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WHEAT SEEDS GERMINATION USING DIFFERENT PHOSPHOMOLYBDATE COMPOUNDS

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Abstract: Although both phosphates and molybdates have been widely used as chemical fertilizer in crop production of cereals, a comparative study for different types of compounds has not been realized yet. In this work we aimed to compare different behavior on seed germination of wheat next polyoxometalates with Keggin type structure: $K_3PMo_{12}O_{40}$, $K_7PMo_{11}O_{39}$ și $K_4[FePMo_{11}O_{39}]$, where the Fe (III). There were prepared solutions of the three compounds at concentrations of 0.1 to 100 μM . The results obtained showed that the presence of Fe (III) chelate bound to polyoxometalate monolacunar $K_7PMo_{11}O_{39}$ does not stimulate seed germination of wheat. Instead, monolacunar Keggin species $K_7PMo_{11}O_{39}$ favorised plant growth in the first days after germination compared with Keggin with complete structure $K_3PMo_{12}O_{40}$.

Key words: Keggin, wheat, molybdate, iron.

INTRODUCTION

The interest for substances that contribute to improving the nutritional properties of the soil, to participate in accelerating stimulate seed germination and plant growth was a fundamental problem of modern human. In recent years, increased attention is given to the impact that these substances can have on soil, plants and human life. The needs for additional mineral intake into the ground to ensure plant growth is obvious, but you have to know exactly which substances can do this as well, so as not to disturb the environment.^{1,2,3}

Polyoxometalates Keggin type are produced by polycondensation of oxoanions of transition metals (Mo, W, V, Nb, Ta) bound together by common corners and edges around another oxoanion, another element (P, Si, B, at). The compounds considered in this paper are: $K_3PMo_{12}O_{40}$, $K_7PMo_{11}O_{39}$ și $K_4[FePMo_{11}O_{39}]$. All three compounds contain in their structures essential elements in major plant growth: potassium, phosphorus, molybdenum and iron. Monolacunar Keggin has chelate ligand action on metal cations and a behavior similar to that of EDTA used in chemical fertilizers.

The order of structural stability for three compounds is: $K_7PMo_{11}O_{39} < K_4[FePMo_{11}O_{39}] < K_3PMo_{12}O_{40}$. Knowing these theoretical aspects, in this paper we intend to follow the influence of the three

solutions of different compounds type phosphomolybdate with Keggin structures can have on seed germination of wheat.^{4,5}

EXPERIMENTAL PART

There were prepared the salts of $K_3PMo_{12}O_{40}$, $K_7PMo_{11}O_{39}$ și $K_4[FePMo_{11}O_{39}]$, using synthetic methods in the literature. For each of these five Keggin polyoxometalates were prepared solutions from 0.1 μM , 1.0 μM , 10 μM and 100 μM . There are three sets of experiments carried out in parallel for each polyoxometalate. Such experiments with $K_3PMo_{12}O_{40}$ solutions were prepared with six germinating wheat grains sorted, washed and dried with distilled water. In the first germinator was placed the control solution (blank) of distilled water, and the following were soaked in solutions of $K_3PMo_{12}O_{40}$ 0.1-100 μM . Preparation of germinators was performed in the same way for $K_7PMo_{11}O_{39}$ and $K_4[FePMo_{11}O_{39}]$ solutions. Germinators were closed and were kept for six days in obscurity at 25°C. On the sixth day they were opened and were measured adventitious roots, radicle, coleoptile and first leaflet. Propagating biomass was determined by dehydration at 105 °C in an oven, until constant mass.^{6,7,8,9} The results were interpreted against the blank using the differential rates:

$$\% \text{ differences} = \frac{(\text{average}_{\text{sample}} - \text{average}_{\text{blank}})}{\text{average}_{\text{blank}}} * 100$$

RESULTS AND DISCUSSIONS

As can be seen in the figure below (Figure 1), the increase in concentration solution of $K_3PMo_{12}O_{40}$ stimulate embryonic root growth, the highest value is obtained using 100 μM solution. Increasing adventitious roots is favored by soaking seeds with $K_3PMo_{12}O_{40}$ and reach even 20% to 100 μM

$K_3PMo_{12}O_{40}$ use. Increasing coleoptile decreases with increasing concentration $K_3PMo_{12}O_{40}$ but positive throughout the studied concentration range. The growth is stimulated more leaflets first to use 0.1 and 100 μM $K_3PMo_{12}O_{40}$ solutions. Increasing biomass is inhibited by all $K_3PMo_{12}O_{40}$ taken into working solutions.^{10,11}

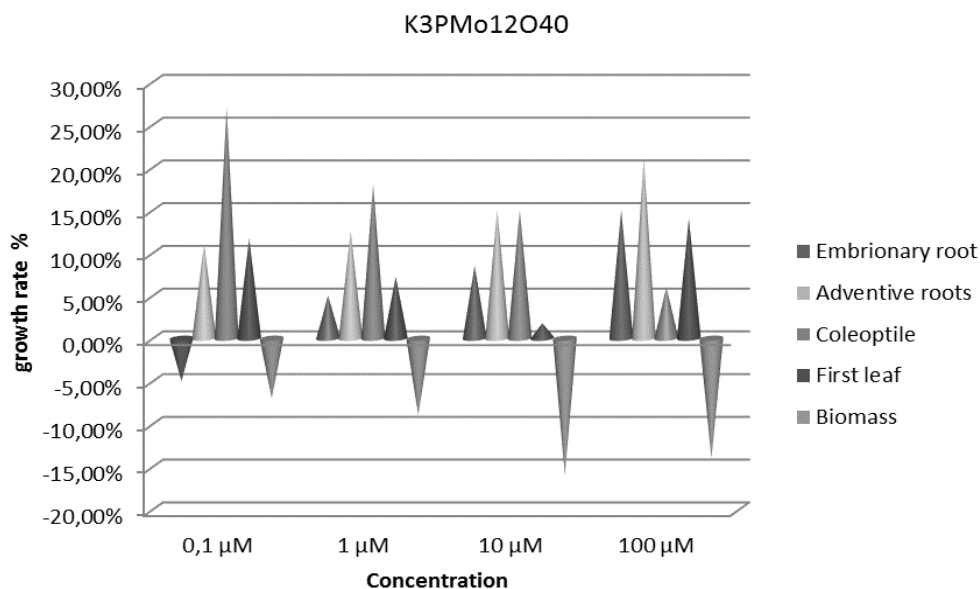


Figure 1. Role of $K_3PMo_{12}O_{40}$ solutions in stimulation of wheat seed germination.

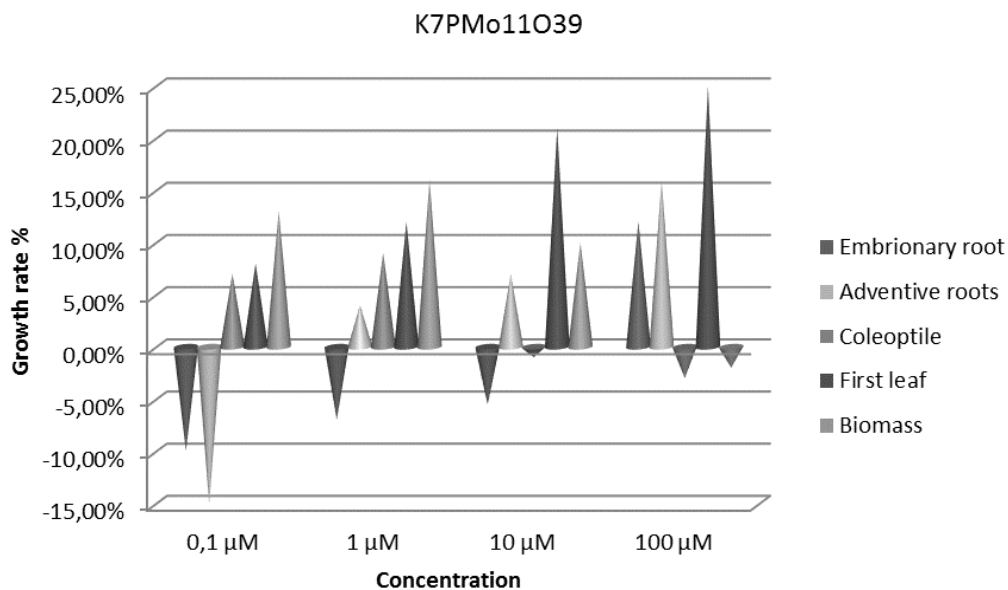


Figure 2. Role of $K_7PMo_{11}O_{39}$ solutions in stimulation of wheat seed germination

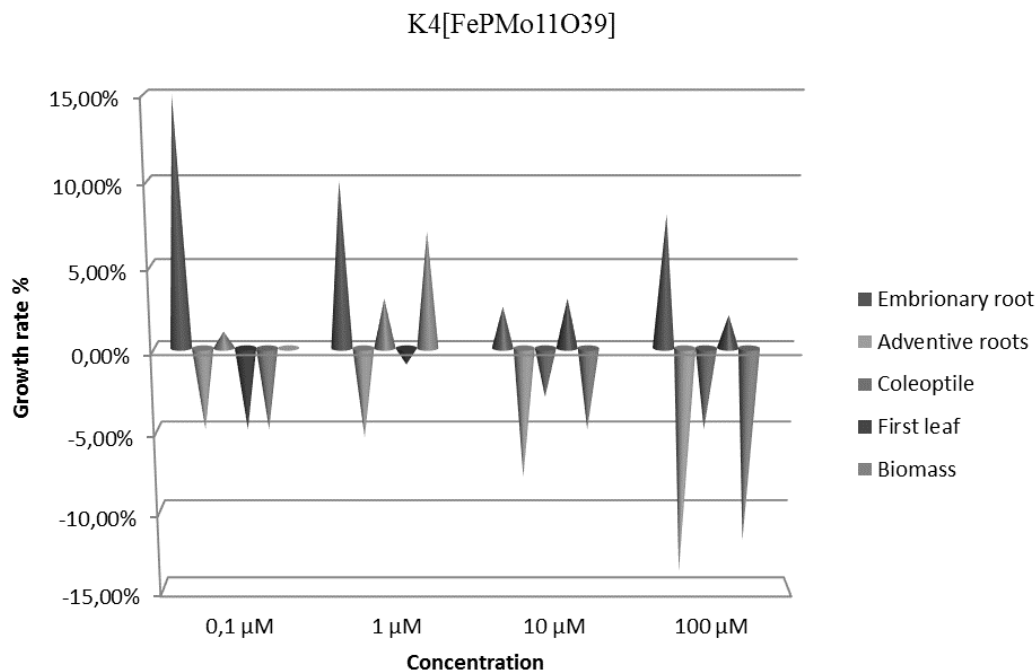


Figure 3. Role of $K_4[FePMo_{11}O_{39}]$ solutions in stimulating of wheat seed germination

When using solutions of 0.1 - 100 μM $K_7PMo_{11}O_{39}$ we have seen a significant increase of the roots, with increasing concentration, while the root growth at low concentrations 0.1-1.0 μM was slightly inhibited.

