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Section 1. Mathematics

Mudar Al Yousef,
Preparing for PhD degree – Damascus University
E-mail: mudar.alyousef1982@gmail.com

THE TRUTH FROM ANOTHER ANGLE

Abstract: The purpose of this paper is to prove that the truth we know might be just a relative term which changes by looking from a different angle.

To this end we will provide a model of 3D Universe, and invite a two- dimensional being to live in.

Here this being lives in the inner curved (lateral) surface of the cone on the circumference of a circle. Because the curvature or the third dimension is infinitesimal, the two- dimensional being thinks that he lives on a circumference of a solid circle in a 2D Universe. In fact he will not understand the real truth of his Universe. Or let's say in other word, he will describe the truth of his Universe as he observes it.

This paper will prove how the understanding of the sun, the concept of day and night and even the whole Universe changes by changing the angle we are looking from. Thereafter we will explain how science and new discoveries make the two- dimensional being believes in new truth.

All the theories, thoughts and ideas included in this paper will be explained mathematically and scientifically, and illustrated through (9) figures.

Keywords: two-dimensional being, inner curved (lateral) surface of the cone, imperceptible curvature, infinitesimal third dimension.

Introduction

Nothing is absolute, everything is relative. What is right today may be wrong tomorrow. It just depends on the way we look to things.

In this paper we will demonstrate that the understanding of truth differs by changing the angle of vision.

To this end we will ask assistance from two- dimensional beings – two-dimensional being will be referred to hereafter as **Z**.

Our mission in this paper is to make **Z** live in a unique Universe, and then watch how he will describe the truth of his Universe.

In a 2D Universe – we three dimensional beings live in a three dimensional Universe on the surface of earth as shown in figure 1:

Sphere 1 (S1) is the earth – Sphere 2 (S2) is the boundary between the earth's atmosphere and outer space. In our world we can move in three spatial dimensions length, width and height (or depth). Our motion is free in two dimensions, but it is not free in the third dimension ($\uparrow\downarrow$).

We cannot go up to sky because of the gravitational force; also the electromagnetic force prevents us from penetrating the ground below us We have two-dimensional vision, but our brain builds a 3D view. This means that we see two dimensions and realize three.

Now let's imagine a two dimensional Universe which is similar to ours. To make this Universe, **Z** must live on a circumference of a solid circle as shown in figure 2:
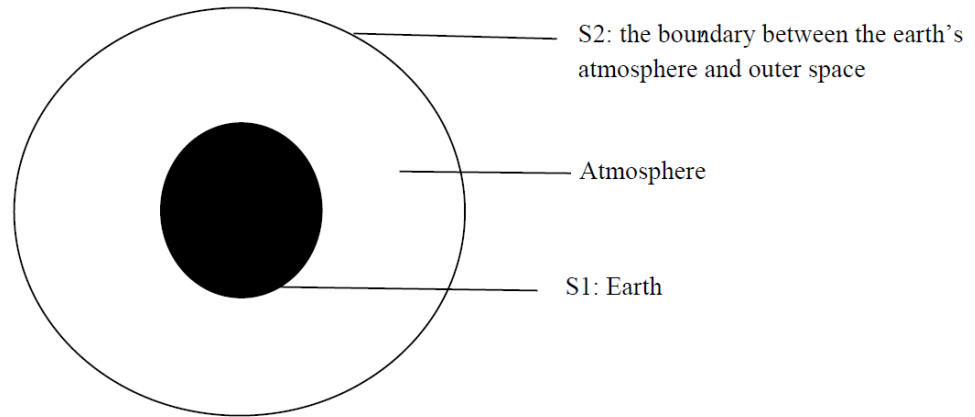
Figure 1. Our Universe
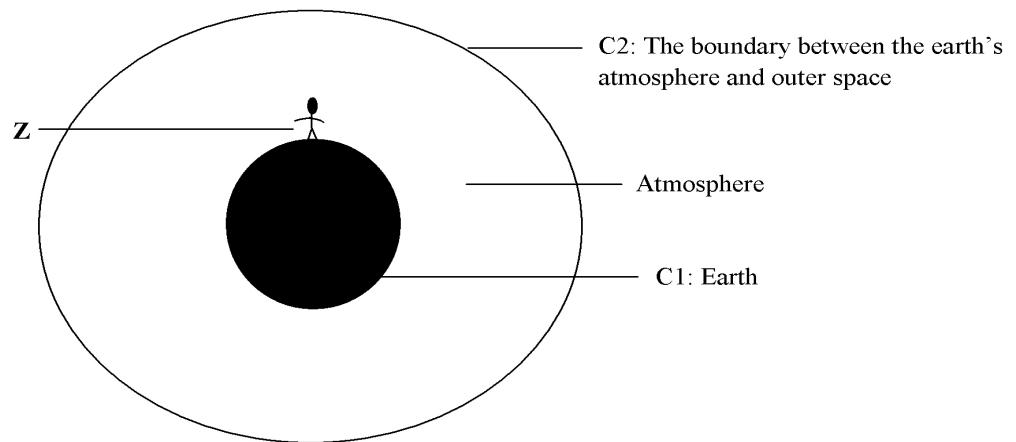
Figure 2. Two dimensional Universe

Circle 1 (C1) is Earth – Circle 2 (C2) is the boundary between the earth's atmosphere and outer space – **Z** can move in two spatial dimensions, his motion has to be free in one dimension around C1 and restricted in the second dimension (↑↓) by the gravity of C1 or any other type of force which pulls **Z** to C1.

This Universe seems really similar to our Universe. But let's try to think out of the box and imagine a new model of Universe.

Out of the Box

In this model we will create a new Universe which is completely different from the above mentioned one.

When **Z** tries to understand and describe this world – within the limits of perceptions – as he is a two dimensional being, he will reach the same re-sults about the life on a circumference of a circle as shown in figure 2.

Z will not understand the truth of his Universe. Only a more developed being will be able to understand this Universe and see the full truth.

In a 3D Universe

Z is designed to recognize only two dimensions; Even if his world is a part of 3D world he will observe it as a 2D world.

Now let's ask the following question: could we able to create a 3D Universe which is appropriate for the life of 2D beings?

Can we make **Z** live in a 3D world without being confused?

Here we will provide a model of a 3D world, and invite **Z** to live in.

In this world **Z** will never know that he is in a 3D world, he will feel relaxed as he is in a 2D world. In fact his new world will be very understandable to him.

In a curved surface of a cone suppose we have an inverted cone with its vertex below its base as in figure 3.
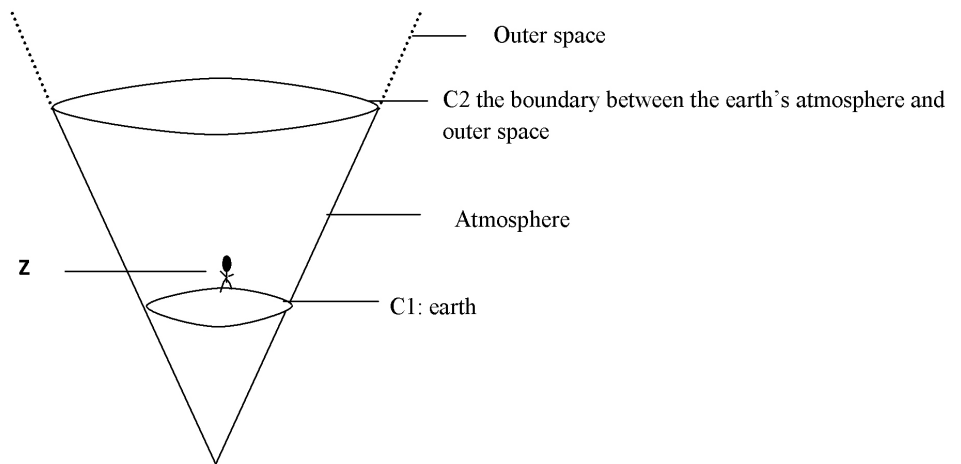
Figure 3. In the inner curved surface of a cone

This cone is definitely a three dimensional shape. Circle 1 (C1) which is a horizontal cross section of the cone represents earth; C2 represents the boundary between the earth's atmosphere and outer space. **Z** lives in the inner curved (lateral) surface of the cone on the circumference of C1.

Earth pulls **Z** by its gravity which means that his motion in one dimension is restricted. The motion in the other dimension is free. **Z** can go wherever he wants moving in a circular path in the curved surface of the cone on the circumference of C1.

**Z** realizes only two dimensions. **Z** doesn't know that he is in a 3D Universe simply because the curvature or the third dimension is infinitesimal.

Even **Z** in this Universe is a 3D being not a 2D being, but in fact it's impossible for him to recognize that because his third dimension is imperceptible.

Nothing in this Universe is a 2D object. All objects which are drawn on the curved surface of the cone are 3D objects with an imperceptible curvature – this curvature caused by the shape of the cone's lateral surface which gives the third dimension to all objects.

To understand that let's draw a line on the surface of our earth. The line seems without any doubt a one dimensional shape, but actually this is untrue.

It is neither a line nor a 1D shape because if we continue drawing the line on the surface of the earth we will finally get a circle.

This means that the line has an imperceptible curvature which gives it a second dimension, but in fact it is impossible for the line to recognize its other dimension.

Even we who draw the line and already know that it is not a line can hardly believe that this line has two dimensions.

Now let's back to **Z** again. **Z** will draw the Universe as shown in the figure (4).

Although **Z** lives in a 3D Universe, he gives a 2D description of it. According to **Z** all 2D beings live on a circumference of a solid circle in a 2D Universe.

Everything in this world is understandable to **Z.** Nothing is unusual.

Actually **Z** will describe the world exactly the same way we do in our world. If **Z** manages to travel around the world, he will reach the same point he started from which makes him sure that the earth is a big circle.

Z believes that if he is at the North Pole and starts digging a hole via the centre of the earth toward the South Pole, he will end up on the surface of the South Pole, but actually he will never reach this point.
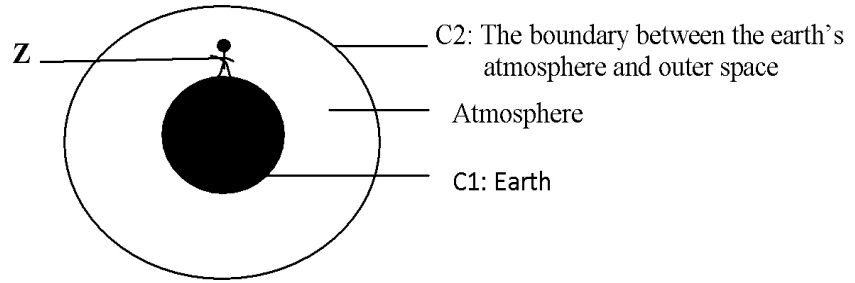
Figure 4. The "cone universe" as drawn by Z
"Notice that Figure 2 and Figure 4 are identical"

In fact there is a big surprise awaits **Z** simply because – as shown in figure 5 – he digs the hole in a direction which is completely different from what he thinks.
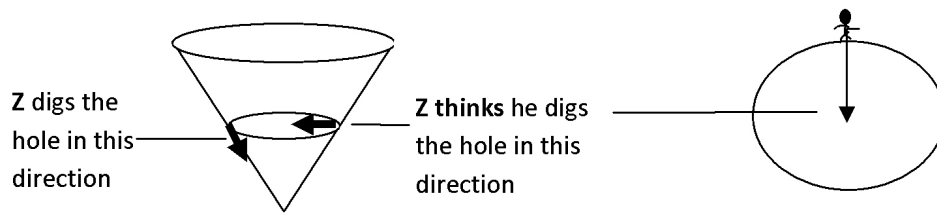
Figure 5. The real and the virtual direction of digging into the earth

The New Earth. In fact when **Z** digs the earth he will reach the other side of the Universe.

