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MICROCONTROLLER USAGE TO STUDY VARIATION IN pH SOLUTIONS IN CONTACT WITH BIODEGRADABLE METALLIC MATERIALS

BY

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Abstract. In this article the authors present the obtaining of a pH sensor based on Arduino modules. We present the main components of the analysed system, parts of the acquisition program code and the component elements. We perform a critical analysis about the advantages of non-stop monitoring of a solution pH using cloud storage possibility, possible applications. Many metallic materials (for example biodegradable alloys) modify the pH environment after a short time of contact through the chemical reactions with the environment. Modification of solutions pH in different environments can be used as a sensor for many applications. The reaction time at pH modification is based on the probe sensibility and the analyze equipment.

Keywords: pH solution; biodegradable materials, analysis; Arduino modules.

1. Introduction

Metallic biodegradable materials represent a new orientation in the medical field, as well as in materials science, combining aspects of

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biocompatibility, bone regeneration correlated with structural analysis, mechanical and corrosion properties. The term “biodegradable material” is recognized worldwide as defining degradable metal biomaterials for medical applications, having experienced accelerated exploitation in recent decades.

Magnesium is a biodegradable metallic material, with the mode of elasticity closer to all biomaterials than the human bone, thus avoiding the appearance of the “stress shield” effect, a phenomenon that occurs mainly in the implants of steel, Co-Cr and titanium alloys (ysi.com/ysi-blog/water-blogged-blog/2015/02/). Magnesium is the fourth cation in the body, Mg2 + being a basic compound for human body metabolism and is also a good nutrient. Classic orthopaedic metal biomaterials greatly help increase the life span of physically traumatized patients, especially the elderly. These implants have two major disadvantages, namely the high longitudinal elasticity and the need for secondary surgery to remove the implant after it has fulfilled its task.

Magnesium is a low specific weight element, having a good vibration damping capacity and a high thermal conductivity. The major disadvantage of this element is the high speed of degradation, which is an impediment for the surgical interventions. Another problem is the release of localized hydrogen, the patient forming temporary subcutaneous inflammation. To improve these impediments, the researchers identified two major directions: by combining magnesium with biocompatible elements and not only, and also by making superficial deposits on the surface of magnesium alloys, constituting a barrier between the tissue and the basic material.

After using stainless materials, Co-Cr-based alloys and titanium biomaterials, which also show a number of shortcomings, the researchers turned to the 3rd generation of biomaterials; Mg-based alloys have proven to be particularly attractive and interesting to study in order to obtain a new class of biocompatible, biodegradable materials. Their purpose is to establish temporary implants, biodegradable in the human body, the main feature being the absence of a new surgery, in order to remove the implant.

The history of biodegradable magnesium implants (Table 1) began immediately after the element was discovered by Sir Humphrey Davy in 1808. The commercial production of metal magnesium by electrolysis was carried out by Robert Bunsen in 1852, which created a small laboratory cell for electrolysis of $MgCl_2$ (Zheng *et al*., 2014).

The major advantage, offered by Mg alloys, which brought Mg to the forefront of research attention, is its adequate mechanical properties, compatible with human bone, its biocompatibility, as well as a corrosion rate that could match the rate for healing the bone tissue. From a physiological point of view, Mg is an essential element in human metabolism and is the 4th most widespread cation in the human body, with an estimated 25 g Mg being stored in the human body, and about half of the whole amount is in the bone tissue. Also, Mg is a co-factor for about 300 enzymatic reactions that occur in the human body and is found in the structure of DNA and human RNA (http://www.romedic.ro/ hipomagnezemie).

Table 1
Selective Reports of Magnesium and Biomedical Applications

Year	Mg (Alloy)	Application	Human/animal model
1878	Mg-pure	Connection wires	Human
1892-1905	High purity Mg	Tubes, wires, plates	Human, Guinea pigs, rabbits and dogs
1903	Mg-pure	Magnesium cylinders as connectors for blood vessels	Dogs
1924	Mg-pure, distillate in vacuum	Wires, plates	Rabbits
1938	Mg-Mn3%; Mg-Al4-Mn0.3%;	Wires, prostheses, screws, tapes	Human, dogs
1951	Mg-Al2%	Wires for coagulation aneurysms	Dogs
1981	Mg-pure	Wires for the treatment of hemangioma	Mice, rabbits

Following previous research in the field of metallic biomaterials and orthopaedic implants, it was considered that biodegradable magnesium alloys are the best solution for the implantation of the implants used in ankle and foot surgery, as well as of the hand and fist, that is, of the small joints of the extremities. The magnesium alloys studied so far, as implant materials, are largely commercial alloys that have been developed for the transportation industry.

Magnesium is an alkaline-earth metal and is therefore only found in combination with other elements. It is found in large deposits of magnetite (magnesium carbonate), dolomite and other minerals, for example talc.

Pure magnesium has a melting point of 650°C (923°K) and a boiling point of 1,090°C (1,363°K). It falls in the category of light metals, having a density of 1,738 kg/m^3, being about 1.6 times less dense than aluminium, 2.6 times less dense than titanium and 4.5 times less dense than steel. The tensile strength of magnesium is higher than of ceramic biomaterials such as hydroxyapatite, while the modulus of elasticity and tension of magnesium flow are closer in value to human bone than the other metallic materials used in osteo-synthesis (Witte, 2008).

a *b* *c*

Fig. 1 – Different forms of production of magnesium and its alloys: *a*, *b* – powder and *c* – bar.

The electrical conductivity of magnesium is lower compared to other metals, such as titanium, ρel = 22.6 μΩ × cm, compared to 55 μΩ × cm of long distance copper titanium, which has a resistivity of 1.7 μΩ × cm. Table 2 presents the main physical and mechanical properties of pure magnesium.

Table 2

Physical and Mechanical Properties of Pure Magnesium

Property	Value
Atomic number	12
Atomic weight (g/moll)	24.3
Crystalline structure	Hexagonal
Density	1,738 kg/m^3
Melting point	650ºC
Boiling point	1,090ºC
Specific heat (la 298 K)	1020 J/kgK
Thermal conductivity	160 W/mK
Electrical conductivity	23 MS/m
Hardness (HRB)	260 MPa
Shear resistance	17 GPa
Flow resistance	65 MPa
Elasticity module	45 GPa
Friction coefficient	0.6 in dry environment 0.08 in a lubricated environment
Poisson coefficient	0.290
Thermal expansion coefficient	24.8 $\mu m \cdot m^{-1} \cdot K^{-1}$

The biocompatibility and the rate of degradation of magnesium-based alloys can be improved by two methods, once by developing alloys with various elements, and by two by depositing thin layers which constitute a barrier between the basic material and the physiological environment. Table 3 presents the main alloying elements of magnesium-based alloys used in biomedical applications.

Table 3
The Main Alloying Elements for Magnesium-Based Biomedical Alloys (Witte, 2008)

Chemical element	Technological aspects	Patofiziological/toxicological aspects
Aluminum	Improves mechanical strength and ductility (hardness of solid solution, precipitation, refining of structure), corrosion resistance and casting ability.	Contributes to stabilizing the alloy elements of titanium alloys; May lead to the destruction of muscle fibers; Susceptible to the occurrence of Alzheimer's disease; 2.1,…,4.8 mg/L – Normal level of Al in the blood.
Calcium	Improves mechanical strength (hardness of solid solution, precipitation, refining of structure) and fluage resistance; reduces the casting ability.	The most widespread mineral in the body; It is mainly found in bone tissues; It is controlled by homeostasis, renal and intestinal skeletal mechanism; 0.919-0.993 mg/L – Normal Ca level in the blood.
Lithium	Reduces mechanical strength, but improves ductility (it turns into a BCC structure); reduces corrosion resistance and density.	Can produce malformations; Dysfunctions of the kidneys and lungs in high concentrations; 2,…,4 ng/g – normal Li level in the blood.
Manganese	Improves mechanical strength and ductility (refining the structure); improves creep resistance; improves corrosion resistance in combination with aluminum.	At high concentrations has neurotoxic character; Contributes to immune system functions, bone growth and blood clotting; Decisive factor in the metabolic circuit of carbohydrate and amino acids < 0.8 μg/L – normal Mn level in the blood.

Table 3
(*Continuation*)

Chemical element	Technological aspects	Patofiziological/toxicological aspects
Rare earth (including Yttrium)	Improves creep resistance and high temperature resistance (hardness of solid solution, precipitation) improves corrosion resistance; reduces mechanical anisotropy.	Several rare elements offer anti-cancer properties.
Silicon	Reduces ductility; improves creep and high temperature resistance; reduces corrosion resistance and casting ability.	
Strontium	Improves mechanical strength and ductility (refining the structure); improves creep and high temperature resistance	
Zinc	Improves mechanical strength, but reduces ductility at high concentrations (hardness of solid solutions, precipitation); improves the casting ability.	Trace element; Immune system element required; At high concentrations is neurotoxic; 12.4-17.4 μmol/L-normal level of Zn in the blood.
Zirconium	Improves mechanical strength, ductility and resistance to high temperatures (sharp refinement of the structure) in the absence of aluminum.	

In general, the alloying elements introduced into the magnesium alloys contribute to the improvement of the various properties. The presence of the alloying elements in the solid solution leads to increasing the hardness of the alloy. At the same time, these elements form with magnesium intermetallic compounds that mainly contribute to refining the microstructure and resistance of the alloy. Impurities that occur frequently in magnesium alloys are: iron, nickel, beryllium and copper. Typically, the maximum concentration of impurities in magnesium alloys can reach up to approximately 0.3%. The pH feature (hydrogen potential) represents the decimal logarithm with a changed sign of the concentration of hydrogen ions in a solution, indicating its acidic or basic character. The notion of pH is expressed quantitatively the acidity (or basicity) of a substance, based on the concentration of ions called hydronium

H_3O +. For experiments, we chose to build our own pH-meter using a microcontroller called the Arduino Nano and a PH-4502C sensor, along with an E-201-BNC probe.

A microcontroller is a "computer on chip" designed and optimized to perform control functions for certain electronic devices. This, from a performance standpoint, is inferior to a "computer on the processor", but it excels on the interaction side with the sensors. There are several types of microcontroller, of which we can enumerate Arduino (Uno, Mega, Mini, Leonardo), NodeMCU, STM32, PIC32. We're going to use Arduino Nano (Fig. 2).