The increase of coleoptile is not significantly affected by $K_7PMo_{11}O_{39}$ solutions. At low $K_7PMo_{11}O_{39}$ concentration (0.1-1.0 μM), growth of premium leaflets is 5-12%, rise significantly to 18-25% at higher concentrations of 10-100 μM $K_7PMo_{11}O_{39}$. Increasing biomass is stimulated in the range 0.1-10 μM concentrations of $K_7PMo_{11}O_{39}$.^{10,12}

Use of the $K_4[FePMo_{11}O_{39}]$ compound stimulated only root growth development and inhibited the plant embryo during the first days after germination, especially at higher concentrations. As shown in Figure 3, the largest increase of embryonic

roots was recorded at sprinkling wheat seeds with 0.1 μM solution of $K_4[FePMo_{11}O_{39}]$.^{10,12,13}

CONCLUSIONS

Solutions of $K_3PMo_{12}O_{40}$ and $K_7PMo_{11}O_{39}$ stimulated germinating of the seeds and the growth of plants during the first six days of life. $K_3PMo_{12}O_{40}$ solutions were more effective in stimulating roots and coleoptile growth, while $K_7PMo_{11}O_{39}$ solutions have favoured the growth of the first leaflets and biomass. Using $K_4[FePMo_{11}O_{39}]$ solutions in μM concentration range 0.1-100, has not proven effective in stimulating germination, growth and development of wheat seedlings in the first days of life.

REFERENCES

- [1] Pope, M.T., Heteropoly and Isopoly Oxometalates, Springer-Verlag, Berlin, Heidelberg, New-York, Tokyo, 1983.
- [2] Borg, S., Brinch-Pedersen, H., Tauris, B., Holm, P. B., Plant Soil, **325**, nr. 1-2, 2009, pp. 15.

- [3] Castleden, C.K., Aoki, N., Gillespie, V.J., Macrae, E.A., Quick, W.P., Buchner, P., Foyer, C.H., Furbank, R.T., Lunn, J.E., *Plant Physiol.*, **135**, nr. 3, 2004, pp. 1753.
- [4] Clark, R. B., *Plant Soil*, **72**, 1983, pp. 175.
- [5] Goss, M.J., Carvalho, M.J.G.P.R., *Plant Soil*, **139**, 1992, pp. 91.
- [6] Inumaru, K., Ono, A., Kubo, H., Misono, M., *J. Chem. Soc. Faraday Trans.*, **94**, nr. 12, 1998, pp. 1765.
- [7] Katsouli, D. E., *Chem. Rev.*, **98**, 1998, pp. 359.
- [8] Maderova, L., Dawson, J.J.C., Paton, G.I., *Water Air Soil Pollut.*, **210**, nr. 1 - 4, 2010, pp. 63.
- [9] Nagajyoti, P.C., Lee, K.D., Sreekanth, T.V.M., *Environ. Chem. Lett.*, **8**, 2010, pp. 199.
- [10] Pope, M.T., Müller, A., *Polyoxometalate chemistry from topology via self-assembly to applications*, Kluwer Academic, New York, Boston, Dordrecht, London, Moscow, 2002.
- [11] Rhule, J. T., Hill, C. L., Judd, D. A., Schinaz, R. F., *Chem. Rev.*, **98**, 1998, pp. 327.
- [12] Riesen, O., Feller, U., *J.Plant Nutr.*, **28**, 2005, pp. 421.
- [13] Soudek, P., Katrušáková, A., Sedláček, L., Petrová, Š., Kočí, V., Maršík, P., Vaněk, M.G.T., *Arch. Environ. Contam. Toxicol.*, **59**, nr. 2, 2010, pp. 194.

A NEW SYNTHETIS METHOD OF $H_5PW_{10}V_2O_{40} \cdot 12H_2O$

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Abstract: In this paper we proposed to find a new method of synthesis of $H_5PW_{10}V_2O_{40} \cdot 12H_2O$, in which at a trilacunar polyoxoanion, $A-Na_9[HPW_9O_{34}] \cdot 11H_2O$ 've added on one unit wolframate and two units of vanadate. To get heteropolyacide, we acidified sample with H_2SO_4 and used ether extraction method at strongly acidic pH. The entire synthesis was conducted at pH 2. To confirm the new structure we used spectral methods like UV-VIS and FT-IR. The chemical composition was determined using AAS -method. The thermal stability of the compound and the number of water molecules was performed by using TG, DTA and DTG. Basisity was determined by potentiometric method.

Key words: Keggin, polyoxometalate, mixed addenda, vanadium

INTRODUCTION

Polyoxometalate chemistry aroused the attention of chemist researchers since the early twentieth century, as it highlighted the ability of polycondensation of inorganic compounds of metals. In 1930, Keggin showed the attachment mode of the atoms in the structure using X-ray diffraction method.

Due to this, polyoxometalates with general formula $XM_{12}O_{40}^{n-}$ were called Keggin compounds. The Keggin compounds are polycondensation products, in which a central tetrahedron XO_4 (X can be almost any element of the periodic table) is encircled by 12 octahedral MO_6 (M is generally Mo (VI) or W (VI), but can also be one up three V (V), Nb (V) or Ta (V)). Octahedrals MO_6 are grouped into four units M_3O_{13} with octahedrals joined by common edges. M_3O_{13} units are connected to one another through the common corners.

The synthesis of heteropolyacide $H_5PW_{10}V_2O_{40}$ was performed before the direct path from oxoanions of components.

Unfortunately, in this way, vanadium ions can occupy random positions within the structure and are great chances to obtain mixtures of compounds with chemical and physical properties less interesting. In our work, $H_5PW_{10}V_2O_{40}$ was obtained by the addition of Na_2WO_4 and $NaVO_3$ at trilacunar Keggin unit, α , $A-Na_9[HPW_9O_{34}] \cdot 11H_2O$. With our proposed method ensures vicinal position of the two vanadium atoms, which greatly increases the catalytic and not only properties of this compound.

MATERIAL AND METHODS

All syntheses of polyoxoanions were done with analytical high-purity chemical reagents. In preparing solutions in all the summaries and studies have used doubly distilled water. Measurements of pH and alkalinity determination were performed with an apparatus Multi 720 Inolab WTW series.

Chemical analysis of transition metal cations was performed by AAS method with a device type Varrian ASA 220. Thermal analysis were performed with a Paulik-Erdely derivatograph OD-103 (20-800 °C) with a scan speed of samples 5°C min⁻¹. FT-IR vibrational spectral analysis was performed on solid pilled samples with a spectrophotometer KCl Biorad FTS 60A, with the possibility of making measurements in the 4000-400 cm⁻¹. Electronic spectra were realised in aqueous solution in the concentration range of 0.01 to 10 mM, with a UV-VIS spectrophotometer, model T-60, working with a range of 190-1100 nm. Electronic spin resonance spectra (RES) were performed with a spectrophotometer Bruker ESP 380, at room temperature.

Synthesis of $H_5PW_{10}V_2O_{40} \cdot 12H_2O$

Synthesis of α , $A-Na_9[HPW_9O_{34}] \cdot 11H_2O$ was performed according to the method of literature. In 100 mL of distilled water were sequentially dissolved 4.0 g (10 mmol) of $NaVO_3 \cdot 4H_2O$ and 3.3 g (10 mmol) of $Na_2WO_4 \cdot 2H_2O$. In small portions, stirring continuously, were introduced 26 g (10 mmol) α , $A-Na_8[HPW_9O_{34}] \cdot 11H_2O$.

The reaction mixture was acidified with 50% H₂SO₄ up to pH 2.0.

The mixture was allowed to react on a water bath boiling at reflux for one hour. The reaction mixture was cooled, was transferred into a separatory funnel and add 50 mL diethyl ether. The stirring and acidification with 50% H₂SO₄ formed etherate polyoxoanion [PW₁₀V₂O₄₀]⁵⁻. This step is repeated twice. The solution containing etherate, was transferred into a dish and allowed to crystallize at room temperature. It will be obtained 20.52 g of H₅PW₁₀V₂O₄₀·12H₂O orange crystals (η = 72.4%).

Spectral data for H₅PW₁₀V₂O₄₀·12H₂O IR: 3420, 1632, 110, 1080, 1057, 970, 880, 805 (cm⁻¹); UV-VIS: 200.5, 253 (nm)

Anal. Calc. (Found) (M = 2832.45): P, 1.09 (1.0); V, 3.59 (3.6); W, 64.91 (65.0); H₂O, 12.0 (11.8)%.

RESULTS AND DISCUSSIONS

From TG data of the thermal analysis method of (Table 1) H₅PW₁₀V₂O₄₀·12H₂O, it can be seen that the weight loss corresponds to 12 water molecules. The first process endotherm about 105 °C corresponding to loss of water of crystallization and is present in both DTA and DTG curves. The exothermic process of the DTA curve from 392 °C is attributed to the destruction of the polyoxoanionic building, followed by a series of exothermic processes in the heat range of 700-800 °C, due to the formation of oxides and possible structural changes of them

Table 1. Thermal analysis of H₅PW₁₀V₂O₄₀·12H₂O

Thermogravimetric analysis		
DTA (° C)	endothermal	107
	exothermal	387
	endothermal	710
		743
DTG (° C)		790
		105
TG		392
	Weight lost (%)	8.69
	H ₂ O	12
	Number molecules	

Basisity was determined by potentiometric titration of a solution of 0.01M H₅PW₁₀V₂O₄₀·12H₂O with NaOH. From the potentiometric curve found that they consumed 5 moles of NaOH per mole of H₅PW₁₀V₂O₄₀·12H₂O, which shows that which shows that in the outer sphere of polyoxoanion Keggin there were five protons.

The FT-IR spectrum of FT-IR al H₅PW₁₀V₂O₄₀·12H₂O (Figure 1) shows a broad band around 3420 cm⁻¹ attributed to the asymmetrical vibration of the O-H bond, $\nu_{as}(\text{OH})$, due to crystallization water molecules. Medium intensity band $\delta(\text{OH})$ of the 1632 cm⁻¹ is attributed to deformation plan vibration of the same bonds. The bands of vibration of the 1100-1000 cm⁻¹ were assigned to the asymmetric stretching band

$\nu_{as}(\text{P-Oi})$. Shoulder presence indicates the existence of links of different lengths P-Oi due coordination atoms such wolfram (tungsten) and vanadium atoms. Very intense band at 970 cm⁻¹ is due to asymmetrical stretching vibration on $\nu_{as}(\text{M-Ot})$ (M is W⁺⁶ and V⁺⁵), where Ot is the terminal oxygen atoms. To link M-Oc, (Oc -atom of oxygen in common corner) achieved a intense band at 880 cm⁻¹, and to link M-Oe-M, (Oe -atom of oxygen in common edge) was obtained intense band at 805 cm⁻¹.

In Figure 2 it can see that the UV-VIS spectra of H₅PW₁₀V₂O₄₀·12H₂O has two load transfer characteristic bands, ν_1 due to electronic transition $d\pi-p\pi-d\pi$ of bonds M-Oc, e-M, which occurs at 253 nm and ν_2 CT, due to transition $d\pi-p\pi$ of bonds M = Ot, which occurs at 200.5 nm.