What a surprise! A new earth and a new space or let's say a new Universe is hidden at the other side of the earth, and the only way to reach it is by digging the earth (see figure 6 below).
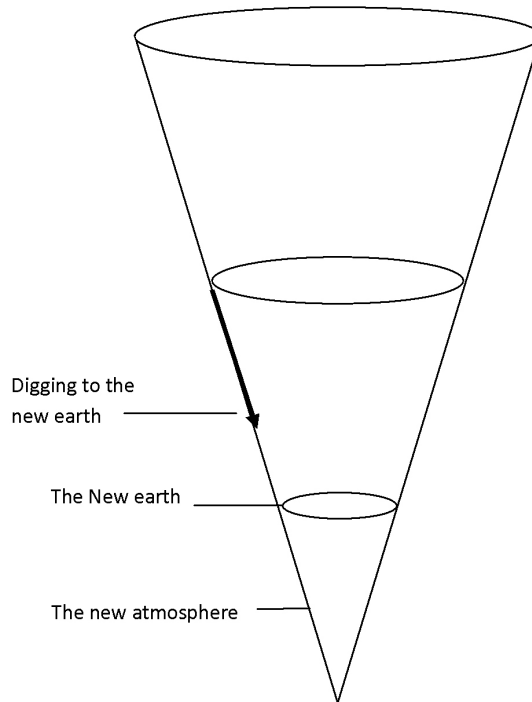
Figure 6. Digging to the new earth

Z used to think that he knew everything about the circle he lives on, but reaching the new earth at the other side of the Universe will for sure make him change all his thoughts.

At the other side of the Universe (The Final Model). If **Z** wants to live in a new earth, he must enter the secret path inside the earth to reach the other side of the Universe.

As shown in figure 7, this Universe is a double cone, C^*1 in the lower nappe is the new earth, C^*2 represents the boundary between atmosphere and the outer space, the upper nappe is infinitive.

Z now lives in the inner curved surface of the cone on the circumference of C^*1.

C 1 is the old Earth.
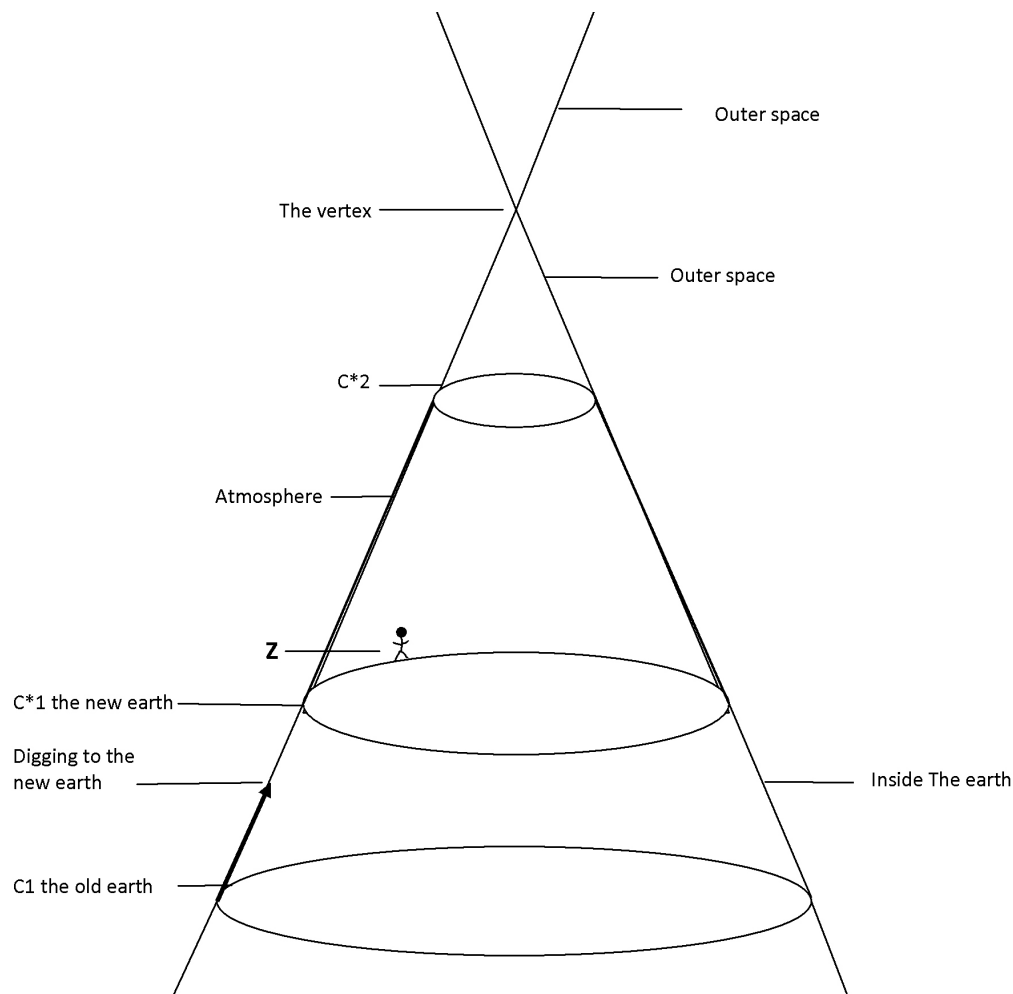
Figure 7. The Final Model

New features of the final model – in addition to preserving all the features of the old cone, there are many other features this model has:

1 – This model means that – when all objects rotate at the same speed – far objects take less time to rotate around the earth than close objects, and then after passing the vertex the opposite happens.

This variation is not due to the differences in the gravity force, but it happens because the cone gradually tapers till reaching the vertex, then it widens again. In other word this variation happens because of the shape of the Universe.

2 – When travelling to the outer space from any point in the earth, **Z** must enter a compulsory corridor– at the vertex – in order to continue his journey in space.

3 – As **Z** goes far in space as his third dimension becomes clearer because the curvature itself becomes clearer until reaching the vertex, and then after passing the vertex the opposite happens.

4 – At the vertex point **Z** can see that the earth is flat simply because at this point all the straight lines that form the side of the cone – the Universe – meet, which mean that the vertex is the point where he can watch the whole Universe.

5 – At the vertex point **Z** will definitely know that he is not a 2D being, because it is impossible for 2D being to see the entire circle as one view.

Here **Z** will definitely believe that the flat earth theory is true, and accept without any doubt that the circle is a flat shape.

Out of the box again

Let's think out of the box again and give a new theory about the sun and the concept of day and night.

Here we will suppose that the sun doesn't exist in the surface of the cone, this simply means that **Z** will never see it, because he sees only what is drawn on his Universe – inner curved surface of the cone.

In this world the sun is a closed 3D object which exists in the 3D space at the center of the cone.

At this position **Z** will never see the sun or even know that there is a sun because this object doesn't belong to his Universe.

So how could we make him see the sun? How could we make the sun rises in the east and sets in the west as our sun does?

Day & night and the sun – suppose that the cone's lateral surface between C*1 and C*2 is covered with a very thin layer (film) which in turn divided longitudinally into two parts, the first one is a reflective surface like a huge mirror (the day), and the other one is a non-reflective surface (the night).

This layer gives the cone's lateral surface an infinitesimal thickness which in turn gives **Z** a new third dimension but it is like the first one impossible to be noticed. See figure 8.
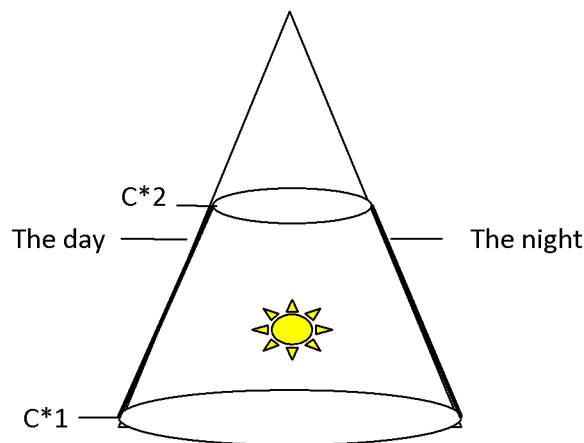
Figure 8. Day and Night in the "Cone Universe"

Cone's lateral surface and (C*1) don't rotate but only day and night rotate around each other, which mean that earth doesn't rotate.

This rotation is responsible for the way **Z** experiences day and night.

The reflective surface works as a huge mirror which reflects the objects that exist in the 3D Universe at the center of the cone.

Z who lives in the curved surface of the cone can't see the reflective images from his angle, but sees only the reflective image of the sun as its rays leave a great effect on the mirror which can be recognized as a circle of light. **Z** can't see the entire circle of the sun because he sees only one dimension, **Z** sees the front part of the circle but his brain realizes this light as a 2D object (circle).
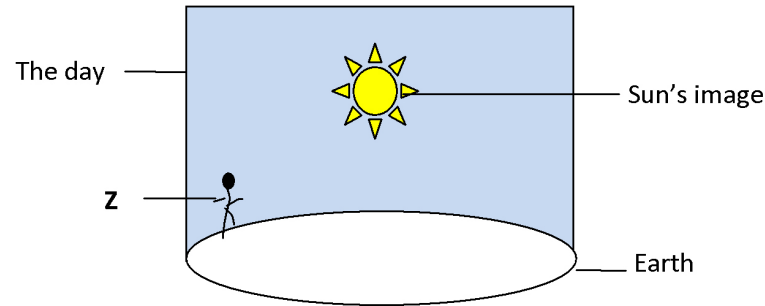
Figure 9. Sun's image on the reflective surface

Z sees the sun as shown in figure 9. This view rotates around the earth enabling all beings to see it.

Now **Z** can experience day when the reflective surface comes into the view, and experience night when the reflective surface leaves and the non-reflective surface comes.

Imagine

Imagine that we live in a surface of 4D shape (Universe), and all the objects are drawn on this surface. Everything in our world is a four dimensional object, and even we human beings have four dimensions but the fourth one is imperceptible.

Imagine that we human beings live in a flat earth – flat sphere.

Imagine that the sun is a 4D object and doesn't belong to our Universe, what we see in our world is only a reflective image of it.

Imagine that we experience day and night not because earth rotates on itself, but because day and night are two surfaces rotate around each other above the earth.

Imagine there is a secret path inside the earth leads to the other side of the Universe.

Imagine there is a certain point in the space where we human beings can watch the whole Universe, and at this point we can see that the earth is flat.

Imagine that spacecraft must enter a compulsory corridor in order to continue its journey in space.

Imagine that our fourth dimension becomes clearer when going far in space until reaching a certain point – the vertex – and then after passing that point this 4D gradually becomes imperceptible.

Conclusion

This research paper is dedicated to prove the relativity of truth, it demonstrated how the truth might take another forms depending on the observer.

For this purpose the author created a special 3D universe and asked a two- dimensional being – referred as **Z** – to live in.

The Universe as provided by this paper is the inner curved (lateral) surface of a Huge Cone, and the life exists on a circumference of a circle – earth – which is a horizontal cross section of the cone.

In fact here all the objects and beings – including **Z** – are drawn on the curved surface of the Cone and has three dimensions, but because the curvature or the third dimension is imperceptible, **Z** couldn't understand the truth of his Universe or realize the existence of the third dimension. He thought that he is a 2D being lives on a solid circle in a 2D Universe.