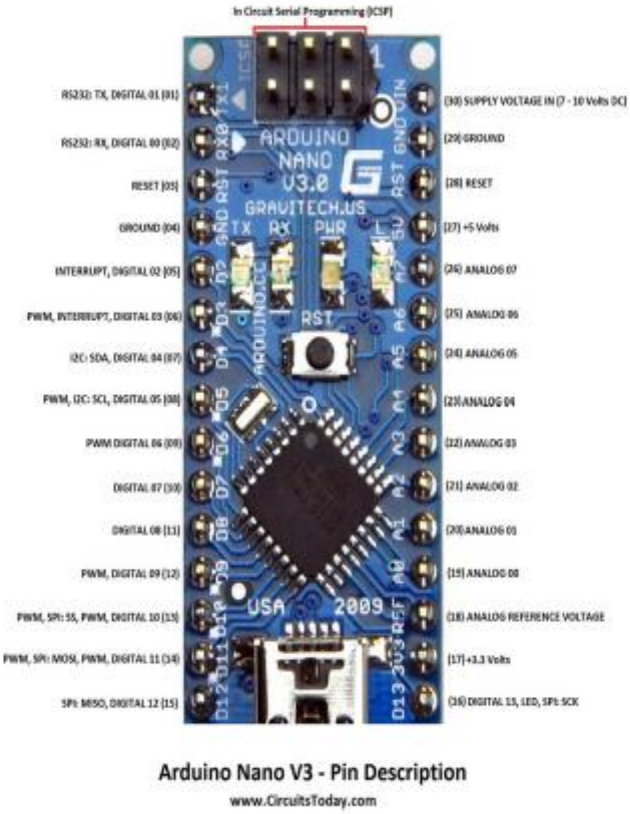


Fig. 2 – Development card Arduino Nano V3 (https://www.circuitstoday.com/category/arduino).

Main Features: Microcontroller: ATmega328, Architecture: AVR, Operating Voltage: 5 V, Flash Memory: 32 KB, SRAM: 2 KB, Clock Speed: 16 MHz, Analog IN Pins: 8, EEPROM: 1 KB, DC Current per I/O Pins: 40 mA, Input Voltage: 7,…,12 V, Digital I/O Pins: 22, PWM Output: 6, Power Consumption: 19 mA and PCB Size: 18 × 45 mm (https://en.wikipedia.org/wiki/ATmega328).

```
#include <Wire.h>
#include
<LiquidCrystal_I2C.h>
LiquidCrystal_I2C
lcd(0x27, 2, 1, 0, 4, 5, 6, 7, 3,
POSITIVE);
#define phPin A0
#define tempPin A1
#define
rezistorThermistor 10000
float phValue=0;
int tempValue = 0;
int probe=0;
int interval = 0;
//Variable for timer
long lastTime = 0;
long minutes = 0;
long hours = 0;
int sensorValue = 0;
unsigned long int
avgValue;
float b;
int buf[10],temp;
void setup() {
  //Initialisers text
  initializationLCD();

initializationSerialMonitor();

Serial.println("nr;pH;Temperature;ti
me"); //Cap tabel serial
  takeValue();
  //Preluare prima valoare
  printSerial();
  //Printare prima valoare
}
void loop() {
  timer();
  takeValue();
}
void timer(){
  if(millis()-lastTime >
60000){
    minutes++;
    if(interval == 0){
      printSerial();
    }
    lastTime = millis();
  }
  if(minutes > 60){
    Hours++;
    minutes = 0;
    if(interval == 1){
      printSerial();
    }}}
```

```
void takeValue(){
  //pH
  for(int i=0;i<10;i++) {

buf[i]=analogRead(phPin);
    delay(10);
  }
  for(int i=0;i<9;i++){
    for(int j=i+1;j<10;j++){
     if(buf[i]>buf[j]){
        temp=buf[i];
        buf[i]=buf[j];
        buf[j]=temp;
      }
    }
  }
  avgValue=0;
  for(int i=2;i<8;i++)
  avgValue+=buf[i];
  float
pHVol=(float)avgValue*5.0/1024/6;
  phValue = -5.78 *
pHVol + 22.88;
  //Temperature
  float tempValueRaw;
  tempValueRaw =
analogRead(tempPin);
  tempValue =
tempValueRaw;
   delay(1000);
   printValueLCD();
}
void printValueLCD(){
  lcd.clear();
    lcd.setCursor(0,0);
  lcd.print("pH:");
  lcd.print(phValue);
    lcd.setCursor(0,1);
  lcd.print(hours);
  lcd.print(":");
  lcd.print(minutes);
  lcd.print(":");
  lcd.print(millis()/1000);
    lcd.setCursor(11,0);
  lcd.print("t:");
  lcd.print(tempValue);
    lcd.setCursor(11,1);
  lcd.print("p:");
  lcd.print(probe);
}
void printSerial(){
  probe++;
  Serial.print(probe);
```

```
  Serial.print(";");

Serial.print(phValue,2);
  Serial.print(";");

Serial.print(tempValue);
  Serial.print(";");

Serial.print(hours);
  Serial.print(";");

Serial.println(minutes);
}
void
initializationLCD(){
  lcd.begin(16,2);
  lcd.backlight();

lcd.setCursor(0,0);
  lcd.print("    pH
Meter    ");

lcd.setCursor(0,1);
  lcd.print("    SIM
2019    ");
}
void
initializationSerialMonitor(){

Serial.begin(9600);

Serial.println("pH Metru");

Serial.println("SIM 2019");
}
```

(https://www.botshop.co.za/how-to-use-a-ph-probe-and-sensor/)

Corrosion resistance tests can be achieved by implanting experimental samples in a SBF solution at 37°C for 24, 48 and 72 hours. The immersion enclosure (Fig. 3*a*), is thermo-static (37°C) and allowed the return the samples position at 180° every 12 hours. Samples must be weighed before and after each period of immersion using a digital balance partner (Fig. 3*b*). After weighing the experimental samples these are cleaned in a solution of technical alcohol in an ultrasonic bath Nahita (Fig. 3*c*) for removing the unstable compounds from the surface.

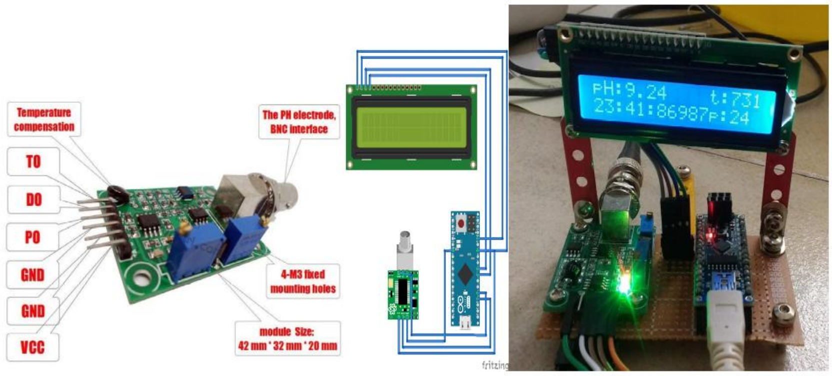
a *b* *c*

Fig. 3 – Equipment used in the immersion corrosion resistance test:
a – thermostatic enclosure; *b* – digital balance and *c* – ultrasonic bath.

The samples were weighed before and after each period of immersion using a digital balance Partner (Fig. 3*b*). After weighing the experimental samples they were washed in a technical alcohol solution in an ultrasonic bath Nahita (Fig. 3*c*) for removal of unstable compounds from the surface. Fig. 4 shows a developed plate for the acquisition of pH values: a) mini-Arduino, pH sensor and display input scheme, b) pH transducer and digital display.

Potentiometric Ph-meters measure the tension between two electrodes, and display the result transformed into a pH corresponding value. They comprise a simple electronic amplifier and a pair of electrodes, or alternatively a combination of electrodes, and a type of display calibrated in pH units. Usually it has a glass electrode and a reference electrode, or a combination of electrodes. Electrodes, or probes, are introduced into the solution to be tested. Depending on the pH of the solution that is in contact with the probe, the sensor sends a certain voltage to the P0 pin, Arduino retrieves that voltage in the Analog0 pin (A0) and converts it to analog signal (0–1,024). To retrieve the pH value, we need to transform that analog signal back into tension with the formula: Analog Signal * 5.0/1024/6 = Tension. After this, this tension shall be applied to a function derived from a straight line. For this, we must use 2 solutions of pH established, one of 4.01 and another of 6.89. According to the manufacturer's specifications, for the pH value of 4.01 we should obtain a voltage of 3.04 V, take for the pH of 6.86 we should get a value of 2.53 V. Due to a problem with the sensor regulator potentiometer, it is not possible to reach such a value, but the values are close and as observed are directly proportional.

With these dots, it builds on the graphic a straight line, and calculates the distance from the y axis and the slope of the straight (offset and slope). To find the pH, the voltage calculated above must be entered in the function of the line (this is y = offset + slope * x), Fig. 5 (Slope + offset * tension = pH value). (https://scidle.com/how-to-use-a-ph-sensor-with-arduino/).



a *b*

Fig. 4 – Developed plate for the acquisition of pH values consisting of *a*) mini-Arduino plate, pH sensor and display input (https://www.botshop.co.za/how-to-use-a-ph-probe-and-sensor/), *b*) pH transducer and digital display.