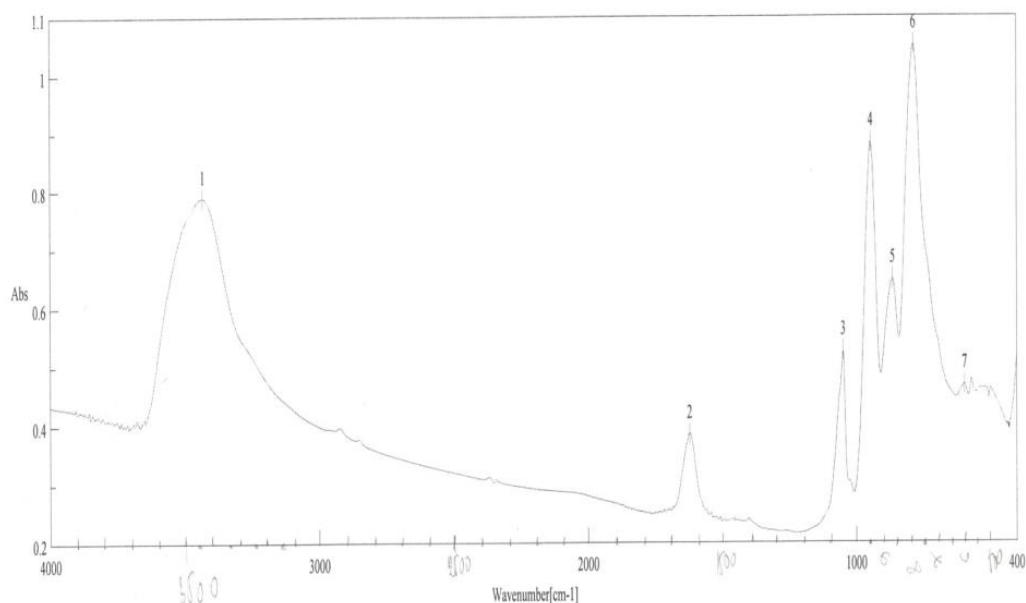


Figure 1: FT-IR spectra of $H_5PW_{10}V_2O_{40} \cdot 12H_2O$

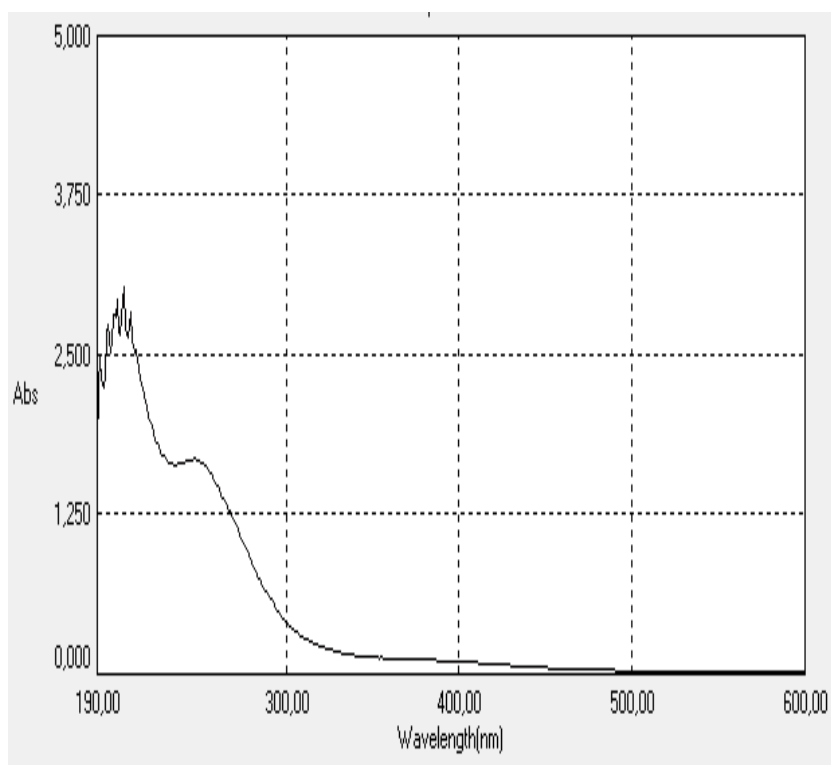


Figure 2: UV-VIS spectra of $H_5PW_{10}V_2O_{40} \cdot 12H_2O$

CONCLUSIONS

The chemical composition shows that the synthesis has led to a compound of known molecular formula $H_5PW_{10}V_2O_{40} \cdot 12H_2O$. UV-Vis analysis data indicate the

phenomenon of polycondensation and obtaining a compound with a Keggin-type structure.

FT-IR spectral data points to obtain a Keggin compound, with a single structure. All the bands obtained are characteristic of this class of compounds

REFERENCES

- [1] Pope, M.T. *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, Berlin, Heidelberg, New-York, Tokyo, 1983.
- [2] Marcu, Gh.; Rusu, M. *Chimia polioxometalaților*, Ed. Tehnică, București, RO, 1997.
- [3] Pope, M. T.; Muller, A. *Angew. Chem. Int. Ed. Engl.* **1991**, 30, pp. 34-48.
- [4] Neumann, R. *Polyoxometalate Complexes in Organic Oxidation Chemistry*, in *Progress in Inorganic Chemistry*, Ed. K. D. Karlin John Wiley & Sons, Inc., Hoboken, NJ, USA., 2007.
- [5] Park, D. R.; Song, S. H.; Hong, U. G.; Seo, J. G.; Jung, J. C.; Song, I. K. *Catal. Lett.* **2009**, 132, pp. 363–369.
- [6] Rudnitskaya, A.; Evtuguin, D. V.; Gamelas, J. A. F.; Legin, A. *Talanta* **2007**, 72, pp. 497–505.
- [7] Sami, P.; Rajasekaran, K. *J. Chem. Sci.* **2009**, 121, pp. 155-161.
- [8] Rhule, J.T.; Hill, C. L.; Judd, D. A. *Chem. Rev.* **1998**, 98, pp. 327-357.
- [9] Knoth, W. H.; Domaille, P. J.; Farlee, R. D. *Organometallics* **1985**, 4, pp. 62-68.
- [10] Domaille, P. J.; Hervé, G.; Téazé, A. *Vanadium(V) Substituted Dodecatungstophosphates*, in *Inorganic Syntheses*, John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2007.
- [11] Cowan, J. J.; Bailey, A. J.; Heintz, R. A.; Do, B. T.; Hardcastle, K. I.; Hill, C. L.; Weinstock, I. A. *Inorg. Chem.* **2001**, 40, pp. 6666-6675.
- [12] Shivaiah, V.; K Das, S. *Proc. Indian Acad. Sci. (Chem. Sci.)* **2002**, 114, pp. 107–114.
- [13] David, L.; Craciun, C.; Rusu, M.; Rusu, D.; Cozar, O. *J. Chem. Soc. Dalton Trans.* **2000**, pp. 4374–4378.
- [14] Rusu, D., Crăciun, C.; Rusu, M.; Pătruț, A.; David, L. *Rev. Roum. Chim.* **2007**, 52, pp. 817–821.
- [15] Gamelas, J. A. F.; Soares, M. R.; Ferreira, A.; Cavaleiro, A. M. V. *Inorg. Chim. Acta* **2003**, 342, pp. 16-22.
- [16] Nakayama, M.; Komatsu, H.; Ozuka, S.; Ogura, K. *Electrochim. Acta* **2005**, 51 (2), pp. 274–280.
- [17] Barteau, K.P.; Lyons, J.E.; Song, I.K.; Barteau, M.A. *Top. Catal.* **2006**, 41 (1–4), pp. 55-62.
- [18] Maestre, J. M.; Lopez, X.; Bo, C.; Poblet, J.-M.; Casan-Pastor, N. *J. Am. Chem. Soc.* **2001**, 123, pp. 3749-3758.

SHORT REVIEW ON CORROSION OF STEEL WATER PIPES

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Abstract. Corrosion and corrosion protection is a particularly important economic factor in loss prevention and combating environmental pollution. Corrosion might be a problem of any engineering field using metals and alloys, especially those where metal interactions are very different medium, such as water supply systems and gas, energy production systems, transportation.

A short review of steel pipes corrosion is presented, in the field of transportation and distribution water grids.

Key words: corrosion, water grid, steel pipes, interdisciplinarity.

INTRODUCTION

Corrosion of metals is a spontaneous natural phenomenon, which in most cases can not be totally eliminated but can be controlled, by corrosion management. As it is said, the solution is often in simplicity: no just solution to a problem innovations are often only rigorous application of knowledge and data accumulated can bring added value.

From the perspective of sustainable development, energy efficiency must be seen in this century more than its definition of engineering, but as a new concept, more comprehensive, not only sociological and philosophical interdisciplinary well. The most important questions are not about science and technology but about society and become the policies, ie education and responsibility, moving from wasting of energy resources in knowledge but a life in harmony with the environment. No need to fear that technology will see a decline because this sustainable approach comes with new scientific challenges.

The interest in a scientific approach to the management of transport networks and water distribution in urban areas began almost a century ago. The particularity of each system, depending on the physico-chemical properties of water transported, soil and air, materials, weather conditions and the continued development of methods for mathematical analysis, statistical modeling possibility of the subjects, makes the this area to be still full of unknowns.

EXPERIMENTAL

The reason these studies are still at the beginning of a road, is that, although it

discusses the importance of interdisciplinary studies, sustainability and environmental protection, many experts are content with their own domain knowledge. Unfortunately, self-sufficiency not only stands in the way of integrated knowledge, but also economic considerations, such as underfunding, both national and local administrations, respectively lack of cooperation between them and research institutes

RESULTS AND DISCUSSIONS

D. McLarty and others¹ debate on sustainable development, including the urban networks of water, which tends to focus on the national and international issues. They presented a new mathematical instrument based on certain databases and to explore prospects for improving sustainability practices by harnessing existing resources and establishing synergistic partnerships with neighboring cities. The paper presents the potential social implications and transdisciplinary methodological issues and barriers to implementation.

D. A. J. Rand ² in the article "A journey on the road to sustainability Electrochemical highlights the benefits of scientific application of electrochemistry to sustainable development. Starting from the premise ongoing development of the world, accompanied by population growth and consequently demand for energy, electrochemistry offers innovative solutions to limit corrosion in fuel cells and environmental protection. Thus, with its attributes versatile and clean electricity is expected widely to assume a larger share of the global energy market. Electrochemical road towards sustainability is a fascinating

journey that should inspire all who seek a clean and safe future for humanity.

R.E. Ricke³ in 2010 reinterprets corrosion studies conducted during 1922-1940 to increase safety exploitation of water pipes may be possible in a new approach, using commercial software packages. The purpose was to identify trends and develop an empirical model for estimating soil corrosion behavior. Studies and linear regression curves of damage did not provide enough correlations between these and soil composition. Applying multiple regression led to some uncertainty with enough empirical models. The solution to limit these uncertainties is the development of more complete data bases, leading to predictions representative

L. S. McNeill and Marc Edwards⁹, in the book "Corrosion of steel pipes". The first chapter presents a guide particularly interesting- "Review of Iron Pipe Corrosion in Drinking Water Distribution Systems": corrosion of iron is one of the most complicated problems and costly facing the water supply system.

Other studies have focused on the development of corrosion inhibitors that may be used for small-scale heating plants⁴. Or to the use of softening additives to limit deposit formation²³.

Ya. A. Kovylyanskii, B. M. Krasovskii, A. V. Grishkov⁶ show that although there are manuals, codes, regulations, etc. for the construction of a transportation and distribution of heated water, they should be updated and should take into account the new conditions imposed by health and safety and the environment, stressing that the need to analyze in detail the criteria for reliability.