Thereafter, the paper has shown that new discoveries lead to a new truth by explaining how digging inside the earth enabled **Z** to reach the other side of the Universe. And then at the new earth the paper demonstrated that travelling to the outer space also lead to a different truth about the Universe and all the existence specially when reaching the vertex point.

Following, the author created a new vision of the sun and the concept of day and night and showed how **Z** gave a description of these natural phenomena which is completely different than their real truth.

Finally, and depending on the new angle of vision suggested by the paper, the author gave a new imagination about our Universe.

Section 2. Machinery construction

Inoyatkhodjayev J.SH.,
Turin Polytechnic University in Tashkent
Tashkent, Uzbekistan
E-mail: j.inoyatkhodjayev@polito.uz

Kambarov I. N.,
Turin Polytechnic University in Tashkent
Tashkent, Uzbekistan
E-mail: ikrom.kambarov@polito.uz

SPARK IGNITION ENGINES QUALITY CHECKING METHOD IN COLD TEST STANDS

Abstract: In this article described vehicle's engines quality checking method during test on machines without ignition, rotating by driving motor and under stationary condition. The aim of the article is that define early burning defects during the engine manufacturing process, in order to improve production line productivity and make manufacturing lines Lean Manufacturing.

Keywords: Cold test, Lean Manufacturing, Sensors.

I. Introduction

In the process of production of modern internal combustion engines, the main part of engine manufacturers test their engines by means of a "hot test", i. e. a test in which the engine is firing. On the other hand, recently, some companies have introduced a "cold test" instead of the hot test, but this method has to be further improved. The essential difference between these two methods is that the hot test aims to verify the engine performance, whilst the cold test aims to verify the anomalies by means of torque, pressure and vibration measurements. Although in the hot test the main anomalies could be detected, in the cold test the fault detection is more simple and effective because the engine is driven by an electrical motor, so that no noise and vibration due to the firing are added.

In the "hot test", each engine must be connected to a test bench which includes a brake and provides the cooling (water, oil and possibly turbo compression air) and the connection with the other auxiliary services in working condition as fuel, gas and air. For this reason, the cost in time for a complete hot test procedure is more than ten minutes. At present, the hot test technology only indicates to the manufacturer which engines are not good for customers, but does not give any more information regarding the causes of the fault producing the malfunction. Moreover, hot tests also give auxiliary costs for oil and fuel consumption, need of trained personal in order to set up the test, auxiliary costs of bench's maintenance, and as said above difficulty of detecting the causes of the faults. On the other hand, the cold test reduces oil and combustible consumption, emissions of $CO - SO_2 - CO_2$. In addition, the introduction of this technology decreases the noise produced during the test as well as the number of personal involved giving reduced costs of testing and fast detection of faults and of their causes.

There are many stages of quality control of its parts, subassembly and final assembly. The so-called Quality Gate- is a quality control station, which is checked 100% of the products passing through the conveyor belt and through which it is impossible to pass the marriage or substandard products to the next station. Cold Test is one such as a gate, and the last automatic station checks 100% manufactured engines.
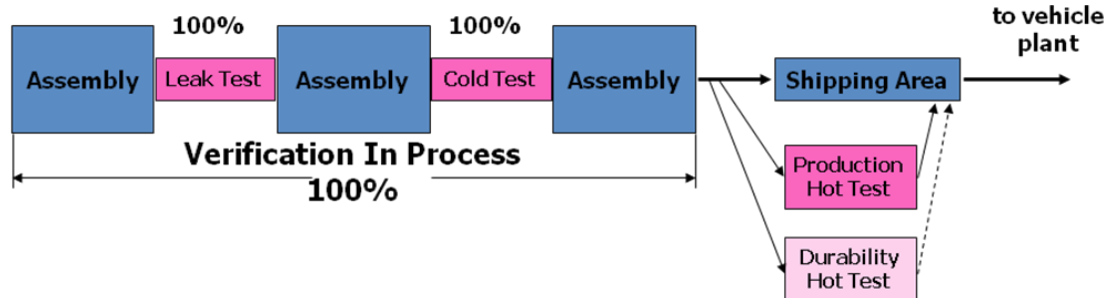
Figure 1. In-line and off-line test production line

Ankit Khurana`s [1] summary about his research is that, the use of a. c. drives that control velocity fluctuations to within [+ or −] 3 percent make it possible to accurately diagnose virtually any assembly defect with amazing levels of accuracy. In addition, cold testing ensures that improperly assembled engines do not leave the manufacturing facility.

During his studies on "Condition Monitoring in diesel engines for cold test application" S. Delvecchio [5] described characteristics of the cold test technology and a monitoring method for quality tests of diesel engines at the end of assembly line. His work concerns evaluation of the engine condition at the end of assembly line based on vibration signals during the cold test.

This article is based on the Cold Test stand results simulations and analysis, and find correlation between engine manufacturing process and engine testing in order to find early burning defects during manufacturing process. The Cold test simulation results obtained by Defect Mapping method, which means artificially creating the most frequent defect and analyze their behavior on engine test cycle. All experimental and simulation data are obtained from General Motors Powertarin Company.

The paper is organized as follows. Section 2 describes the experimental apparatus, the test conditions and the data acquisition system; Section 3 shows the comparisons between several features and the results achieved.

II. Experimental Apparatus

The experimental investigations are carried out on a 1.5 l DOHC (Double Overhead Camshaft) gasoline engine produced by General Motors Powertrain, 4 – cylinder 4 – stroke with eight valves.

Figure 1. 1.5 L DOHC engine

JW FROEHLICH (Germany) has designed the cold test bench Figure 2. The results presented in this paper concern two specific speed phases: 120 and 1000 rpm.
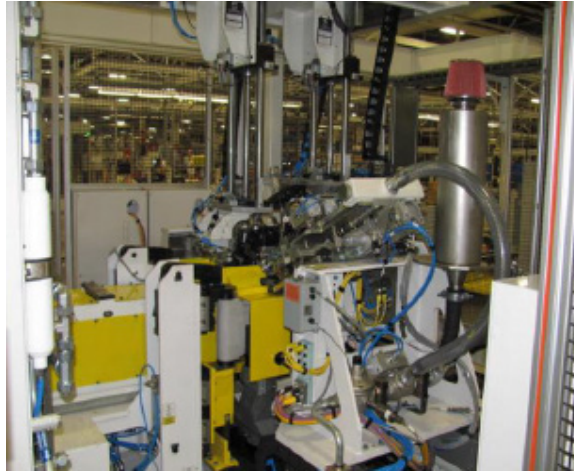
Figure 2. Cold test stand

In the cold test the engine is driven by an electric motor via a coupling unit and it is maintained in a non-combustion state. During the test cycle, that is controlled automatically, measurements of torque, vibration, and pressure are simultaneously acquired.

The test stands computer generates control signals to operate engine subsystems like the ignition and cam phases. The basic test signals are monitored and analyzed by the cold test stand comput-ers as the engine motored. Data acquisition is synchronized to the engine crankshaft. Test points are compared to high and low limits. Based on limits comparison the engine either accepted as normal or rejected as abnormal. The data acquisition system panel (see Figure 3), collects and processes data through dedicated test algorithms and compares them to the threshold value in order to take a pass/fail decision.
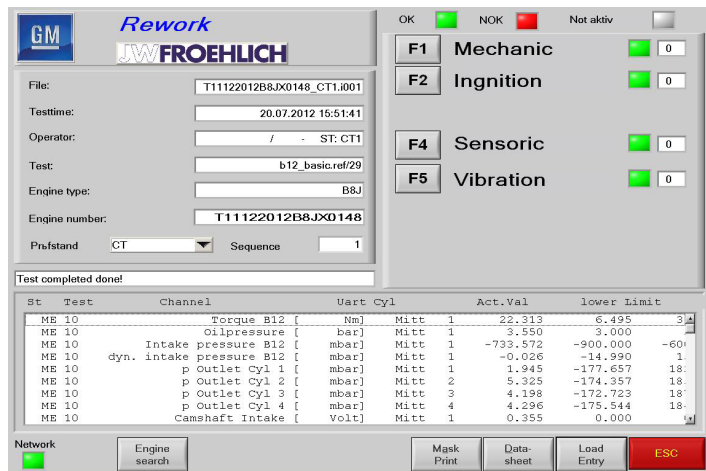
Figure 3. Data acquisition system panel for Cold Test

Data acquisition panel summarize information about number of defective or not defective parameters of the tested engine. Cold Test stand gives us engine intake and exhaust pressure, oil pressure, motoring torque, crankshaft and camshaft sensor signals and other parameters.

III. Results and discussion

In the case of the quality control application, requirement is that low computational costs. In this work, this requirement is considered and the goal is to obtain suitable features with threshold values, as shown in Figure 4. As said, in Section 2, two experimental phases are carried out in order to evaluate the engine behavior.

Figure – 4,w represents us engine outlet pressure distribution in cylinder – 1, while it is checked under 120 RPM. Cold test results in lower RPM of motor gives more precise pressure distribution.

Such small RMP only possible in cold test, due to the fact engine driven in the motor and only motor can give such condition.
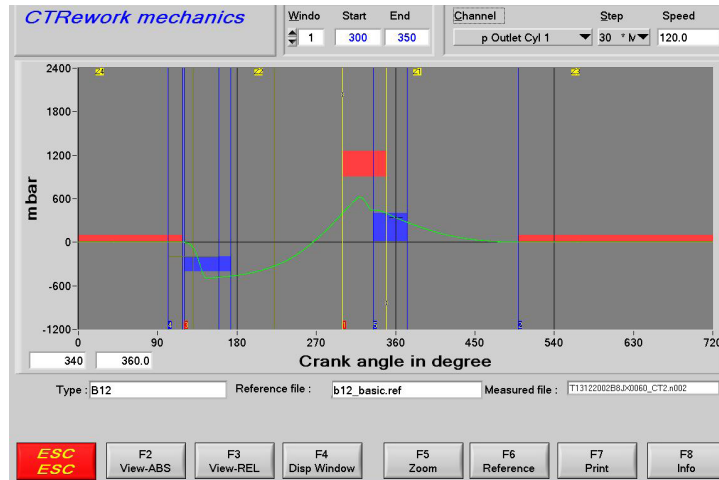
Figure 4. Outlet pressure distribution in cylinder-1 (at 120 RPM)

The outlet pressure distribution of the cylinder-1 shows us four working phases of the engine (Intake, Pressure, Expansion and Exhaust).During intake and compression phases outlet pressure does not match with pressure specification of the manufacturing process, the pressure specifications for outlet pressure is set around – 200/ – 300 mbar for intake and around 700–1200 mbar for compression phase but in this example outlet pressure is measured around – 450 mbar for intake process and 600 mbar for compression which cause to fail the engine from this process. During the reworking process of this test-failed engine all electric, mechanical and manufacturing parameters examined and root cause of the problem to improve manufacturing process quality.
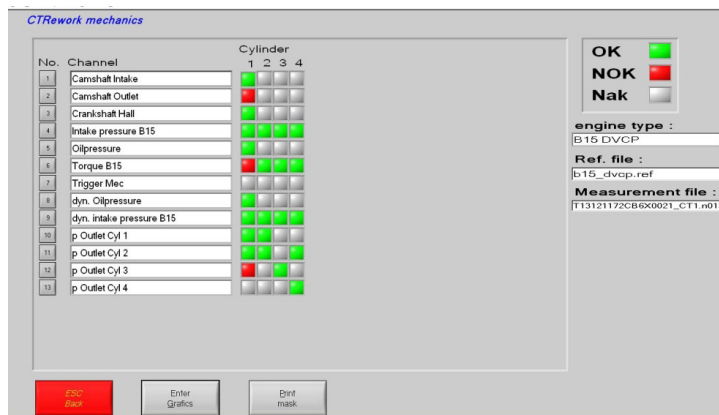
Figure 5. Mechanical panel of the Cold test (Note: Green squares represents us OK parameters and Red squares represent us NOK parameters)

Figure 5, represents us outcome results of the sensors (pressure, torque, cam phase and etc.) installed in the engine. In general, it gives us mechanical parameters of the engine. We can see from me-

chanical panel outlet and exhaust parameters are failed, while intake mechanical parameters show good results. Not specified torque in cylinder 1 can be the result of changing time phasing of valves,

wrong opening and closing time and as a consequence fuel injection at not desired time.

