoparticles, and 3-trimetoxi-silil-propil-methacrylate (TMSPM) as coupling agent. For the deposition of thin films, the spin-coating method was used.

The electrical measurements of dielectric thin films were done using a metal-insulator-metal (MIM) devices fabricated to study the dielectric constant of the films as function of frequency (measured at 1 MHz). Electrical results show a weak trend of the dielectric constant of the hybrid films with different MMA molar ratio. More importantly, the PMMA-SiO_2 hybrid films showed a higher dielectric constant than SiO_2 and PMMA layers, due to the presence of additional C-O-C bond. For the calculation of dielectric permittivity, the thickness of thin films was measured using cross-section SEM micrographs and the value of dielectric permittivity was calculated using electrical capacitance formula.

KEYWORDS: thin films, dielectric, PMMA-SiO_2, nanoparticles

1. Introduction

Thin-film transistors (TFTs) based on hybrid materials present great interest for different potential applications in portable devices, sensors, radio-frequency (RF) identification tags, smart cards, and backplane circuits for active matrix displays and flexible electronics among others. In the latest years, the technology has been focused on the development of new materials, which can be easily processed at low temperature in different large-area of applications, which are compatible with different substrates for transparent flexible electronics.

The dielectric gate used in flexible devices requires a lot of conditions to be promising materials.

The transistor parameters critically depend not only on the thickness and the dielectric properties of the gate insulator but also on the interface formed between dielectric and semiconductor layers, where the trapped charge has strong influence on the device electrical behaviour [1].

Recently, SiO_2, TaO_2, Ta_2O_5, ZrO_2 and HfO_2 transition metal oxides were demonstrated as premise for high-k dielectric materials in submicron range technology [2, 3].

The SiO_2-PMMA hybrid system was synthesized using the sol-gel method [4, 5]. The sol-gel process is one of the most convenient methods to achieve the proper linking between the organic and inorganic phases at the molecular scale. Furthermore, the sol-gel route is suitable to produce a multi-functional hybrid.

The hybrid materials could provide the following advantages over organic polymers for optical waveguide applications: (1) The incorporation of the inorganic moiety into polymer matrix could improve the thermal and mechanical properties; (2) the incorporation of inorganic moiety decreases the C-H bonding density in the waveguide materials and thus reduces the optical loss; (3) the large polarizability difference between the organic and inorganic moieties possibly induces an increase of the anharmonicity of the C-H bond and thus the NIR spectra could be shifted for the optical window of the used light source [6].

Although the SiO_2 thin films are limited in utilisation as dielectric gate due to the band gap which increase to 9eV. In different condition of utilisation, the thin film became semiconductor, that is why is used in combination with MMA that in the presence of UV light it turns into in PMMA. The

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presence of new C-O-C bond decrease the energy band gap. To have dielectric properties the thickness of thin films must be under 100 nm. Here is report the first attempts of fabrication bellow 160° C of hybrid thin films containing silica oxide nanoparticles by modified sol-gel route in which a 3-trimetoxysilylpropyl methacrylate (MPS) coupling agent is used to have a good interaction between the SiO_2 nanoparticles and methylmethacrylate monomer. SiO_2 was used as precursor for the inorganic (oxide) part and methyl methacrylate (MMA) as precursor of the organic polymeric component. The molar ratio between SiO_2 and the polymethyl methacrylate was adjusted to ensure the adherence, flexibility and good dielectric properties of the films.

2. Experimental

2.1. Preparation of sols and thin films

SiO_2 nanoparticles, 3-trimetoxysilylpropyl methacrylate 98% (MPS), methylmethacrylate 99% (MMA) and absolute ethanol 99.99% (Et-OH) purchased from Sigma-Aldrich were used for the preparation of hybrid films.

For the sol preparation, the silicon dioxide was dissolved into absolute ethanol at room temperature. The MPS coupling agent and the methyl methacrylate monomer was added successively.

