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ANALYSIS OF SULFAMETHAZINE IN CHICKEN EGGS FROM AGRICULTURAL AND FAMILY AGRICULTURAL FARMS

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Abstract: *Residues of antibiotics, used in veterinary medicine, end up in animal-derived edible tissues (meat and offal) and products (milk and eggs). Residues of the medicine as antibiotics in consumed food could have direct adverse effects on the human health. The main goal of this study is to study the Sulfamethazine (SMZ) presence in the chicken eggs. The samples were taken from 260 eggs which were randomly collected from a local market in Oradea City, NW-Romania. ELISA screening method (enzyme-linked immunosorbent assay) was used for the SMZ analysis. Were led a comparative study of the presence of SMZ in the eggs components: shell, yolk and albumen from samples coming from agricultural and family agricultural farms*
Key words: sulfamethazine, ELIZA, chicken egg

INTRODUCTION

To ensure the safety of the food supply has a great importance to consumers. Therefore, to facilitate international trade, government agencies and international bodies must establish standards, guidelines, and regulations that food producers and trade partners need to meet, respect, and follow. Today, antimicrobial drugs are used in food-producing animals to treat and prevent diseases and to enhance growth rate and feed efficiency. Such use is fundamental to animal health and well-being and to the economics of the livestock industry. However, these uses may result in residues in foods and have been linked to the emergence of antibiotic-resistant strains of disease causing bacteria with potential human health ramifications [1]. Many factors influence the residue profiles of antibiotics in animal-derived edible tissues (meat and offal) and products (milk and eggs), and in fish and honey [2].

A consequence of the use of veterinary drugs (including antibiotics) in food-producing animals is the production of residues of the drug in the edible tissues [2]. Residues of the medicine as antibiotics in consumed food could have direct adverse effects on the complex microflora that inhabit the human gastrointestinal system, with potentially disastrous consequences for the consumer. Another potential consequence is exposure of the human consumer to bacteria that, having been exposed to the drug through the treated animal and having survived the exposure, are less susceptible to that antibiotic. People who develop a human disease resulting from exposure to these bacteria may find that the causative organisms are resistant to antibacterials used in human medicine and the disease refractory to standard treatments. Adverse impacts on the human consumer resulting from years, or even decades, of exposure to residues of a veterinary antibiotic in the food would be very difficult to trace back to the source of the problem. A primary goal of national and international regulatory frameworks for the use of veterinary drugs, including antimicrobials, in food-producing animals is to ensure that authorized products are used in a manner that will not lead to non-compliance residues [1].

However, analytical methods are required to rapidly and accurately detect, quantify, and confirm antibiotic residues in food to verify that regulatory standards have been met and to remove foods that do not comply with these standards from the marketplace. The ELISA (enzyme-linked immunosorbent assay) technique was developed through the pioneering work of Engvall and Perlmann [3] in the 1970s. By immobilizing the reagents to a surface, the facile separation of bound and unbound material is achieved, making ELISA a powerful tool for the measurement of analytes in crude sample preparations [4]. In

its simplest form, ELISA is based on an enzyme catalyst and UV/VIS detection. It is a technical protocol highlighting the antibodies against viruses and bacteria or specific antibodies against a specific type of virus, so the analysis reveals not the pathogen but determined the enzyme activity that binds to antigen or antibody, thus giving indication of the amount of antagonistic substance produced against it.

The conversion of the substrate to product either generates a signal or releases an ion that reacts with a secondary compound, resulting in a change that can be measured spectrophotometrically or electrochemically. Traditional ELISA typically involves the use chromogenic reporters and substrates, which generate an observable colour change and the majority of ELISA applications reported in the literature or commercially available for antibiotic residue analysis, are based on such reporters [5,6].

ELISA has been routinely used as a qualitative, semi-quantitative, or even quantitative screening technique in official residue control and quality control laboratories since the late 1970s and hence, is a well established bioanalytical technique. ELISA is generally accepted as a cost-effective and highly specific laboratory based method that does not require the need for expensive equipment in its most basic operation [7,8].

The main goal of this study is to pursue in eggs one of the wide use antibiotic, Sulfamethazine (sulfadimidine)-SMZ, which has remarkable effect on controlling and curing livestock and poultry diseases [9].

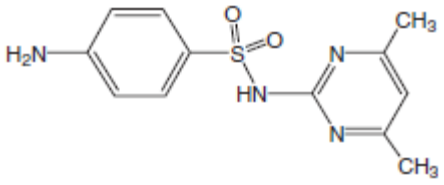

Figure 1. Sulfamethazine (sulfadimidine) 4-Amino-N-(4,6-dimethylpyrimidin-2-yl) benzenesulfonamide; $C_{12}H_{14}N_4O_2S$

SMZ and its metabolites is easy to remain in animal body; also has considerable side effect on human, which can cause faint, headache, exhaust, nausea, vomit, etc; lead to haemolytic anaemia, a vacuity of granulocyte, allergic reaction and damage urinary and nervous system; cause the increasing tolerance of drugs [10]. It was regulated that maximum SMZ residue limit in animal food and feed is 100 ppb in America, China, and EU [11].

MATERIALS AND METHODS

The studied eggs were randomly collected from a local market in Oradea City, NW-Romania. 260 eggs were studied during the summer 2012. 180 eggs were purchase from Agricultural Farms and 180 from Family Agricultural Farms.

Were used ELISA Ridascreen® R-Biopharam AG, Darmstadt, analysis Kits for SMZ.

Sample preparation affects all the later assay steps and therefore is critical for unequivocal identification, confirmation, and quantification of analytes. It includes both the isolation and/or pre-concentration of compounds of interest from various matrices and also makes the analytes more suitable for separation and detection. Sample preparation typically takes more than 70% of the total analysis time. Sample pretreatments for the analysis were as follows: two grams (2±0.05g) of homogenized egg samples was mixed with 4ml of ethyl acetate and then vortexed vigorously for 2 min. This was followed by centrifugation at 2000×g for 10 min. Afterward 400 ml of supernatant was evaporated to dryness at 60 ^oC under a gentle flow of nitrogen. The residue obtained was then re-suspended in 200 µl of 10 mM of phosphate buffer (pH 7.4) before analysis [12].

For a comparative study of the SMZ accumulation in the egg samples were processed separately from each egg the: shell, yolk, albumen.

The spectrophotometric measures were done at 450 nm.

RESULTS AND DISCUSSIONS

The results obtained for the SMZ screening in the eggs samples are presented in table 1.

The obtained data confirmed the fact that SMZ is present in the eggs of the chickens taken as samples from both sources: Agricultural Farms and Family Agricultural Farms. The values are under the maximum SMZ residue limit in animal food and feed.

In the samples taken from Agricultural Farms the total SMZ/egg average value is almost double as value comparative to the egg samples from Family Agricultural Farms. It is evident that the Agricultural Farms because of the largest poultry flock are dealing with much more risks and incidents of diseases then the Family Agricultural Farms and therefore are using more often antibiotics.

The comparative study of the SMZ detected in the component parts of the studied eggs (table 2) reveal that about 60 % of the antibiotic is accumulated in the yolk, meantime that in the shell is less than 10% and the yolk contains almost double SMZ then the albumen of the egg.

Table 1. The results obtained for the SMZ screening in the eggs samples (shell, yolk, albumen)

Value SMZ/egg $\mu g\ kg^{-1}$	Agricultural Farms Egg sample			Family Agricultural Farms Egg sample		
	Shell	Yolk	Albumen	Shell	Yolk	Albumen
Minimum	0.12	4.07	2.25	0.10	2.07	1.19
Maximum	4.83	76.59	38.57	2.16	30.09	18.27
Average	3.22	38.68	21.54	1.85	21.18	9.47

Table 2. The SMZ percent in the eggs parts (shell, yolk, albumen)

% SMZ/egg	Agricultural Farms Egg sample	Family Agricultural Farms Egg sample
Shell	5,07	5,21
Yolk	60,97	65,16
Albumen	33,96	29,13

CONCLUSIONS

Sulfamethazine (SMZ) determined by enzyme immunoassay, shows considerable advantages regarding sensitivity, detection limit, technical equipment and time requirement.

Antibiotics as SMZ, can have impact on living organisms, as any other synthetic chemical we are using in our daily life, and it is present in the chicken eggs in measurable concentrations.

The eggs samples from Agricultural farms are richer in SMZ then the eggs from Family Agricultural farms (almost in ratio 2:1) probably because in the Agricultural Farms because of the bigger flock is more risk and incidents of diseases then the Family Agricultural Farms and therefore are using more often antibiotics.

The SMZ detected is under the maximum Sulfamethazine residue limit in animal food and feed (100 ppb).

The SMZ is present in yolk, albumen and shell, in the approximate ratio: 12/6/1.

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WASTE RECOVERY A WASTE WATER SOLUTIONS WITH PALADE ION

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Abstract. *This paper aims to recovery of the transition metal by means of chemical reduction, using wastewater containing palade ion in hydrochloric acid medium, derived from ceramic substrate activation of chemical resistance to 0.5w, 1w, 2w, the manufacture of components passive electronic.*
Keywords: wastewater, palladium, reduction, hypophosphite.

1. INTRODUCTION

Treatment the waste water containing transition metals, in this case palladium,is a priority imposed by environmental legislation management of material resources, and the re-use of compounds particular technical importance.

It is known a method for the recovery of palladium of the spent catalysts containing palladium, which have in their composition from 0.01 to 0.5% palladium metal found on Al_2O_3 suport.

The catalyst used was subjected to a thermal process at 410-460 ° C after which the palladium has been extracted as palladium chloride by refluxing with a hot solution of hydrochloric acid 1:1. Palladium chloride so obtained is adjusted to pH 1.9 to 2.3 and then by treatment with formic acid cooking , the reduction of palladium metallic.

For waste water containing palladium chloride in hydrochloric acid medium resulting from the operation of the activation ceramic substrate, the method chosen for the chemical reduction of an appropriate reducing agent , hypophosphite sodium.

General procedures are known and acidic wastewater treatment containing metals, including precipitation with different precipitation agents, ion exchange, electrodialysis, osmosis , electrodeposition.

Palade ion chemical reduction method with sodium hypophosphite is effective and easily affordable, convenient favored values of standard electrode potentials for palade ion and reductant selected.

Acidic waters with palladium chloride are heated to 70-75 ° C , followed by chemical reduction palladium ion with solution 0.5 M of sodium hypophosphite in excess of 10% , and by decantation , the precipitate obtained palladium is agglutinate in a period of 10-12 hours (at normal temperature). [1, 9]

The supernatant is removed and neutralized with 20% sodium hydroxide to pH=7, as environmental legislation.

2. EXPERIMENTAL

2.1. Materials and methods
2.1.1 Materials and equipment

The reagents used were as C.P. Merck, Fluka, or Bucharest reagent: complexone 0.05 M; HCl 1:1 vol.; thorium nitrate, metalocromic indicator, solution 10% ammonium acetate, potassium iodide 10%, buffer pH 10, xylenol orange, distilled water, Berzelius glasses, Erlenmeyer vessels. We used volumetric solution one factor. [2, 3, 5, 6]

Laboratory equipment included glassware Class A +, magnetic stirrer with hot plate, distillate device and redistilled water, G4 filter crucible , digital pHmeter pH 100 (INM) Bucharest, automatic burette and microburette .