Based on the above figure we can analyze all 4 – cylinders of the engine and directly see in which cylinder there is problem and with which mechanical parameter. When we face with mechanical defects, such technology gives us information where to concentrate during the manufacturing process and for which systems.

IV. Conclusion

The Cold test gives the same simulation outcomes for several engine parameters, such as engine torque, NVH, spark plug ignition etc. So all these results can be linked with manufacturing process to define early burning defects, different impacts on engine parameters, which lead to fail engine under specific test cycle. As a summary, the following outcomes can be obtained:

• the Cold test is specific machinery which defines most of the defects in the engine, the defects are localized and the repair can be immediately;

• the test cycle simulations outcomes obtained individual forms for every single cylinder, which help to improve and better to concentrate on specific type of defects;

• the Cold test gives opportunity to check mechanical, electrical parameters of the engines under low load condition (120–1000 RPM), which makes testing process more easier;

• with analyzing Cold test results and making correlation with manufacturing process we can enhance FTQ (First Time Quality) of the produced engine, which lead to make manufacturing line more close to Lean Manufacturing.

• the Cold test gives opportunity to analyze quality of the engine assembly process and machining process also checks desired functioning of the sensors and some components.

The future direction is to improve this method for a higher number of experiments and to evaluate several techniques for the diagnostic of the faults analyzed in the present work.

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Orumbayev Rakhimzhan Kabiyevich,
Doctor of Engineering Sciences, professor at
Almaty University of power engineering & telecommunications

Kibarin Andrey Anatolievich,
Candidate of Engineering Sciences,
head of "Heat power units" department at
Almaty University of power engineering & telecommunications

Korobkov Maksim Sergeevich,
Engineer at Almaty University of power engineering & telecommunications
E-mail: korobkovmax@gmail.com

Khodanova Tatyana Victorovna,
Senior lecturer at Almaty University
of power engineering & telecommunications

DESIGN-BASIS AND EXPERIMENTAL JUSTIFICATION OF BI-RADIATED SCREENS INSTALLATION IN PTVM-125 (KVGM-145) WORKING ON FUEL OIL

Abstract: This paper shows that in case of use of bi-radiated screens and decrease in thickness of radiating layer, there won't be any significant loss in efficiency of radiant heat transfer. And enlargement of heat transferring surfaces inside of firebox would lead to increase of general share of radiant heat transfer and decrease of firebox exhaust temperature. Besides that, the use of bi-radiated screens would improve heating efficiency of PTVM-100 boiler by 25%. Usefulness of bi-radiated screens was tested on KV-GM-42 hot water boilers operated on fuel oil at boiler houses of LLP "Almatyteplocommunenergo, called "Yuzhnaya" and "UVRK".

Keywords: Hot water boiler, bi-radiated screen, heat transfer by radiation and convection, reliability improvement, operating efficiency.

Introduction

Economical rates of average capacity hot water boilers operated on gas and fuel oil are considered to be quite high. Nevertheless, degree of screen tubes' metal use is only about 38%. Tubes of furnace screens in PTVM-100 hot water boilers are located very close and almost touching each other (in case of Ø 60 mm screen tubes mounted on a boiler's wall, the distance between tubes is only 3m). It significantly decreases the coefficient of use of convective tubes' surface, transferring heat only by their own projection. Thus, the most part of screen tubes facing brickwork does not take part in the process of heat transfer.

Intensity of radiant heat transfer between gas environment and heated surface does not depend on hydrodynamic conditions and is determined mostly by temperature conditions and radiant ability of combustion products, in our case these products are fuel oil or gas fueling the torch of PTVM boiler, and the volume of heat transfer mostly depends on heating surface.

In conditions of having a very thick gas layer, when it's degree of darkness (Degree of darkness – how dusty the gas layer is) is quite high, it was considered that the intensity of radiant heat transfer is enough and there were no measures undertaken to improve this value. It was not a problem, and

moreover it was considered that intensity of radiant heat transfer in radiation part of the boiler unit is rather high and corresponds to practical requirements, until these boiler units reached their limits in terms of capacity. Nevertheless, in case of hot water boilers with 116+ MW capacity the question of increase of radiant heat transfer and share of radiant component during heat transfer becomes very important.

Design-basis and experimental justification of bi-radiated screens

One of the ways to increase share of radiant component during heat transfer and the degree of use of radiant heating surfaces is to apply bi-radiated screens in fireboxes of hot water boilers. Authors of this paper suggest new design of PTVM-125 (KVGM-145) hot water boiler with bi-radiated screens, which provides significant improvement in terms of reliability of convective heating surfaces, and allows to increase PTVM-100 boiler's efficiency by 25% [1; 2].

In conditions of having a thick gas layer, when it's degree of darkness is rather high, intensification of radiant heat transfer may be performed by means of temperature increase in radiant layer (increase of heat load), but this always leads to increase of exhaust temperatures and decrease of boiler's general operating economy as well. Amount of radiant heat transfer also depends on temperature on walls of heated surface, which is important for hot water boilers and PTVM-125 hot water boiler with cold walls of two bi-radiated screens of a boiler in particular. However, such temperature is defined only by technological conditions of boiler unit.

According to scientific researches [3–6], the radiant heat transfer has it's defined maximum value. Max. value is reached under certain temperature conditions and depends also on dustiness of gas flow. Degree of darkness of fuel oil torch depends on temperature of radiant layer. The higher the temperature is the lower degree of darkness becomes. It happens so due to the fact that with temperatures of 1500 °C and higher, significant effect on degree of darkness is provided by dissociation of CO_2 and H_2O gases.

High temperature of radiant layer leads to decrease of triatomic gases content due to their partial dissociation. Degree of CO_2 and H_2O gases dissociation depending on temperature is quite well researched [5; 6].

Radiant heat transfer between gas layer and wall, except already mentioned factors, also depends on dustiness of the flow. At the same time increase of flow dustiness increases the degree of it's darkness. In case of high temperatures the effect of dustiness increases especially well.

We have performed an analysis of radiant heat transfer process between gas layer and wall taking into consideration the dissociation of triatomic gases in relatively uncontaminated flow resulting from combustion of fuel oil in PTVM-100 boiler's and new PTVM-125 boiler's fireboxes.

All calculations of heat transfer coefficient from gas layer to on-wall screens, depending on temperature of gas layer and temperature of wall, were brought into accordance with [3–6].

Calculation results of radiant coefficient of heat transfer from fuel oil torch to on-wall screens of PTVM-100 and PTVM-125 boilers [1] for relatively clear flow are shown on figure 1.

At the same time effective thickness of fuel oil torch's radiant layer determined for PTVM-100 hot water boiler $S = 6$ m (figure 2 a), and for PTVM-125 boiler $S = 2,5$ m (figure 2 b).

Two curves showing the dependency of radiant heat transfer coefficient on flow's temperature (torch) t_f, are illustrated on diagram (figure 1) for wall's temperature $t_w = 500$ °C and $t_w = 1000$ °C.

$CO_2 = 13\%$; $H_2O = 11\%$; $S = 6,0$ m for PTVM-100; $S = 2,5$ m for PTVM-125

$1 - \alpha_1$ according to Hottel and Smith's data, $2\text{-}\alpha_1$ according to Karasina and Timofeeva's data.

Observed heating load of furnace volume is 453×10^3 kcal/(m^3×hour)

If we look on figure 1, we would see that curves of dependency of fuel oil torch $\alpha_1 = f(t_f)$ have obvious maximum. Maximum value of radiant heat transfer coefficient with the wall temperature equal to

$t_w = 500\ °C$, may be observed when the temperature of fuel oil torch's gas flow is equal to $1700\ °C$, and un-der the temperature of $1000\ °C$ the maximum value α_1 shifts to the left for $150\ °C$ and equals only to $1550\ °C$.
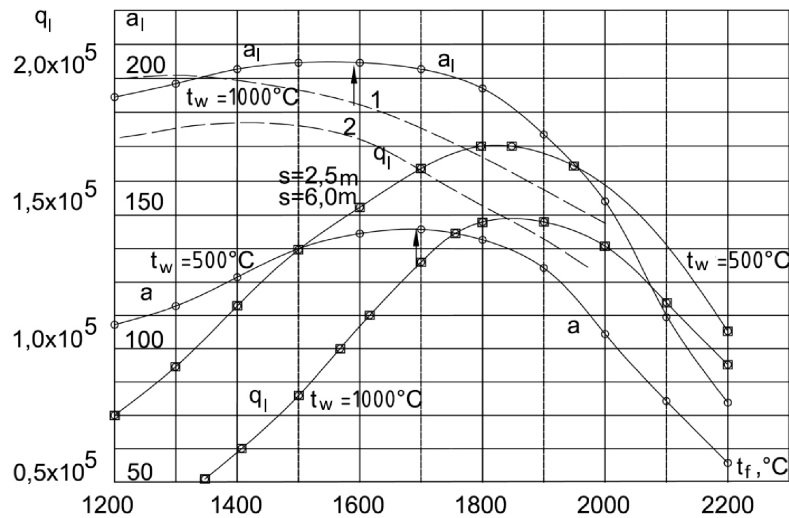
Figure 1. Dependency of q = f (t$_f$) and a = f (t$_f$) for fuel oil

a)   b)
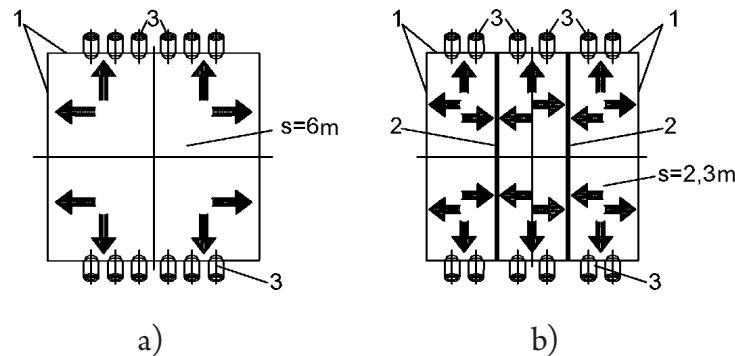
Figure 2. Radiant heat transfer diagram; a) inside of a stock PTVM-100 boiler's furnace; b) with two bi-radiated screens on PTVM-125; 1 – Side screens; 2 – bi-radiated screens; 3 – torches

Therefore, increase of temperature inside the furnace or firebox of a boiler has it's optimal value for radiant heat transfer coefficient α_1.

The same diagram illustrates the values of heat-flux density coming from gas flow of fuel oil torch to the wall q_1 $(kcal/m^2 hour)$. These curves q_1 of t_f have maximum values for heat-flux. Moreover, the position of this maximum value for $t_w = 500\ °C$ is reached with temperature of the flow equal to $t_f = 1850\ °C$. If the temperature of the wall is $t_w = 1000\ °C$, this maximum shifts $50\ °C$ to the right of the scale and already reaches the value of $1900\ °C$.