For the dielectric film deposition, two sol compositions corresponding to SiO_2:MMA molar ratios of 1:1 and 4:1 were prepared (Table 1). Each sol was aged at 50 °C until it became transparent and provided good viscosity for the film deposition. The resulting homogeneous solution was spin-coated onto cleaned n-doped silicon substrates, covered by sputtering with a tantalum layer of 100 nm thickness. The post-deposition treatment of films consisted in 10 minutes hot plate thermal treatment at 160 °C and exposed at UV radiation (λ = 254 nm) emitted by an H 466.1 UV lamp. For electrical characterization, aluminium contacts (~300 nm in thickness) with different areas were evaporated through a shadow mask on top of the hybrid dielectric film.

Table 1. *Investigated samples*

Sample symbol	**Molar ratio** SiO_2:PMMA/number of layers	**Thickness of the film** (nm)	**Capacitance, C** (F) $*10^{-10}$ (medium value)	ε_r
P1	(1:1) /1 layer	170	4.3	1.9
P2	(1:1) / 2 layers	330	4.1	4.7
P3	(4:1) / 1 layer	220	3.5	2.3
P4	(4:1) / 2 layers	400	3.2	4.5

2.2. Thin films characterization

The surface and cross-section morphology of the hybrid films were investigated by scanning electron microscopy (SEM) using an EOL JSM-7500F/FA microscope and by high resolution transmission electron microscopy (HR-TEM) using a Tecnai TM G2 F30 S-TWIN microscope equipped with a STEM/HAADF detector.

The I-V and C-V curves of the hybrid films were measured by including them into a Metal-Insulator-Metal (MIM) structure (Fig. 1), using Agilent 4156 and HP 4277A Analysers, respectively, at 1 MHz.

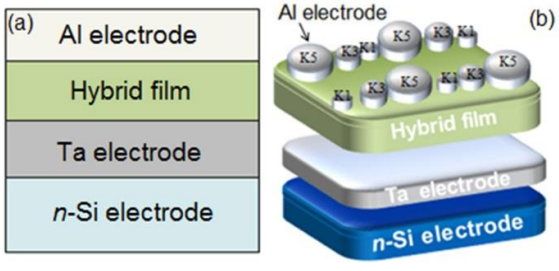

Fig. 1. *Schematic representation (a, b) of MIM structure used for the measurement of I-V and C-V characteristics of thin films*

3. Results and discussion

The hybrid thin films of SiO_2-PMMA, deposited with 1 and 2 layers had the thickness value between 250 and 400 nm, respectively. SEM images onto thin films surface, deposited with one layer shows a non-homogenous, discontinuous aspect regarding the distribution of nanoparticles, a high roughness of the

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film consisting of agglomerates porous and not uniform of spherical particles embedded in the polymeric mass. In these agglomerates formed by the embedding of spherical SiO_2 we can distinguish the spherical form of initial nanoparticles.

The roughness determined by the presence of nanoparticles affects the structure of aluminium electrodes deposited by thermal evaporation for electrical measurements (Figure 2-6).