Wastewater treatment containing of palladium ion are taken account two concentrations representative of palladium ion .

Determination palladium concentration of waste solutions is volumetric, by back-titration excess complexone III with thorium nitrate, to pH=3, in the presence of xylenol orange

indicator. Equivalence colour of solution turns to red.

Wastewater with containing 1243mg Pd/dm^3, to pH 1.6 due to the presence of hydrochloric acid, submit analysis palladium content complexometric volumetric method.

Taking the analysis of 25 ml of waste water, in which added 10 ml of disodium salt ethylenediaminetetraacetic acid 0.05 M. Excess complexone back titrate a volume 3.85 ml of the thorium nitrate solution to 0.05 M, in the pH of the reaction mass to pH 3.

Determining factor thorium nitrate solution is 1.08. 1ml Complexone III of 0.05M; corresponds to 5.32 mg Pd., and 1 ml of 0.05 M complexone III, corresponding to 1.08 ml of $Th(NO_3)_4 \cdot 5H_2O$; 0.05 M.

Palladium ion calculation is done according to equation:

$$Pd=(10-V_{titrat} \cdot F_{Th(NO3)4 \cdot 5H2O}) \cdot m_{Pd} \cdot \frac{1000}{25}$$

$$Pd=(10-3,85 \cdot 1,08) \cdot 5,32 \cdot \frac{1000}{25} =$$

$$=(10-4,158) \cdot 5,32 \cdot 40=5,842 \cdot 5,32 \cdot 40=$$

$$=1243,178 \text{ mg Pd/dm}^3$$

2.1.2. Working mode:

Palade ion reduction in hydrochloric acid medium at pH 1.6 there is according to the reaction equation. [4, 7, 8]:

$Pd^{2+} + H_2PO^{2-} = Pd + H_2PO^{3-} + H_3O^+$ (1)

$Pd^{2+} + 2e = Pd$ $E=+0,987V$ (2)

$PdCl^{4-} + 2e = Pd + 4Cl^-$ $E_0 = +0,623V$ (3)

$H_2PO^{2-} + e = P + 2OH^-$ $E_0 = -2,051V$ (4)

$H_3PO^{2-} + H^+ + e = P + 2H_2O$ $E_0 = -0,51V$ (5)

a) Using 250 ml of waste water containing 310.7 mg of Pd which requires 310.7 mg of sodium hypophosphite with an excess of 10%, which means a total of 6448 ml of hypophosphite .

So if 1 ml of 0.05 M sodium hypophosphite has a content of 53 mg $NaH_2PO_2 \cdot H_2O$ will use 6.448 ml hypophosphite .

The waste water is heated to a temperature of 70 ° C and add the solution sodium hypophosphite as calculated stoechiometric , 6.448 ml under stirring.

After this process the check test to see whether there was complete reduction of Pd^{2+}. This test is carried out with a solution of 10% potassium iodide. In the case of the pink coloration disappears after verification that the palladium is absent below the limit of 0.8 ppm.

Recovery palladium may be revalue as palladium chloride. Palladium by treatment with royal water and returning back with concentrated hydrochloric acid . Hydrochloric of dark brown solution is brought to dryness by evaporation under energy ventilation 2-3 or , is achieved $PdCl_2$.

b) It is taken into 250 ml of waste water containing 105 mg Pd/liter.

In this case the required 105 mg of sodium hypophosphite monohydrate and an excess of 10%, which is a total of 115.5 mg hypophosphite (115.5 mg is equivalent to 2.18 ml reagent).

Reducing the palade ion , along with the precipitation of the amorphous form of palladium occurs at 70°C. The precipitate is left to decantation for 10-12 hours and then filtered.

Method regenerative treatment of aqueous waste solutions with palade ions in hydrochloric acid medium, by chemical reduction followed by precipitation, decanting and filtration takes place as shown in fig.1.

Analysis of palladium content of waste water is carried out by back-titration of the excess complexone III 0.05 M with thorium nitrate 0.05 M in the presence of xylenol orange at pH=3, adjusted with 10% aqueous ammonium acetate . The equivalent color of the solution changes from yellow to red .

In determining factor thorium nitrate solution by titration with complexone III to pH=2-3 adjusted with nitric acid and ammonium acetate 10% as appropriate.

Palladium can be determined spectrophotometrically by measuring the color intensity of the palladium complex yellow with dimethylglioximă alcoholic solution 1% was extracted into chloroform, the acid pH of 0.7-1 pH units, at a wavelength of 366 nm [6].

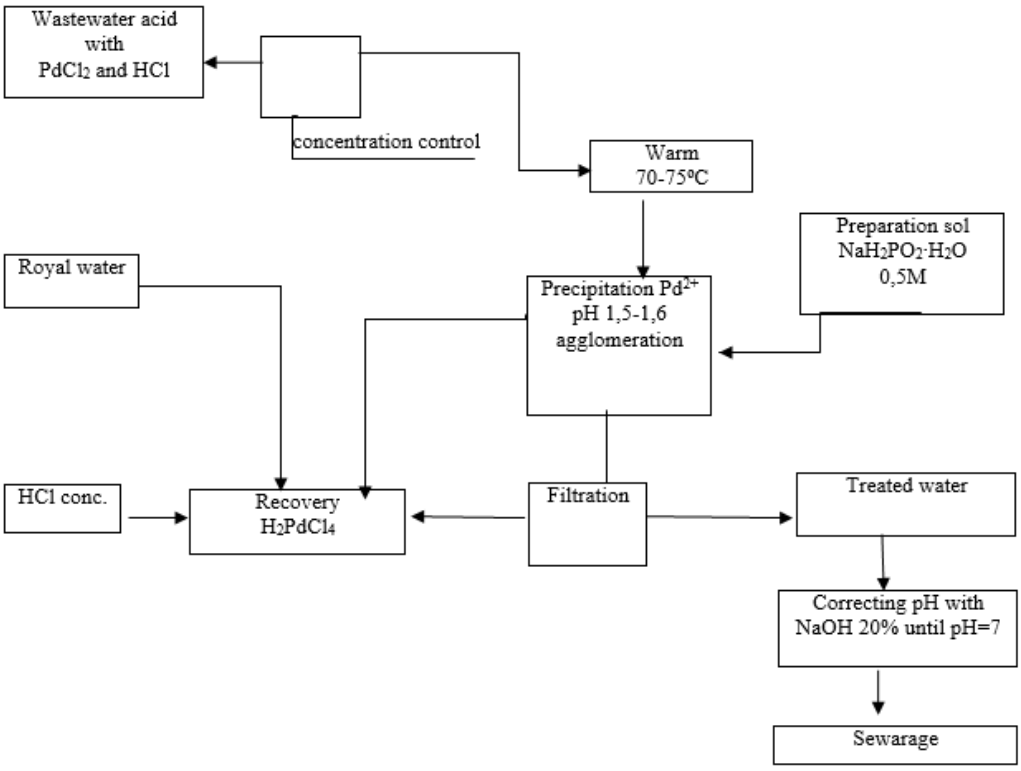

Fig. 1. Treatment of aqueous waste containing palladium chloride.

3 RESULTS AND DISCUSSION

The concentration of palladium ions in the waste water analyzed ranged from 300-1300 mg Pd/dm^3.

Chemical reaction equation the reduction of palladium with sodium hypophosphite used is as follows:

$$PdCl_2 + H_2O + NaH_2PO_2 \rightarrow Pd + 2HCl + NaH_2PO_3$$

The difference values of the standard electrode potentials allow chemical reduction reaction in good condition, with yields recovery above 99% after a reaction rate noticeable. (Correlation between initial and final concentrations ion of palladius with respect to time).

Analysis of the initial and final concentrations palladium ion in wastewater and treated water, is about volumetric method, easily approachable and quick.

The supernatant was neutralized with sodium hydroxide solution 10% until the pH value from 7 to 8.5, you can flush drains.

4. CONCLUSIONS

Following the survey, I found that chemical reduction method applied in this case has several advantages:

- Use as the reaction medium acidity wastewater;
- Avoid possibility re-dissolution palladium hydroxide in excess of base;
- Using a slight excess of reagent to the stoechiometric requirement;
- Lead the recovery of palladium in water and reintroduction in the technological.

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PRELIMINARY STUDIES CONCERNING ELECTRICITY GENERATION IN MICROBIAL FUEL CELLS

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Abstract: *A microbial fuel cell (MFC) is a bioreactor that converts chemical energy of organic compounds into electrical energy through catalytic reactions of microorganisms under anaerobic conditions. The recent energy crisis has increased the interests in MFCs among researchers as a possible alternative way to generate electrical power or hydrogen from biomass without increasing the net carbon emission into the environment. MFCs can also be used in wastewater treatments to break down organic matters. Power output and efficiency are significantly affected by the types of microbes in the anodic chamber of the MFC, the fuel cell configuration and the operating conditions. Currently, the applications of MFCs are somehow limited because of their low power density in the range of several W/m^2. A miniaturised microbial fuel cell operated with mediator and different microorganisms was developed and the influence of the external load on the composition of the anodic biofilm microbial community was investigated in this MFC fed with glucose and Saccaromyces Cerevisae used as source of electrogens. The purpose of these preliminary studies was to determine the effect of external resistance on biofilm formation and power output. The internal resistance in MFCs can be affected by the anolyte and catholyte composition, pH, the electrode material and structure, the electrode polarisation and by the microbe's characteristics*.

Keywords: microbial fuel cell, biofilm formation, microbial composition

1. INTRODUCTION

In recent years the intensive use of fossil fuels (oil, natural gas) has accelerated and this fact has triggered a global energy crisis. In this context, renewable bioenergy is considered as one of the ways to alleviate the energy crisis and avoid global warming.

Technologies based on microbial fuel cells represent the newest approach regarding the electricity generation from biomass or sewage using bacteria and microorganisms.

In addition, there is a trend of miniaturization and portability of computers, computing and communications devices. These applications require small and light energy power sources that are able to support operation over long periods of time, especially in remote places. Moreover, progress in medical sciences lead to the design and use of a growing number of implantable powered devices (pacemakers). These devices require energy sources that work for extremely long periods of time, as their replacement requires surgery. Ideally, the implanted devices could use natural body "fuels", and thus would continue to draw power as long as the patient lives.

Biofuel cells offer potential solutions to all these problems by taking from nature the power generation solutions and adapting to our own needs. They consume the available substrates from renewable sources and turn them into secondary products, with electricity generation.

Because MFC (microbial fuel cells) use concentrated chemical energy sources, they can be small and light, and fuel can be purchased even from a living organism (e.g. blood glucose).

The first observations and experiments on generating electricity using bacteria-based systems were performed by Potter et al. in 1911 [1, 2], but in the next half century only a few practical applications have taken place in this area. In the early '90s a lot of studies regarding microbial fuel cells have been carried out. However, the accomplished experiments have required the presence of chemical mediators or of electron carriers, capable of transporting electrons from the cell towards exogenous electrodes. The most important breakthrough occurred in 1999 when it was

discovered that the presence of these mediators is not required for electron transport.