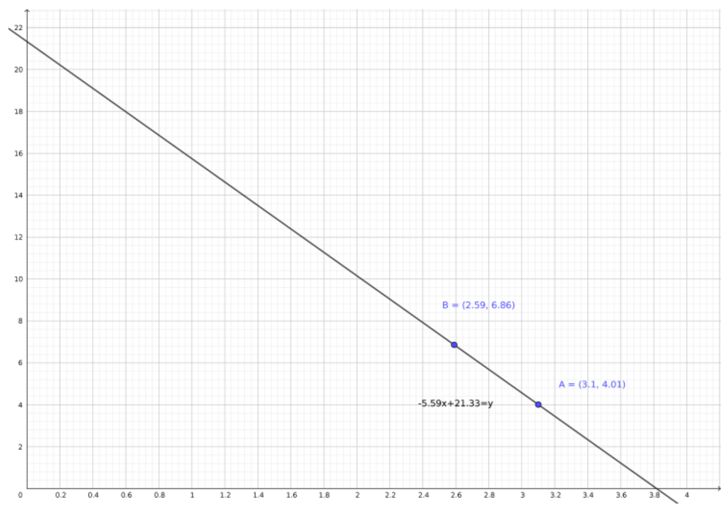


Fig. 5 – Determination of the parameters necessary to transform the experimental stresses into pH values.

For taking over the pH, the microcontroller will provide 10 pH samples and from these, will delete the maximum values and will average the rest of the values.

3. Conclusions

Biodegradable alloys have more and more applications in the medical field. Following the interaction with the biological media, for example a SBF solution, magnesium-based alloys interact intensely from the first hour of immersion forming on the surface a layer of compounds based mainly on oxides. The interaction between the alloy and the liquid medium leads to a change in the pH of the solution over time. This change was recorded using a mini-Arduino development board that retrieved the data from a digital pH transducer connected via a BNC jack to a pH probe. The results were transferred in real time to a computer where the recorded data were processed and interpreted. It is proposed to create a program, a possibility being the Java programming environment, for the acquisition of data from the Arduino work interface and their automatic storage in a file as well as the implementation of a Rasberry Pi3 system for computer replacement.

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UTILIZAREA MICROCONTROLLER-ULUI
PENTRU STUDIUL VARIAŢIEI SOLUŢIILOR DE pH ÎN CONTACT
CU MATERIALE METALICE BIODEGRADABILE

(Rezumat)

În acest articol autorii prezintă obţinerea unui senzor de pH bazat pe module Arduino. Prezentăm principalele componente ale sistemului analizat, părţi din codul programului de achiziţie şi elementele componente. Autorii au efectuat o analiză critică

cu privire la avantajele monitorizării non-stop a pH-ului unei soluţii folosind posibilitatea de stocare în cloud dar şi alte aplicaţii posibile. Multe materiale metalice (de exemplu, aliajele biodegradabile) modifică mediul de pH după un timp scurt de contact prin reacţiile chimice cu mediul înconjurător. Modificarea pH-ului soluțiilor diferite poate fi utilizată ca senzor pentru multe aplicaţii. Timpul de reacţie la modificarea pH-ului se bazează pe sensibilitatea sondei, echipamentul de analiză şi prgramul realizat.

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OBTAINING AND CHARACTERIZATION OF GEOPOLYMERS SUITABLE FOR HEAT PROCESSING EQUIPMENT'S

BY

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Abstract. By looking back into our history as human beings, we can easily observe that the world has become more dependent on energy, now more than ever. With a crowder and an increasingly polluted planet, we have reached the point where we must take any measure, no matter how insignificant it may seem, to reduce the pollution of the planet, stopping the consumption of natural resources in order to obtain the energy that sets us in motion. In order to, researchers have understood that the need to develop new ways to save energy and raw materials, in the same time, stopping pollution, is critical for our future. Inspired by the natural geosynthesis of earth, scientists have developed a new material, called geopolymer. This new material is achieved by combining a hard material (with high percentage of aluminosilicate) to an alkaline solvent, together with other constituents, technique that is called geopolymerisation. This material is presenting great properties and can be used in a wide diversity of products starting from a ceramic brick to a reentry shield of space shuttle. This article, is intended to be a brief review of geopolymers and its uses, and few considerations, for which believe, the possibility of using a geopolymer as refractory material.

Keywords: eco-friendly materials; geopolymers; refractory materials; thermal characterisation.

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1. Introduction

As our society is growing at a rapid rhythm (global population is around 7.8 billion people) the need for energy conservation and waste reduction has become more and more critical. Due to the fact that the industrial sector is one of biggest consummator of energy and resources (Singh, *et al*., 2019), therefore one of the biggest polluters (Vardhan *et al*., 2019), the reuse of waste for new materials developing becomes a society must.

A mineral waste which presents significant interest in the last decades is fly ash (Zerfu and Ekaputri, 2016; Lahoti *et al*., 2019). This is a silico-aluminium or low calcium waste (Ostwal and Chitawadagi, 2014), that can be used in multiple applications, primarily in construction industry (Aldred and Day, 2012), *e.g*. concrete, pavements, recipients for containment and immobilization of radioactive wastes (Vereshchagina, 2018), refractory ceramics (Lahoti *et al*., 2019; Bernal *et al*., 2012; Vilches *et al*., 2005) and because of its elemental structure, a source of geopolymerization reaction. Due to these properties fly ash gives great mechanical strength (Jindal, 2019) and good fire (Luna-Galiano *et al*., 2015) and chemical resistance (Burduhos Nergis *et al*., 2018; Albitar *et al*., 2017), which gives a boost to creativity and further applications.

2. What is a Geopolymer?

According to the literature (Davidovits, 1991; Davidovits, 2002; Duxson *et al*., 2006), the geopolymers term was introduced in 1976 by Joseph Davidovits, and defines an alkali aluminosilicate binder. These materials have been originally intended and developed as a fire-resistant material alternative to organic thermosetting polymers after a series of unfortunate fires in Europe (Davidovits *et al*., 2019). The transformation of kaolinite into tridimensional tecto-aluminosilicates used for the polycondensation of organic resins at low temperature is very similar with the thermosetting method of these materials (Duxson *et al*., 2006). The nanocomposite that results from the process looks like an artificial rock, also named by J. Davidovits, “man-made rocks” (Luukkonen *et al*., 2018).

Since cost and final product properties are the most important parameters, researchers identify a wide variety of waste material to choose from, such as: metakaolin (Hao *et al*., 2015), red mud (Lemougna *et al*., 2017), fly ash (Longhi *et al*., 2019) etc. Considered to be a green material (Liew *et al*., 2017), the production of geopolymers emits only 169 kg CO_2/m^3 compared to Portland cements that release 306 kg CO_2/m^3 at the same characteristics (Zerfu and Ekaputri, 2016), therefore, it presents a decrease of the emission of about CO_2 45%.

3. How are Geopolymers Obtained?

Geopolymers are obtained by mixing a rich in aluminium and silicone oxides solid material (aluminosilicate) with an alkaline solution and other constituents (Burduhos Nergis *et al*., 2019), depending on the desired properties. The base material can be a natural mineral (Bondar *et al*., 2011), *e.g*. clay, kaolinite etc. or "waste" materials (Embong *et al*., 2016) such as fly ashes, slags, red mud etc. The activation solution is usually based on sodium (hydroxide or silicate) or potassium (hydroxide or silicate) which are soluble alkali metals (Burduhos Nergis *et al*., 2018).

The curing time is short, during the first hour a man can walk on the geopolymers concrete surface, after 4 hours a car can be drive on it, while after 6 hours it is ready for a commercial jet to land on it (Davidovits *et al*., 2019). Sialate, an abbreviation for silicon-oxo-aluminate, consists of SiO_4 and AlO_4 tetrahedra linked by sharing all the oxygens (North and Swaddle, 2000).

Geopolymerization, takes place in three major stages: dissolution, where the solid part of material (alumino-silicates) dissolves due the presence of water and alkali activator presence; the reorientation, where changes take places at atomic level; and solidification, when most of the water is eliminated (at 20°C or up to 1,000°C) and the final form of the geopolymeric material is obtained (Xu and Van Deventer, 2002). Due to its fast synthetization geopolymers have been introduced in multiple applications, especially to its refractory characteristics.

4. What are Refractory Materials?

Refractory materials are those natural or artificial materials, that are able to withstand at high process temperatures without melting (in excess of 1,000°C), and have low thermal conductivity (Lahoti *et al*., 2019). Other than this main characteristics, refractory materials must have high mechanical and thermomechanical properties, with high corrosion resistance, to function like a barrier between the walls of heat chamber and the hot charge, in the same time preserving the process heat.

Refractory products can come in preformed shapes or unformed compositions-also called monolithic refractories; as refractory ceramic fibers-that resemble with home insulation, but much higher insulation temperature; as for the majority production of refractory products, ceramic bricks. As for shapes and sizes, they can be small and complex with delicate geometry; others, can come in blocks, precast or fusion-cast blocks, that are massive and could weigh few tons (Parmar *et al*., 2018).

The most used refractory materials are these based on aluminium (alumina), silicon (silica) and magnesium (magnesia); also, calcium oxide (lime) and fire clay-that presents interest at large scale (Parmar *et al*., 2018).

Starting from a simple ceramic brick, to the sophisticated reentry shields for the space shuttle, it is right to assume that without refractory materials the world as we know would not exist. In some way, refractory materials are essential to any of industrial operation that include high temperature processes.

Refractory materials can be considered 'energy-concentrated' materials; using more monolithic materials and less high-fired bricks provide energy conservation in refractory production. Even so, the entire cycle starting with production of the material and its application, must be considered, as highly energy-consuming refractory materials may be preferred if they save energy in their application due its long life. Therefore, by development of nano graphitized black containing MgO-C bricks carbon emissions can be decreased, while the thermal shock resistance, corrosion and oxidation resistance are significantly improved.

5. Conclusions

Refractory materials development starts form a trial-and-error approach, using natural materials as base materials, into a high innovative industry, which use composite oxide-carbon-metal systems; it has grown to meet the iron and steel industry and become a vast territory of research, with an evolution process far from complete. Geopolymers presents an increasing interest as a high-quality material within refractory applications, due to their excellent mechanical properties, durability, abrasion resistance, chloride diffusion rate etc. Moreover, any source of aluminosilicate can be used for this material, such as fly ash, metakaolin or common clays.