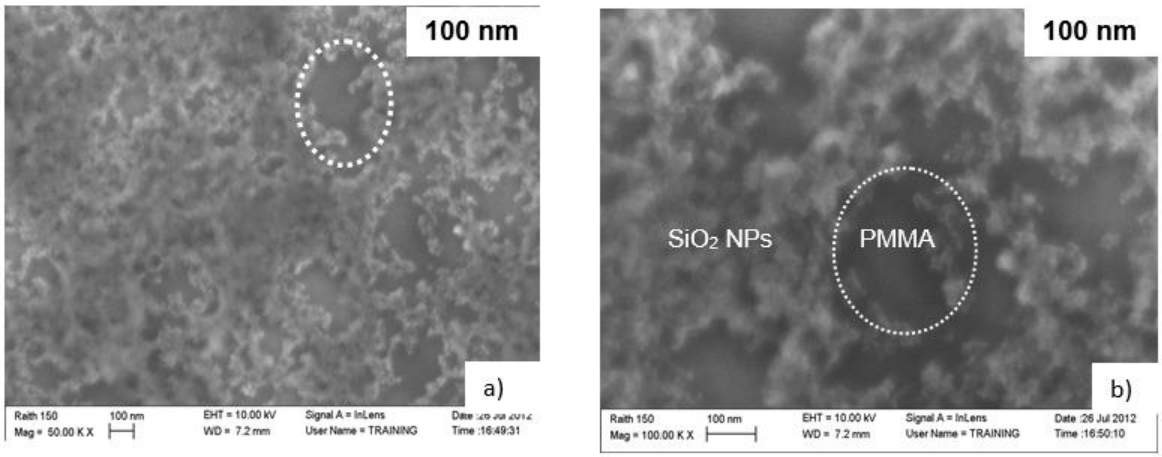


Fig. 2. *SEM images top-view of SiO_2-PMMA (1:1) 1 layer (a) and detail (b)*

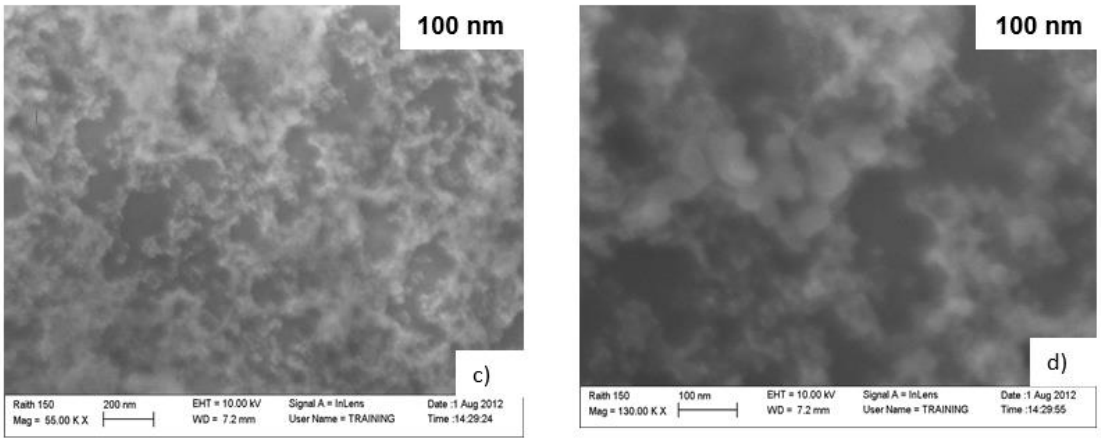
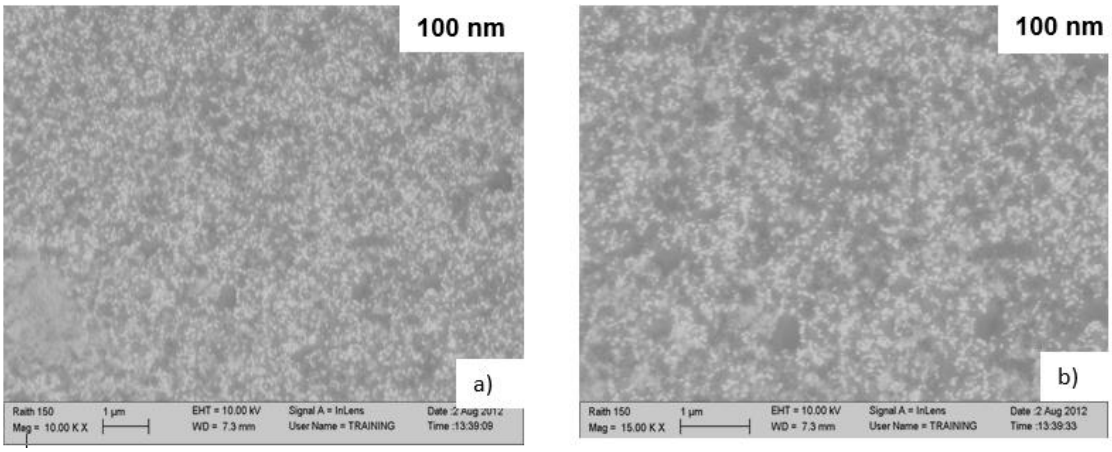