Biofuel cells use biocatalysts for the conversion of chemical energy into electrical energy. Because most organic substrates undergoes combustion with energy evolving biocatalytic oxidation of organic substances by oxygen or other oxidants, at the electrode interfaces, provides an effective way of converting chemical energy into electrical energy. Abundant organic raw materials such as methanol, organic acids or glucose, can be used as oxidation substrates and molecular oxygen or H_2O_2 can act as substrate for the reduction reaction.

2.OPERATING PRINCIPLE OF BIOCHEMICAL FUEL CELLS

The present world energy crisis has raised interest in researchers for microbial fuel cells as a possibility to generate electricity or hydrogen directly from biomass without carbon emissions into the environment. Also, these fuel cells can be used successfully in industrial and sewage wastewater treatment to decompose organic matter. Another way to use these microbial fuel cells is the biosensors (sensors for monitoring the biological oxygen consumption).

As the power generated by microbial fuel cells is somehow low, it does not comply with the needs for a large scale wastewater treatment. In fact, the only microbial fuel cell with potential practical application is that of a sediment-based design which produces current by incorporating the anode in that sediment and it is connected through an electrical circuit to a cathode placed in the aerated seawater. This system is feasible to generate power for sensors and telemetry devices in remote ocean areas.

A microbial fuel cell is a bioreactor that converts chemical energy from chemical bonds of organic compounds into electricity, based on catalytic reactions of microorganisms under anaerobic conditions.

Terminal voltage and energy efficiency are significantly influenced by the type of microorganisms in the fuel cell anode compartment, its configuration and operating conditions. Currently, practical applications of microbial fuel cells are limited due to low specific power values obtained (a few hundred mW/m^2). Therefore efforts are being made to improve energy performance and reduce costs of construction and operation of these cells

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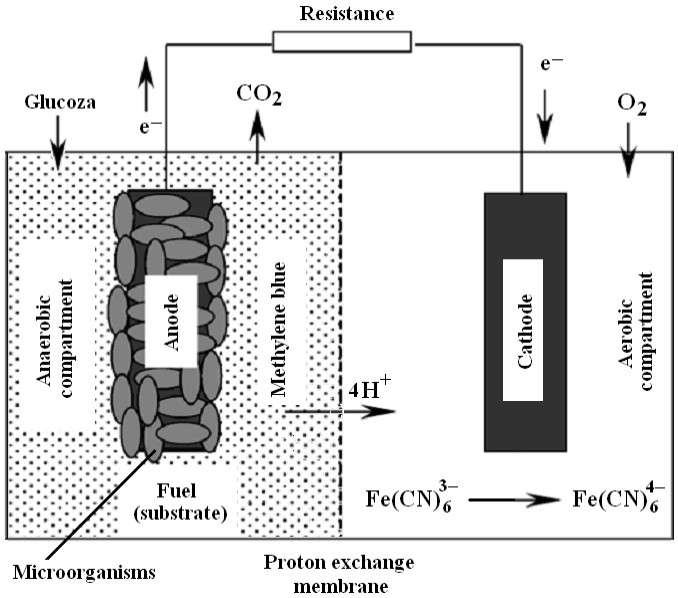

Fig. 1. Schematic representation of a microbial fuel cell [5]

Figure 1 presents a diagram of a typical microbial fuel cell for electricity generation. It consists of an anode and a cathode compartments, separated by a proton exchange membrane (PEM). The presence of oxygen in the anode chamber will inhibit the generation of electricity process. Therefore the system must be designed to maintain separate microorganisms and oxygen present in the catholyte. This separation can be achieved by placing a separating membrane, which provides charge transfer between the electrodes, forming two separate compartments: the anodic compartment, where microorganisms grow and the cathodic compartment, where the electrons react with catholyte [3, 4, 5].

The microorganisms from the anodic compartment of microbial fuel cell oxidize added substrate and generate electrons and protons in this process. Carbon dioxide results as a product of the oxidation reaction. However, there is no net carbon emission because carbon dioxide from renewable biomass comes from the atmosphere through the photosynthesis process. Electrons are transferred to the cathodic compartment through an external circuit and protons cross the exchange membrane shifting towards the cathodic compartment. Electrons and protons are consumed in the cathodic compartment, combining with oxygen to form water.

The electrolyte solution is an oxidizing agent, which takes electrons from the cathode. In the electron transfer circuit related to the microorganism cell one of the oxidizing agent is the oxygen. However, this is not very effective, as it would require large volumes of flowing gas; a more convenient solution is to use an oxidizing agent.

The connection of two electrodes in the external circuit is made of electrical wires, having inserted a resistive component (e.g. resistance, electrical bulb etc) and also the internal circuit contains a salt bridge or an ion exchange membrane. Selective membranes allow protons which are produced in the oxidation reaction to pass from anodic to the cathodic compartment [8, 9, 10].

Electricity generation is achieved by separating the microorganisms and the oxygen or any other final acceptor resulting in an anaerobic anodic compartment.

The electrochemical reactions taking place at the two electrodes are shown below using as an example the acetate ion:

Anodic reaction :

$$CH_3COO^- + 2H_2O \xrightarrow{\text{microorganisms}} 2CO_2 + 7H^+ + 8e^- \quad (1)$$

Cathodic reaction :

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \quad (2)$$

The overall cell reaction is represented by the decomposition of the substrate to carbon dioxide and water, with concomitant generation of electricity as a by-product. Based on the two redox reactions at the electrodes, a microbial type bioreactor can generate electricity on electron flow from anode to cathode in the external circuit.

Generally, there are two types of microbial fuel cells: with mediators and without mediators. Microbial fuel cells without mediators are recently discovered and their operation is not very well explained, due to several factors affecting the optimal working conditions, such as: the nature of microorganisms used in the system, the type of ion exchange membrane, temperature. Usually, the used bacteria have electrochemically active redox enzymes such as cytochromes on the outer membrane that can transfer electrons outside.

Microbial fuel cells use inorganic mediators that enter in the electrons transport chain from cells and extract the transferred electrons. The mediator crosses the outer lipid membrane of the cells and the plasma wall, and then begins to release electrons from the electron transport chain, which normally would be taken over by oxygen or other intermediaries. The reduced form of mediator leaves the cell charged with electrons, which are carried to the electrode, where they are discharged; this electrode becomes the charge generator anode (negatively charged electrode). The release of electrons means that the mediator is oxidized to its original state, making it ready to repeat the process. It is important to note that this process may take place only under anaerobic conditions; if oxygen is present then it will capture all the electrons, because it has higher electronegative character than the mediator.

Under aerobic conditions, when microorganisms consume the substrate (sugar), they produce carbon dioxide and water. However, when oxygen is not present, the microorganisms produce carbon dioxide, protons and electrons, according to

the following oxidation reaction:

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^- \quad (3)$$

In a microbial fuel cell, the anode is the final electron acceptor recognized by bacteria in the anodic compartment. Therefore, microbial activity is strongly dependent on anode redox potential. Recently, it was discovered that there is a Michaelis-Menten type dependence between anode potential and nominal generated power, so there is a critical value of anodic potential that can get the maximum value of nominal power for a microbial cell.

MFC's reach a maximum working voltage of 0.3 to 0.7 V. The value of generated voltage is a more difficult problem to predict than in case of a chemical fuel cell. In a microbial cell, it takes time for bacteria to colonize the electrode and to create enzymes and structures needed to transfer electrons outside the cell. Even the electric potential of a pure culture can not be predicted with precision.

In biological systems, the potentials are usually pre-adjusted to a neutral pH, because the cytoplasm of most cells has a pH = 7.

When the voltage is positive, the reaction that occurs is exothermic. In this case, the variation of Gibbs free energy is negative. Total voltage is represented by the difference between the anodic and cathodic potential:

$$E_{ref} = E_{cat} - E_{an} \quad (4)$$

The potential is corrected for standard conditions and for pH = 7.

If the system's thermodynamic limits the total produced power, it is expected that the measured anodic potential to approach the calculated maximum potential. Typically, the maximum cathodic potential is 0.4 V, with a working potential of 0.25 V, even using a platinum catalyst. With the exception of oxygen, the most widely used catholit is hexacyanoferatte $Fe(CN)_6^{3-}$:

$$K_3[Fe(CN)_6] + e^- \rightarrow K_4[Fe(CN)_6] \quad (5)$$

3.COMPONENTS OF MICROBIAL FUEL CELLS

The main challenge in achievement of a microbial fuel cell is to identify materials and design, which optimizes the energy generation process and the coulombic efficiency but also minimizes the costs of a reliable and reproducible system.

The main components of a microbial fuel cell are anode, cathode and selective membrane [11, 12, 13].

In Table 1 are presented the components of a microbial fuel cell and also the materials used for their construction

Table 1. Basic components of microbial fuel cells

Components	Materials	Observations
Anode	graphite, graphite felt, carbon, Pt, Pt black, reticulated vitreous carbon	necessary
Cathode	graphite, graphite felt, carbon, Pt, Pt black, reticulated vitreous carbon	necessary
Anodic compartment	glass, polycarbonate, Plexiglas	necessary
Cathodic compartment	glass, polycarbonate, Plexiglas	optional
Proton exchange system	- proton exchange membrane: Nafion®, Ultrex, polyethylene, poly (styrene-co-divinylbenzene) - salt bridge, porous porcelain diaphragm	necessary
Electrocatalyst	Pt, Pt black, MnO_2, Fe^{3+}, polyaniline, electronic mediator immobilized on the anode	optional

1.1. The anode has reached the highest level of development through the use of graphite fibre brush-type electrodes. The selection of membranes or other material separating the anode – cathode compartments is an important step for the development of these devices, due to high cost and general effect of increasing internal resistance.

Anodic material must have the following characteristics: high conductivity, non-corrosive characteristics, high specific surface area, high porosity, cheap, easy to produce in larger dimensions.

Among the anodic materials it can be mentioned:

- carbon paper, carbon cloth, foams and RVC; These materials have high conductivity and are suitable for the growth of microorganism. Carbon paper is rigid and fragile, but easy to connect to a conductor. The stainless steel or titanium conductors have better behaviour than copper.
- graphite rods, felt, foam, granules, plates and sheets

Graphite rods were used in several studies especially due to their high conductivity and relatively well-defined surface, but present the disadvantage of a reduced surface area for growth of microorganisms. In terms of current density, this parameter was studied in comparison (Chaundhuri and Lovley, 2003) using Rhodoferax ferriducens in a two-compartment microbial fuel cell.

So it was found that the graphite felt produces 2.4 times more current than graphite rods, mainly due to the large surface area.

- fibres and graphite brushes
- conductive polymers
- metals and metal plating.