This diagram also illustrates dependency of $\alpha_1 = f(t_f)$ (dashed line), built according to Hottel and Smith's data [5], and dependency 2, obtained according to data of Karasina and Timofeeva [6].

Therefore, the heat-flux density value q_1 also has maximum value under certain temperature of screen tubes' wall.

Calculations, suggested by authors of this paper, with consideration of CO_2 and H_2O dissociation (under set temperature of fuel oil torch), have shown that the thinner radiant layer was getting the lower heat transfer value was appearing to be. But, due to quite low temperature of bi-radiated screen walls, the rate of heat transfer remained on a high level, and enlargement of the surface leads to increase of radiant heat transfer share and decrease of exhaust gases

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temperature, which justifies the usefulness of bi-radiated screens (figure 2 b) installed in furnace volume of PTVM-100 hot water boiler.

Optimization of installation of two bi-radiated screens between torches and parallel to their axes is caused by calculations of wall temperature. Bi-radiated screens' wall temperature should correspond to maximum of heat transfer coefficient, with certain adjustments when choosing the particular thickness and height of bi-radiated screen tubes' lining in the core area of fuel oil torch, if such necessity would appear in order to increase the durability of screens.

But for the new PTVM-125 boiler an area of interest lays to the left of the maximum α_1 (figure. 1), because it determines the most favorable conditions of heat transfer during enhanced temperature levels in core area of the torch and up along the firebox till cold discharged tubes.

To the left of the maximum value point α_1 curves on diagram are quite flat, thus the chosen temperature of a gas layer (wake of fuel oil torch) is 100–200 °C below the temperature of it's most favorable value would not lead to significant loses of radiant heat transfer coefficient α_1 from gas flow (fuel oil torch) to the wall.

From practical perspective, the most favorable value may be chosen from quite wide range of flow temperature values, at which the radiant heat transfer coefficient α_1 from gas flow (fuel oil torch) to the wall would have the maximum value for two bi-radiated screens.

As far as PTVM-125 hot water boiler with two bi-radiated screens is concerned, it's range of favorable values for clear gas flow (fuel oil torch) may lay only within 1400–1700 °C range.

Effective operation of cold screens (inlet water temperature equals to $t_{water} = 70 °C$) was tested on KV-GM-42 hot water boilers operating on fuel oil at boil-er houses of LLP "Almatyteplocommunenergo, called "Yuzhnaya" and "UVRK" [7; 8]. Unlike PTVM-30 MS, KV-GM-42 hot water boiler (which substituted old PTVM-30 MS) has the festoon screen is actually a bi-radiated type of a screen. Boilers' modernization (cold bi-radiated festoon screen, convective surface was enlarged by 220m², firebox's volume also was enlarged by 9m³) allowed to reach 42 Gcal/hour of heat production rate, which is 1,4 times more than on old PTVM-30 MS boilers, and to increase reliability of boilers if operated on fuel oil.

Model calculations of PTVM-125 hot water boiler with two bi-radiated screens, made by authors of this paper using BOILER DESIGNER software [9], showed that temperature of firebox exhaust gases before entering convective packs decreased by 150 °C, in which case convective packs are operating in more favorable temperature conditions similar to temperature conditions of Π-shape hot water boilers. Screen surfaces absorb about 33% of heat if boilers is operating on gas, and about 40% if boiler is operating on fuel oil.

Conclusion

Therefore, we can make a conclusion that effective operation of bi-radiated screens, which are going to be installed on PTVM-100 hot water boilers with purpose of heat production rates increase up to 145 MW, was practically justified using design-based method of calculation and tested on boilers of average and low capacities. Suggested modernization of PTVM-100 boilers uses the whole already existing infrastructure of CHPPs and boiler houses, leaving even side screens of boilers untouched. Such modernization would cost about 39,7 $ millions (US dollars), which is way more cheaper in comparison with installation of new heat production facilities.

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Section 3. Medical science

Nechytailo Elena Yurievna,
Bukovinian State Medical University
Assistant, medical faculty
E-mail: vmz2@yandex.ua

PATHOPHYSIOLOGICAL ASPECTS OF HEMODYNAMIC DISORDERS IN DIABETIC PATIENTS WITH CRITICAL LIMB ISCHEMIA

Abstract: Pathophysiological mechanisms of complications development in patients with diabetes are considered in the article. The pathogenesis of surgical complications, first of all, is associated with a decrease in the velocity of volumetric blood flow in the distal parts of the lower extremities and in the phenomena of sensory neuropathy.

Keywords: diabetes mellitus, diabetic foot, microcirculation, angiopathy, neuropathy.

Нечитайло Елена Юрьевна,
Буковинский государственный медицинский университет
ассистент, медицинский факультет
E-mail: vmz2@yandex.ua

ПАТОФИЗИОЛОГИЧЕСКИЕ АСПЕКТЫ НАРУШЕНИЙ ГЕМОДИНАМИКИ У БОЛЬНЫХ САХАРНЫМ ДИАБЕТОМ С КРИТИЧЕСКОЙ ИШЕМИЕЙ КОНЕЧНОСТЕЙ

Аннотация: В статье рассматриваются патофизиологические механизмы развития осложнений у больных сахарным диабетом. Патогенез хирургических осложнений, прежде всего, связан с уменьшение скорости объемного кровотока в дистальных отделах нижних конечностей и явлениями сенсорной нейропатии.

Ключевые слова: сахарный диабет, диабетическая стопа, микроциркуляция, ангиопатия, нейропатия.

Сахарный диабет (СД) является одной из самых серьезных современных медико-социальных и экономических проблем многих стран. По данным Международной диабетической федерации, сегодня в мире СД болеют около 382 млн. человек [9]. Из-за распространенных осложнений, в основе которых лежат микро- и макроангио-патии, эта патология приводит к тому, что около 75% больных умирает от сердечно-сосудистых осложнений. Даже в момент установления диагноза СД более 50% больных уже имеют сосудистые диабетические осложнения, а стоимость амбулаторной медицинской помощи при наличии осложнений возрастает от 3 до 13 раз [2; 5; 9].

Согласно литературным данным, факторами риска сосудистых нарушений у больных СД является длительное течение болезни, неконтролируемая гипергликемия, избыточная масса тела, нефропатия, нарушение микроциркуляции и эндотелиальной функции сосудов, нейропатии и другие [4; 6; 7]. Ухудшение общей гемодинамики и интенсивности микроциркуляции сопровождается нарушениями метаболизма тканей и снижением локальной температуры дистальных частей тела. Локальная температура конечностей отражает состояние кровенаполнения и интенсивности кровотока и у пациентов с СД она часто снижается, а в случаях воспаления или судомоторной нейропатии, наоборот, может локально повышаться [3; 6; 8]. Наиболее частым хирургическим осложнением у больных СД является синдром диабетической стопы, в основе которого лежит критическая ишемия нижних конечностей, часто в сочетании с нейропатией и остеоартропатией [4; 5; 8]. В то же время, для своевременной диагностики, эффективного лечения и предупреждения осложнений у пациентов с СД существует необходимость в понимании патофизиологических механизмов нарушений общей гемодинамики и микроциркуляции, их соотношения с другими факторами риска.

Целью нашего исследования было определить взаимосвязь между отдельными патофизиологическими компонентами формирования сосудистых нарушений у больных СД.

Материал и методы. Под нашим наблюдением находилось 87 пациентов с СД 2 типа в возрасте от 43 до 89 лет (в среднем 65,8 ± 1,1 года) (57 мужчин и 30 женщин) госпитализированных по поводу хирургических проблем. Пациенты были разделены на 2 группы: в первую группу (47 пациентов) вошли больные СД с разной хирургической патологией, но без ишемических и гнойно-некротических осложнений со стороны нижних конечностей, во вторую группу (40 пациентов) были включены больные СД с критической ишемией ног и гнойно-некротическими осложнениями. Все пациенты были комплексно обследованы. Состояние микроциркуляции оценивалось при биомикроскопии сублингвальной слизистой по стандартным параметрам. Определение эндотелиальной дисфункции проводили с помощью функциональных проб: эндотелийзависимой дилатации – с применением пробы с нитроглицерином, эндотелийзависимого спазмирования – с локальной холодовой пробой. Исследование проводилось с помощью цифрового USB микроскопа Supereyes B008 с сенсором 5 Мп, увеличением от 10 до 500 раз и с программным обеспечением производителя. Локальную термометрию проводили инфракрасным пирометром DT-8836. В качестве базальной температуры принималось измерение, проведенное над проекцией сонной артерии. Вычислялась разница температуры в различных участках в процентах к базального показателя. По данным термометрии пальцев ног по формуле [1] рассчитывался показатель объемного кровотока (мкл/с). Наличие сенсорной нейропатии определяли на стопах по состоянию отдельных видов чувствительности (болевой, тактильной, вибрационной, температурной). Полученные результаты обрабатывались статистически с использованием программы Statistica 6,0 (StatSoft). Для утверждения о достоверности различий учитывалась общепринятая в медико-биологических исследованиях величина уровня вероятности p < 0,05.

Результаты исследования и их обсуждение. Длительность СД у обследованных пациентов колебалась от 3 до 15 лет (в среднем 8,9 ± 1,8 года), причем у 32,2% больных продолжительность болезни была более 10 лет. Преобладала среднетяжелая форма болезни (56,3%), реже было тяжелое течение (39,1%). Большинство больных (45,9%) получало терапию пероральными сахароснижающими препаратами, несколько меньше использовали инсулин (32,2%) или комбинированную терапию (28,2%). Среди осложнений СД кроме

поражения нижних конечностей частыми были также ретинопатии и нефропатии. Избыточная масса тела, которая считается одним из факторов риска развития заболеваний сердечно-сосудистой системы, в нашей работе была зарегистрирована у большинства лиц – средний показатель ИМТ по группе составил 27,5 ± 0,46 кг/м², чаще пациенты имели избыточную массу тела (51,7%), реже – ожирение (21,8%), нормальные показатели ИМТ были у 23 пациентов (22,9%). Часть пациентов страдала гипертонической болезнью (20,2%), а средняя величина систолического давления у обследованных составила 133,1 ± 1,9 мм Hg и диастолического – 82,9 ± 1,2 мм Hg, причем у пациентов второй группы систолическое давление было достоверно выше (138,6 ± 3,0 против 128,3 ± 2,1 у пациентов первой группы, $p < 0,05$). Уровень сахара крови при поступлении был в пределах от 4 до 21,6 ммоль/л, средний показатель у обследованных составил 10,6 ± 0,57 ммоль/л и был несколько выше у пациентов второй группы (11,3 ± 0,8 ммоль/л, против 9,8 ± 0,7 ммоль/л у пациентов первой группы, $p = 0.24$).

Комплексное обследование пациентов включало измерение температуры различных участков тела. Средние показатели температуры на нижних конечностях были следующими: паховая область – 34,8 ± 0,22 Cº, подколенная зона – 33,7 ± ± 0,19 Cº, тыл стопы – 31,6 ± 0,38 Cº, подошвенная поверхность – 31,1 ± 0,39 Cº, большие пальцы ног – 30,7 ± 0,45 Cº. Температура в паховой области мало отличалась от базальной, но в дистальных отделах разница температуры возрастала. У одного из обследованных, с ампутированной правой стопой, на левой ноге снижение температуры в нижних отделах было около –30%, с клинической угрозой возникновения некроза пальцев. Из анализирования температурных данных были исключены три пациента, с явлениями судомоторной дисфункции с ангидрозом и повышенной температурой стоп, как следствие автономной нейропатии.