The pipes used for transportation of fluids are protected from corrosion or by using chemical additives or by the application of the coating to the inner surfaces of the annular weld zone⁷.

It was also investigated the effect of chloride ions, corrosion behavior and passivity of a X80 pipeline steel in a solution of bicarbonate - carbonate using electrochemical and photo-electrochemical⁸. A stable passive state occurs in both the absence and the presence of chloride ions. Their presence initiates the pitting corrosion. Increasing lighting leads to an acceleration of anodic dissolution of steel.

Outside water content (dissolved oxygen, chloride ions) to mount network should not be neglected the phenomenon of

galvanic corrosion (bimetallic), which occurs at the contact of two metals with different electrochemical potential, which acts as a file, more active metal such suffering anodic dissolution³³.

K.W. Nam, D. W. Kim, N.S. Kim, K.Y. Seong¹⁰ shows that the corrosion resistance of galvanized steel pipe increases if the heat treatment thereof, drying in two stages at 170 or 190 ° C, with control of corrosion at the expense of silicon oxide which is formed during the heat treatment. It was noted that the corrosion resistance of steels undergo aging tensions grow considerably²⁶.

A. I. Balitskii, R. K. Melekhov, S. G. Polyakov¹¹ explains the mechanism of corrosion fatigue, which occurs in desert areas or semi-desert pipelines, protected by cathodic protection or protective coatings. The mechanism of corrosion fatigue is directly related to the balance carbon / bicarbonate, resulting in a very narrow asset-liability transition accompanied by decarburization of steel. A possible cause could be corrosion fatigue and microstructure of steel¹⁰. Experience suggests that the inner surfaces immediately adjacent to the external welds are susceptible to corrosion fatigue as a result of thermal and mechanical effects caused by the welding³².

The presence of dissolved oxygen and stagnation of water in the installation rise to pitting corrosion^{38,43}. A method of limiting the occurrence of scale was found to be to apply an electric field to the system¹⁶, the effect on the environment considerably less than in the case of the water treated by demineralization by ion exchange.

The use of corrosion inhibitors for closed loop proves an effective way of saving money, but also increase the quality of work provided as uniform a distribution network^{19,21,29,30}. The effect of phosphonates reduces corrosion of carbon steel, one of the most promising is the zinc salt of the hydroxy - ethylene - diphosphoric acid, resulting in an increase of the protective properties of silicate film on the inner surface of steel pipe²¹. Unfortunately, in certain situations, the only limitation is the use of corrosion inhibitors, which clearly alters the quality requirements of water²⁹.

E. A. Grin¹³ believes that operational reliability and life time of pipes related to a centralized heating system can be analyzed by investigating the mechanical properties and fracture toughness parameters related or a failure analysis³⁹. Although well

known that an increase in temperature can lead to an increase in the speed of chemical reactions, changing the dissolved oxygen content, the rate of diffusion coefficient of the thermal activity, the solubility of salts, organic corrosion¹⁶.

In laboratory experiments with cultures isolated from thermophilic microorganisms staple urban heat supply systems, increasing the iron sulphate - reducing bacteria may accelerate the corrosion rate of the steel plates used in the pipes. Micro-organisms have been shown to be widely present in the alloy steel pipe networks, a solution is the elimination of additional water supply, the oxygen re-introduced into the system¹⁹. Closely monitoring the bacteriological content and chlorination will increase the security of supply, and quality of water supplied to the beneficiary²⁸.

The renewed interest on corrosion prevention and control is due to the enormous costs arising from repairs due to corrosion. One of the unexpected problems that can lead to microbiologically influenced corrosion failure is premature (MIC). Biofilms tend to form where there are flaws in the surface. Stagnation of water or untreated water entering the system favors their development. Once formed biofilm, the final elimination of microorganisms is extremely difficult, which makes maintaining cleanliness is vital. To prevent this, it is recommended visual inspections, but the use of chemical and biochemical sensors. Another option would be to develop biological products, environmentally friendly, to destroy biofilm³⁷.

Corrosion causes not only direct material losses but may be responsible for many accidents and disasters that occur in cities, due to water leakage from pipes used: sewage, heat distribution networks, water supply networks. Cracked pipes and leaky pipe joints allow water to enter the soil, leading to the formation of water lenses that raise groundwater levels. All these produce flooding in foundations and therefore is ultimately a threat to buildings. Water leaks from pipes can affect roads, which are gradually dug to repair the pipes. Repairers after replacing defective pipes ditches filled with soil or sand excavated without consolidation and covered with a mixture of asphalt cement. These known operations gradually lead to a rapid deterioration of the road, especially in heavy traffic areas or large temperature gradient, specific continental

climate, air pollution and the presence of dust and even accidents¹⁸.

Corrosion control by introducing automated systems and monitoring chemical parameters of water and / or steam in a centralized heating system is not a fad, but a necessity²² and is performed using data acquisition systems, sensors and software programs dedicated , such as the sensor for determining the oxygen content, fast and efficient technique for the prevention of corrosion.

O. V. Endrukina, V. N. Voronov, P. N. Nazarenko⁵ shows that monitoring systems to chemical parameters for cogeneration plants and power depends on its specific characteristics. Cherepet plant analysis allowed to conclude that the failure rate of surface warming decreased by approximately 46% within 5 years due to these monitoring systems chemical parameters of water.

M. Froling, C. Holmgren, M. Svanström²⁵ conducted a study on the life cycle of the transportation and distribution systems, related to a centralized heating system and considers particularly important, its mapping, depending on the type of materials used and the IR effect on the environment.

Naphtali A. Groysman Brodsky³¹ explains the interaction between material corrosion as a medium, which leads to deterioration of the quality of both. The author argues that most costs of corrosion can be reduced and increased quality control measures, failure analysis, dissemination of knowledge and experience exploitation which use automated techniques and monitoring. The author claims that the corrosion is a phenomenon, and the quality of a philosophical concept and proposes a quality management system that includes controlling corrosion at all levels: design, manufacture, installation, maintenance, practice, research and regulations and recommends that each industry to thus calculate the exact cost of failures and the possibility of its predictability.

L. R. Pendrill³² discusses the risks of incorrect decisions H. Källgren conformity assessment associated with sampling and uncertainty measurements addressed in terms of decision theory and the testing costs compared to the costs associated with the consequences of incorrect decisions.

Engineering decision making in an analysis tube wear can be done through a so-called system based on knowledge -

knowledge-based systems (KBS)²⁶, an interactive design and analysis cycle encompassing experience engineers operating, thereby increasing productivity, energy efficiency implicitly analyzed system. Science is based on the experience of preventing failures personnel serving system. Therefore cataloging, creation of databases, seemingly unimportant, ability to communicate and transmit information about possible failures are critical aspects to prevent industrial disasters.

K. A. Grantham Lough, R.B. Stone, I. Y. Tumer³⁵ created in this database and a spreadsheet program that allows an analysis of the risk of failure in the design phase, known as RED method (risk in early design).

A. Restrepo, J. Delgado and F. Echeverria⁴⁰ make an assessment of current conditions and life cycle of a plant for drinking water. Consider buried pipes and a large amount of data related to soil chemistry. Statistical techniques have led to a pattern of occurrence of pitting corrosion.

Benjamin D. Craig will describe the corrosion failure modes that cover both general corrosion, uniform and localized corrosion forms, showing that the latter can produce disasters, even before being identified (pitting corrosion). Material selection from the stage design is a must, and

thermal analysis of a system failure is as important as the electrical systems, which are usually applied³⁹.

Roland Huet comes to underline once again the interdisciplinary nature of the failure analysis. Determining the root cause and causes mechanical failures is a complex process that requires expertise from many fields of engineering: materials science, mechanics, thermal engineering, fluid mechanics, without neglecting biology, statistics, computer science and human factors, all contributing to the overall image analyzed the problem⁴¹.

CONCLUSIONS

The interest in a scientific approach of the corrosion management of transportation and distribution water networks in urban areas began almost a century ago. The particularity of each system, depending on the physico-chemical properties of transported water, soil and air, materials, weather conditions and the continued development of methods for mathematical analysis, statistical modeling possibility of the subjects, makes the this area to be still full of unknowns.

REFERENCES

- [1]. D. McLarty, N. Davis, J. Gellers, N. Nasrollahi, E. Altenbernd, *Sisters in sustainability: municipal partnerships for social, environmental, and economic growth*, Sustainable Science, 2014, DOI 10.1007/s11625-014-0248-6.
- [2]. D. A. J. Rand. *A journey on the electrochemical road to sustainability*, Journal of Solid State Electrochemistry (2011) 15:1579–1622, DOI 10.1007/s10008-011-1410z.
- [3]. R. E. Ricke, *Analysis of Pipeline Steel Corrosion Data From NBS (NIST) Studies Conducted Between 1922-1940 and Relevance to Pipeline Management*, Journal of Research of the National Institute of Standards and Technology 115 (5), 373-392 (2010).
- [4]. Yu. V. Balaban - Irmenin, N. G. Fokina, Corrosion Inhibitors for Small-Scale Heat-Supply Systems, Protection of Metals, 2008, Vol. 44, No. 7, pp. 698–703, Original Russian Text © Yu. V. Balaban-Irmenin, N. G. Fokina, 2008, published in Korroziya: Materialy, Zashchita, 2007, No. 7, pp. 28–32, DOI:10.1134/S0033173208070096.
- [5]. O.V.Endrukina, V. N. Voronov, P. N. Nazarenko, *Analyzing the Efficiency of Using a Chemical-Engineering Monitoring System.Taking a District Power Station As an Illustration*, Thermal Engineering, 2006, Vol. 53, No. 8, pp. 600–604. © Pleiades Publishing, Inc., 2006, Original Russian Text © O.V. Endrukina, V. N. Voronov, P. N. Nazarenko, 2006, published in Teploenergetika, DOI:10.1134/S0040601506080040.
- [6]. Ya. A. Kovylyanskii, B. M. Krasovskii, A. V. Grishkov, *Reliability and Quality of Heat Supply As Priorities of SNIIP (Construction Code and Regulations): Heat Supply Networks*, Thermal Engineering, 2006, Vol. 53, No. 8, pp. 663–668. © Pleiades Publishing, Inc., 2006, Original Russian Text © Ya. A. Kovylyanskii, B. M. Krasovskii, A. V. Grishkova, 2006, published in Teploenergetika, DOI:10.1134/S0040601506080155.