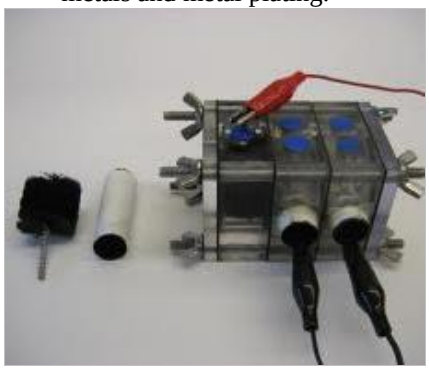

Fig. 2. Microbial fuel cell with carbon brush anode and tubular cathode [6]

3.2. In bicameral microbial fuel cells membranes are used to separate the anolit from the catholit. These membranes must be permeable to protons, but should be a barrier to the transfer of other chemical species between microbial fuel cell compartments. Membranes are used to reduce the organic substrate flow from the anode to the cathode and also the oxygen flow from the cathode to the anode (oxygen is toxic to exo-electrogene bacteria), improving coulombic efficiency.

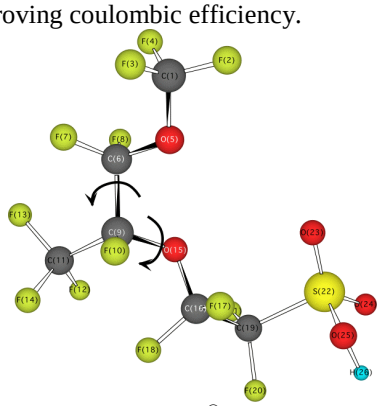

Fig. 3. Nafion 117® membrane [7]

The main disadvantages of separation membranes are the high cost and the fact that it slightly decreases the energy performance of the system as a result of increased internal resistance.

Membranes used in existing applications are of two types:

- cation exchange membranes: Nafion 117®, CEM
- anion exchange membranes. It was found that protons can be efficiently transported also by other chemicals used as pH buffer (phosphate anions).
- bipolar membranes;
- ultrafiltered membranes.

3.3. The presence of a catalyst is the necessary basic feature for the cathode. However, recent studies have shown promising results for the replacement of a noble metal catalyst by a transitional metal or other compounds that do not contain noble metals.

The mechanism of electrochemical reactions taking place at the cathode is difficult to determine because the electrons, protons and oxygen should converge on the catalyst surface in a three-phase reaction (solid catalyst, air and water). Catalyst placed on a conductive surface requires exposure to both water and air, so that protons and electrons from these phases to reach the same active reaction area of the catalyst.

At the cathode achievement are used the same materials as the anode, except that for the cathode is necessary, but not required, the presence of a catalyst (platinum for the reduction of O_2).

Among the cathode materials it can be mentioned:

- cathodes made of platinum or platinum-coated metal;
- metal cathodes;
- carbon cathodes with platinum catalyst;
- carbon cathodes with non-platinum catalyst. in different geometrical shapes:
- plain carbon cathodes;
- tubular cathodes covered with carbon;
- bi-cathodes.

3.4. Microorganisms and exo-electrogens bacteria

Electrochemically active biofilms are of great importance in the natural environment, mainly in metals oxidation and reduction, in the minerals dissolution, in the carbon cycle and complexing phosphorus compounds and heavy metals.

Anaerobic bacteria have evolved over millions of years using various methods to reduce the compounds needed to maintain metabolism, all without the involvement of oxygen necessary for respiration [14, 15].

Most anaerobic bacteria can only transfer electrons to soluble compounds (nitrates, sulphates) that can diffuse through the cell membrane inside the cell.

Bacteria that have evolved have been able to use several different types of electronic acceptors, also transferring electrons outside the cell. Such bacteria are called exo-electrogens. Exo-electrogen bacteria differ in their capacity to carry electrons directly outside the cell, allowing them to function in a biochemical fuel cell.

Biochemical reactions inside the anaerobic bacteria may be carried out on different levels of temperature, depending on the tolerance of bacteria, from moderate temperature (15–35°C) to high temperatures (50–60°C) or low temperature (<15°C).

Exo-electrogen bacteria that produce electricity without mediators are:

- Gammaroteobacteria and Schewanella;
- Deltaproteobacteria and other members of Geobacteracae;
- Firmicutes and Clostridia;
- mediators generating bacteria;
- Pseudomonas Aeruginosa;
- Geothrix fermentans, from Geobacter genus type.

3.5. For any biological process substrate is important because it serves as a source of carbon and energy. Substrate affects not only the bacterial community full composition in anodic biofilm, but also microbial fuel cell performance, including the value of specific power and coulomb efficiency.

The most common types of substrates are:

- acetate – a simple substrate, extensively used as carbon source to induce electro-active bacteria; is preferred because of its inertia to other alternative types of microbial conversions at room temperature (fermentations and methane-genesis);
- glucose – another substrate commonly used in microbial fuel cells;
- lignocellulosic biomass.

Abundance and regenerative capacity of lignocellulosic materials from agricultural residues make of this type of substrate a potential source of cheap energy production. However, lignocellulosic biomass can not be used directly by microorganisms in MFC power generation. First this type of biomass must be converted to monosaccharide or other low molecular weight compounds. It was not found yet effective microorganisms to convert pentose (the main component of lignocellulosic hydrolysates) to bioethanol.

Other types of substrates involved in electricity generation are: synthetic waste water, waste water from the beer industry, starchy waste water, waste water from the paint industry, cellulose and chitin, inorganic substrates.

4.EXPERIMENTAL

4.1. Construction and operating conditions of the microbial fuel cell

Microbial fuel cell is achieved from polycarbonate and contains two circular compartments, anodic and cathodic, each having a volume of 27 mL, with an open side and two supply holes at the top, as in Figure 4. These compartments are assembled using screws, washers and nuts, being separated by a proton exchange membrane (Nafion®, DuPont USA), with an active area of 18 cm^2. Membrane was pre-treated by hydration in doubly distilled water for 24 hours before use. Each compartment contains one graphite electrode in the form of disc with a diameter of 4.8 cm

(active surface area 18 cm^2).

The electrodes are provided with connecting wires that make the connection to external electrical circuit. Ohmic resistance of the electrodes and connecting wires is 3 kΩ, measured with an ohmmeter. The distance between electrodes is 3.4 cm.

The design shape of assembled microbial fuel cell is shown in Figure 5:

Fig. 4. Components of the microbial fuel cell used in the experiments

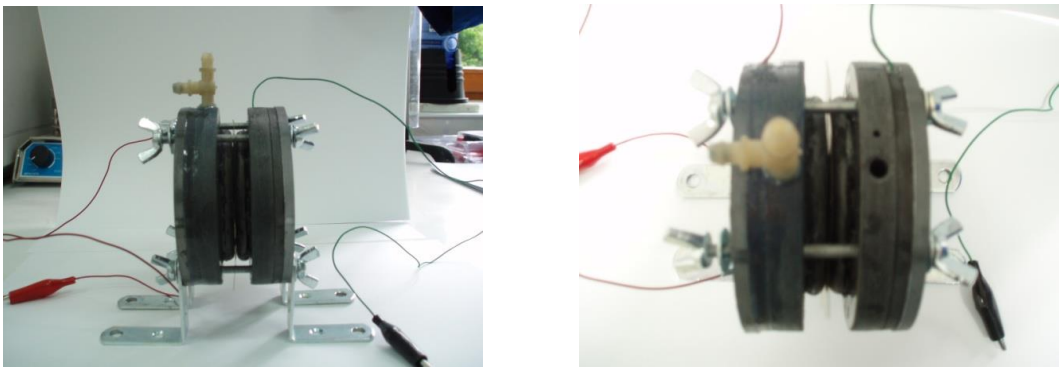

Fig. 5. The assembled microbial fuel cell

4.2. Electrolyte solutions and microorganisms

Anodic compartment was inoculated with a solution containing a suspension of microorganisms (Saccaromyces Cerevisae) in 0.1 M Na_2HPO_4 and NaH_2PO_4 buffer solution. The necessary nutrient for the feed of microorganism is based on 1M glucose solution and the mediator used is a 0.01 M methylene blue solution. After filling, the anodic compartment was closed to ensure an anaerobic environment. As a catholit in cathodic compartment was used a 0.02 M potassium hexacyanoferrate $K_3[Fe(CN)_6]$ solution.

Experimental measurements were performed at room temperature 25 ± 1°C. In order to form the biofilm on the anode surface, experimental measurements were initiated after a period of 30 minutes since inoculation.

Redox potential values of anodic and cathodic reactions are:

E_0 = +11 mV/Ag, AgCl (methylene blue) (6)

E_0 = +430 mV/Ag, AgCl (potassium hexacyanoferrate)(7)

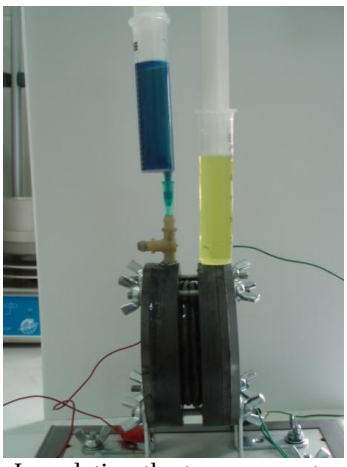

Fig. 6. Inoculation the two compartments of the fuel cell with the electrolytes

4.3. Electrical and electrochemical measurements

In the external electric circuit one

has placed a variable resistance (0 – 1000 Ω) connected to the two electrodes.

The nominal fuel cell voltage was monitored every 10 s by measuring the potential difference between anode and cathode, with VoltaLab 40 potentiostat, connected to a computer for data acquisition. Electrical power P was calculated with the formula:

$$P = I \cdot V \qquad (8)$$

where V – electrodes potential measured versus Ag/AgCl saturated, V, I – current intensity, A.

Polarization tests were achieved by varying the external resistance, then reading current and voltage value at the stabilization point. Internal Ohmic resistance, which refers to the resistances amount of electrodes, electrolyte, membrane and interconnectors on charge transfer process was calculated according to the relation derived from Kirchoff's law for a circuit in that the value of electrical resistance connected to power source is known:

$$R_{int} = \frac{V_{OCP}}{I} - R \qquad (9)$$

where V_{OCP} – open circuit voltage, I – current intensity at the resistance value R, R – electrical resistance.

5.RESULTS AND DISCUSSION

Figure 7 presents the nominal fuel cell voltage evolution under investigation. It can be noticed there is a sharp, gradual rise of the voltage in the first 30 minutes, followed by a further slower increase, then a period of stabilization around 500 mV values, approximately 2 hours after inoculation At the end of this investigation the anode and cathode surfaces were microscopically examined; on the anode was observed a thin layer, coloured in deep blue, which represents the biofilm formed by the microorganism's colony. This fact indicates that the tested microorganisms were oxidized the substrate and thus generating voltage

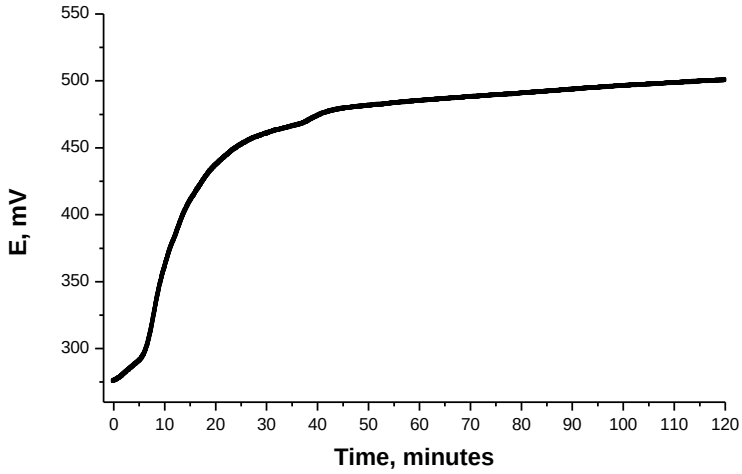

Fig. 7. Evolution in time of nominal fuel cell voltage

Figure 8 shows the experimentally determined nominal voltage and specific power, calculated according to relation (8), depending on current intensity values and implicit on variable resistance values of the circuit. From these curves can be observed that the maximum power value obtained is about 60 mW at a current intensity of 200 μA (external resistance R = 750 Ω). For this maximum value was calculated the internal resistance that is equal to 2 kΩ.