Fig. 3. *SEM images top-view of SiO_2-PMMA (4:1) 1 layer (a) and detail (b)*



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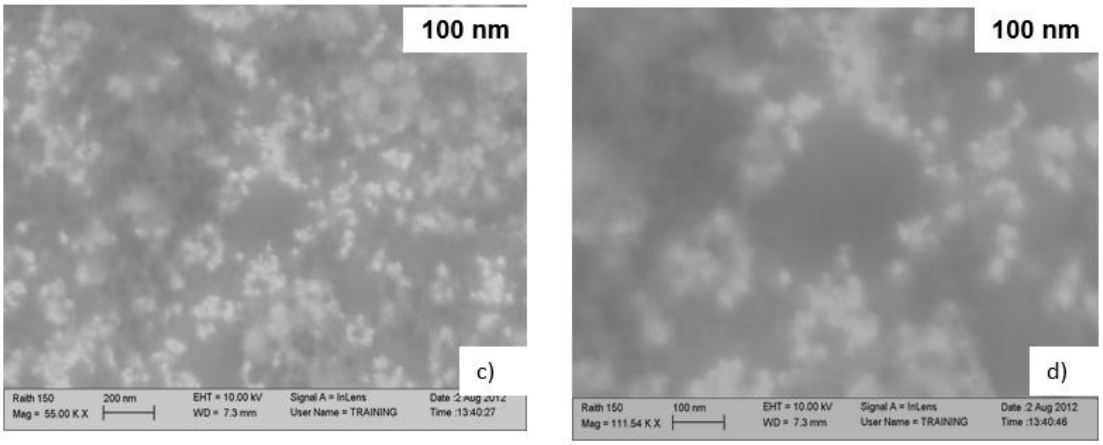