- [7]. V. Yu. Chernov, Evaluation of the corrosion resistance of pipes made of carbon low alloy steels, *Materials Science*, Vol. 38, No. 1, 2002.
- [8]. H. B. Xue, Y. F. Cheng, Passivity and Pitting Corrosion of X80 Pipeline Steel in Carbonate/Bicarbonate Solution Studied by Electrochemical Measurements, *Journal of Materials Engineering and Performance*, (2010) 19:1311–1317, ASM International DOI: 10.1007/s11665-010-9631-3.
- [9]. L. S. McNeill, M. Edwards, Chapter 1. Review of Iron Pipe Corrosion in Drinking Water Distribution Systems, <http://www.ebookspdf.org/download/aggressive-water-corrosion.html>, http://www.nuflowtech.com/Portals/0/pdfs/Iron_Pipe_Corrossion.pdf
- [10]. K. W. Nam, D. W. Kim, N. S. Kim, K. Y. Seong, Characteristic of Corrosion Resistance under Different Heat Treatment Conditions of Coated Zinc Coating Steel with Cr-Free Solution, *AETA 2013:Recent Advances in Electrical Engineering and Related Sciences Lecture Notes in Electrical Engineering* Volume 282, 2014, pp 635-643.
- [11]. A. I. Balitskii, R. K. Melekhov, S. G. Polyakov, Carbonate Stress Corrosion of the Mains, *Materials Science*, vol.33,(2), 1997, 242-249.
- [12]. J. T. Bulger, B. T. Lum, J. L. Luo, Microstructural effect on near-neutral pH stress corrosion cracking resistance of pipeline steels, *Journal of Material Science* (2006) 41:5001–5005, DOI 10.1007/s10853-006-0131-7.
- [13]. E. A. Grin, *Operational Reliability and Longevity of the Feed Pipelines of Power Units at Thermal Power Stations*, *Thermal Engineering*, 2006, Vol. 53, No. 8, pp. 648–654. © Pleiades Publishing, Inc., 2006, Original Russian Text © E. A. Grin, 2006, published in *Teploenergetika*.
- [14]. ***Corrosion and Corrosion Protection of Underground Steel Pipelines, SSS Korrosionsschutztechnik, <http://www.scribd.com/doc/234865532/Corrosion-Protection-Underground-Pipelines>
51. G. V. Vasilenko, *The Effect of Oxygen Concentration on the Corrosion of Heat Supply Networks and Heat Exchangers*, *Thermal Engineering*, 2007, Vol. 54, No. 2, pp. 156–158. © Pleiades Publishing, Inc., 2007, Original Russian Text © G. V. Vasilenko, 2007, published in *Teploenergetika*, DOI:10.1134/S0040601507020140.
52. G. V. Ushakov, *Antiscaling Treatment of Water by an Electric Field in HeatSupply Networks*, *Thermal Engineering*, 2008, Vol. 55, No. 7, pp. 570–573. © Pleiades Publishing, Inc., 2008, Original Russian Text © G. V. Ushakov, 2008, published in *Teploenergetika*.
53. L. S. McNeill, M. Edward, *The importance of temperature in assessing iron pipe corrosion in water distribution systems*, *Environmental Monitoring and Assessment* 77: 229–242, 2002, Kluwer Academic Publishers.
54. L. M. Bobylev, *Avoiding emergencies and catastrophes due to leaks of oil, gas, water and industrial effluents from pipelines*, *Chemical and Petroleum Engineering*, Vol. 38, Nos. 5–6, 2002, Translated from *Khimicheskoe i Neftegazovoe Mashinostroenie*, No. 5, pp. 43–46, May, 2002.
55. F. F. Chausov, P. S. Dedyukhin, O. A. Bartenev, M. A. Pletnev, *Corrosion and scaling inhibitor distribution in complicated hydraulic networks*, *Chemical and Petroleum Engineering*, Vol. 38, Nos. 9–10, 2002.
57. E. P. Rozanova, G. A. Dubinina, E. V. Lebedeva, L. A. Suntsova, V. M. Lipovskich, N. N. Tsvetkov, *Microorganisms in Heat Supply Systems and Internal Corrosion of Steel Pipelines*, *Microbiology*, Vol. 72, No. 2, 2003, pp. 179–186. Translated from *Mikrobiologiya*, Vol. 72, No. 2, 2003, pp. 212–220.
58. Yu. V. Balaban - Irmenin, A. M. Rubashov, N. G. Fokina, *The Effect of Phosphonates on the Corrosion of Carbon Steel in Heat-Supply Water*, *Protection of Metals*, 2006, Vol. 42, No. 2, pp. 133–136. © Pleiades Publishing, Inc., 2006, DOI:10.1134/S0033173206020044.
59. L. M. Zhivilova, *The State of Work on Automated Monitoring and Control of Water Chemistry at Power Stations and Prospects for Their Future Development*, *Thermal Engineering*, 2006, Vol. 53, No. 8, pp. 626–632. © Pleiades Publishing, Inc., 2006, DOI: 10.1134/S0040601506080088.
60. E. V. Makarova, V. I. Sharapov, *Some Thermal Engineering Aspects of Protecting the Condensate–Feedwater Path of a Cogeneration Station against Corrosion*, *Thermal Engineering*, 2006, Vol. 53, No. 8, pp. 633–638. © Pleiades Publishing, Inc., 2006, E. V. Makarova, V. I. Sharapov, 2006, DOI:10.1134/S004060150608009X.

61. L. Kontsevoi, S. A. Kontsevoi, *Unified Water Chemistry for Circulation HeatTransfer Systems*, Thermal Engineering, 2006, Vol. 53, No. 8, pp. 639–643. © Pleiades Publishing, Inc., 2006, DOI:10.1134/S0040601506080106.
62. M. Froling, C. Holmgren, M. Svanstrom, *Life Cycle Assessment of the District Heat Distribution System*, International Journal of Life Cycle Assesment, 2004, 9 (2), 130-136, (ISI).
63. M. Alvarado, M. A. Rodriguez-Toral, A. Rosas, S. Ayala, *Decision-making on pipe stress analysis enabled by knowledge-based systems*, Knowledge and Information Systems, 2007, 12(2):255–278, DOI 10.1007/s10115-007-0076-4.
64. A. E. Kuzmak, A. V. Kozheurov, L. A. Efimenko, V. Yu. Ilyukhin, O. V. Konovalova, *Strain ageing and corrosion resistance of pipe steel*, Chemical and Petroleum Engineering, Vol. 44, Nos. 3–4, 2008.
65. C. C. Chien, C. M. Kao, C. W. Chen, C. D. Dong, H. Y. Chien, *Evaluation of biological stability and corrosion potential in drinking water distribution systems: a case study*, Environmental Monitoring Assessment (2009) 153:127–138, DOI 10.1007/s10661-008-0343-1.
66. Yu. V. Balaban-Irmenin, N. G. Fokina, *Internal corrosion inhibitors for pipelines carrying deaerated heating water*, Power Technology and Engineering, Vol. 41, No. 5, 2007, 306-312.
67. Yu.V.Balaban - Irmenin, N. G. Fokina, N. N. Spirin, L. I. Pravdina, *Use of varrios methods for suppressing internal corrosion of the thermal network at the Novomoskovsk state regional electric power plant*, Power Technology and Engineering Vol. 42, No. 6, 2008, 356-358
68. A. Groysman Naphtali Brodsky, *Corrosion and Quality*, Accreditation Quality Assurance (2006) 10: 537–542, DOI 10.1007/s00769-005-0034-3
69. L. R. Pendrill, H. Källgren, *Optimized measurement uncertainty and decision making ib the metering of energy, fuel and exhaust gases*, Measurement Techniques, Vol. 51, No. 4, 2008.370-377.
70. P. M. Singh, J. Mahmood, *Stress Assisted Corrosion of Waterwall Tubes in Recovery Boiler Tubes: Failure Analysis*, Journal of Failure Analysis and Prevention, (2007) 7:361–370, DOI 10.1007/s11668-007-9063-z.
71. F. Elshawesh, K. Abusowa, H. Mahfud, H. Ezuber, *Stress-Corrosion Cracking and Galvanic Corrosion of Internal Bolts from a Multistage Water Injection Pump*, Journal of Failure Analysis and Prevention, (2008) 8:48–53, DOI 10.1007/s11668-007-9109.
72. K. A. Grantham Lough, R. B. Stone, I. Y. Tumer, *Failure Prevention in Design Through Effective Catalogue, Utilization of Historical Failure Events*, Journal of Failure Analysis and Prevention, (2008) 8:469–481, DOI 10.1007/s11668-008-9160-7.
73. J. I. Mickalonis, *Failure Prevention by Short-Time Corrosion Tests*, Journal of Failure Analysis and Prevention, (2005) 4:46-53 © ASM International, DOI: 10.1361/154770205X55027 1547-7029.
74. R. A. Lane, *Corrosion Costs - Under the Microscope: Understanding, Detecting, and Preventing Microbiologically Influenced Corrosion*, Journal of Failure Analyse and Prevention, (2005) 5:10-12, 33-38 © ASM International, DOI: 10.1361/154770205X65891.
75. S. C. Dexter: “Microbiologically Influenced Corrosion,” Corrosion: Fundamentals, Testing, and Protection, vol 13A, ASM, Handbook, ASM International, 2003, pp.398-416.
76. B. D. Craig, *Material Failure Modes, Part III: A Brief Tutorial on Corrosion- Related Material Failure Modes*, Journal of Failure Analyse and Prevention, 2006, 2:12-19 © ASM International, DOI: 10.1361/154770206X99262.
77. A. Restrepo, J. Delgado, F. Echeverria, *Evaluation of Current Condition and Lifespan of Drinking Water Pipelines*, Journal of Failure Analyse and Prevention. (2009) 9:541–548, DOI 10.1007/s11668-009-9291-5.
78. R. Huet, *The Interdisciplinary Nature of Failure Analysis, Practical Failure Analysis*. 2(3), 2002, 17-22, Proceedings of Failure Prevention through Education: Getting to the Root Cause. The conference was presented 23–25 May 2000, in Cleveland, Ohio, by ASM International.
78. E. B. Bieberich, R. O. Hardies, *TRIDENT Corrosion Control Handbook*, DTIC Doc.: AD-B120 952, David W. Taylor Naval Ship Research and Development Center, Naval Sea Systems Command, DTRC/SME-87-99, Feb 1988.
79. G. Pantazopoulos, *Analysis of Leakage Failure in a Domestic Hydraulic Installation Assisted by Pitting Corrosion of Water Tube*, Journal of Failure Analyse and Prevention, (2009) 9:479–485, DOI 10.1007/s11668-009-9274-6.

TREATMENT WASTEWATER WITH A LARGE VALUE OF CHEMICAL DEMAND OXYGEN COMING FROM COPPER PLATING (PART I)

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Abstract: The wastewater coming from copper plating have a large quantities of anion tartrate as result of chemical composition of initial solution (g/L⁻¹), like Seignette salt, that's means a very high oxygen chemical demand measured as KMnO₄ mg L⁻¹, in accordance with-STAS , NTP 001,- and NTP 002.

Because alkaline pH of these spent solution (9-10) , it is necessary to acidify between 5-6,5 pH, for the purpose of eliminate anion tartrate in the best conditions through chemical precipitation with calcium chloride 1M, in a large excess, under the mechanical stirrer, optimal pH, and optimal dose of reagent for quantitative precipitation tartrate anion. After four hours necessary crystallization process, the precipitate formed can be decantated, filtered and eliminated in the first step of cleaning by this proposed method.

The calcium tartrate product of solubility, $7,7 \cdot 10^{-7}$ allowed to elaborate technical procedure to decrease CCO-Mn up to the allowed limit.

Key words: tartrate, precipitation, calcium chloride, pH.

INTRODUCTION

There are known many assortments wastewater containing copper or other heavy metals coming from plating works as well as by electrical and chemical procedure^{1,11}.

The discharge of galvanic industry wastewater containing heavy metals is one of the largest sources of water pollution. In this case also organic free compound and copper complex with anion tartrate.

The removal and recovery useful transitional metals is made by different methods like: precipitation, precipitation and coagulation with aluminium or iron salt, electrodialysis technique, activated adsorption carbon process, ionic exchange, indirectly osmoze, concentration through extraction, extraction with suitable organic solvents, cementation, oxidation or chemical reduction with chemical reagents^{4,7,8}.