Since the cathodic reaction is potassium hexacyanoferrate reduction, the cathode potential remains constant, therefore changes in nominal fuel cell voltage is due to change in anode potential, thus biofilm formation and growth on anodic surface.

The low energy efficiency of fuel cell depends also on factors that can not be quantified, namely the accumulation of metabolites, biomass growth, diffusion through the substrate and electron-consuming competitive reactions (formation

of gaseous hydrogen, methane gas, etc.) or reduction of gaseous oxygen that diffuses through the membrane.

5.CONCLUSIONS

Microbial fuel cells have gained much attention in recent years as a way to convert the organic waste, including wastewater or ligno-cellulosic biomass, into electricity. Electricity generation from microorganisms can become an important form of bioenergy in the future, since microbial fuel cells (MFC) allows the extraction of electricity from a wide variety of complex dissolved organic waste and also from renewable biomass sources. Variations in generated power values can be attributed to changes in the overpotential of activation, ohmic or concentration values within the investigated microbial fuel cell. Variations in ohmic drop voltage and concentration overpotentials have relatively constant values as a result of similar operating conditions. Variations in generated power, as an indicator of energy performance, with external resistance value may be associated with low levels of anodic activation overpotentials, which are influenced by the electrochemical activity of reducing microorganisms at the anode.

In conclusion, one may suggest that changes in anode potential depending on external resistance represent the main criterion for selecting the type of electrochemically active microorganism used.

It is expected that, over time, given the interest and resources invested in this area of research, generated power density to reach values that makes biochemical fuel cell used in other applications.

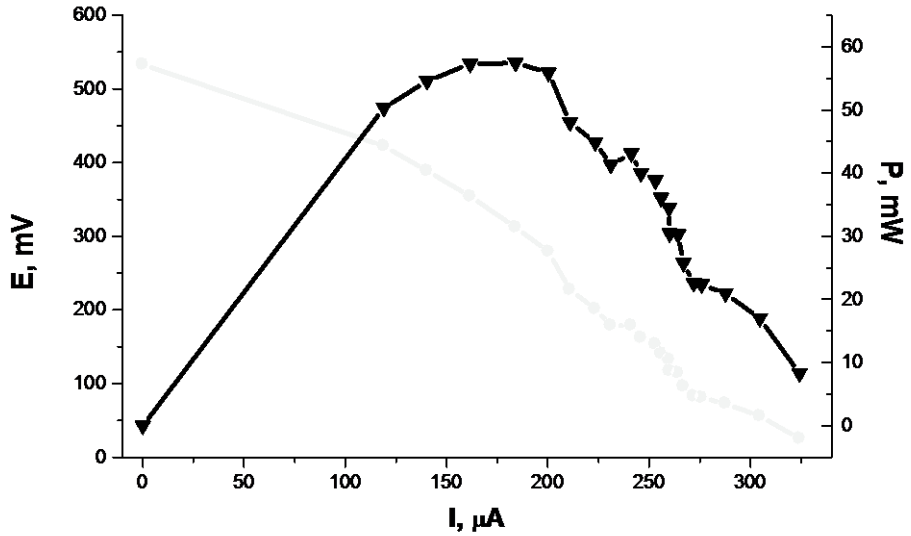

Fig. 8. The influence of external resistance values against nominal voltage and specific power

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CORROSION AND SCALING TENDENCIES IN GEOTHERMAL WELLS NEARBY ORADEA

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Abstract: *Aquifer fluid composition has been determined by analysis made on water samples collected from a production well in Felix geothermal area. The obtained data was used to monitor any possible chemical change in the field. In order to assess the corrosion processes in exploitation equipments there were determined the corrosion rates for the studied well and were performed experiments with corrosion inhibitors, monitoring their efficiency. The control of mineral depositions was done by tests in order to check the good performance of additives to avoid deposition formation, by measuring the change in pressure across a capillary tube in conditions of using different dosage of additives.*
Key words: additive treatment, mineral deposition

1. INTRODUCTION

The north-western part of our country has a good geothermal potential, being exploited a high number of low-temperature geothermal wells.

The major problem encountered during wells production, which affects the heat transfer surfaces, having as results a serious loss of efficiency and production is scaling due to mineral depositions and to corrosion. Without effective chemical control, this might lead to the eventual shutdown of the production for cleaning[1].

This paper presents the research results obtained for a geothermal well located in Baile-Felix resort, nearby Oradea, which supplies geothermal water for heating and for swimming pool for the local community.

The corrosion and scaling problems suggested the necessity of laboratory investigations.

A first objective was to obtain a reliable composition of these waters and then to determine the corrosion rate and the scale deposits and to try to find out the best additive which control corrosion rate and deposition formation.

2. EXPERIMENTAL METHODS

2.1 Thermal water analysis

Waters from the selected geothermal well was sampled and the main components were analysed in the laboratory by the methods[3] briefly mentioned in table 1. The wellhead temperatures measured during collection of water samples were in the range of 40-42ºC.

Table 1. Applied water analysis

Constituent	Type of analysis
Cl^-	Volumetric
HCO_3^-	Volumetric
SO_4^{2-}	Volumetric
NH_4^+	Volumetric
Ca^{2+}	Volumetric
Mg^{2+}	Volumetric
Fe^{3+}	Spectroscopy in VIS
Na^+	Flamphotometry
K^+	Flamphotometry
SiO_2	Spectroscopy in VIS
pH	Electrometric
Mineralization	Gravimetric

2.2 Determination of corrosion rates

In order to calculate the corrosion rates, in the present paper was applied the gravimetric method, in static and also in dynamic conditions. Corrosion tests were conducted using carbon steel coupons, being done by the same material of the exposed pipe to fluids from Felix well. The metal coupons were treated first with a diluted HCl solution, then washed with distilled water, alcohol and dried. The surfaces of the coupons were measured and they were weighed to 0.001 g accuracy

before introducing them into the test. The water bath was kept at constant temperature of 25ºC, respectively 40ºC. The measurements were done for periods ranging between 360 and 1440 hours. The effects of corrosion for each coupon were noticed by taking into account the changes in weight after immersion in the geothermal water.

In lab conditions was studied the performance of different additives by the use of gravimetric method. The used coupons were from the same material as the pipe. The methods for preparation of the coupons and the timing were exactly like in the case without any treatment. As anti-corrosion additives were used disodium phosphate and tiouree, in different concentrations, trying to find out the minimum dosage needed to prevent corrosion.

2.3 Chemical deposition control

A laboratory test was done in order to control the calcium carbonate deposit[2,5,6]. The geothermal water from the well was pumped at constant flowrate through a stainless steel capillary tube immersed in water bath at 40^0C. Any calcium carbonate deposition reduces the bore of the tube, being followed of an increase in pumping pressure. The rate of change in pressure across the capillary tube was monitored. The chemical additive was maintained at a low concentration of 2 mg/l during the test and was measured the time needed to reach a pressure difference of 0.08 atm. Then were increased the dosages of additive, in order to get the proper dosage, which gives a longer time related to the deserved price.

3. RESULTS AND DISCUSSIONS

The results of chemical characteristics of analysed geothermal waters are shown in table 2. The measured pH at sampling was 6,5.

As seen from Table 2, the studied waters can be classified as calco-bicarbonated waters. It can be anticipated calcium carbonate deposition in exploitation equipments. Mineralization is rather high, being about 0.7 g/l. The pH is slightly acid. The high carbon dioxide content, which at the waters' pH is especially in the form of bicarbonate, associated with the chloride content, gives a tendency of corrosion of the pipes, that could be amplified by the water temperature around 40^0C at the wellhead.

Calculation data for the corrosion process of the coupons immersed in geothermal water from well are summarized in table 3, comparative at the wellhead temperature and at lower temperature and illustrated in fig.1.

Table 2. Chemical composition of studied waters

Constituent	Concentration, in mg/L
Cl^-	28,9
HCO_3^-	382,5
SO_4^{2-}	260,8
NH_4^+	0,064
Ca^{2+}	180,8
Mg^{2+}	25,4
Na^+	18,2
K^+	4,9
SiO_2	27,2
Fe^{3+}	0,011
Mineralization	698

Table 3. Corrosion rate results

Temp, [ºC]	Weight loss, [g]	Exposed time, [hours]	Corrosion rate, [g/m^{2}hour]	Corrosion rate, [mm/year]
40	0,2682	360	0,45153	0,5012
	0,2424	576	0,25505	0,2831
	0,2091	720	0,17604	0,1954
	0,1585	1080	0,08892	0,0987
	0,0696	1440	0,02928	0,0325
25	0,2422	360	0,40775	0,4526
	0,2385	576	0,25090	0,2785
	0,1915	720	0,16117	0,1789
	0,1371	1080	0,07694	0,0854
	0,0550	1440	0,02315	0,0257

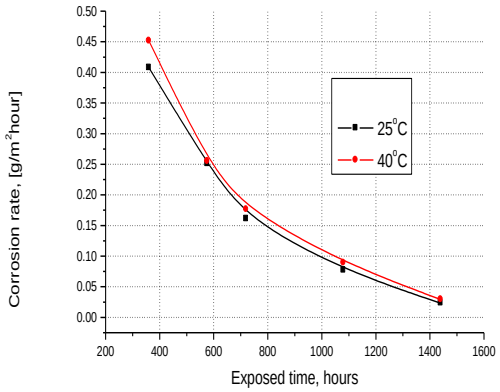

Figure 1. Changes of corrosion rate in time

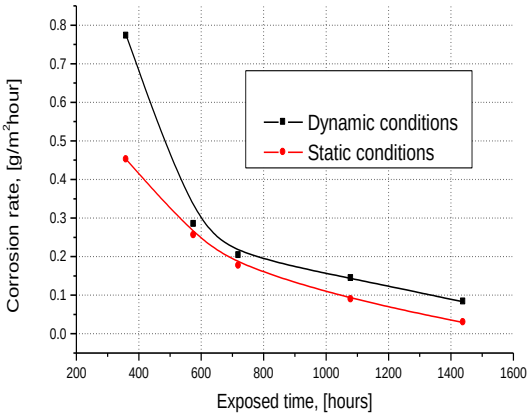

Figure 2: Changes of corrosion rate in time, at 40^0C

By analysing the corrosion process of the coupons exposed in geothermal water from the studied well, you can notice that the corrosion process is more accurate in the first month of testing and it decreases in time, being almost stable in the second month, which is explained due to corrosion products, with a passive action, formed on the coupons surface.