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OBŢINEREA ŞI CARACTERIZAREA GEOPOLIMERILOR DESTINAŢI ECHIPAMENTELOR PENTRU PRELUCRĂRI LA CALD

(Rezumat)

Privind înapoi în istoria noastră ca fiinţe umane, putem observa cu uşurinţă că lumea a devenit dependentă de energie, acum mai mult ca niciodată. Cu o planetă din ce în ce mai populată şi poluată, am ajuns la punctul în care trebuie să luăm orice măsură, oricât de neînsemnată ar părea, pentru a reduce poluarea planetei, în special prin oprirea consumului de resurse naturale folosite pentru obţinerea energiei, care ne pune în mişcare. În acest sens, cercetătorii au înţeles că nevoia de a dezvolta noi modalităţi de a economisi energie şi materii prime este esenţială pentru viitorul nostru. Inspiraţi de geosinteza naturală a pământului, oamenii de ştiinţă au dezvoltat un material nou, numit geopolimer. Acest material este obţinut prin combinarea unui material dur (cu un procent ridicat de aluminosilicat) cu un solvent alcalin, precum şi alţi constituenţi, printr-o tehnică cunoscută sub numele de geopolimerizare. Geopolimerii prezintă proprietăţi deosebite şi pot fi utilizaţi într-o mare varietate de produse, pornind de la o cărămidă ceramică până la un scut de reintrare în atmosferă al unei navete spaţiale. Acest articol prezintă pe scurt geopolimeri, precum şi posibilitatea utilizării acestora ca materiale refractare.

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GENERAL VIEW OF BIODEGRADABLE ZINC ALLOYS

BY

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Abstract. Biodegradable metals have attracted great attention in recent years. In addition to biodegradable metals such as Mg and Fe studied early, Zn, an essential element with the osteogenic potential of the human body, is considered and studied as a new type of biodegradable metal. Zinc seems to address some of the major engineering problems which magnesium and iron could not handle it when it comes to applications for biomedical implants; hence the increase in the number of metal research studies in recent years. Unfortunately, pure Zn is soft, fragile and has low mechanical strength, which requires further improvements to meet clinical requirements. Although pure zinc has unsatisfactory mechanical properties, the addition of alloying elements was a simple approach to improve these properties.

Zinc-based alloys successfully meet the unclear requirements for use in next-generation biodegradable implants. Zinc implants exhibit excellent biocompatibility in vivo, but it has been found that inhibit attachment and viability in vitro conditions. The development of new zinc alloys used in biodegradable implants has emerged as a popular trend in the last few years. Zinc is an essential element in the human body. Plays an important role in many fundamental cellular processes. Zinc implants have a low corrosion rate.

Keywords: metals; zinc; zinc alloys; biodegradable; implants.

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1. Introduction

Zinc is one of the most important element for the human body. The adult human body has about 2-3 g of zinc with biological function, enzyme catalytic variants that play a crucial role in the cellular neuronal system (Kaur *et al*., 2014). Zn serves as a co-factor in all several classes of enzymes, as well as in several classes of proteins. In addition, zinc ions play an important role in regulating blood pressure (Tapiero and Tew, 2003). In high blood pressure, the level of zinc of zinc is decreasing in serum, lymphocytes and bones, while in the heart, erythrocytes, kidneys, liver, adrenal glands and spleen increases (Tubek, 2007a; Tubek, 2007b). Furthermore, zinc-induced changes in cardiomyocyte ionic currents were observed, suggesting that it is possible to expand and grow intracellular under conditions of cardiomyocyte pathology (Turan, 2003).

Also, zinc plays an important role in the immune system. It has been reported that immune function is definitely synchronized with zinc, as both increasing and decreasing zinc levels lead to impaired immune function. Finally, zinc is crucial for bone tissue growth and mineralization. Zinc stimulates bone formation and mineralization by directly activating aminoacyl-tRNA synthesis in osteoblastic cells and stimulates cellular protein synthesis. In addition, zinc inhibits osteoclastic bone resorption by preventing the formation of osteoclast-like cells from marrow cells (Yamaguchi, 2015). With the exception of pure zinc, various zinc alloys have been developed and tested in vitro and in vivo. The tests are proving that Zn alloys have mechanical properties comparable to those of Mg and Fe alloys. Zn-based materials avoid some major disadvantages that have been observed for biodegradable materials based on Mg and Fe. Mg-based materials are usually degraded too quickly to support sufficient mechanical support. It also creates unwanted hydrogen gas pockets, possibly harmful around the implantation location (Yang *et al*., 2017). Fe-based materials degrade relatively slowly and produce voluminous corrosion products, difficult to remove from the human body. In addition, ferromagnetism of Fe-based materials prevents MRI use after implantation. The difference between Mg and Fe-based materials and Zn-based materials is that they degrade at an ideal rate and exhibit satisfactory biocompatibility.

2. Zinc Alloy Systems Designed for Biomedical Applications

Over ten types of zinc alloy systems have been developed for industrial and biomedical applications, as described in Fig. 1. The main considerations for the development of these alloys were different.

Mechanical property was the most important aspect for zinc industrial alloys, while biocompatibility was most important for zinc biomedical alloys. Industrial zinc alloys were shown to be largely Zn-Al based, high Al content, which was strongly avoided in the biomedical field. Most biomedical zinc alloys contained nutrients or potential nutrients.

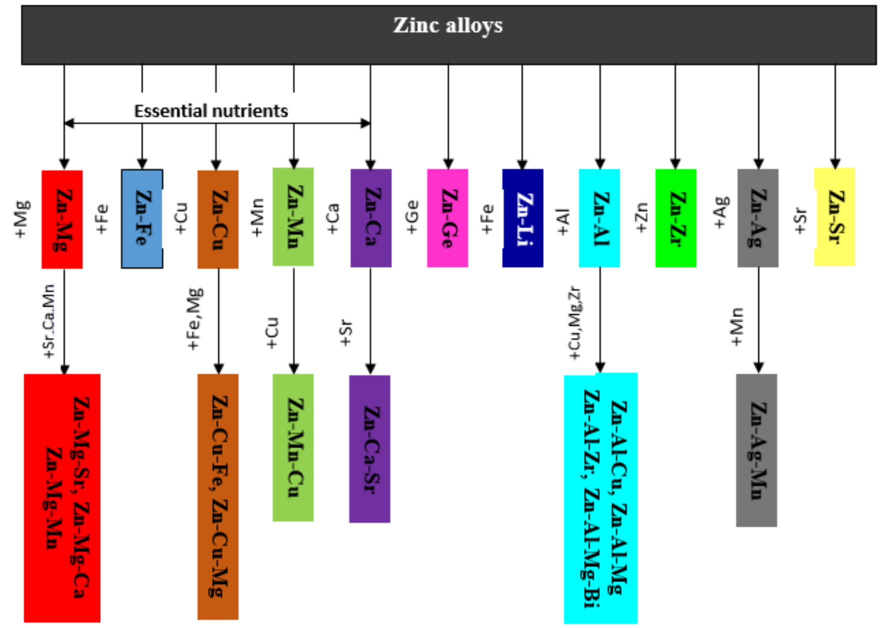

Fig. 1 – Zinc alloy main systems.

2.1. Zn-Mg System

The Zn-Mg system is one of the most studied alloying system from biodegradable Zn alloys. Mg has less than 0.1wt% solubility in Zn at 364ºC. As cast Zn-Mg alloys contain primary dendrites and a mixture of lamellar eutectic Zn and Zn_2Mg_{11}. This was confirmed by both the phase diagram and the metallographic observations. Homogenization could eliminate the lamellar details of the eutectic phase, making it homogeneous. Hot extrusion activated dynamic recrystallization (DRX) and created a microstructure composed of recrystallized Zn grains and precipitated by this alloy which were distributed along the extrusion direction (Yang *et al.*, 2018). The existence of Zn_2Mg_{11} refined the grain structure by creating stress concentration and inducing particle stimulated nucleation, which gradually saturated as the Mg content increased. (Robson *et al.*, 2009). Once the Mg increased, most of the studied Zn-Mg alloys showed a dramatic reduction in ductility and a change in the fracture mode from ductile to cleavage due to the increase in volume. The hard Zn_2Mg_{11} phase caused the mechanical mismatch between the Zn_2Mg_{11} phase and the Zn matrix phase, which made the phase boundaries a perfect place for crack initiation.

Couple elements, including Mn, Ca and Sr, were added to the Zn-Mg binary system to obtain ternary alloys. The strength and ductility of Zn-Mg-Sr and Zn-Mg-Mn alloys were effectively improved after hot rolling (STU from Zn-1wt% Mg-0.1wt% Sr and Zn-1wt% Mg-0.1wt% Mn alloys reached 300.1 MPa, respectively 299.0 MPa) (Liu *et al*., 2016; Zberg *et al*., 2009).

2.2. Zn-Li System

Li has a solubility of about 0.1 wt% in Zn, which is equal to 1%. A eutectic reaction occurs at about 403ºC, and the resultant β-$LiZn_4$ is changed to α-$LiZn_4$ at 65ºC. Many of the researchers claimed that the low-Li Zn-Li alloys were composed of α-$LiZn_4$ and Zn at RT. The Zn-Li alloy system exhibited outstanding mechanical properties, greater than 200 MPa and all STUs greater than 300 MPa (Zhao *et al*., 2017).

2.3. Zn-Zr System

Zr, the alloying element, is almost insoluble in Zn. A small addition of the Zr element to Zn resulted in precipitation with a stoichiometry of $Zn_{22}Zr$ inside the grains, as well as to the grain boundaries forming a dual-phase microstructure. The formed alloys have a higher resistance than pure zinc, which was due largely to refining the grains. Anyway, the resulting strength may not be excellent enough and require further improvement. Zn-Zr alloys with more than 0.05 wt% Zr showed a ductile fracture mode with a visible collapse phenomenon during tensile tests (Wątroba *et al*., 2018).

2.4. Zn-Al System

Al has a solubility of about 1.14 wt% at 381ºC and about 0.7 wt% at 277ºC in Zn. The Zn-Al alloy system undergoes a transformation of the eutectic phase to 381ºC. The eutectic networks appeared at the grain boundaries at Zn-1.0 wt% Al (Mostaed *et al.,* 2016). After the heat treatment for 48 hours, most of the eutectic network dissolved and only small particles remained, resulting in a solid solution Zn supersaturated together with small precipitates. Subsequent extrusion created equiaxed grains of relatively larger size than Zn-Mg alloys. This was due to the lack of restriction of grain growth by the particles in the second phase. The texture evaluation revealed basal poles inclined towards the extrusion direction, which was caused by a combination of basal and pyramidal slip. Developed ternary Zn-Al-Mg and quaternary Zn-Al-Mg-Bi as alloys for biomedical applications, it was found that their mechanical properties were not attractive. Zn-Al-Cu commercial alloys have been a potential candidate for biodegradable zinc alloys. These alloys exhibited a softening during tensile tests and an obvious asymmetry in traction compression.