Асимметрия распределения температуры поверхности кожи наблюдалась как на левой и правой конечностях, так и между ангиосомами одной стопы. Значительная разница температуры между левой и правой ногой была у восьми пациентов. Так, у пациента 82 лет была отмечена наибольшая разница между стопами – градиент температуры на тыльной части левой стопы составил –20,5%, в то время как на правой он был всего – 6,0%, а на подошве соответственно –31,0% и –9,0%. В пределах одной стопы у четырех пациентов наблюдалась почти двухкратная разница между ангиосомами, чаще страдала латеральная часть стопы.

На основании полученных температурных данных рассчитывался показатель характеризующий состояние микроциркуляции – скорость объемного кровотока. Его средняя величина для больших пальцев ног составила 23,9 ± 1,76 мкл/с (с колебаниями от 8,2 до 58,4 мкл/с). Скорость кровотока у пациентов второй группы была достоверно ниже, чем у пациентов из первой группы. На пальцах левой ноги она была соответственно 20,9 ± 1,8 мкл/с (против 29,7 ± 3,3 мкл/с у пациентов первой) и на правой ноге 19,7 ± 1,6 мкл/с (против 28,5 ± 3,9 мкл/с у пациентов первой) ($p < 0,05$). В свою очередь, снижение скорости кровотока коррелировало с эндотелиальной дисфункцией ($r = 0,32$, $p < 0,05$), преимущественно из-за ухудшения эндотелий зависимой дилатации.

По мнению многих исследователей, одним из основных патофизиологических механизмов развития критической ишемии нижних конечностей является поражение периферических нервов – сенсорная, моторная или автономная нейропатия [2]. У наших пациентов мы оценивали наличие наиболее распространенной сенсорной нейропатии. Она была диагностирована в 47,0% пациентов первой группы и у 87,5% – второй ($p < 0,05$). Нарушение объемного кровотока в зависимости от наличия нейропатии указывает на взаимосвязь с ней. У пациентов первой группы наличие явлений нейропатии практически

не влияло на кровоснабжение нижних конечностей. В то же время у пациентов с осложнениями она ассоциировалась с ухудшением кровотока – при наличии нейропатии он составил 19,7 ± 1,3 мкл/с, при отсутствии – 24,3 ± 0,7 мкл/с (p < 0,05). Эти данные указывают на ведущую патофизиологическую роль нарушений микроциркуляции, при которых нейропатия выступает вторичным отягчающим фактором.

Таким образом, при формировании хирургических осложнений СД мы наблюдали у пациентов комплекс патофизиологических факторов: не корригированный уровень гликемии, избыточная масса тела, повышение системного артериального давления, сенсорная нейропатия, уменьшение скорости объемного кровотока в дистальных отделах нижних конечностей, замедление метаболических процессов результирующее в снижении локальной температуры. Патогенез развития хирургических осложнений сахарного диабета, прежде всего, связан с уменьшением кровотока в концевых участках сосудистого русла, что приводит к угнетению метаболизма за счет ишемических явлений. Этот процесс захватывает не только мягкие ткани, но и нервные волокна, функции которых нарушаются и формируется патологический круг с дисрегуляцией метаболических процессов.

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Section 4. Technical sciences

Begjanova Gulrukh Bfhtiyarovna,
doctor of philosophy (Ph. D.) in technics, senior scientific research,
research and test center "Strom" Institute of General and
inorganic chemistry of Academy of Sciences of the Republic of Uzbekistan
E-mail: gulrukh-begzhanova@rambler.ru

Iskandarova Mastura Iskandarovna,
doctor of technical Sciences, Professor,
head of the scientific-research and test center "Strom" Institute of General and
inorganic chemistry of Academy of Sciences of the Republic of Uzbekistan
E-mail: mastura-iskandarova@rambler.ru

TECHNOLOGY OF OBTAINING PORTLANDCEMENT WITH THE USE OF A NEW ACTIVE MINERAL ADDITIVE – "FOSFOZOL"

Abstract: The information on the new active hydraulic additive "Fosfozol" obtained by autoclaving a mixture of ash and phosphogypsum in certain proportions, which exerts a double effect on the cement, regulating the timing of its setting with simultaneous increase in the strength of cement stone with significant savings in the clinker constituent of cement is given. The peculiarities of chemical interactions and phase transformations are revealed both in the synthesis of the additive itself in the autoclaving process and in the formation of the cement composite with hardening of cement containing up to 20% the additive "Fosfozol".

Keywords: industrial waste, ash and slag, phosphogypsum, mineral composition, autoclave treatment, hydrate compounds, chemical activity, cement additive, double action, clinker saving, cost price, ecology.

Introduction. At cement plants in Uzbekistan, additional Portland cements are produced in accordance with GOST (State Standard) 10178–91 "Portland cement and slag Portland cement". "Technical conditions". This type of cement is produced by the joint grinding of Portland cement clinker, gypsum stone and additives of natural or technogenic origin.

Formulation of the problem. According to the method developed by the team of "Elemental" LLC, an unconventional additive to cement, obtained by hydrothermal treatment under pressure of a mixture of phosphogypsum and ash and slag in the medium of saturated water vapor, is supplied to the cement plants of the republic under the name "Fosfozol". The standard of the Republic of Uzbekistan O'z DSt 2830: 2014 regulates the total content of additives, including additives "Fosfozol" to 20% without reducing the design grade of cement. According to Amendment No.2 to O'z DSt 2830: 2014, in the production of Portland cement using phosphosol compositions as additives, gypsum stone is not used. To organize the release of portland cement with the

addition of "Fosfozol" at cement plants in Uzbekistan, it is necessary to conduct complex tests to optimize their composition and chemical production of production parameters and establish the conformity of properties to the requirements of existing regulatory documents.

Materials research methods, equipment and instruments. To study the effect of the non-traditional additive "Fosfozol" (Ts (organization standard) 24249595–01: 2014 "Fosfozol": Active mineral additive for cements – Technical specifications"), the clinker of JSC Bekabadcement O'z DSt 2801 was used for the physical and mechanical properties of Portland cement: 2013 "Portland cement clinker. Technical conditions". The chemical compositions of the starting materials are given in Table 1.

Table 1. – Chemical compositions of raw materials

Material	Oxide content,%									
	loss on ignition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	R_2O	other	Σ
Phospho-gypsum	15.50	14.56	1.92	0.62	25.25	1.45	37.23	3.19 P_2O_5–0.40	–	100
Ash-slag	11.09	45.71	20.10	7.30	9.32	2.37	0.86	1.61	1.64	100
Clinker	0.42	20.9	6.26	4.40	62.8	3.97	1.23	–	0.02	100
Fosfozol	19.52	29.44	12.49	2.00	21.7	0.48	8.56	0.18	5.64	100

The physical and mechanical properties of cements with the addition of "Fosfozol" were determined in accordance with the requirements of GOST 10178 according to the methods of GOST 310.1–310.4. Investigations of the physicochemical properties of cements with the addition of "Fosfozol" were performed by chemical-analytical, X-ray diffraction (XRF) (on the X-ray unit "DRON-2" at a shooting speed of 2 degrees per minute using α-quartz as an external standard) by research methods.

Results and its discussion. It has been established that in the process of hydrothermal treatment of a mixture of phosphogypsum and ash and slag, in addition to gypsum minerals (two-water, semi-aqueous calcium sulfates), hydrate neoplasms of hydrosulfoaluminate and hydrosilicate structures also form, which increase the hydration and hydraulic activity of the product obtained. The chemical activity of the "Fosfozol" additive is characterized by the absorption of 54,5 mg CaO from the saturated lime solution for 30 days, which corresponds to the minimum permissible activity characteristic for the group of artificial (technogenic) aluminosilicate hydraulic additives. Consequently, the additive "Phosphosol" belongs to the group of chemically active mineral additives of artificial origin, classified according to chemical composition as acidic, and by chemical activity as hydraulic. It is known that during the interaction of acidic hydraulic additives with Portland cement, additives react with calcium hydroxide Ca $(OH)_2$, which is released during hydrolysis and hydration of clinker silicate minerals, forming calcium hydrosilicates (CSH), which increase the structural density and anticorrosive properties of cement stone [1; 2].

The diffractogram of the additive "Fosfozol", reveals the presence of a wide range of products of chemical interaction of minerals ash and slag and phosphogypsum (Fig. 1). In the composition of the additive "Fosfozol", According to (Table. 2), reflecting the mineral composition of the additive "Fosfozol", in its composition there are both gypsum minerals (divalent, semi-aqueous calcium sulfates), and hydrate neoplasms of hydrosulfoaluminate and hydrosilicate structures. During cement hardening, these hydrate products play the role of "crystals" – crystalline seeds and serve as "centers of crystallization", around which the emergence of new embryos of crystals of hydrosulfoaluminates

and calcium hydrosilicates is accelerated. This accelerates the hydrolysis and hydration of aluminate and silicate minerals of Portland cement due to the removal of Ca^{2+} ions from the liquid phase, which, in turn, accelerates the process of structuring the compaction of the structure of the cement dispersion with the formation of a composite with high strength values [3].
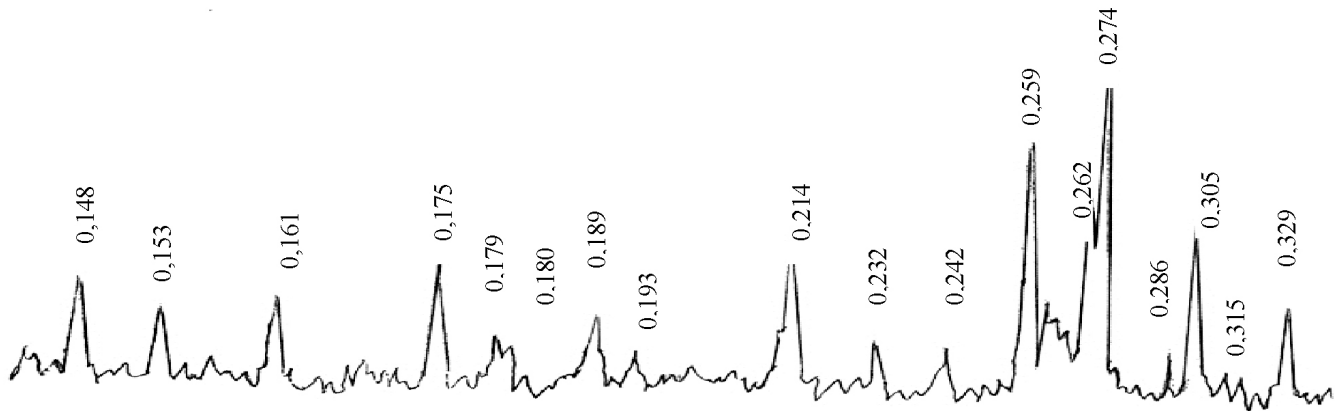
Figure 1. Diffractogram of the additive "Fosfozol"

Table 2. – Mineralogical composition of the additive "Fosfozol" according to the X-ray-phase analysis

№	Minerals		Diffraction reflections, nm
	Name	Formula	
1	Two-water gypsum	$CaSO_4 2H_2O$	0.315; 0.305; 0.286; 0.278; 0.259; 0.214; 0.189; 0.179; 0.153.
2	Gypsum hemihydrate (bassanite)	$2\,CaSO_4.H_2O$	0.278; 0.232; 0.189; 0.179
3	Hydrosulfoaluminates of calcium	$C_3A.\,CaSO_4.12H_2O$ $C_3A.\,CaSO_4.31H_2O$	0.3.03; 0.257; 0.242
4	Low basic calcium hydrosilicates	$C_2SH\,(A)$; $C_2SH\,(C)$; $C_2SH\,(B)$	0.329; 0.260; 0.241; 0.276; 0.189; 0.180
5	Hydrosilicates of the tobermorite group	C_4S_5H; C_4S_3H; $C_6S_2H_3$; $CSH\,(B)$; $CSH\,(A)$; $C_3S_2H_3$	0.296; 0.278; 0.274; 0.214; 0.180; 0.174.160; 0.153; 0.148.
6	Two-calcium silicate	α-C_2S; $\beta-C_2S$	0.278; 0.262; 0.215; 0.180; 0.175.
7	Portlandite	$Ca\,(OH)_2$	0.262; 0.193; 0.179.