Also for the anion contents there are the same possibility, but is very important to take into account the concentration of anions and then to propose the more economically procedure and method, using cheap reagent^{5,6}.

In this paper we are studied removal tartrate anion from copper waste water work plating, by chemical precipitation method , using calcium chloride 20% concentration, the influence of

pH, quantities of reagent, optimal time of decantation and separation from aqueous phase. Wastewater coming from chemical copper plating are residual tartrate, that means a high amount of organic charge.

The technologies treatment existing (chemical oxidation, coagulation/flocculation, ozonation, anaerobic biological treatment), have a certain efficiency extraction degree in removal of organic charge^{12,14}.

Adsorption is a cheap technique. One of the advantage is the possibility to use a large variety of low-cost waste materials from industry and agriculture , but it is adequate, after the first step of primary removal through chemical precipitation of calcium tartrate.

Chemical oxygen demand (COD) gives information on the oxygen required by a water for oxidation of almost all water soluble substances, the exceptions being a number of compounds containing nitrogen and only very slightly soluble hydrocarbons.

STUDY AREA

This paper reports the removal and decreasing of (COD) parameter for the pollution assessment of the plating bath corresponding method for electrolessly a copper on the metal surface.

Copper, (COD) and pH have been chosen as indicators of the pollution degree of the studied area.

It was measured the copper concentration, pH and COD.

METHODS, TECHNIQUES, MATERIALS

A number of 10 wastewater sample was collected from galvanic plating, in which copper was analyzed by flame atomic absorption spectrometry (FAAS), using a spectrometer AAS-30 the content of copper. It was found 0,700g Cu/L. The content of copper was confirmed also by volumetrically method with Titriplex III 0,01M (F=1) and murexide like indicator at pH 8. The optimal technical conditions for copper determination, were as below^{10,13}: Halogen cathode lamp; HCL, Wave length:

324,8 nm, Slit :0,3 nm, Sensibility: [ppm] : 0,04, Flame: air / C₂H₂ leen

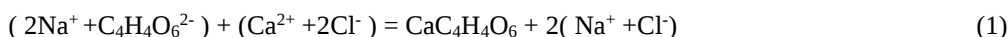
The COD content was made according to STAS-CCO-Mn, volumetrically, using chemical pure Merck, Riedel -de Haen and Fluka Chemie reagent. Anion tartrate was eliminated by chemical precipitation with calcium chloride 20% solution, 100% excess, against stoichiometric ratio.

The finally value of allowed COD is : max 70mg/L (NTP-001)

Synthetic solution of sodium potassium tartrate, was prepared for etalon, test and analysis against KMnO₄ solution and sulfuric acid.

RESULTS AND DISCUSSIONS

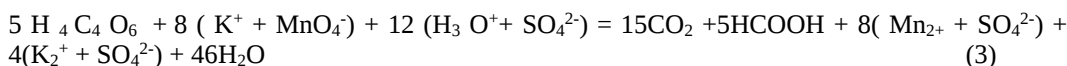
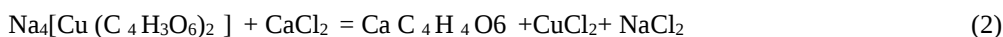
The precipitation of free anion tartrate follows next equation:



Tartrate anion reacts with potassium permanganate in the presence of sulfuric acid, when is reduced to formic acid according to equation.

In alkaline domain, copper ion and anion tartrate forms a chelate compound⁹ which has a stability constant equal to 6.

The copper tartrate complex could be destroyed also through chemical precipitation with the same reagent, calcium chloride at 5,5-6,5 pH.



From (2) and (4) equations, could observe that theoretically, 5,40 mL KMnO₄ 0,01N (F=1), can oxidizing 000.1 mg H₂C₄O₆²⁻(4)

At the beginning of treatment, wastewater have had 3.5 g of total tartrate anion. It was determined COD upon 10 mL filtered solution, after precipitation with calcium chloride.

Effect of pH

The results are presented in table 1. The influence of calcium chloride excess are presented in table 2.

The optimum pH value is between 6-6,5 and reagent excess could be 100% for calcium chloride 20%.

The white, crystalline, insoluble calcium tartrate is removal through decantation and filtration. COD had a good improvement to low value of potassium permanganate consumption. Copper ion remained in soluble form, besides calcium cation and could be prepared for recovery by chemical reduction method

The calibration copper curve was made by FAAS technique, as fallows in table 3

Table 1. Influence of pH and extraction degree values.

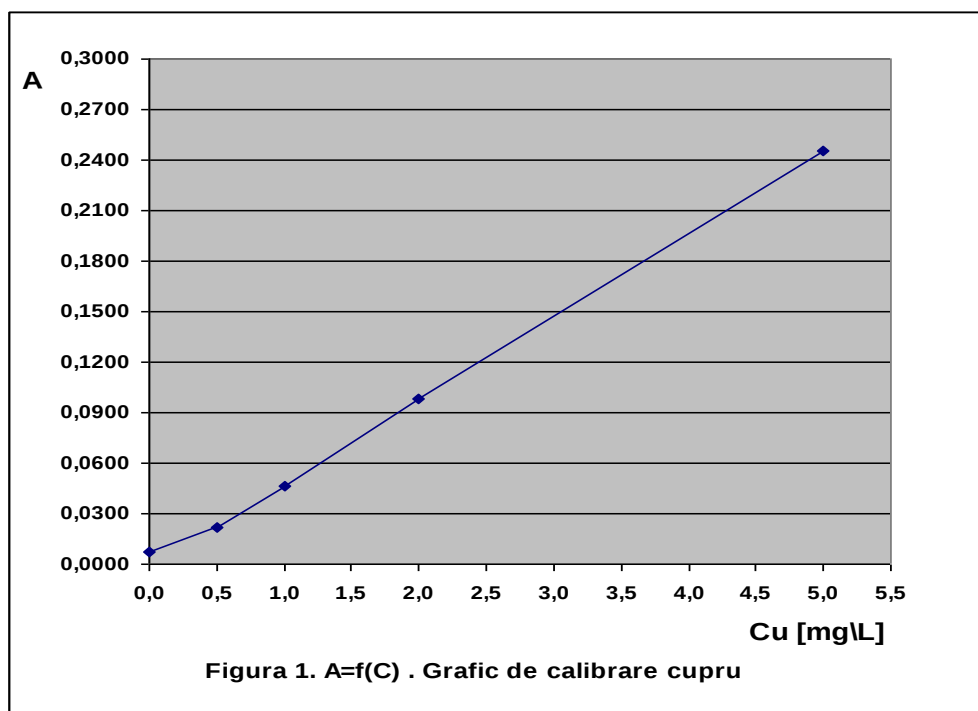
Nr.	pH	G, %	V _{KMnO4} 0,01N
1	1,0	0	68,05
2	2,0	25,67	50,63
3	3,0	38,45	41,88
4	4,0	66,88	22,54
5	5,5	82,90	11,63
6	6	82,90	11,63

Table2. Excess of reagent and extraction degree G %,.

Nr.	Reagent excess, %	G %,.	V _{KMnO4} 0,01N
1	25	82,20	12,11
2	50	86,45	9,22
3	100	92,67	4,98
4	150	98,02	1,34
5	200	99,40	0,41

Table 3. Calibration curve for copper (concentration, absorbance)

Nr.	Cu [mg/L]	Corr. Absorbance	A	Std. Dev. [Mg/L]
1.	0,00	0,0069	0,0069	0,0111
2.	0,50	0,0219	0,0219	0,0001
3.	1,00	0,0467	0,0467	0,0002
4.	2,00	0,0980	0,0980	0,0003
5.	5,00	0,2458	0,2458	0,0013



CONCLUSIONS

A large content of organic compound could be eliminated in form of calcium tartrate, a white crystalline, insoluble precipitation, from spent alkaline solution coming from copper chemical plating works.

At the beginning of treatment, the content of copper was determined by FAAS and organic charge by volumetrically titration with KMnO₄ in acid range 2-2,5 of sulfuric acid.

The optimal pH, for this case, could be realized around 5,5-6,5 units pH. For the low values of pH, the extraction degree, G %, had a little importance and G, did not exceed 40-60%. Growing pH values, the extraction degree, G%, had 83%, for the reagent excess equal to 10%, starting from (2).

For a higher quantities of calcium chloride 20%, 40-80%, excess, the

precipitation of calcium tartrate is more evidently, COD has low value determined in mL KMnO₄ 0,01N/L. The most acceptable extraction degree is obtained for 100 % solution 20% calcium chloride excess against stoichiometric rapport: anion tartrate: calcium, practically 99,40% elimination of organic compound, according to extreme limit of discharge.

REFERENCES

- [1]. BAZAN, J.K., BISANG, J.M., :Journal of Applied Electrochemistry, **(34)**, 2001, p. 501;
- [2]. BURTICĂ, G., VLAICU, I., NEGREA, A., PODE, R., PODE, V., MICU, D.,:Tratamentul efluenților reziduali, Editura Politehnica, Timișoara, 2000, p. 274-292;
- [3]. CORDAȘ, E., FRENȚIU, T., PONTA, M., RUSU, A.M., FODOR, A., Analiza prin spectrometrie atomică, editată și tipărită de Institutul Național de Optoelectronică-INOE, București, 1998, p. 191-200;
- [4]. FUMIO, N., KAZUMI, B., MASAHIRO, Y., YOSHINORI, W., Journal of . of the Minino and Materials Processing, Japan, **(120)**, 2004, p. 209-216;
- [5]. GAVRIȘ, G., "Chimia mediilor poluate", Editura Universității din Oradea, 2003, p. 120-130;
- [6]. GAVRIȘ, G., Chimia mediilor poluate. Caiet de lucrări practice, 2003, Editura Universității din Oradea, 2003, p. 19-23
- [7]. ILEA, C. G., DORNEANU, S., IMRE, A., ILEA P., Studia Universitatis, Babeș-Bolyai, Cluj-Napoca, *Chimia*, **(1)**, 2005, p. 3-5;
- [8]. KANG, S.Y., LEE, J.U., KIM, K.W., Environmental Technology, **(26)**, 2005, p. 615-624;
- [9]. LOURYE, Y., : Aide mémoire de chimie analytique", Edition Mir, Moscow, 1975, p.130-139;
- [10]. MACAROVICI, C., Analiza chimică cantitativă anorganică, Editura Academiei R.S.R., București, 1979, p. 257-259;
- [11]. ONICIU, L., GRUNWALD, E., Galvanotehnica, Editura Științifică și Enciclopedică, București, 1983, p. 466-477;
- [12]. SRINIVASA, K.R., SARANI, D., DASH, P.K., CHAUDHURY, G., :Journal. of Chemical Technology and Biotechnology, **(77)**, 2002, p. 1107-1113;
- [13]. SEASIN, W.,:Atomic absorption spectrophotometry, Moscow, 1971, p. 155-156;
- [14]. ZAMANI, H. A., RAJABZADEH, G., FIROUZ, A., GANJAL, I M. R., Journal of analytical chemistry, **62**, **(11)**, 2007, p. 1080;

GEOCHEMICAL MODELLING OF LOW-ENTHALPY THERMAL RESERVOIRS

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Abstract: A well known geothermal area is located along the north western side of our country. Considering the wellhead temperatures of the waters, the geothermal areas are classified as low-enthalpy. The high geothermal potential has supplied heating both for residential and commercial spaces, industrial processes and for recreational purposes. Chemical study for the characterization of the geothermal waters and water-rock interaction is of great significance when a geothermal well has been exploited. For geochemical evaluation of selected thermal reservoirs, fluid samples were obtained from several wells. Using the analytical data of the wellhead samples, the aquifer fluids feeding the selected wells were modelled with the aid of specific simulation programs.