Fig. 4. *SEM images top-view of SiO_2-PMMA (1:1) 2 layers (a) and detail (b-d)*

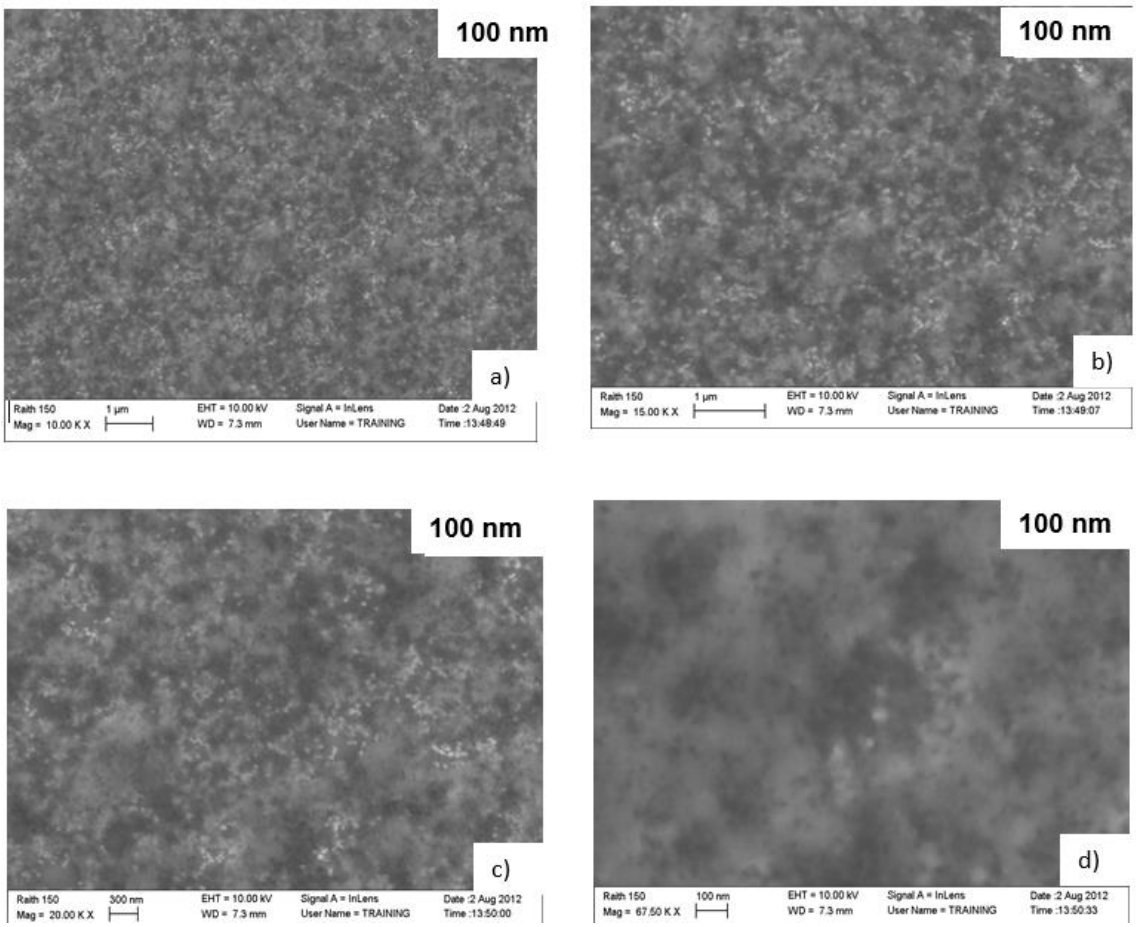

Fig. 5. *SEM images top-view of SiO_2-PMMA (4:1) 2 layers (a) and detail (b-d)*

The SiO_2-PMMA films deposited with two layers, 1:1 and 4:1 molar ratio shows a higher degree of coating with oxide nanoparticles of substrate surface. However, the increase of the nanoparticle concentration caused the porosity and non-uniformity in the film thickness (Fig. 6).

As we can observe in Fig. 6, the increase of roughness affects the Al electrodes structure deposited onto thin film surface by the thermal evaporation for the electrical properties.

The thickness of the films is thinner for (1:1) than for (4:1) molar ratio, about 200 and 470 nm, respectively, because the higher concentration of SiO_2

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provides higher sol viscosity and roughness. For both films, the SEM images show a morphology without phase separation between the organic and inorganic components. The roughness of the thin film layer determines the irregularity of Al electrodes.

Fig. 7 shows the I–V characteristics of the investigated films, at gate voltages from 4 to +4 V. The leakage current density is ranging from 10^{-6} to 10^{-1} A/cm^2 and from and 10^{-6} to 10-2 A/cm^2 in the case of 1:1 and 4:1 molar ratio, respectively. Further studies are considered to correlate the dielectric behaviour of films with the effect of temperature and duration of post-deposition thermal treatment.