2.5. Zn-Ca and Zn-Sr Systems

The alloying elements Ca and Sr have almost no solubility in zinc; thus, $CaZn_{13}$ and $SrZn_{13}$ are formed in weakly alloyed zinc. Binary alloys Zn-Ca, Zn-Sr and ternary alloys Zn-Ca-Sr were developed as new biodegradable metals. These alloys were designed to perform specific biological functions during the bone fixation process, based on the simultaneous release of the nutrients Ca, Sr and Zn (Li *et al*., 2015). The mechanical properties were improved by rolling and extrusion 250 MPa and 11% (UTS, elongation) for the Zn-Ca binary alloy and at 260 MPa and 20% for the Zn-Sr binary alloy, which were better than those for pure zinc, but still not enough (Wątroba *et al*., 2018). Adding the third alloying element, Mg, did not change the phase composition, but deteriorated both the strength and ductility of the Zn-Ca and Zn-Sr binary alloys.

2.6. Zn-Ag System

The Ag alloying element has high solubility of about 2.5 wt% in zinc at 200°C. Adding the Ag alloying element greatly enhances tensile strength by enriching the solid η-Zn solution, refining the grain structure and generating $AgZn_3$ particles (Sikora-Jasinska *et al.*, 2017). This effect continued as Ag increased without affecting ductility. Making the EBSD analysis it showed that the texture formed by extrusion facilitated the pyramidal slip and resulted in excellent ductility of Zn-Ag alloys. The perfect combination of strength and ductility has made Zn-Ag alloys one of the most promising Zn alloy systems in terms of mechanical properties.

2.7. Zn-Cu System

Cu has a medium solubility in Zn at a high temperature, but gradually decreases to almost zero at RT. The cast Zn-Cu alloys are composed of the Zn matrix and the ε-$CuZn_5$ dendrites, confirmed by XRD and SEM (Niu *et al*., 2016). The homogenized treatment at over 350ºC did not give rise to an obvious change in the microstructure. After extrusion, the dendrites were crushed and rearranged along the extrusion direction to form large $CuZn_5$ clusters. The refined grains near the $CuZn_5$ phase could be produced by DRX enhancement due to the localization of stress near the large and hard groups of the second phase. Zn-Cu alloys exhibited excellent traction properties, which were gradually improved without loss of ductility as the amount of Cu increased. This was incredible, given the large particle size of $CuZn_5$ in Cu Zn-4wt%. Zn-Cu alloys with high Cu content showed a visible work softening after stretching to over 20%. The Mg and Fe elements were introduced into the Zn-Cu alloy system as the third alloying element. The addition of Fe was not successful, as a concomitant decrease in strength and ductility was observed, while alloying with Mg improved Zn-Cu resistance to the detriment of ductility. This was similar to that observed in the Zn-Mg alloy system, that excessive addition of Mg would reduce the ductility of the Zn-Mg alloy (Tang *et al*., 2017a; Tang *et al*., 2017b).

2.8. Zn-Mn System

Mn, the alloyng element, has a solubility of about 1% in zinc at 400ºC. The study of Zn-Mn binary alloys identified the $MnZn_{13}$ phase when the amount of Mn was greater than 0.4 wt%, while a single-phase structure was observed at 0.2 wt% Mn. Compared to Mg, Mn had a very different effect on the mechanical properties of extruded Zn alloys (Sun *et al*., 2017). Both, UTS (ultimate tensile strength) and elongation of Zn-Mn alloys increased when a small amount of Mn was added. As Mn content increased, UTS decreased, and elongation increased to over 70%. The twinning could contribute to the strengthening of zinc alloys with a low content of Mn, and this contribution decreased as the addition of Mn increased. Zn-Mn-Cu ternary alloys were created and investigated, with special attention being paid to the phase compositions and solidification behaviors and it was found that the addition of Cu further optimized the resistance of Zn-Mn alloys to the price of ductility (Shi *et al*., 2018).

2.9. Zn-Ge System

The Zn-Ge alloy is a new developed zinc alloy for biodegradable applications reported from 2018. The Ge element has no solubility in Zn. Ge had a prominent effect on the refining of the cast zinc grain and thus strengthened the zinc matrix (Jin *et al*., 2018). Further optimization of the mechanical properties was obtained by hot rolling the Zn-5wt% Ge alloy, which created a more uniform (Tong *et al*., 2018).

3. Conclusions

Last years have seen a fast growth in the research and development of zinc-based medical devices. The interest for zinc based alloys is due to their biological and biodegradable properties that fit to the human body. Zn is one of the common and essential element of the human body, playing essential roles in human health. Moreover, zinc remote the limitations inherent in iron and magnesium, both pure and allied. Main limitations includes better corrosion rates, easier casting and machining. In this paper, the progress of zinc-based alloys was presented and discussed.

Challenges were discussed regarding the mechanical compatibility of zinc and zinc-based alloys to evaluate their feasibility as biodegradable metals.

The results show that although zinc alloys are not perfect, nothing has proven that their disadvantages are fatal. Leaving aside the advantages, the use of pure Zn is limited regarding the mechanical properties due to insufficient strength, plasticity and hardness for most medical applications. Alloying with different elements and refining grain sizes by thermomechanical processing is a common practice to alter the mechanical properties of the main metallic materials.

Some types of zinc alloys have been developed with non-toxic and biocompatible alloying elements. Were obtained adequate mechanical properties to serve as structural support for arteries or bone, with promising preliminary results in cell culture and small animal models. For example, Zn-Mg and Zn-Al with alloy concentrations less than one percent have improved mechanical properties and have obtained adequate strength and ductility. All that happens without using excessive amounts of potentially toxic alloying elements.

The mechanical properties of these materials are considerably improved from casting, followed by extrusion to perfect the grain size. Zinc-based materials have many potentials, including a guarantee of sufficient mechanical support using strong zinc alloys and applying additive manufacturing techniques, as well as severe plastic deformation to optimize their mechanical properties. Next-generation of zinc implants will need to have corrosion rates tailored to optimize favorable cell responses. Also need to minimize toxicity and negative inflammatory reactions, specific to the host tissue.

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ANALIZA GENERALĂ A ALIAJELOR DE ZINC BIODEGRADABILE

(Rezumat)

Metalele biodegradabile au atras atenţii considerabile în ultimii ani. Pe lângă metalele biodegradabile precum Mg şi Fe studiate timpuriu, Zn, un element esenţial cu potenţialul osteogen al corpului uman, este considerat şi studiat ca un nou tip de metal biodegradabil. Zincul pare să abordeze unele dintre principalele probleme de inginerie asociate cu magneziul şi fierul atunci când vine vorba de aplicaţii pentru implanturi biomedicale; de aici se explică şi creşterea numărului de studii de cercetare asupra metalului în ultimii ani. Din păcate, Zn pur este moale, fragil şi are o rezistenţă mecanică scăzută, ceea ce necesită îmbunătăţiri suplimentare pentru a satisface cerinţele clinice. Deşi zincul pur are proprietăţi mecanice nesatisfacatoare, adăugarea de elemente de aliere a fost o abordare simplă pentru îmbunătăţirea acestor proprietăţi. Aliajele pe bază de zinc fac fată cu succes cerinţelor neceare pentru a putea fi folosite la implanturi biodegradabile de generaţie următoare. Deşi implanturile de zinc prezintă o biocompatibilitate excelentă in vivo, s-a descoperit că inhibă ataşarea şi viabilitatea celulelor în condiţii in vitro. Dezvoltarea de noi aliaje pe bază de zinc utilizate la implanturi biodegradabile a apărut ca o tendinţă populară în ultimii câţiva ani. Zincul este un oligoelement esenţial în corpul uman şi joacă un rol critic în numeroase procese fundamentale celulare. Implanturile de zinc prezintă o rată scăzută de coroziune.

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SHORT DESCRIPTION OVER THE CORROSION RATE ON IRON-BASED BIODEGRADABLE METALS

BY

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Abstract. Over time, metallic biomaterials have been designed to be corrosion resistant. This is the main aspect that has been taken into consideration in most scientific works on medical devices in the past. Nowadays, tissue engineering is focusing its attention on the degradation mechanism of biomaterials, which revolutionizes the engineering of implants, thus paving new ways of addressing to the corrosion of biomaterials. The necessity in the medical world of some materials to be actively involved in the healing process led to the emergence of biodegradable metals, which would represent a support for a necessary period of time, after which it could progressively degrade once the medical function was accomplished. So many metallic materials have been developed to satisfy from the point of view of the reconstructing of tissues. The corrosion process was also followed in the case of iron-based alloys, pure Fe and Fe-Mn alloys, as having the most promising results in vivo. The future of the development of biodegradable metals focuses on a very good biocompatibility, mechanical stability and control over the degradation process. Important properties in the degradation process could be

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obtained from studies conducted on the human body interaction with iron-based biomaterials during corrosion (Hermawan, 2012).

Keywords: biodegradable metals; corrosion; iron-based alloys.

1. Introduction

Iron is considered to have relatively very slow degradation rate *in vivo* (Peuster *et al*., 2006) and its ferromagnetic property is an issue for medical implants. New Fe-based alloys showed important mechanical properties and a faster degradation rate (0.44 mm/year) than pure Fe (Hermawan *et al*., 2007). It resulted in new austenitic alloys due to the alliances of 30-35 wt% Mn, following which some alloys turned into antiferromagnetic ones. As a result, the alloys have become compatible with the magnetic field just like that of MRI. Also, due to the nontoxicity of Mn in the cardiovascular system, it has made it a suitable alloying element for the production of biodegradable materials for stents. Currently, the existing proposals for new materials focus on Fe-Mn-Pd (Schinhammer *et al*., 2010), Fe-Mn-(Co, C, Al etc) alloys (Liu and Zeng, 2011) as having a favorable behavior from the point of view of the mechanical properties but also of the corrosion rate, although without an *in vivo* test. Layer depositions were considered for better control over the material degradation period, the most appropriate being the coating of degradable ceramics or polymers. Regarding the stents from biodegradable metals, the most favorable results of the purity of the metal would be obtained by powder metallurgy (Datta *et al*., 2011; Wegener *et al*., 2011) and electro-deposition (Moravej *et al*., 2010a). The classical methods of thermal, thermo-mechanical treatments are also taken into account to achieve the desired properties.