Key words: geothermal potential, modelling

INTRODUCTION

The first wells were drilled in the Western Plain. Considering the outstanding special therapeutic properties of the geothermal water in Băile Felix, where the microclimate is ideal for recreation and the landscape is pleasant, it has become an attraction for the investments in tourism, recreation and health. Băile Felix is nowadays the most famous thermal spa, which contains abundant treatment indoor and outdoor facilities. Its geothermal reservoir is currently exploited by wells with depths between 50 and 450m, with wellhead temperatures in the range of 36–48°C. The geochemical assessment of an area requires a detailed study of the chemistry of thermal fluids and gives information on any change in surface manifestation, but gives also information of possible manifestation which would happen into the reservoir. In this paper were studied two low-temperature geothermal wells, 4003 and 4012 from Baile Felix.

METHODS OF STUDY

The results of analysis of main elements in the water samples from the studied wells will be interpreted for each well. First, in order to have a classification of the waters, the Schoeller diagram was used. It utilizes the equivalent concentration of sulfate, carbonate, chloride, magnesium, calcium and the sum of the alkali ions,

sodium and potassium on the y-axis and these elements are lined up on the x-axis in this order. Each water sample is represented on the diagram by a line water sample.

The Piper diagram can be used to classify water samples as alkali-bicarbonate water, sodium-chloride water, magnesium-sulfate water etc. It is made up by two triangular diagrams, one for plotting the proportions, in equivalent concentrations, of the main cations and the other for the equivalent concentrations of the main anions. Parallel lines are drawn from the triangular shapes into a diamond shape where the lines cross.

The Durov diagram utilizes the same triangular diagrams as the Piper diagram, which are connected into a square, adding total dissolved solids and pH of the water samples in connecting rectangles. All the diagrams were calculated by the AqQa program⁶.

For an initial classification, in terms of the major anions: bicarbonate, chloride, sulphate, a triangular diagram⁴ will be used. The position of a data point in this diagram is obtained by evaluating the percentage of each anion relative to the sum of the concentrations, in mg/l of all three constituents.

By the use of Giggenbach⁵ and Arnorsson¹ triangular diagram we'll get information regarding water-rock equilibrium. This diagram with Na/1000, K/100 and $\sqrt{Mg}$ can be used to divide waters into fully

equilibrated with rock at a given temperature, partially equilibrated and immature water, that means dissolution of rocks is not followed by equilibration.

Silica-enthalpy mixing model was developed in order to estimate the temperature of a deep hot water component in mixed waters in springs or discharge from shallow drillholes.

Changes in water temperature, pressure, pH and mineral saturation may occur when the fluid is tapped from geothermal reservoir by production wells. As a consequence, minerals can precipitate within the wells, in pipelines and other surface equipments. The saturation index, $\log Q/K$ is an indicator of the degree of saturation of water with respect to a mineral. When the ionic activity has a higher value than the theoretical solubility ($Q > K$), the saturation index is positive, indicating a supersaturation with respect to the particular mineral considered. If $Q = K$, geothermal water is in equilibrium with the mineral in respect.

The computer program WATCH² was used to calculate the saturation indexes for particular mineral phases believed to occur in the reservoir of Baile Felix field. This application is useful in prediction of scaling tendency in a particular geothermal system.

RESULTS AND DISCUSSIONS

The results of the chemical analysis of the main elements in the water samples were plot in different classification diagrams. The Schoeller diagram (Figure 1) for the studied geothermal waters indicated that waters are as calcium-bicarbonated type with relatively high sulphate concentration, especially for the well 4012. The Piper diagram (Figure 2) also indicates the calcium-bicarbonated waters with a high content of bicarbonate and also sulphate is high and, within cations, magnesium. By the Durov diagram (Figure 3) mineralization is higher for well 4012 compared to 4003. The presented diagrams were constructed using the AqQa program.

The triangular diagram (Figure 4) on the relative concentrations of the three major anions indicated that the data points for the geothermal waters from well 4012 plot in the

field of peripheral waters, while for well 4003 closer to the field of steam heated waters.

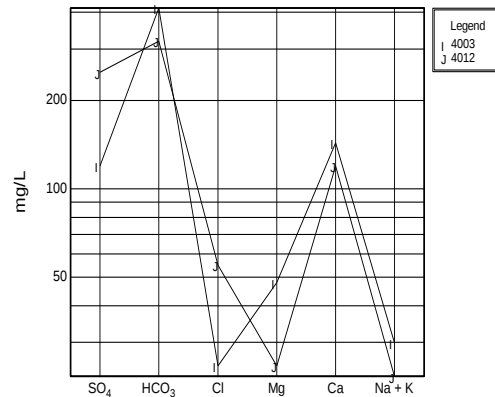


Figure 1. Schoeller diagram for the water samples

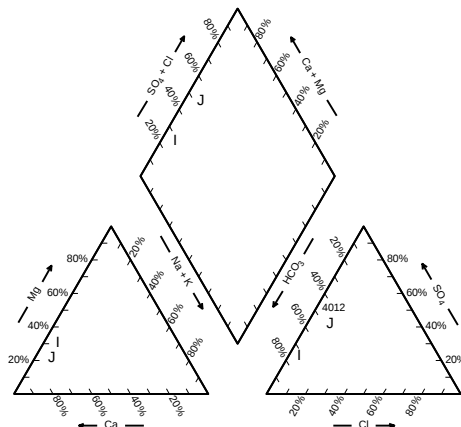


Figure 2. Piper diagram for the selected water samples

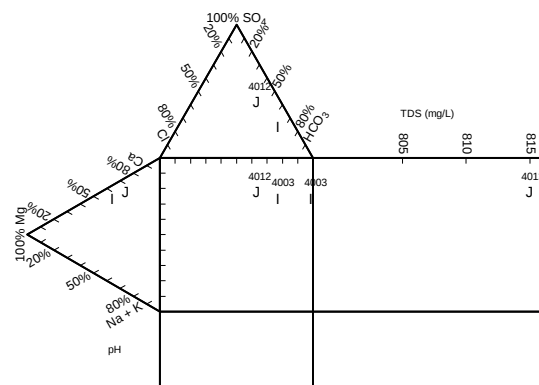


Figure 3. Durov diagram

The Na-K-Mg ternary diagram (Figure 5) plot in the immature region for both studied wells, having a high Mg concentration. Since this

implies that these waters have not attained equilibrium with the reservoir rocks it would be inaccurate to use them to get the Na/K geothermometer temperature.

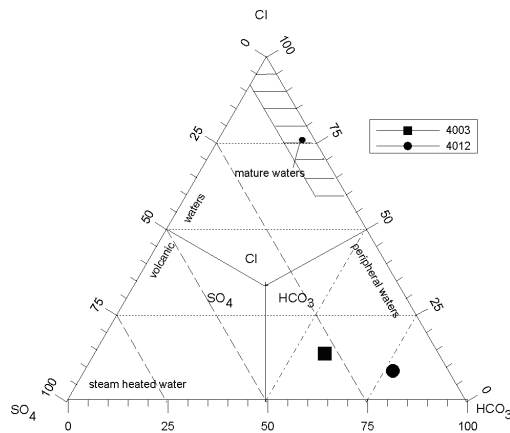


Figure 4. Major anions ternary diagram

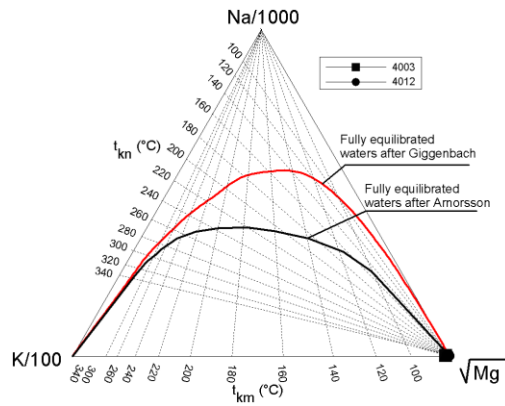


Figure 5. Na-K-Mg equilibrium diagram

The wellhead temperatures measured during water sampling were 45°C and 43°C. In order to find out the temperature into the reservoir, the diagram (Figure 6) plots silica versus the enthalpy of water, the intersection points of the “cold water - geothermal water” line with the solubility of chalcedony curve giving the silica content and the enthalpy of the deep hot water component as: 192 respectively 261 kJ/kg for the wells 4003 and 4012.

Deep water temperatures obtained from the steam tables³ are 46°C for the deep geothermal water from well 4003 and 60°C from well 4012. These temperatures indicate a shallow feed reservoir, based on the fact that the depths of the wells is low and well-sustained the reservoir pressure.

Figure 7 shows the results for the saturation indexes of calcite calculated for each well using WATCH simulation program, first at the wellhead temperature and then at lower temperatures, which can be attained after geothermal waters utilization.

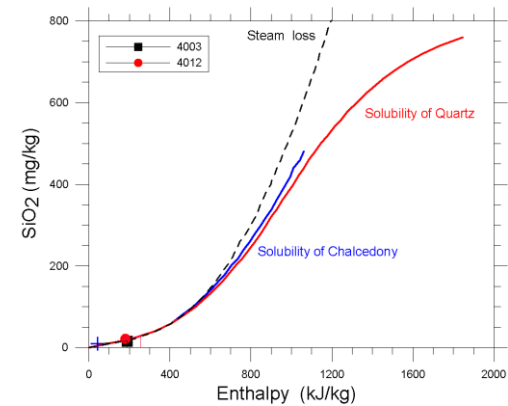


Figure 6. Dissolved silica-enthalpy diagram

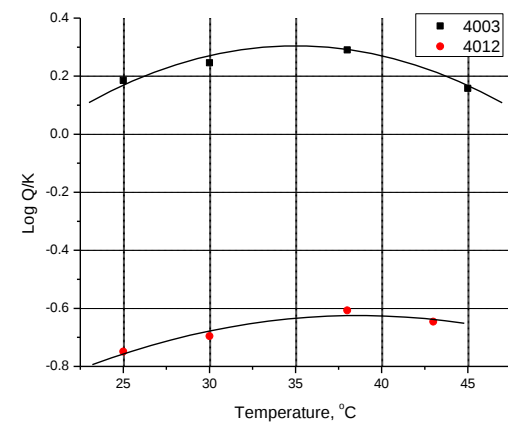


Figure 7. Prediction of saturation state of calcite

By figure 7 can be assessed scaling with respect to calcite at the wellhead temperature and also at the lower temperatures for geothermal well 4003. For the other well there is no expect of any calcium carbonate scale, the saturation index having negative values.

CONCLUSIONS

Waters from important production wells from Baile Felix were taken in this study. The results of the laboratory analysis were interpreted by the aid of specific programs. The type of water was found out as bicarbonated-calcium-sulphate, as was demonstrated also by Schoeller, Piper and Durov classifications. Bicarbonated was the dominating anion.