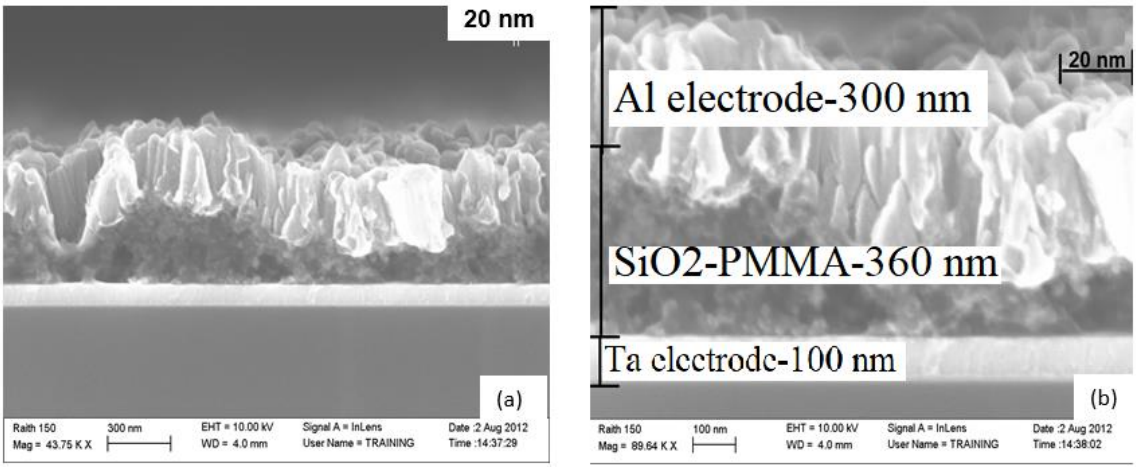

Fig. 6. *SEM images top-view of SiO_2-PMMA (4:1) 2 layers (a) and detail (b)*

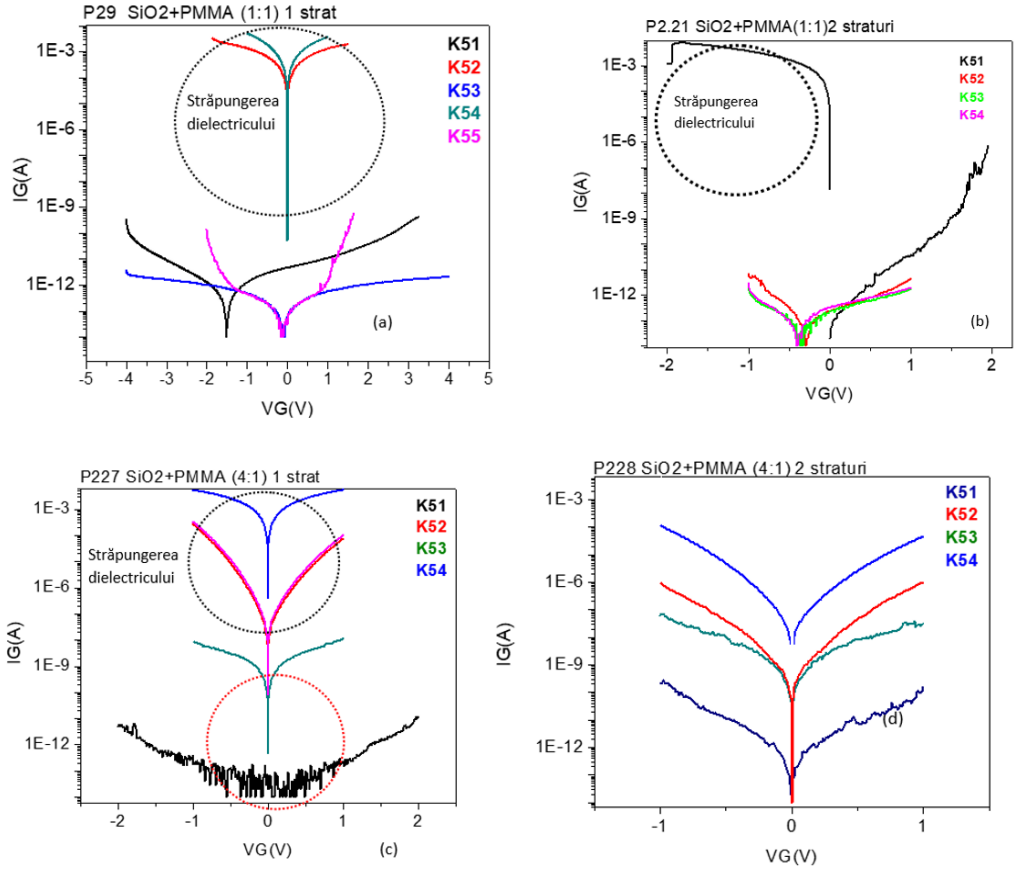

Fig. 7. *I-V characteristics for SiO_2:PMMA-1:1 (1 layer and 2 layers) and SiO2-PMMA -4:1 (1 layer and 2 layers)*

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From the C–V curves of the investigated films, the dielectric constant was calculated. The values of 1:1 and 4:1 molar ratio hybrid film was determined from the C–V measurements in the voltage range from -15 to +15 V, at 1 MHz. The dielectric permittivity of a material is proportional to its electronic polarization. Materials with polar groups (i.e. C=O, OH) usually have large dielectric constants due to the orientation of their electrical dipoles in the electric field. Taking also into consideration the fact that the hydroxyl group has the highest molar polarization [4, 20], by adding different molar ratio of the precursor, the dielectric constant increases from about 1.9 to 4.5 with increasing the SiO_2:MMA ratio from (1:1) to (4:1).