Experimentally it was observed a uniform corrosion in the first half of testing period and later then a tendency to pitting corrosion.

Comparing the tests made at the wellhead temperature in static, respectively in dynamic conditions (figure 2), it was recorded almost a double corrosion rate in dynamic conditions compared to static ones.

Trying to protect against corrosion, were done experiments at the wellhead temperature, in static conditions, by the use of two anti-corrosion additives, being recorded the effects on corrosion rates in time. The results are summarized in table 4.

Table 4. Dependence of corrosion rate on inhibitor

Time, hours	Corrosion rate without inhibitor, g/m^2 hour	Corrosion rate in presence of inhibitor, g/m^2 hour			
		Na_2HPO_4. mg/L		CH_4N_2S. mg/L	
		25	50	25	50
360	0.45153	0.2135	0.1122	0.3216	0.2311
576	0.25505	0.1267	0.0948	0.1790	0.1357
720	0.17604	0.0899	0.0403	0.1248	0.0982
1080	0.08892	0.0302	0.0103	0.0722	0.0503
1440	0.02928	0.0100	0.0084	0.0215	0.0092

It can be seen a better efficiency of disodium phosphate.

The supersaturation of calcium carbonate[4] was controlled by tripoliphosphate additive, trying different concentrations, in order to check the lowest concentration of additive when precipitation of calcium carbonate does not form.

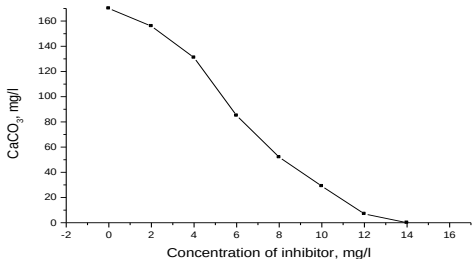

Figure 3. Deposition control

It was found out (figure 3) that the phosphate additive gives good results. It can be used in concentration of 12 mg/L in order to avoid calcium carbonate deposition.

4. CONCLUSIONS

Chemical analysis of water samples collected from selected geothermal well from Băile Felix indicated that these waters present a high bicarbonate content and calcium is the most dominant cation. It was also noticed a high sulphate content.

At low pH, the presence of chloride and of dissolved oxygen into the geothermal water represent factors which affect the exploitation equipments by stimulating the corrosion processes.

After gravimetric research in static and dynamic conditions it can be concluded a double corrosive tendency in dynamic conditions.

The analysis were done at temperature of 40ºC, which is the wellhead temperature of the well taken in this work and at 25ºC, temperature that can be reached by utilization. Corrosion is more pronounced at the beginning of the exposed period. Then the corrosion rate tends to establish to a value with one order smaller. At the production temperature, 40ºC, corrosion is higher. It was considered the anti-corrosive protection with additives. There were made experiments with a precipitation additive, disodium phosphate and an adsorptive additive, tiouree. It was recorded the better efficiency of disodium phosphate additive, because, even at a 25 mg/L dosage reduces significantly the corrosion rate of the coupons.

In laboratory conditions, by using an installation which allows measuring the pressure, in a capillary tube, as the precipitation takes place, were performed tests with anti-scaling additive. It was proven the efficiency of the tripoliphosphate additive.

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NITROGEN COMPOUNDS REMOVAL FROM MUNICIPAL WASTEWATER

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Abstract. *The paper is a short review on nitrogen compounds removal, as ammonia, nitrate, nitrite, from municipal waste water, containing primary information of nitrogen chemistry, consideration on the physical-chemistry methods of removal and also on the most popular wastewater nitrification systems[1].*
Keywords: municipal waste water, nitrification-denitrification treatments.

INTRODUCTION

The use of water becomes in time more impractical but the water resources. Human activities, from cities, industry or irrigation systems are discharging effluent which becomes the supply of water for other users. Not only intensive agriculture [2,3], but also the nuclear industry[4] are the main pollution source for the drinking water. The admission levels for nitrate in CE is 50 $mg.L^{-1}$ (adults) -15 $mg.L^{-1}$ (children) [3,5,6], high levels of nitrate concentration leading to serious medical problems.

Chemicals as metallic salts or complex organic compounds are increasing frequency in the waterways. They enter the drinking water and eventually end up in the wastewater. Primary and secondary waste treatment processes could be not very effectively in removing these chemicals.

For years, dilution and purification of the effluent in the receiving stream was considered acceptable. Because these streams have more pollutant loadings, natural processes are not enough in these days. Often is necessary some more treatment than primary and secondary wastewater. In the last years, some physical, chemical, and biological processes come into light in the wastewater technology. Currently wastewater technologies which have been used for advanced wastewater treatment are the following: filtration, adsorption, chemical oxidation, reverse osmosis, nitrate removal by denitrification, phosphorus removal.

Ammonia removal could be done by the biological nitrification of wastewater and after that the denitrification, which involves the conversion of nitrate nitrogen ions (NO_3^-) to gaseous nitrogen (N), as shown on the left side of nitrogen cycle (figure 1).

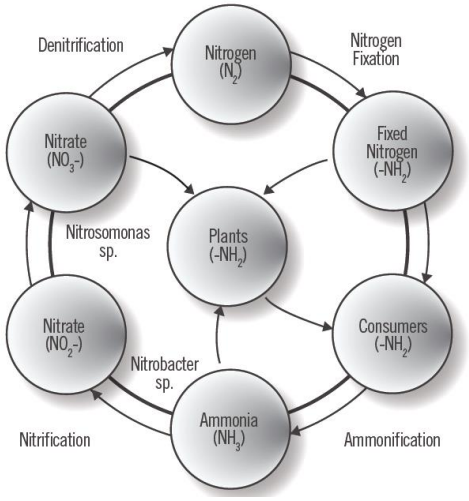

Figure 1. Nitrogen cycle[7].

EXPERIMENTAL AND DISCUSSION

The removal of ammonia from wastewater treatment becomes a a very important operation in special for the lands where agriculture is done intensively. One method of ammonia removal is the biological nitrification of wastewaters, a process where ammonia is converted to nitrate using aerobic autotrophic bacteria in the treatment process.

The process of nitrification is a two-step process for removing ammonia from wastewater and this is done by the utilization of two types of autotrophic bacteria that oxidize ammonia to nitrite (nitrosomonas) and then oxidize nitrite to nitrate (nitrobacter). Biological nitrification systems are projected to convert the entire amount of ammonia into nitrate[1,7].

The two types of autotrophic bacteria need proper biomass concentrations, in a specific environmental conditions (temperature, pH, alkalinity, etc.), enough time for the treatment process, and an increased amount of air, more that requires, for the treatment of biochemical oxygen demand only. A different factor that should be take in consideration in projecting of wastewater treatment plants, that assure biological nitrification is the low alkalinity. Adding sodium hydroxide or other chemicals in order to increase the alkalinity may be needed.

The treatment processes which are recomended for biological nitrification at wastewater treatment plants are :

- conventional activated sludge system(figure 2)
- extended aeration treatment systems(figure 3).
- sequencing batch reactor(figure 4)
- fixed film (figure 5)
- membrane bioreactor(figure 6)
- lagoon systems (figure 7)

The **conventional activated treatment** process (figure 2) has the advantage that the proven treatment process is able of treating many types of wastewater and is easier to operate, comparative with other treatment processes.

Figure 2. Wastewater conventional system[1].

Conventional activated sludge treatment processes that were projected for biochemical oxygen demand removal only could be changed to assure biological nitrification, too. Constructing conventional activated sludge treatment processes have the disadvantage of being are very expensive. Aeration basins and clarifiers are usually built of concrete and demand expensive mechanical equipment (blowers, pumps, clarifier mechanisms, etc). Conventional treatment processes are also more sensizitive to bulking sludge from filamentous organisms.

Extended aeration treatment processes (figure 3) are similar to conventional activated sludge treatment processes and involve: aeration basins, clarifiers, return activated sludge, and waste activated sludge processes. The most important difference is the longer hydraulic and solids residence times in the process. The hydraulic residence time is typically around 24 hours and the sludge residence time is over 20 days at design flow rates and organic loadings [1]. Having sufficient air, the nitrification will take place faster in extended aeration processes.

Figure 3. Conversion of ammonia in a diffused aeration system [1].

Because of these longer times for hydraulic and solids residence, the extended aeration treatment processes can assure the better quality effluent for any kind of wastewater. Extended aeration processes are easier to operate than conventional activated sludge treatment process. With a sufficient amount of oxygen, extended aeration treatment processes can assure raised levels of biological nitrification. The main disadvantage to extended aeration treatment processes consist in the dimension of the facilities that are required to guarantee longer times for the

hydraulic and solids residence. The cost of building these types of processes is bigger because the aeration basins and clarifiers are mainly made of concrete and because of the costs of the mechanical equipment.

Sequencing batch reactors (figure 4) are using extended aeration activated sludge treatment process, the difference being that the aeration and clarification processes are taking place in the same reactor basin, having the next steps: fill, react/aeration, settle, and decant. Wasting usually occurs during the react/aeration step[1]. Having sufficient air, the hydraulic and solids residence times could be changed in such a manner to activate the nitrification in the reactor basin.

Figure 4. Photo of sequencing batch reactors[8].

The most important advantage of the treatment process is the lower dimension of the treatment system. Using the combination of the aeration and clarification steps into one basin, the processes can be controlled, measuring the time for each step to assure the required quality of the treated effluent. This type of treatment process, to be performance requires professional operations personnel, with long practice in working and maintenance of these devices. The majority of the municipal systems also need multiple reactor basins and equalization tanks.

Biochemical oxygen demand removal and biological nitrification could be done by **fixed film treatment**[1] process: trickling filter/activated sludge treatment process, rotating biological contactors, or moving bed bioreactors. In the place of the microorganisms that treat the wastewater suspended in the liquid, the microorganisms are placed to fixed media and treat the wastewater as it flows through the reactor. The trickling filter/activated sludge treatment process also includes plastic media for the microorganisms to develop on packed inside a tower where wastewater is used for treatment. The trickling filter is followed by a conventional activated sludge process. Fans, blowers, clarifiers and pumps are necessary. Rotating biological contactors are made of a series of closely packed plastic circular disks that are partially submerged and rotated through the wastewater to be treated. Microorganisms develop on the disks and aeration is accomplished as the disks are exposed to the air during rotation.

Figure 5. Fixed film treatment system.[9].

Moving bed bioreactors include plastic media that is immersed in the wastewater in a separate basin with screens to keep the media in the basin. They are built in the manner of conventional aeration basins for biochemical oxygen demand removal and are projected specifically for biological nitrification only. Utilization of the trickling filters/activated sludge treatment process have the advantage of both processes. Trickling filters are more energy efficient and the activated sludge process holds off scaling material from creating lower effluent quality.

These types of systems can also reduce the footprint necessary for the conventional activated sludge treatment processes.