2. Materials and Processes

Fe-Mn binary alloys were subjected to the sintering powder process to obtain metallic biomaterial (Hermawan *et al*., 2008), in which case 20-30wt% Mn powder and pure Fe of the highest quality were used, subjected to a series of cold rolling and re-sintering cycles. At the Fe-20Mn and Fe-25Mn alloys, consisting of phase's γ and φ, the strength was the highest of 702 ± 11 MPa for Fe-20Mn and 723 ± 19 for Fe-25Mn, but they showed less ductility 7.5 ± 1.5%, 4.8 ± 0.4%, respectively and degradation rates of 0.5 ± 0.1 mm/year for both. The Fe-30Mn and Fe-35Mn alloys, consisting of phase γ presented a lower strength, 518 ± 14MPa for Fe-30Mn and 428 ± 7MPa for Fe-35Mn, but higher ductility of 19.0 ± 1.4% for Fe-30Mn and 32.0 ± 0.8% for Fe-35Mn, and also a better degradation rate 0.7 ± 0.1 mm/year for both. It could also be noted that magnetic susceptibility decreased with the increase in Mn content to these alloys.

The electroforming technology was used by Moravej *et al*. (2010a), on films of pure Fe. Depending on the electro-deposition current density, differences were observed in the texture and microstructure of the resulting pure Fe: at 2 A/dm^2 resulted a uniform degradation and a strong texture of <111>//ND with an average grain size of ~4 μm. Subsequently, after annealing it was reached a lower yield strength to 270 ± 6MPa, and ductility being improved to18.4 ± 4%. These results were better than those obtained from the conventionally cast pure Fe. The conclusion resulting from the tests that have been made on static and dynamic degradation *in vitro* (Moravej *et al*., 2010b) is that pure electroformed Fe presents a faster corrosion rate than conventionally cast pure Fe, thanks to fine-grain structure and structural defects obtained from the electroforming.

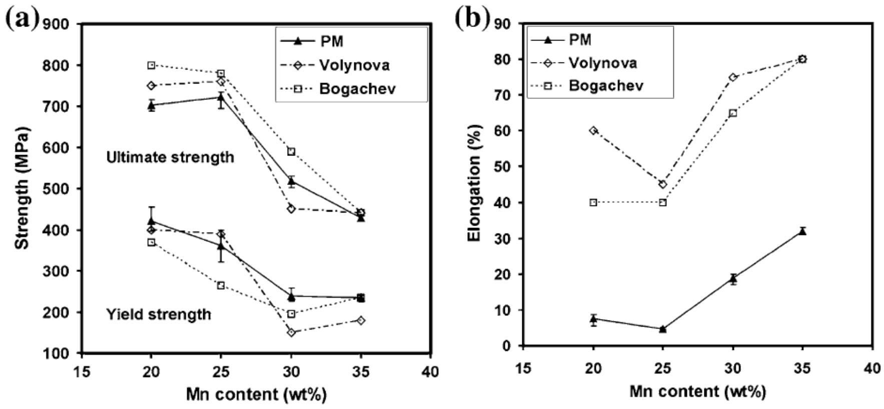

Fig. 1 – Comparison of: *a*) tensile and yield strength, and *b*) elongation of Fe-Mn developed by Powder Metallurgy to the cast counterparts developed in (Bogachev *et al*., 1972; Volynova, 1984). Adapted with permission from John Wiley and Sons (Hermawan *et al*., 2010).

Fig. 1, shows the difference between the mechanical properties of the Fe-Mn alloys produced by powder metallurgy with those obtained by classical casting. Regarding the yield strength values are comparable, but the difference is that the maximum elongation for alloys produced by sintering is considerably lower than that shown by the cast alloys, due to the presence of a larger number of pores and inclusions.

3. Degradation Behavior

Following static degradation tests using the immersion method in the modified Hank solution, Fe-Mn alloys produced by powder metallurgy showed a degradation rate of about 0.23,…,0.24 mm/year, the differences between the types of alloys being not significant, as well as about pure Fe immersed in

Ringer's solution. a similar rate of 0.20,…,0.22 mm/year was observed. Due to the long immersion time (one week) a low degradation rate resulted, and a short polarization time (15 min) caused the layer formed during the degradation to stop further corrosion (Hermawan, 2012). By potentiodynamic polarization it was concluded that with the decrease of the content in Mn, the corrosion rate increased.

Dynamic tests on the degradation in modified Hank solution (Hermawan *et al*., 2010) to which a 4 Pa shear stress was applied, in order to simulate human coronary artery, were able to make possible a view on the ionic release process of Fe and Mn in the environment of degradation.

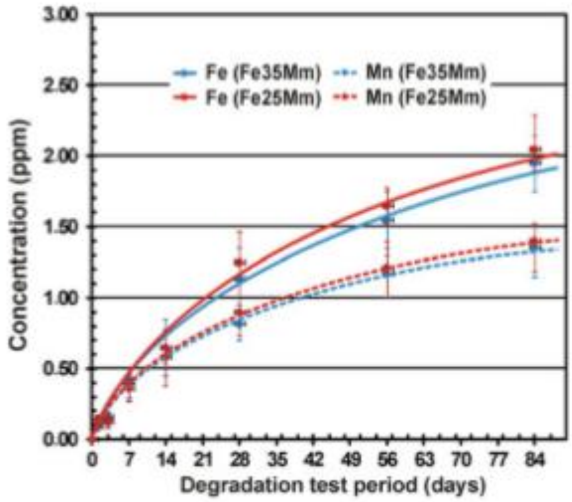

Fig. 2 – Concentration of Fe and Mn ions in degradation medium as a function of immersion time for Fe-25Mn and Fe-35Mn measured by AAS (Hermawan *et al*., 2010).

It can be observed that both alloys release ions without large difference up to 14 days, after which Fe-25Mn is characterized by a higher ion release than Fe-35Mn. However, the average concentration after 3 months of 2 ppm for Fe and 1.4 ppm for Mn at the Fe-25Mn alloy shows a rather low concentration, which shows the insolubility of the degradation products, namely iron hydroxides and Ca/Ph. It was found that the very slow ion exchange was influenced by the fact that the degradation products adhered to the surface, slowing the process. It was possible to make a connection between the depth of the corroded layer and the duration of degradation, that is, after 3 months at Fe-25Mn the layer depth was 13 µm and that of Fe-35Mn 110 µm. Thus the degradation rate was set at 520 and 440 µm/year, respectively (Hermawan, 2012).

4. Conclusions

Fe-Mn alloys with different content in Mn, produced by re-sintering with the help of powder metallurgy and subjected to cold-rolling treatments have presented mechanical, physical and even magnetic properties suitable for the development of medical implants. In vitro tests on the rate of degradation of Fe-Mn alloys showed a better corrosion rate of 520 µm/year than that of pure Fe, which corresponds to a rate of 220-240 µm/year. Fe-Mn alloys can be considered as important candidates in the production of degradable biomaterials, these having a good compatibility and a favorable degradation rate for medical research. Compared to the minimum requirement of ASTM F138 for SS316L, the mechanical properties of Fe-Mn alloys are superior except the elongation.

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SCURTĂ ANALIZĂ A VITEZEI DE COROZIUNE A BIOMATERIALELOR METALICE PE BAZĂ DE FIER

(Rezumat)

De-a lungul timpului, biomaterialele metalice au fost proiectate pentru a fi rezistente la coroziune. Acesta este aspectul principal care a fost luat în considerare în cele mai multe lucrări ştiinţifice asupra dispozitivelor medicale, în trecut. În zilele noastre, ingineria ţesuturilor îşi concentrează atenţia asupra mecanismului de degradare a biomaterialelor, care revoluţionează ingineria implanturilor, pavând astfel noi modalităţi de abordare a coroziunii biomaterialelor. Necesitatea în lumea medicală a unor materiale de a fi implicate activ în procesul de vindecare, a dus la apariţia metalelor biodegradabile, ceea ce ar reprezenta un sprijin pentru o perioadă de timp necesară, după care s-ar putea degrada progresiv odată îndeplinită funcţia medicală. Materialele metalice au fost dezvoltate pentru a satisface din punctul de vedere al reconstrucţiei ţesuturilor. Procesul de coroziune a fost urmărit şi în cazul aliajelor pe bază de fier, a Fe pur şi aliajelor Fe-Mn, având cele mai promiţătoare rezultate in vitro. Viitorul dezvoltării metalelor biodegradabile se concentrează pe o biocompatibilitate foarte bună, stabilitate mecanică şi control asupra procesului de degradare. Proprietăţi importante în procesul de degradare ar putea fi obţinute din studii efectuate pe interacţiunea corpului uman cu biomaterialele pe bază de fier în timpul coroziunii.

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STUDY ON THE EXTERME WEAR OF THE CONVEYOR BAND OF A RUBBER BAND FEEDER IN THE CONSTRUCTION OF A HYDROCARBON PAVMENT MIXTURE PREPARATION PLANT. IDENTIFYING THE CAUSES OF THE EVENT

BY

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Abstract. The study presented in this paper disscus the causes that acted as a starting point of an accidental extreme wear of the rubber band in the construction of a feeding equipment placed at the input end of a rotating cylindric dryer, both equipments being components of a complex instalation destined for the preparation of hydrocarbon pavement mixtures. They are shown, starting from available initial data, the feeding equipment description by its main characteristics, its role in the installation and, chronologically, the course of events. They are listed in the form of a logical chain of argument, the objective causes and the possible subjective causes that led to the failure occurrence. Based on the general rules of reliability control and maintenance organisation, the possible causes in the event occurrence are being investigated and specific comments are being made. After drawing conclusions some recommendations are being proposed in view of enhancing the machine reliability and, about the way of acting in similar situations.