4. Conclusions

SiO_2:PMMA hybrid dielectric thin films for flexible electronics were successfully prepared by sol-gel methods below 200 ºC. SiO_2 nanoparticles were embedded in amorphous matrix and the dielectric properties were determined for films with 1:1 and 4:1 molar ratio. The use of 3-trimetoxysilylpropyl methacrylate (MPS) as coupling agent improves the compatibility between the organic and inorganic phases, it allows obtaining homogeneous and roughness thin films without phase separation. The I-V curves show a leakage current between 10^{-12} and 10^{-9} A, and a constant capacitance in bias range ± 15 V. Dielectric constant of 4.5 was obtained for the hybrid films with 4:1 molar ratio. Further investigation will be continued to establish the conditions required to prepare stoichiometric nanocrystalline SiO_2 phases from alkoxide precursor embedded into polymer matrix.

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AUTOMATIC IDENTIFICATION OF FLYING BIRD SPECIES USING COMPUTER VISION TECHNIQUE FOR ECOLOGICAL DATA ANALYSIS

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ABSTRACT

The aim of this study is to propose a bird detection algorithm. Bird detection is useful for the counting and dynamics of bird study. Neural networks are used for bird detection and the first step is to learn to classify bird species based on previous experiments. We further develop a proof of concept for the meta-data fusion which indicates that the fusion of elevation data can be used to increase the accuracy of the model, and to decrease its coverage error, in particular.

KEYWORDS: bird detection, automatic, computer vision

1. Introduction

An area of interest in environmental studies is monitoring animal populations to better understand their behaviour, to determine population dynamics [1-3]. Birds can be automatically recognized and/or classified using the latest computer vision technologies. The aim of this study is to propose a bird detection algorithm, created for bird recognition. Bird detection is useful in bird dynamics and counting. Neural networks are used for bird detection and the first step is to learn to classify bird species based on previous experiments [4]. Several fields need birds' detection.

Bird species are an important biodiversity indicator able to describe changes in sensitive ecosystems and, therefore, counting bird populations and their behaviour analysis are a quantifiable method to determine levels of changes. Birds can be monitored by ecologists to determine population fluctuations and to assess biodiversity.

A large number of technical challenges emerge in the visual analysis technologies in natural environments. These include challenges concerning light variation, variation of distance to the objects to be detected, robust object detection, tracking objects in crowded environments. Also, there are many challenges in tracking articulated bodies, such as in the case of birds with the aim of birds' detection [5]. Artificial intelligence algorithms combining computer vision technologies generate reliable results, though errors cannot still be eliminated.

The object classification has been a major interest of research in the computer vision and machine learning communities during the last years, and a lot of progress has been made in developing algorithms and techniques [6-8]. The concern in the topic of detection of objects, a variety of techniques have been issued and many datasets are available for use as training for artificial intelligence techniques. These techniques include feature encoding methods, such as the Fisher vectors (FV) and the Histogram Encoding through to the more recent developments of deep learning algorithm [9-10].

Authors used the motion detection though these methods may however require important computational resources, but simpler methods, such as the background subtraction is working even on low computational power, such as the embedded system and the Raspbery Pi is preferred to others. One of the traditional motion detection algorithms used for tracking objects has been the Kalman Filter.

In many studies the main goal was to be able to track birds and count it. For our case, tracking the bird is necessary for further analyse trajectory. In our case, we store the past information and calculations concerning the speed and trajectory, when new image frames come in from the video footage [10-11].

The aim of this study is to propose a bird detection algorithm. We further develop a proof of the concept for the meta-data fusion, which indicates that fusion of elevation data can be used to increase the accuracy of the model, and decrease its coverage error, in particular.

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2. Experimental procedure

The field experiment was carried out in Galati, near the Danube River, where there is an important amount of bird species. For monitoring bird activities, a spot towards the Danube was chosen with the elevation of 30 degrees of camera point of view towards the sky, where bird's activities were relatively high. Videos were recorded at 1080p as the birds were relatively small and generally far away from the cameras. Two GoPro Hero 4 cameras were installed at the four corners of the field. Videos were recorded at 30 frames per second during the morning hours from 7:00 am to 9:00. The experiments were conducted between September 20 and 25 in the year of 2019. The conceptual steps for application are described in Fig. 1.