The main disadvantages to fixed film treatment technologies are the increased high solids retention time requirements, pumping energy required, the potential for rotten egg odors, and the potential for snails and filter flies. The moving bed bioreactors treatment process also requires higher levels of dissolved oxygen.(up to 7 mg/L)[1].

The **membrane bioreactor treatment** process[1] have three mainly components: 1) anoxic basins, 2) pre-aeration basins, and 3) the membrane bioreactor basins. Rough wastewater have to be screened through a fine screen prior to the anoxic basin. From the anoxic basin, mixed liquor goes into the pre-aeration basins and then into the membrane bioreactor basins. The membranes are placed in the membrane bioreactor basins where wastewater is passed through the membranes and permeate pumps deliver the effluent to the disinfection process prior to discharge[1]. The membranes eliminate the necessity for secondary clarification, Pumping is required as in the same way as in conventional treatment processes. The membrane bioreactor treatment process produces a high quality of the effluent, without any additional operations, will assure both biological nitrification but also nitrogen removal, fitting into a less area, but there are outgoing costs connected to the operation devices and also with purchasing replacement membranes.

Figure 6.Membrane bioreactor treatment system[10].

The costs of operation and maintenance of these systems are higher because they need more power and more operator attention.

L**agoon treatment** systems [1] are not projected to provide more than biochemical oxygen demand and total suspended solids removal. Biological nitrification takes place, having enough long hydraulic and solids residence times, the proper temperature and sufficient oxygen. Hydraulic residence times have to be extended to at least five to seven days in the aeration process, higher temperatures must be maintained, and enough oxygen have to be assured. A mixed liquor recycle system could be involved to keep a high enough biomass to promote the growth of nitrifying bacteria.

Figure 7. Lagoon treatment system [11]

Lagoon treatment systems have the primary advantage of having building low costs and they are easier to operate and maintain comparative to mechanical wastewater treatment systems. Basins are built mainly by excavation , very little concrete is required. In this case, expensive mechanical equipment (pumps, clarifier mechanisms) are not required. Unfortunately, it is harder to control the parameters that influence effluent quality such as wastewater temperature, wasting, return rate, and oxygen levels in lagoon treatment systems [1].

The effluent quality may fluctuate, that means there are needed facilities projected to be be more versatile in design and operation. The facilities use very large areas, these kind of system is recommended only for small treatment systems.

After ammonia was converted in nitrate/nitrite, the denitrification treatment will be applied following the cycle below (figure 8).

Biological denitrification [7] is realized in anaerobic conditions by heterotrophic bacteria that use nitrate during the fermentation of organic carbon materials. Contrary to nitrification, in which only Nitrosomonas and Nitrobacter bacteria are necessary, a relatively large range of bacteria could done the denitrification. These include Pseudomonas, Micrococcus, Achromobacter, and Bacillus. These groups accomplish nitrate reduction through the process of nitrate dissimulation[1]. In nitrate dissimulation, nitrate or nitrite replaces oxygen in the

respiratory processes of the organism under anoxic conditions. Due to the ability of these organisms to "eat" either the oxygen bound in nitrate or free oxygen, these organisms are named *facultative heterotrophic bacteria*.

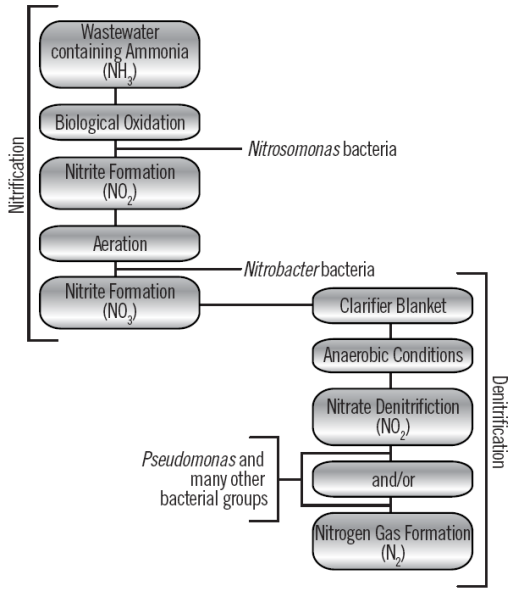

Figure 8. Nitrification-Denitrification Cycle [7].

Denitrifiers are able of an assimilation process where nitrate/nitrite is converted to ammonia. Ammonia is then utilized for the bacterial cell's nitrogen requirements. If ammonia is already present, assimilation of nitrate need not occur to satisfy cell requirements. Electrons pass from the carbon source (the electron donor) to nitrate or nitrite (the electron acceptor) to promote the conversion to nitrogen gas. This involves the nitrifiers' "electron transport system" and releases energy from the carbon source for use in organism growth. This electron transport system is similar to that used for respiration by organisms oxidizing organic matter aerobically, except for one enzyme. Because of this close relationship, many facultative bacteria can shift between using oxygen or nitrate (or nitrite) rapidly and without difficulty[7].

In wastewater treatment, organic carbon is the pollutant to be removed, and oxygen must be added. In denitrification, it is nitrate that is removed, and a carbon source must be available. If an insufficient amount of organic carbon is available for denitrification, sufficient carbon (such as methanol) is added to accomplish the nitrate removal.

For the nitrates removal from the potable water, various methods have been proposed: chemical reduction [12,13], physical–chemical processes [14-16], biological methods [17,18], electrochemical reduction of nitrates on different electrodes: Pt [19,20], Pd [21, 22], Cu [23-28], Ag[27], Ni [29,30], Rh [31], Sn[32], Pb [33], binary alloys [34], CuSn [35], CuZn [36], PdRh1.5/Ti [37], metallic electrodes modified by *upd* deposition [38-41] or *opd* deposition [20, 26, 42–35].

Transforming nitrate/nitrate in nitrogen gas, could also be a challenge using electrochemical treatment methods, based on nitrogen cicle, but taking in consideration the reactions with electron transfer.

CONCLUSIONS

Removal of nitrogen compounds from municipal wastewater, but also resulting mainly from agriculture, animal farms or nuclear industry is following the scheme :

ammonia→nitrate→nitrite→nitrogen gas

As it could be seen there are many types of conventional activated sludge treatment processes for the nitrification process as: complete-mix, plug flow, and step feed treatment. They all have the same basic layout of an aeration basin and secondary clarifier with return and waste activated sludge pumps. The conversion of ammonia occurs in the aeration basins. Because the duration of the required time for nitrification, more than for biochemical oxygen demand removal, there are not recomanded high-rate and contact stabilization activated sludge treatment processes. All the presented method has advantages or disadvantages, and one option is not the best solution for all systems and a good consulting engineer can assist with evaluating all of the options before recommending the best solution for each system. The gaseous product is primarily nitrogen gas, but some nitrous oxide or nitric oxide may also result during denitrification.

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ESTIMATION THE RESERVOIR TEMPERATURE BY USING THE SILICA- ENTHALPHY MODEL OF GEOTHERMAL WATER RESULTING FROM FOUR WELLS SITUATED IN THE WEST ROMANIA

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***Abstract**: The paper presents the estimation of the geothermal reservoirs temperature using the silica-enthalphy model. The reservoirs temperatures were calculated with chalcedony geothermometers, by Watch simulation program. There were proposed to estimate the deep waters temperatures using the silica- enthalphy model and to compare this temperatures with the temperatures resulting from geothermometers which were calculated by the Watch program. We establish the chemical data of the water in 2010. Based on the chemical composition by these of Watch simulation pogram, they were estimated the minerals which can precipitate during production of the studied wells.*

Keywords: geothermal water, silica- enthalphy model, geothermometer, Watch program

1. INTRODUCTION

The geothermal energy has been used for heating, for industry, and for generation of electricity. In our country the geothermal reservoirs are mainly located in the western part. This paper presents the estimations the deep water temperature for geothermal water resulting from: well 4699 from Cighid, well 4175 Tăşnad, well 4777 Mădăras and well 507 Livada. 4699 geothermal well is situated in the yard of the hospital for children with severe handicap from Cighid, located at about 3,5 km south-west from Ghiorac town and 4 km far from Ciumeghiu village. Starting 1998 geothermal energy from Cighid was use the water for heating the hospital.

Geothermal well 507 from Livada drilled in the year 1979. Currently geothermal water used up to heating of houses, to heating of social objectives, to heating of a greenhouses and to swimming place the summer.

The drilling 4175 from Tăşnad is situated in the county Satu –Mare. The utilization of geothermal energy from Tasnad is done for heating military unit, to heating of a greenhouses and to heating of houses. Well 4777 from Mădăras is situated in the northern part of village, near swimming place. Water extracted is drived in thermal swimming place.

The reservoirs temperatures were estimated using the silica- enthalphy model. Watch program show us the deep waters temperatures, calculated which geothermometer chalcedony, geothermometer quartz and geothermometer Na/K.

2. EXPERIMENTAL DATA

In this paper we utilized Watch program for calculus deep waters temperatures.

The Watch program predict possible scaling what occured during the utilization of geothermal water and with geothermometers indicates the reservoirs temperatures.

Geothermal waters from Cighid and Madaras were analysed by using standard analytical methods.

The results are presented in tables 1.

In this paper we utilized Watch program for calculus deep waters temperatures. The Watch program predict possible scaling what occured during the utilization of geothermal water and with geothermometers indicates the reservoirs temperatures.

The use of geothermometers is based on the supposition that there is an equilibrium between minerals from the rocks of the reservoir and the fluid from the reservoir.

TABLE 1. Characteristics of geothermal water from Cighid, well 4699 and Madaras, well 4777 in mg/l, in 2010.

Chemical Characteristics	Well Cighid 4699	Well Madaras 4777
pH	8,0	7,2
Na^+	1205	1490
K^+	10,2	22,5
Ca^{2+}	19,1	8,4
Mg^{2+}	3,3	5,2
Cl^-	743	607
SO_4^{2-}	28	160
HCO_3^-	2150	2720
SiO_2	48	30,5
Fe^{2+}	-	0,7
CO_2	1550	1900
Mineralization	4295	5200

The chemical composition of the surface fluid is controlled as main by the composition of the minerals from the reservoir and the temperature. Arnorsson and Fournier [1] concluded that the solubility of some components of the geothermal fluid is controlled by the temperature.

The temperatures resulting from geothermometers which were calculated by the Watch program are presented in table 2.

TABLE 2. Temperatures resulted by Watch program calculations.

Well	T (quartz) °C	T (chalcedony) °C	T(Na/K) °C
Tasnad	86,5	96,0	39,8
Madaras	77,5	95,6	48,6
Cighid	90,9	104,5	116,0
Livada	150	59,7	289,9

Is noticed as temperature calculated by chalcedony geothermometer [2] is very close to the production temperature of majority geothermal waters than the values given by the other geothermometers.

Another way to estimate the reservoir temperatures is by using the silica-enthalpy mixing model [2]. On the strength of contained of silica from geothermal waters and of surface reservoir temperatures we caused the enthalpy for geothermal fluids.The results are presented in table 3

TABLE 3. Concentration SiO_2, temperatures and enthalpy of surface for wells from Cighid, Livada, Tasnad and Madaras.