Keywords: equipment reliability; return drum; objective and subjective cause of an event; event tree; bearing shell; slack.

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1. Introduction

Obtaining materials for pavements is an important step in infrastructure modernisation and maintenance. Installations for preparing such materials are usually being constructed by combining individual machines (Oprescu *et al*., 1977).

Short length conveyor bands, known also as feeding bands (Răileanu *et al*., 2002) are important elements in this industry. This kind of equipment has specific characteristics when used individually (Simionescu *et al*., 1991; Simionescu *at al*., 1995). Sometimes coupling into greater installation can cause adjustment problems and this paper approach one of them.

Reliability and maintenance of construction installations, because “they have to work” during the whole hot season is very important because of contractual constraints and achieving it is not so easy to fulfil (Smith, 2001; Smith and Hinchcliffe, 2004).

The paper aims to put into discussion the case of accidentally extreme wear of the conveyor band, basic component in the construction of a rubber band feeder in the construction of a hydrocarbon pavement mixture preparation plant.

Based on the initial data available, it is desired to formulate a set of hypotheses on the possible causes involved in this degradation as preparation in building a cause consequence scenario.

Based on such an approach, and following punctual detailed investigations, recommendations can be made in view to increase the reliability of this equipment.

2. Initial Data

In order to formulate plausible hypotheses about the causes of equipment or installation failures, it is necessary to understand as accurately as possible the conditions under which a particular event occurred.

This requires at least information on:

– the functional role of the part in the construction of the machine;

– the working conditions of the machine and its role in the installation to which it belongs;

– the technology of fabrication.

For “big equipment” sometimes the condition of transport and events during it are also valuable.

Based on the knowledge of these elements, it is possible to identify the type of stresses to which the part is subjected under normal operating conditions and the value of these stresses. Having those as a benchmark one can then identify deviations from normal state and also make some scenario of “what could go wrong type” and in this manner to find what exactly could become a certain cause of failure.

3. Machine Description and Overall Functional Role

The band feeder, on which this work is carefully directed, is part of an installation for the production of hydrocarbon pavement mixtures, an installation characterized by a maximum productivity of 120 t/h, having intermittent operation.

The feeder is part of the category of conveyor machines with continuous operation of band conveyor type, the specificity of the different name coming from the short length, corroborated with the designed functional role (Răileanu *et al*., 2002). Some technical data according to the manufacturer's technical book are given in Table 1.

Table 1
Equipment General Characteristics

Characteristic	Description
Center distance	3.5 m
Belt speed (maximum value)	1.58 m/s
Power	3 kW; 380 V
Revolution number (maximum)	126 rot/min
Capacity	320 t/h
Year of production	2018
Construction with two upper rollers positioned in the trough at 30 degrees	
Upper roller – 24 pcs	ϕ 89 x 250 mm
Lower roller with rubber rings – 2 pcs	ϕ 63,5 x 108 x 750 mm
Drive drum – rubber surface – (neck journal)	ϕ 220 x 720 mm – (50 mm)
Return drum – (neck journal)	ϕ 220 x 750 mm – (40 mm)
Band width	650 mm
Band thickness	8 mm
Number of textile inserts	2 pcs

In the given installation, the band feeder is the assembly that performs the proper supply of the dryer of the installation with granular mineral material (sands, quarry or gravel sorts crushed or uncrushed, dosed according to the prescribed recipe), necessary for the manufacture of hydrocarbon pavement mixtures.

The feeder picks up the granular material from the band conveyor of the plant pre-dispenser and unloads it in the dryer Figs. 1 and 2.

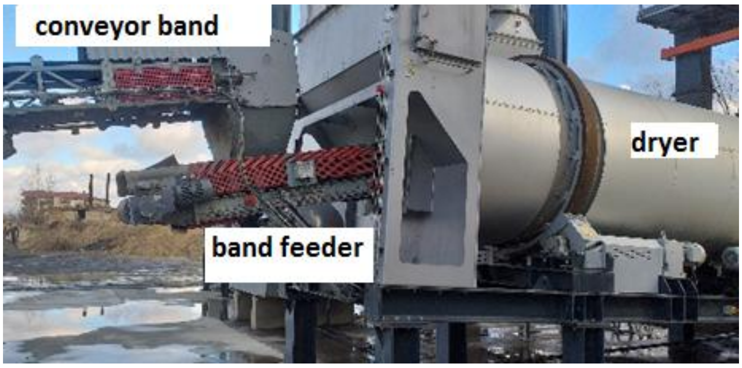

Fig. 1 – Position in the installation of the rubber band feeder.

Its operation is ordered by the operator of the installation, depending on the material requirements and the specific conditions of humidity, ambient temperature, dosage, quantity and type of finished product ordered, etc. resulting in a variable transport speed.

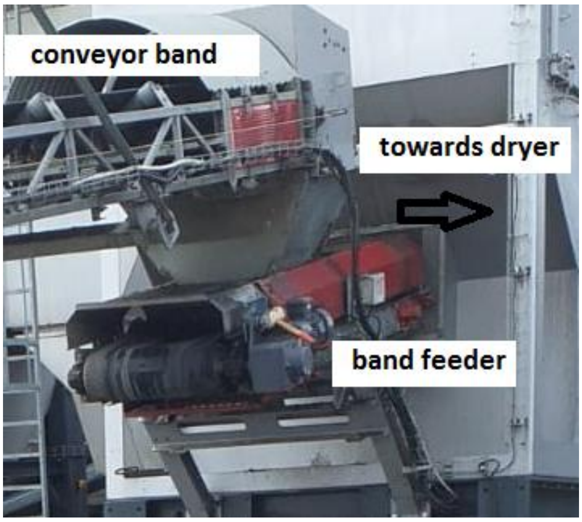

Fig. 2 – Position in the installation of the rubber band feeder. Detail.

Its operation is ordered by the operator of the installation, depending on the material requirements and the specific conditions of humidity, ambient temperature, dosage, quantity and type of finished product needed etc. resulting in a variable transport speed.

The equipment can be used, as a subassembly of the installation and correlated with it, at a maximum productivity of 150 t/h (for a certain type of mixture with reduced mixing time), but by design, it can ensure a maximum productivity inscribed on the nameplate of 320 t/h.

The equipment is positioned upwards with the angle of the longitudinal axis at 10 degrees from the horizontal.

The drive of the rubber band is made using an asynchronous electric motor - reducer group of 3 kW, with the possibility of speed variation by changing the frequency of the electric current.

The motor – reducer group and the drive drum of the feeder are being positioned at the lower side of the equipment and the construction do not have a deviation drum for ensuring the possibility of regulation for the contact angle between band and the drive drum having rubber surface.

The band tensioning system, in classic construction with tensioning screw, acts on the drive drum system and is also positioned at the bottom.

This construction is required because the upper part holding the return drum is inaccessible during operation; it enters inside the tubing that covers the rotating drum of the dryer for a distance of about 1.5 meters.

The lubrication of the bearings of both machine drums, which are made with oscillating bearings with one row of balls, is done with a manual lubrication system, at the prescribed interval of 1000 operating hours.

Fig. 3 – Drive drum – rubber surface. Detail and wear of the rubber band.

The upper part of the conveyor, where the unloading is performed, works at a higher temperature than the ambient environment, a temperature that can reach up to 90 degrees Celsius, being near the hot gas outlet resulting from the heating of mineral aggregates inside the dryer.

The rubber band of the feeder continuously transports material at ambient temperature and thus is permanently “cooled” by it. Therefore, the rubber band does not overheat during operation.

At the end of a working day or of a command, when the supply to the system must be switched off, when the dryer must be switched off and ventilated in order to reduce the temperature, the automation system of the entire installation ensures the continuous power supply of the band feeder, not allowing the conveyor band to stop and overheat.

In conclusion, the overheating of the band that may occur is not significant and can not lead to its thermal damage.

4. Event Investigation. History of Interventions

After a number of approximate 1150 hours of use, an unjustified lateral movement of the rubber band on the return drum of the band feeder was found.

It was decided to assume the continuing of operation in these inappropriate conditions and the acceptance of a wear of the rubber band following the next logic tree analysis structure (Smith and Hinchcliffe, 2004).

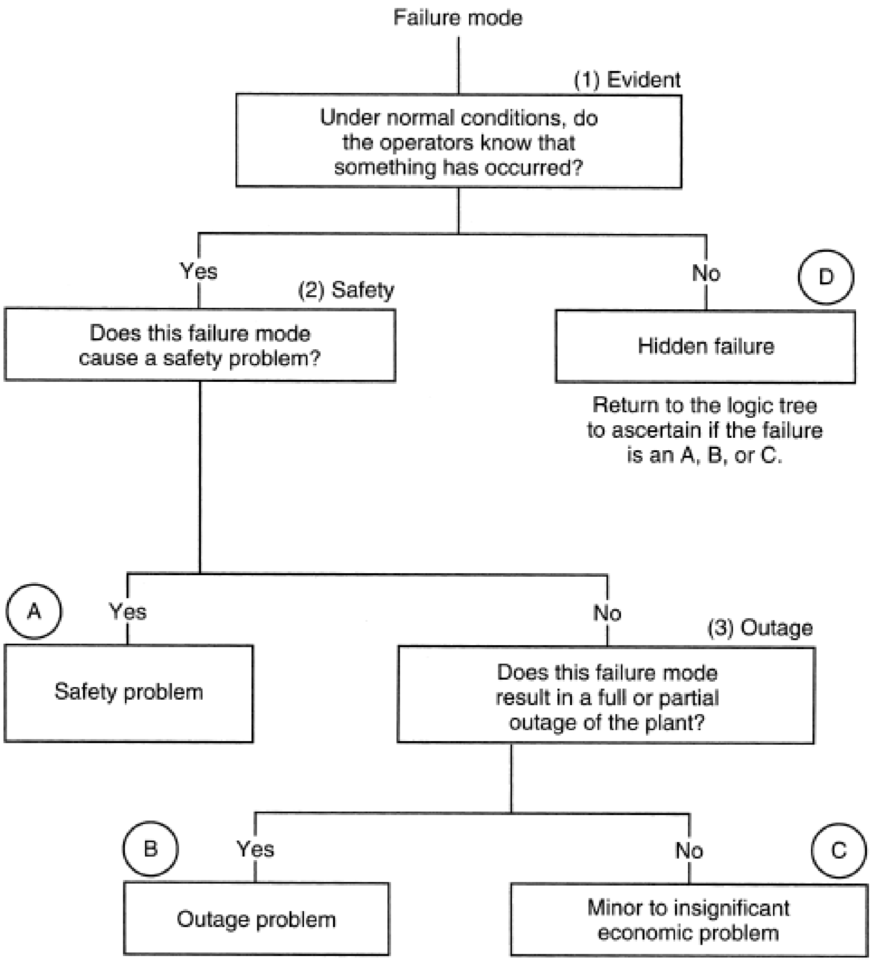

Fig. 4 – Logic tree analysis structure (Smith and Hinchcliffe, 2004).