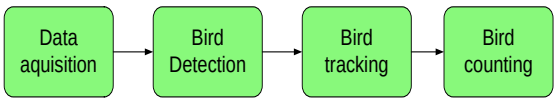

Fig. 1. *Steps for the application*

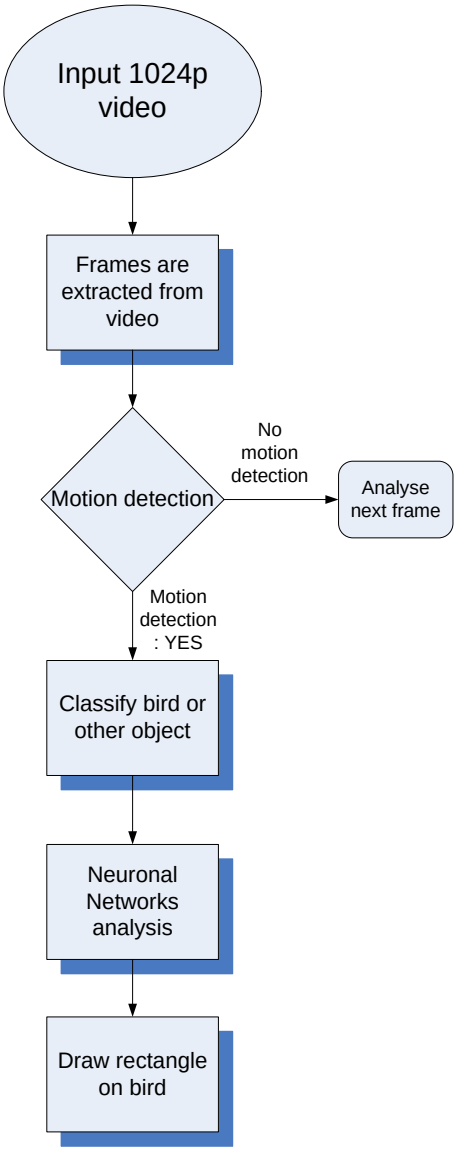

Fig. 2. *Algorithm for bird recognition*

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The data acquisition is the first step, followed by bird detection, which is the topic of the present paper. The bird tracking and counting are used to produce the data for ecology purposes. We used as online processing a laptop with i3-8145U processor, 8 GB RAM. As development environment we used Visual Studio along with OpenCV library.

The neural library we used is Keras. The algorithm for bird recognition is taking into account motion detection in order to detect object in the scene to be analysed (Fig. 2). Not all of the moving objects in the sky are birds. Airplanes or even clouds happened to be detected as moving objects.

The neuronal networks analysis is able to classify the objects and exclude those that are not birds. The birds are marked with a rectangle (Fig. 4 and 6), regardless of the wing positions.

Fig. 3. *Cameras Field of View*

Fig. 4. *Detection of bird*

Fig. 5. *Detection of bird*

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3. Results and discussions

To be able to store shape, for a later study concerning bird species detection, we store shape for several frames, until the bird is out of the focus of camera. Many improvements could be made in motion concerning the mathematical morphology analysis, taking into account the wings dimensions and the motion to be done on the binary images. The neuronal networks have been trained using morphology operators in order to compensate imperfections to the potential "blobs" that represent moving objects. The morphology operators are taking into account bird position in flight. These positions were generated using real images of bird flying.

This approach also might better result as it allows for birds to be detected as separate birds and avoid the situations when multiple regions of the bird moving are detected as bird.

Results showed that the detection rate is up to 97% and false positive are very low, under 4%, in case of scene depicting random objects. We also need to note that the experiments were conducted during clear sky during morning.

We further develop a proof of the concept for the meta-data fusion, which indicates that fusion of elevation data can be used to increase the accuracy of the model and decrease its coverage error, in particular.

4. Conclusions

Neuronal networks along with computer vision allows development of reliable results for bird detection. Possible ways forward are to tune the hyper parameters of the neural networking information concerning the weather status (rain, air pressure, humidity, position of the sun).

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