To study the physical and mechanical properties, experimental cements with a different dosage of the "Fosfozol" additive were made, taking into account that the content of SO_3 (VI) oxide in it was 8,56%. It is established that all samples of experimental cements with the additive "Fosfozol" meet the requirements of regulatory documents for SO_3 content (2,33–3,06), so when they are milled, additional gypsum stone is not introduced. This means that the addition of "Fosfozol", while performing a dual function, acts as an active mineral additive and a regulator of the timing of setting the cement. The shots containing "Fosfozol" are characterized by higher grindability, and at the

same milling time have a fineness within the range of 2–6% of the residue on the No. 008 screen, while the PC – D0 cement is 10%. The reaction rate of the reaction of experimental cements with water differs little from those of PC – D0 cement: the process of their setting starts is extended by 15–30 min. However, the setting time of the experimental addi-tional cements corresponds to the requirements of GOST 10178–85. The rate of durability of cements with increased dosage of ki "Fosfozol" in the initial terms has a slowed down character. However, in the period from 28 to 360 days, the strength set is ac-celerated and their hydraulic activity by 1 year is an average of about 60,0 MPa (Table 3).

Table 3. – Results of physical and mechanical tests of cements with the additive "Fosfozol"

Conventional designation of cement	Water-cement ratio of 1: 3 so-lution	Strength limit, MPa, with bending and compression, through:							
		3d		7d		28d		360d (1 year)	
		R_{bend}	R_{comp}	R_{bend}	R_{bend}	R_{comp}	R_{comp}	R_{comp}	R_{comp}
PC-D0	0.380	**5.0**	**12.7**	**6.0**	**25.2**	**7.0**	41.5	7.9	**59.9**
PC-F15	0.376	3.8	9.3	5.4	21.2	7.0	42.0	7.3	59.2
PC-F20	0.376	**3.3**	**8.8**	**5.3**	**20.2**	**6.8**	40.2	7.3	**61.6**
PC-F25	0.398	3.3	8.6	5.3	20.7	6.7	38.1	7.7	**59.8**
PC-F0	0.400	3.3	8.6	5.2	19.8	6.0	28.0	8.0	47.3
PC-F35	0.392	3.2	8.4	4.9	19.8	5.7	27.4	7.9	58.2

Currently, the additive "Fosfozol" on an indus-trial scale is used at JSC "Akhangarancement" with the release of Portland cement brands PC 400 D20, PC 400 KD20 and PC 400 KD30. A test is being con-ducted to introduce the technology of production of these cements at JSC "Bekabadcement".

Conclusion. The additive "Fosfozol" is a new type of cement additive consisting solely of man-made raw materials and, when injected into Portland cement, it has a double action: replacing a significant part of the expensive clinker component, it acceler-ates the process of the formation of cement stone and simultaneously regulates the setting time of its setting. Portland cement with an additive "Fosfozol", for all quality indicators meet the requirements of GOST 10178–85 "Portland cement and slag Port-land cement. Technical conditions". If the chemical composition and other characteristics are in ac-cordance with the requirements of the standard of organization Ts 24249595–01: 2014 "Fosfozol. Ac-tive mineral additive for cement. Technical specifica-tions", an additive in the amount of 15–20% ensures the production of cement of the brand PC 400 D20, which have a sufficiently high resistance to the effects of climatic factors and can be used for the manufac-ture of mortars and concretes.

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Iskandarova Mastura Iskandarovna,
doctor of technical Sciences, Professor,
head of the scientific-research and test center "Strom" Institute of General and
inorganic chemistry of Academy of Sciences of the Republic of Uzbekistan
E-mail: mastura-iskandarova@rambler.ru

Atabaev Farrukh Bakhtiyarovich,
doctor of philosophy (Ph.D.) in technics, senior scientific research,
research and test center "Strom" Institute of General and
inorganic chemistry of Academy of Sciences of the Republic of Uzbekistan
E-mail: atabaev-farruh@mail.ru

Eminov Ashraf Mamurovich,
doctor of technical Sciences, Professor,
The state unitary enterprise "Fan va Tarakkiyot"
of Tashkent State Technical University
E-mail: ashraf.52@mail.ru

ENERGY EFFICIENT TECHNOLOGIES OF PROCESSING OF WASTE OF ENRICHMENT OF TUNGSTEN ORES IN BUILDING MATERIALS INDUSTRY

Abstract: The article presents the results of studies on the possibility of using stale waste secondary enrichment tails of tungsten ore deposits Ingichka as a complex raw material for producing cement clinker, the main component of mineral of the composition (press powder) for production of chemically bonded extruded wall stones by dry pressing, and additives-filler for obtaining an extension of the Portland cement that meets the requirements of GOST (State standard)10178-85 applicable to the cement PC 400 D20.

Keywords: waste enrichment of tungsten ores, secondary raw materials, aluminosilicate component, ferrous mineralizer, additive in cement, additional cement, press powder, semidry pressing, non-fired brick, energy-efficient, conservation-environment, mountain ecology.

Introduction. The constant increase in volumes generated in mining and processing industries of various types of waste and storing them in storage, leads to adverse effects of such facilities on the environment [1–3]. In recent years, our country pays great attention to the reduction of the raw resources from mining wastes and their integrated use. In mineral processing waste is generated, which represent a suspension of fine solid particles in water. From concentrator tailings hydrotransport sent to waste storage, which represent the waste processing indus- try. Perspective on the content and reserves of use- ful components are the tails of enrichment of ores of ferrous and non-ferrous metals [5–7]. Tailings is more convenient for the disposal and use of than the blades, because they, first, more homogeneous, and secondly, represent already crushed, sometimes graded material. The most promising for use in con- struction waste in dry methods beneficiation – tail- ings dry magnetic separation, dry gravity. The devel- opment trend of building materials in Uzbekistan is focused on reducing the cost of fuel and energy

resources per unit of output and increase of cement production through maximum involvement in the production process of local raw materials of natural and anthropogenic origin, not worsen the quality of cement and other construction products.

Formulation of the problem. Due to the fact that the waste tailings secondary enrichment of tungsten ores presented alumino-silicate minerals with inclusions of different oxides, they find wide application in the production of clinker and cement. At the same time, the development and application of technology for clinker, cements and additional wall materials with the use of waste from mining and processing plants is not only technologically feasible option of energy and resource saving in the production of construction products, qualitative indicators are not inferior to traditional analogues and physico-mechanical properties meet the requirements of the normative documents, but the actual solution to the problem of environmental protection.

Materials research methods, equipment and instruments. When conducting experimental studies as the starting materials are used: Portland cement clinkers JSC "Kizilkumcement" and JSC "Ahangarancement", gypsum, secondary waste tailings of beneficiation of tungsten ore deposits Ingichka. Chemical composition of starting materials was determined according to GOST (State standard) 5382–91, calculating the composition of raw material mixes for firing of clinkers was carried out according to a special program in accordance with the "Departmental norms of technological designing cement plants". Chemical and mineralogical composition of the clinkers was regulated by the requirements of O'z DSt (State standard of the Republic of Uzbekistan) 2801:2013 "Portland cement Clinker. Technical conditions". The suitability of waste secondary enrichment of tungsten ores tailings as an additive to cement was determined by the indicators of its strength in compression, and then calculated according to the criterion of Student in accordance with the methodology of GOST 25094. Physico-mechanical properties of cements with the

addition of the specified waste is defined according to the methods GOST 310.1-310.4. Identification of conformity of the results obtained - according to GOST 10178-85. Testing of non-fired building stone, obtained by dry pressing press powder, including waste secondary enrichment of tungsten ores tailings was conducted in accordance with the requirements of GOST 7025 and 8462.

Results and its discussion. Chemical composition of composite samples of waste secondary enrichment of tungsten ores include oxides (wt.%): SiO_2; Al_2O; Fe_2O_3; CaO and MgO, which predetermines the possibility of its use as a component of raw mix for clinker burning, supplements filler for the production of added cement and the main component of the molding powder to obtain a non-fired building bricks by dry pressing (tab. 1). Characteristic is the high content in its composition Fe_2O_3 is (14,90 %), which gives the possibility to use it as a glandular mineralizer in the formation of a raw mix for clinker burning. The main minerals are kaolinite, wollastonite, hematite, the remainder are represented by quartz, which is confirmed by data of x-ray phase and thermal analyses [4; 5]. As the main components of the raw mix for clinker burning were also used limestone industrial sector "Podzemgaz" and igneous rocks – gabbro (table. 1). Calculated compositions of raw mixes and clinker for cement works and buildings construction purpose according to GOST 10178-85. The results of the calculations are given in (table. 2).

On the basis of the calculations were prepared raw material mixture. Characteristics of sludge from a raw mixture comprising limestone "Podzemgaz" – 76,44%, gabbro – of 11.53%, waste of flotation of 12.03% clinker synthesized from the raw material mixture is optimal composition given in table. 2. Raw slurry, characterized by the following technological parameters: the weight of 1 liter of slurry – 1500 g; humidity – 38%; spreadability – 60 mm; fineness of grind on the residue on the sieve No. 008 – 16%, after drying, subjected to calcination at a temperature of 1380–1400° C with an exposure of 30 min.