Contractual obligations regarding the delivery of finished material led to this postponement of an immediate intervention for the detailed finding and repair of the defect, but during this time repeated adjustment attempts were made by means of the tensioning system (screw tensioning system), attempts which did not had the expected lasting effect.

It is the case known as “frequent problem repetition” (Smith and Hinchcliffe 2004). In such conditions, “there is never enough time to know why the equipment failed, let alone enough time or information to know how to correct the deficiency permanently. The result is that the same problem keeps coming up over and over. This repetitive failure problem is often discussed in terms of root cause analysis, or more appropriately the lack thereof. Unless we understand why the equipment failed and act to remove the root cause, restoration to service may be a temporary measure at best, and the cycle not only continues but is reinforced” (Smith and Hinchcliffe 2004).

The operation with the observed defect was done for a period of about 10 hours, approximately 700-850 tons of transported material, and the total wear resulting from rubbing the band by contact with the chassis of the assembly was about 50 mm on the left side in the direction of the band drive.

When it was decided to carry out the remedial intervention, the team of mechanics found a major deficiency, attributed to the manufacturer of the machine, namely an assembly error, as the objective cause of the event.

Specifically, when mounting the ball bearings in the bearing shell on the left side, in the direction of band drive, an impermissible slack was found, caused by the lack of a spacer ring, for blocking movement (safety).

This allowed the oscillation of the return drum along the axis on a variable length, with a maximum amplitude of about 3 mm.

Because of the return drum position, inside the dryer and covered by it, this malfunction was impossible to be seen by the operator and it became more and more severe.

5. Discussion

From the findings, several hypotheses can be formulated which, in succession, present a coherent, logically arguable causal chain.

One can agree that the event we discuss, can be easily considered as an early stage failure for this kind of equipment.

“The complexity of modern engineering products and systems ensures that system failure does not always follow simply from component part failure.

Factors such as:

– Failure resulting from software elements;

– Failure due to human factors or operating documentation;

– Failure due to environmental factors;

– Common mode failure whereby redundancy is defeated by factors common to the replicated units can often dominate the system failure rate" (Smith, 2001).

The literature states that "early failures, are usually related to manufacture and quality assurence, *e.g.* welds, joints, connections, wraps, dirt, impurities, cracks, insulation or coating flaws, incorrect adjustment or positioning" (Smith, 2001) and our situation can easily be included in this type of event.

We look for the two types of causes that can lead to an event or an accident, namely objective causes and subjective causes.

One objective cause of the event is clearly determined by the finding of the absence of an element in the construction of a bearing that supports the return drum which has a role in guiding the band in a correctly determined direction.

In order to determine the subjective causes, attention must be paid to people through the omissions or mistakes that they may make, based on the inadequate dimensioning of the workload or by the level of insufficient technical training in relation to the specifics of the job served.

Literature states that "in the early stages of product deployment, there is some residual of substandard parts, materials, processes, and workmanship that escapes the factory test and checkout actions, and thus remains in the product at its point of initial use and operation. These substandard items generally surface rather quickly relative to the total product lifetime, but initially they produce a failure rate that is larger than the expected long-term failure rate. As these problems surface and are removed, the population failure rate will decrease and a stabilization of the population λ will occur. This first phase of the cycle is called the *infant mortality stage*" (Smith and Hinchcliffe, 2004).

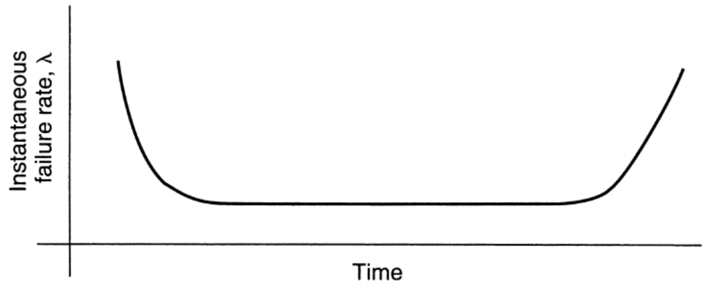

Fig. 5 – The reliability "bathtub curve" (Smith and Hinchcliffe, 2004).

Discussing post factum the possibility of early detection of the defect, one could speculate on an incorrect quality control performed at the manufacturer or of some problems appeared due to the incorrect handling or transport of the machine. Both causes are of a subjective nature, implying multiple possibilities related to the non-fulfillment of the work tasks of some employees, in the category of omissions or mistakes.

Continuing chronologically, in the first phase of operation of the new machine, during the tests at commissioning, it was not possible to immediately detect the assembly error, the probable cause being a subjective nature, namely the lack of experience of the team that put the installation into operation. Moreover, at this stage the only possibility of detecting the defect would have been the appearance of an unexpected additional sound produced due to oscillations along the axis of the return drum.

It should be noted that in the specific noise conditions of such an installation it is very difficult to detect such a noise even by a qualified person.

During the operation of the new machine, the operator could probably see at some point the appearance of changes in the operation of the band feeder but interpreted them, based on his own experience, which can not be attributed to him.

It is known and accepted that during the running-in and warranty periods of such equipment it is natural that fine adjustments or more should appear as necessary.

It is also possible that in this period of acclimatization with the new job, the person who served the machine should not raise the issue of a manufacturing defect but consider that the unpredictable elements that occur are due to lack of self-exercise in the operation of the machine, as is natural.

The situation could also be misinterpreted, namely the fact that the stretching of the band was not done properly, the technical solution being less common and the experience being therefore limited. This was accompanied also by a new objective cause, namely the lack of technical documentation provided by the manufacturer of the indications on the parameters of the tensioner adjustment - “failure due to operating documentation” (Smith, 2001).

Once the degradation of the operating conditions begins, the hypothesis of the growth of a pre-existing slack and the appearance of additional wear in the improperly mounted bearing can be formulated. The tendency of the band to move in the direction of the defective bearing can be explained by the direction of the results of the forces that appear and manifest in the presence of the slack.

We can appreciate the existence of a resulting component of inertial forces, acting both vertically and along the axis in both directions capable of producing vibrations during work.

Also due to the existence and increase of the slack in the bearing, it can be understood a decrease in the tensile force on the bearing side. Implicitly the frictional force and therefore the adhesion between the drum and the conveyor belt is lower than necessary and supports the motivation for the slight repositioning of the band in the direction of the bearing and then, the contact of the band with the machine chassis.

The appearance of band wear due to contact with the chassis is accompanied by thermal phenomena, expansion, rippling and additional inertial forces producing vibrations.

Repeated attempts to solve the problem of misalignment by additional band tensioning were not effective due to, at least the above motives, and in addition subjected the band to very large tensile forces which, coupled with improper operation led to assumed wear and finally to the necessity of changing it.

6. Conclusions and Recommendations

Faulty installation of a bearing support for the return drum of band feeder investigated, found only after severe wear of the conveyor band, initially led to the progressive misalignment of the rubber band and the improper operation of the machine.

Under the conditions imposed by compliance with delivery contracts, the voluntary shutdown of a hydrocarbon pavement mixtures preparation plant in the construction of which the machine is part and its verification, were not possible. By assuming the situation of premature wear of the band, the defect continued its action and finally produced greater consequences then expected.

Due to the severity of the defect and its aggravation manifested by the appearance and increase of the bearing slack, the necessary adjustment measures, achieved by stretching the band, were effective only for a short period and the misalignment reappeared.

The combination of the objective causes with the subjective causes mentioned above eventually led to the accidental extreme wear of the band and the unforeseen need for its urgent replacement in the installation.

Under the given conditions, the identification of the manufacturing defect was not possible without stopping the installation and de-tensioning the conveyor band.

In similar situations, it is recommended to stop the feeder, de-tension the belt by means of the tensioner, check the clearances in the bearings of the return and drive drums and remove any errors.

It is also recommended to submit a request to the manufacturer regarding the conditions for the correct extension of the band.

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STUDIU PRIVIND UZURA EXTREMĂ A BENZII DE TRANSPORT A UNUI ALIMENTATOR CU BANDĂ DE CAUCIUC DIN CONSTRUCȚIA UNEI INSTALAȚII DE PREPARARE A MIXTURILOR ASFALTICE. IDENTIFICAREA CAUZELOR EVENIMENTULUI

(Rezumat)

Studiul prezentat în această lucrare discută cauzele care au acționat ca punct de plecare a unei uzuri extreme accidentale a benzii de cauciuc din construcția unui alimentator plasat la gura de încărcare a unui uscător cilindric rotativ, ambele echipamente fiind componente ale unei instalații de preparare a mixturilor asfaltice. Sunt arătate, pornind de la datele inițiale disponibile, descrierea alimentatorului prin intermediul principalelor sale caracteristici, rolul său în instalație și, în mod cronologic, cursul evenimentelor. Sunt enumerate, într-un lanț logic argumentabil, cauzele obiective și posibilele cauze subiective, care au dus la apariția defectului. Pe baza regulilor generale privind controlul siguranței în funcționare și organizării întreținerii sunt investigate cauzele posibile ale apariției evenimentului și sunt formulate comentarii specifice. După concluzii sunt propuse câteva recomandări în scopul îmbunătățirii siguranței în exploatare a utilajului și a modului de acțiune în situații similare.