Calcium varies from 144 mg/L at well 4003 to 120 mg/L for well 4012. The geothermal water from well 4003 appears to be a steam heated water, while water from well 4012 looks like a peripheral water.

The silica mixing model results have been used to infer the location of the major aquifer feeding the well, the deep water temperature being almost the wellhead temperature for well 4003 and a bit higher for well 4012. This

proves that the feedzone is shallow, close to surface and supplies the geothermal water which flows up through the wells.

In low-enthalphy wells like the studied ones in Baile Felix, the main scaling problem is due to calcium carbonate precipitation. As described previously, by computer simulation, the sample from well 4003 is supersaturated with respect to calcite.

REFERENCES

- [1] Arnorsson, S. (1991). In: Applications of geochemistry in geothermal reservoir development. F. D'Amore, UNITAR/UNDP publication, Rome, pp.145
- [2] Arnorsson, S. and Bjarnason, J.O. (2004). The speciation program WATCH, version 2.3. Orkustofnun, Reykjavik.
- [3] Keenan, J.H., Keyes, F.G., Hill, P.G. and Moore, J.G. (1969). Steam tables, John Wiley, N.Y., pp.162
- [4] Giggenbach W.F. (1991). In: Application of geochemistry in geothermal reservoir development. F. D'Amore, UNITAR/UNDP publication, Rome, pp.119
- [5] Giggenbach W.F. (1988). Geochim. Cosmochim. Acta, 52, pp.2749
- [6]*** (2006). The Spreadsheet for water analyses, Rock Ware, AqQa.

CHEMICAL METHOD FOR TREATMENT WASTEWATERS WITH CHROMATES

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Abstract: Chromium is used for plating and in chrome steel. The chromates [chromium (VI)] have many industrial uses as pigments, catalysts, fungicides. The waste waters with chromate are usually presented in industries side by oxalic acid produced at aluminum protection surface. This paper proposed a very cheap method for reciprocally treatment due to function as a bidentate ligand of oxalic acid in the form of dianion with many transition metals ions. Preparation of oxalate chromate potassium salt was made in form of $K_3[Cr(C_2O_4)_3]$ anhydrous, using a suitable ratio from oxalic acid, potassium chromate and sulfuric acid. The crystals have been deposited, filtered and washed with ethanol. The product is dried and the yield calculated as a percentage based on chromium is dried.

key words: chromate, waste waters, oxalic acid

INTRODUCTION

There are a lot of dates and experimental research about treatment of waste waters containing Cr(VI) which can appears from different sources in a various concentration as diluted solutions or concentrated fluids.

The most investigated sources are electroplating works, tanneries, pigments, where chromate anion concentration begins with 5-50 ppm and may be attends 200-1000 ppm¹⁻³.

The treatment of waste waters with chromium hexavalent shape content are made by chemical reduction method, using reactive agents like $FeSO_4$, Na_2SO_3 , $NaHSO_3$, $Na_2S_2O_5$, SO_2 gaseous, $(Fe + H_2SO_4)$ or electrochemically. All the reduction reactions had taken place in acid range, pH 2-2,5 in the presence of sulfuric acid usually. By electrochemical reducing it is known a suitable method involving coagulation process assured by $Fe(OH)_3$.

If besides of chromate anions there are an eloxal process (on

aluminium) with oxalic acid, then appears also waste waters with oxalic acid.¹ The high concentration of oxalate anion in the presence of sulfuric acid might be a good notification for reciprocally treatment waste waters coming from chromium electroplating and waste waters coming from aluminum protect surface by eloxal process.

* hexavalent chromium could be reduced by oxalic acid in the presence of sulfuric acid

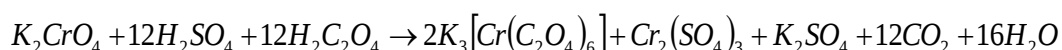
* it could be obtained a new trivalent chromium compound in the shape of oxalate/chromium complex.

METHODS, TECHNICS, MATERIALS

All the reagent were chemically pure or ultra pure: Merck, Fluka, Reanal in the next order: potassium chromate 0,1M sulfuric acid 1:2 vol, potassium permanganate 0,1N (F=1), oxalic acid 0,5M (F=1), Mohr salt 0,1N (F=1), sodium hydroxide 0,1N (F=1), standard chromium etalon 0,05 mg/mL, deionised water.

The apparatus were: analytical balance Toledo, spectrophotometer UV-VIS, IR-Spectrophotometer KBr cell, magnetic stirrer. The hexavalent chromium content was titrimetrical determined with Mohr salt 0,1N and potassium permanganate 0,1N in sulfuric acid range., pH 2. Oxalate anion was analysed titrimetrically with potassium permanganate on boiling⁴. The traces of hexavalent chromium untransformed in

chromium oxalate complex compound was photometrical determined by means of diphenylcarbazide at 573 nm, together with Cr(III), between 1 and 20 mg/l. The cation Cr(III) was eliminated by precipitation with sodium hydroxide at 60⁰C and pH 9⁵. In the filtrate was determined Cr(VI). The chemical equation to obtain oxalate chromium potassium salt compound is:



It was prepared one saturated potassium chromate solution acidified with sulfuric acid at 70-80⁰C, under magnetic stirrer, was added a little quantities from 0,5M oxalic acid as long as solution has a violet color.

After chemical reaction, a violet crystals of K₃[Cr(C₂O₄)₆] have been separated.

STUDY AREA

The influence of the oxalic acid concentration upon extraction degree of a K₃[Cr(C₂O₄)₆] was studied in accordance with Table 1.

Table 1. The influence of oxalic acid excess upon chromium oxalate complex obtaining^{6,7}

K ₂ CrO ₄ 0,1M [mL]	H ₂ SO ₄ 2N [mL]	H ₂ SO ₄ 0,5M [mL]	Excess H ₂ C ₂ O ₄ %
20	2	12	0
20	2	16	33,33
20	2	18	50
20	2	20	66,66
20	2	24	100

Table 2. The conversion of hexavalent chromium to K₃[Cr(C₂O₄)₆]

Oxalic acid excess %	Cr ⁺⁶ filtrate [mL]	Mohr salt 0,1N [mL]	KMnO ₄ 0,1N [mL]	Reduction Cr(VI) to Cr(III), %	Cr ⁺⁶ residual [mg/L]
0	32	10	8,3	60,26	429,84
33,33	31	10	8,8	71,63	307,09
50	35,3	10	9,3	79,03	226,26
66.66	31	10	9,8	91,81	88,02
100	31	-	-	99,80	2,07

RESULTS AND DISCUSSIONS

The results presented in Table 2, allowed to calculate the formula

conversion percentage from Cr(VI) to Cr(III), as follows:

$$C, \% = \frac{N_i - N_f}{N_i} \cdot 100 \quad (2)$$

$$C, \% = \frac{2 \cdot 10^{-3} - \frac{4}{30} \cdot (10 - F_{KMnO_4}) V_{filtrat} \cdot 10^{-4}}{2 \cdot 10^{-3}} \cdot 100 \quad (3)$$

where:

N_i = initial mol number of chromium (VI),: $2 \cdot 10^{-3}$

N_f = final mol number of chromium (VI)

The residual hexavalent untransformed chromium was calculated from Table 2 and formula (3). The excess of oxalic acid

increase the extraction degree up to 99,80% being a good factor for process efficiency and a cheap complexation reagent.

The chromium oxalate complex was determined by IR spectrophotometer (Germany) and its diagram shows in figure 1 (see below).

$$Cr(VI)_{res} [mg/l] = \frac{4}{30} \cdot (10 - F_{KMnO_4} \cdot V_{KMnO_4}) \cdot V_{filtrate} \cdot A_{Cr} \quad (4), \text{ where } A_{Cr} = 52,00$$

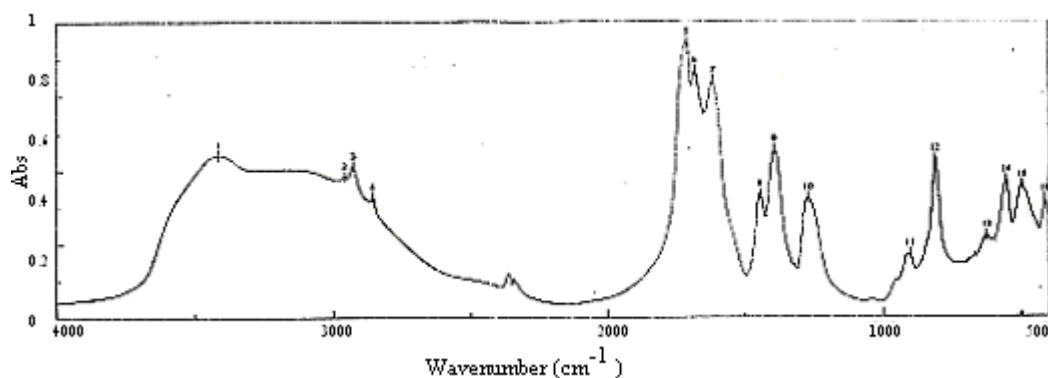


Figure 1: IR spectrum of oxalic acid (HOOC-COOH)

The IR-spectrum analysis is representative for oxalate anion between wave numbers of our compound. The vibration from 900 cm^{-1} corresponds to C-C bond. The signals between 1650-1200 cm^{-1} attribute to vibration band from C=O

and C-O bonds. The last vibration band is very large and dues by O-H bond. In spectrum can see deformation bands, δ_{H-O-H} between 1700-1640 cm^{-1} and δ_{O-H} from 1450 to 1210 cm^{-1} .

CONCLUSIONS

- The reciprocal treatment of hexavalent chromium and oxalic acid presented in waste waters coming from electroplating surfaces works, might be successfully applied as well as, the both concentration are large
- The optimal excess of oxalic acid are 100%
- The maximum extraction degree was 99% into. $K_3[Cr(C_2O_4)_6]$
- Chemical analysis of chromate untransformed made by photocolometric and titrimetric methods, confirming 99% extraction degree.
- The IR spectrum confirmed the structure and composition of chromium oxalate complex.
- By reciprocal treatment it was realised a sub-product and the cleaning in the same time waste waters with chromate anion, oxalic acid and sulphuric acid

6. REFERENCES:

- [1] Grunwald, E. and Oniciu., L. (1980), *Galvanotechnics*, Scientific and Encyclopedic Publishing House, Bucharest;
- [2] Dash. P., Srinivasa Rao. K, Sarani. D., and Roy. P. (2002)., *Jnl. of Chem. Techn. and Biotechn.*, (77). pp 1107-1113;
- [3] Bazan J. K., Bisang . J. M. (2001) . *Jnl. Appl. Electrochem.*, (34). pp 50-54;
- [4] Macarovici, C. (1979). *Inorganic quantitative chemical analysis*, Romanian Academic Publishing House, Bucharest;
- [5] Gavriș, G. (2003). *Environment polluted chemistry*, Publishing Univ. House, Oradea;
- [6] Olaru, R., Suteu, D., and Păduraru, C. (1998). *The utilization of celulozic materials for waste water deppolution*, *Chem. Jm*, (7). pp 123-128;
- [7] Gavriș, G., Iovi, A., and Sebeșan, M. (2005). *Stady of the cleaning process of the waste water with zinc ions content*, *Chem.. Bull. Politehnica Univ.Timișoara*, 50 (64), pp 166-168.

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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.

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

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