Well	SiO_2 (mg/l)	Temperature to surface,°C	Enthalpy [kj/kg]
Cighid 4699	43	80	335,2
Livada 507	120	89	372,91
Tasnad 4175	40,1	70 – 74	297,49
Madaras 4777	66,5	50	209,5
Cold water	20	10	42

It is assumed that the surface geothermal water is the result of mixing of hot geothermal water with cold water. The intersection point with the solubility curve for chalcedony gives the enthalpy of the deep hot water component and its temperature is obtained from steam tables, Model silica-enthalpy for wells: 4699 Cighid, 4175 Tăşnad,

4777 Mădăras and 507 Livada was presented in figures 1, 2, 3, and 4.

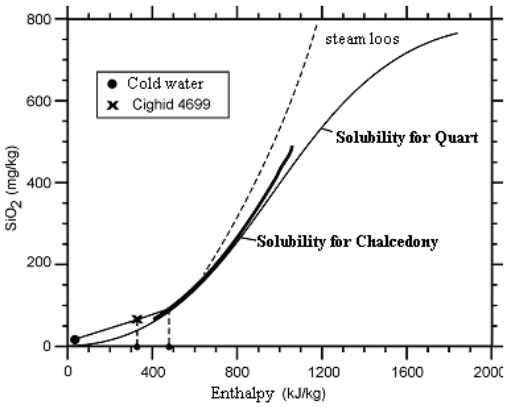

Fig. 1. Diagram of dissolve silica-enthalpy.

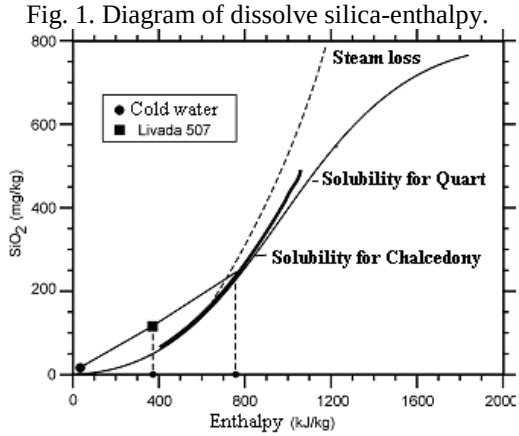

Fig. 2 Diagram of dissolve silica-enthalpy.

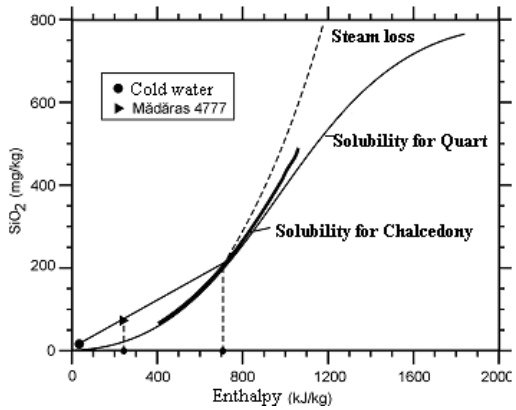

Fig. 3. Diagram of dissolve silica-enthalpy.

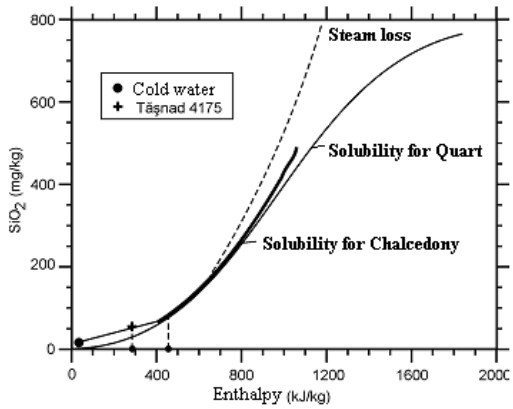

Fig. 4. Diagram of dissolve silica-enthalpy.

3. RESULTS AND DISCUSSIONS

The reservoir temperatures finded out with silica-enthalpy model are presented in table 4.

The results obtained by the Watch program are presented in figures 5 and 6.

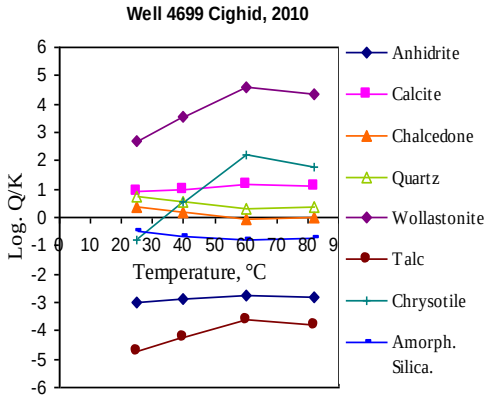

Figure 5. Log.Q/K vs temperature for selected water from well 4699 Cighid, in 2010

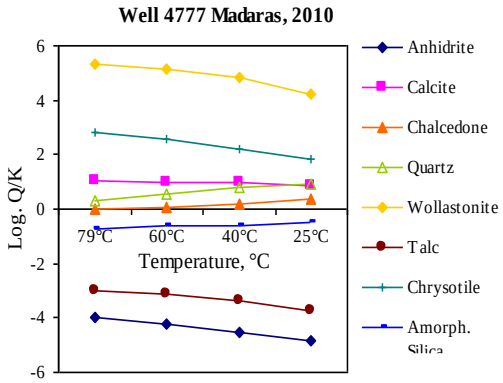

Figure 6. Log.Q/K vs temperature for selected water from well 4699 Cighid, in 2010

At Livada, well 507 the temperature calculated by mixing model is 186,1°C, and for well 4777 of Mădăras the temperature calculated by mixing model is 167°C, therefore differed the temperature calculated by chalcedony geothermometer. The difference compared to the wellhead temperature is assumed to be due to mixing with cold water in the upper layers or due to contact by the cold rocks.

At Tăşnad, well 4175 and at Cighid, well 4699 this temperature calculated by mixing model is 113,4°C, respectivly 106,1°C. For this geothermal wells, the temperatures calculated by chalcedony geothermometer is 96,0°C for geothermal water of Tăşnad and

104,5°C for geothermal water of Cighid. The temperatures calculated by chalcedony geothermometer is very close to the production temperatures of geothermal waters from Tăşnad, well 4175 and from Cighid, well 4699.

By the use of the program it was calculated the ionic activity Q corresponding to different minerals in the brine and it was compared with the theoretical solubility, K, of the respective minerals.

When Q < K the saturation index is negative and the solution is undersaturated with respect to the mineral considered. When Q >K the solution is supersaturated and when Q = K the solution is exactly saturated or in equilibrium with the mineral in respect.

Changes in water by cooling within the system during utilization can by modelled and subsequent changes in chemistry evaluated. This is an important tool for the assessment of scaling problems.

The saturation indexes were calculated for the following minerals: calcite, quartz, talc, chrysotile and wollastonite.

The saturation indexes were calculated for the following minerals: wollastonite, chrysotile, calcite and quartz.

TABLE 4.Temperatures resulted by silica-enthalpy model calculations.

Well	SiO_2 (mg/l)	Enthalpy in reservoir, [kj/kg]	Hot water temperature in reservoir, °C
Cighid 4699	43	476,28	113,4
Livada 507	120	780,62	186,1
Tasnad 4175	40,1	451,01	107,4
Madaras 4777	66,5	701,40	167
Cold water	20	42	10

TABLE 5. The values of saturation indices of minerals may be separated by cooling the geothermal water in the 4699 well at different temperatures in Cighid, in 2010.

Temp. °C	Log.Q/K (Anhyd.)	Log.Q/K (Calcite)	Log.Q/K (Chalc.)	Log.Q/K (Quartz)
82	-2,791	1,125	0,011	0,34
60	-2,759	1,165	-0,041	0,281
40	-2,891	1,007	0,179	0,524
25	-2,989	0,897	0,361	0,711
Temp. °C	Log.Q/K (Talc)	Log.Q/K (Wollast.)	Log.Q/K (Chrysot.)	Log.Q/K (Amorph. Silica.)
82	4,349	-3,779	1,795	-0,748
60	4,617	-3,64	2,197	-0,783
40	3,531	-4,224	0,536	-0,643
25	2,718	-4,698	-0,786	-0,511

TABLE 6. The values of saturation indices of minerals may be separated by cooling the geothermal water in the 4777 well at different temperatures in Madaras, in 2010.

Temp. °C	Log.Q/K (Anhyd.)	Log.Q/K (Calcite)	Log.Q/K (Chalc.)	Log.Q/K (Quartz)
79°C	-4,006	1,012	-0,011	0,313
60°C	-4,205	1,002	0,055	0,577
40°C	-4,538	0,989	0,188	0,771
25°C	-4,841	0,873	0,384	0,903
Temp. °C	Log.Q/K (Talc)	Log.Q/K (Wollast.)	Log.Q/K (Chrysot.)	Log.Q/K (Amorph. Silica.)
79°C	5,341	-2,986	2,812	-0,746
60°C	5,154	-3,125	2,542	-0,632
40°C	4,813	-3,372	2,233	-0,591
25°C	4,232	-3,719	1,824	-0,464

4. CONCLUSIONS

The reservoir temperatures indicated by the calculated chalcedony geothermometer is closer to the production temperatures of the water than the values given by the other geothermometers.

The reservoir temperature calculated by silica-enthalpy mixing model is rather higher than the temperature given by the chalcedony geothermometer and the wellhead temperature, which indicates a mixing of hot water from the reservoir with the infiltrated cold water in the upper layers. A simulation program was used to estimate the depositions which can be formed at different temperatures reached during geothermal water utilization. It is better to avoid scales before they occur. In case of mineral depositions inside the pipes a mechanical removal is not convenient.

Geothermal waters with a scaling tendency must be treated by chemical method in order to prevent the deposits.

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First name SURNAME[1], First name SURNAME[2] (10 pt bold)

[1]Affiliations and addresses (10 pt)Affiliations and addresses (10 pt)

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Abstract: *Abstract of 50-120 words (10 pt italic). It contains concise information about: objectives of the work, the results obtained, conclusions*

Key words: List 2-6 keywords. (l0 pt, italic).

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The paper has to be written in English. Each paper should be concise including text, figures and tables. Authors are kindly requested to submit a paper a hard copy or in electronic format in Microsoft Word file form. Acceptable versions are MS-Word 2003, 2007, 2010. The suggested structure of the main text: Introduction; Methods, techniques, materials, Study area; Results and Discussions; Conclusions; References. (10pt)

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- Use A4 format (210 x 297 mm),
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All tables and figures follow the References or could be inserted within the text. Tables, together with figures should be placed in their order of appearance in the text. Tables should be numbered consecutively. Table captions containing the number of the tables, followed by the caption, and should be placed above the table. Tables should be clearly captioned and all symbols should be properly explained in either the table or its caption.

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(Report)

[2] Carter, B., and Connell, C. (1980). Moa Point Wastewater Treatment Plant and Outfall Study, Report for the Wellington City Council, Wellington, pp. 31.

(Book)

[3] Grady, C.P.L., and Lim, H.(1980). Biological Wastewater Treatment Theory and Application, Marcel Dekker, New York, pp. 375.