Table 1. – Chemical composition of raw materials

№	Raw components	loss on ignition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Прочие	Σ
1.	Limestone "Podzemgaz"	38.25	5.08	0.84	0.36	51.65	1.26	0.08	2.50	100
2.	Flotation waste deposits Ingichka	8.30	47.5	6.10	14.30	21.00	2.10	0.13	0.57	100
3.	Gabbro	2.15	44.01	19.65	6.99	13.35	6.95	–	6.90	100

Table 2. – Chemical compositions of the optimal composition of raw slurry and clinker from him

Material name	The content of oxides of, %									
	loss on ignition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	KH	n	p
Raw slurry	30.1	14.3	3.40	2.97	43.3	2.1	–	0.91	2.32	1.07
Clinker	–	20.2	4.50	4.20	60.9	3.1	–	0.91	2.32	1.07

On diffractogramme annealed samples identified reflect all the major clinker phases: C_3S (d/n = 0.303; 0.297 078; 0.274; 0.261; 0.231; 0.218; 0.192; 0.181; 0.175) nm; C_2S (d/n = 0.288; 0.279; 0.278; 0.274; 0.261; 0.228; 0.218; 0.198) nm; C_3A (d/n = 0.270; 0.220; … 0.192) nm; C_4AF (d/n = 0.277; 0.266; 0.263; 0.192 …) nm. Line free of calcium oxide are absent, indicating complete absorption in the process of roasting. The microstructure of clinkers is characterized by a fine-grained structure, the clinker grains clearly formed (Fig. 1). The actual chemical composition of the clinker was consistent with the calculated data.
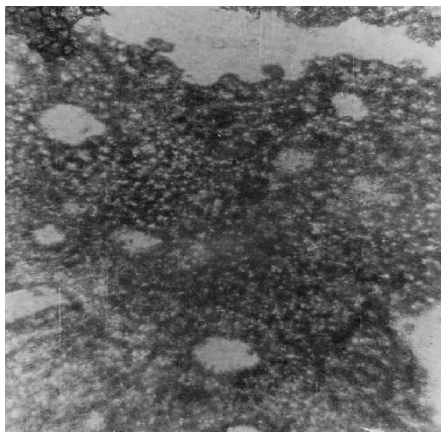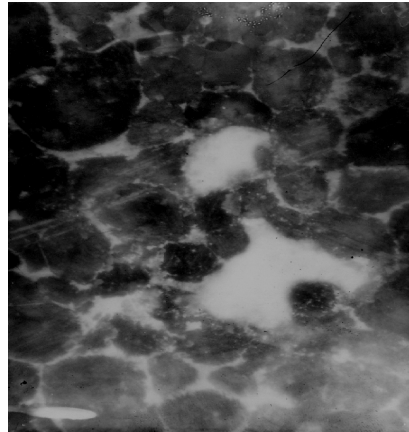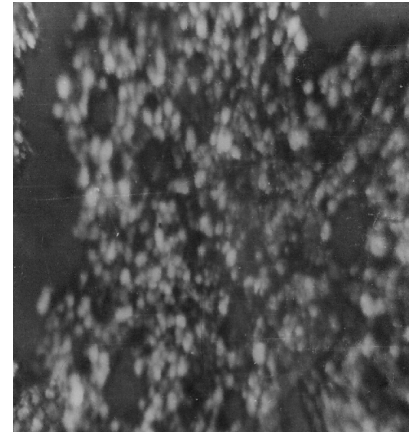
Clinker 1.	Clinker 2.	Clinker 3.*

Figure 1. Microstructure of experimental clinkers

From the synthesized clinkers characterized by the following mineralogical composition, %: C_3S – 59.52–53.75; C_2S – 14.58–20.42; C_3A – 6.19–6.98; C_4AF 11.97–12.72, the method of selection of point samples three samples taken for the preparation of cement to determine their physical-mechanical indicators. A selection was made of the party of clinkers, annealed at a temperature of 1360° C (No. 1), 1380° C (No. 2) and 1400° C (No. 3), after which they were subjected to grinding in laboratory ball mill in

the presence of 5% gypsum. The results of physico-mechanical tests are given in (table. 3).

Physical and mechanical tests established that the content of SO_3, the fineness, water demand, setting time experienced cements meet the requirements of GOST 10178–85. At 28 days age of normal hardening of all three samples experienced cements detect compressive strength of 41.3–42.2 MPa, which corresponds to the brand of cement is "400".

Table 3. – Physico-mechanical properties of the experimental cements

Numbers of cements	SO_3, %	Fineness (residue on sieve No. 008), %	Water/ cement ratio	Setting time, hours-min.		Compressive strength, MPa age (days):		
				start	end	3	7	28
Cement No.1	2.10	12.5	0.39	2-15	4-20	15.1	25.0	41.3
Cement No.2	2.22	12.0	0.39	2-10	4-10	16.2	26.7	42.2
Cement No.3	2.15	12.8	0.39	2-20	4-10	16.0	26.5	41.5

Physical and mechanical tests established that the content of SO_3, the fineness, water demand, setting time experienced cements meet the requirements of GOST 10178-85. At 28 days age of normal hardening of all three samples experienced cements detect compressive strength of 41.3–42.2 MPa, which corresponds to the brand of cement is "400".

In order to determine the suitability of waste for secondary enrichment of tungsten ore tails as a mineral additive for the production of additional ore, tests were conducted to determine their hydraulic activity by the criterion of Student. According to O'z DSt 901-98, paragraph 4.2, as additives for cements can be used materials if their effectiveness is confirmed by results of tests of additives according to GOST 25094. It is established that the value criteria of Student for the departure of secondary enrichment of tungsten ores amounted to 2.45, which is more than his standard value of $t = 2.17$. Consequently, the waste is considered to have withstood the test of compressive strength suitable for use as additive to produce additional cement. Using 10, 15, 20 % of the waste tailings secondary enrichment of tungsten ores were made by experienced incremental cements, which were produced by joint grinding of clinker, additives and gypsum. The results of physico-mechanical tests of cements showed that the added cement at 28 days age of normal hardening have a compressive strength within to 36,7 and 41,8 MPa. With the introduction of 10–15% of the additives, their compressive strength by 2–4 % higher strength without additional cement [6; 7]. The increase in the content of additives in cement up to 20% leads to a sharp decrease of 10,4 % the strength of cement.

Conclusion. The suitability of the secondary enrichment of tungsten ore tails from the Ingichka deposit as a complex aluminosilicate and iron component during the formation of raw mixtures in the production of clinker has been established. Cements based on synthesized clinkers according to technological parameters meet the requirements of GOST 10178–85 for portland cement grade PS 400 D0. The process of curing cement based on clinkers synthesized from raw mixtures prepared using the waste of secondary enrichment of tungsten ore tails in an amount of 11 to 13%, as well as the process of hydration and hardening of Portland cement produced in cement plants of the republic using traditional aluminosilicate components and costly glandular mineralizers. It is shown that using up to 15% of the waste of secondary enrichment of tungsten ore tails as a filler additive allows to obtain general Portland cements without reducing their brand strength. The investigated additive, by the nature of the main effect on the properties of cement, can be attributed to the components of the real composition of cement, which provides savings of the clinker component in the production of additional cement of the brand PC 400 D20.

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Hurmamatov Abdugoffor Mirzabdullaevich,
E-mail: gafuri-19805@mail.ru

STUDYING OF MECHANICAL IMPURITY CONCENTRATION INFLUENCING OF HYDROCARBONIC MIXES ON CLEANING EFFICIENCY IN HYDROCYCLONE

Abstract: In article are given results of researches on revealing of temperature influence degree. density. viscosity and flow rate at purification of oil-gas condensate mixes from mechanical impurity in a centrifugal field. The content of mechanical impurities in the composition of crude oil. gas condensate and their mixes has been studied. In addition. results of research on purification of oil-gas condensate mixes of mechanical impurity in various ratios of components of raw materials (oil – 10÷50%; gas condensate – 50÷90%) and temperature (from 100° C to 500° C). are given. as well as influence on efficiency cleaning in hydroclone at purification of hydrocarbonic mixes on various ratios of mechanical impurity is studied (from 5% to 15%).

Keywords: oil. gas condensate. centrifugal field. hydrocyclone. viscosity. density. hydrocarbonic mix. mechanical impurity.

Introduction. Hydroclones are successfully applied in many industries and show good results. Their advantages are such as the small sizes. working efficiency. a simple design and possibility of combination of devices in one big complex. But in such device. simple on a design. difficult hydrodynamic process proceeds. Sedimentation in a centrifugal field of non-uniform systems is much more effectively. than gravitational sedimentation therefore it is used to division of smaller particles of mechanical impurity [1; 2]. In the course of oil refining products of corrosion of devices and pipelines. catalytic dust. the smallest particles of the bleaching clay. mineral salts can fall into oil products. Pollution of oil and oil products can occur also at storage and transportation. Mechanical impurity in fuel can lead to a contamination of fuel-supply lines. filters. increase in wear of the fuel equipment. breaking of power supply of the engine. The same impurity in oils and greasings can cause obstruction of oil pipelines. breakage of the lubricant equipment. and seizure on surfaces. From mechanical impurity the sand and other solid particles abrading metal surfaces are the most dangerous [3; 4].

Objects and methods of research. As object of research is oil. gas condensate and their mixes. On a basis of the mentioned above. experimental installation was collected by us for division of oil-gas condensate mixes from mechanical impurity and pilot studies at various ratios of oil and gas condensate were conducted [7]. Experiments were carried out a speed of an oil-gas condensate stream at 15 m/s. At first defined change of density and viscosity of oil. gas condensate and their mixes at various temperatures. that is from – 20° C to 98° C [6]. In experiments the composition of raw materials was changed: oil – 10÷50%; gas condensate – 50÷90%. Experiments were conducted at temperatures of 10÷50° C. In studies of concentration of mechanical impurity in the composition of hydrocarbonic mix artificially added within 5÷10% and 15%. In order to determine mechanical impurity in the composition of hydrocarbonic raw materials it was used a weight method [3].

Results and their discussion. Results of pilot studies are summarized and given in tables 1÷3.

Table 1. – Results of pilot studies on determination of efficiency of purification
of oil and gascondensate (gc.) mixes at various ratios of components
and temperatures (content of mechanical impurity 5%)

t. °C	Efficiency of cleaning at various structures of raw materials%				
	10% oil – 90% gc.	20% oil – 80% gc.	30% oil – 70% gc.	40% oil – 60% gc.	50% oil – 50% gc.
10	0.28	0.35	0.36	0.40	0.42
20	0.19	0.27	0.29	0.33	0.36
30	0.12	0.19	0.22	0.21	0.25
40	0.11	0.18	0.18	0.19	0.24
50	0.10	0.17	0.18	0.18	0.22

Table 2. – Results of pilot studies on determination of efficiency of purification
of oil and gascondensate (gc.) mixes at various ratios of components
and temperatures (content of mechanical impurity 10%)

t. °C	Efficiency of cleaning at various structures of raw materials%				
	10% oil – 90% gc.	20% oil – 80% gc.	30% oil – 70% gc.	40% oil – 60% gc.	50% oil – 50% gc.
10	0.26	0.30	0.31	0.37	0.39
20	0.18	0.27	0.27	0.33	0.35
30	0.09	0.17	0.20	0.17	0.23
40	0.08	0.15	0.17	0.16	0.2
50	0.08	0.13	0.15	0.13	0.19

Table 3. – Results of pilot studies on determination of efficiency of purification
of oil and gascondensate (gc.) mixes at various ratios of components
and temperatures (content of mechanical impurity 15%)

t. °C	Efficiency of cleaning at various structures of raw materials%				
	10% oil – 90% gc.	20% oil – 80% gc.	30% oil – 70% gc.	40% oil – 60% gc.	50% oil – 50% gc.
10	0.20	0.27	0.29	0.31	0.37
20	0.15	0.23	0.24	0.30	0.33
30	0.075	0.15	0.18	0.15	0.2
40	0.071	0.13	0.15	0.14	0.19
50	0.069	0.10	0.12	0.11	0.17

As seen from table 1 that content of mechanical impurity as a part of hydrocarbonic mix (at ratios of 50% oil + 50% gas condensate) decreases from 0.42% to 0.22%. at the expense of increase in their temperature from 10 °C to 50 °C. The further increase in temperature to 50° C at ratios of 30% of oil and 70% of gas condensate is observed increase of efficiency of cleaning of hydrocarbonic raw materials of mechanical impurity. content of mechanical impurity as a part of hydrocarbonic mix from 0.36% decreases to 0.18%. In table 3. decrease in the content of mechanical impurity from 0.29% to 0.12% is also observed. at ratios of hydrocarbonic mix of 30% of oil and 70% of gas condensate at temperatures 10÷50 °C. During the pilot studies temperature of an oil-gas condensate stream rose more than 50° C. but to the economic point of view it is not accepted. effect too it isn't noticeable.

Results of comparative pilot studies on definition of the content of mechanical impurity in the composition of hydrocarbonic mixes are also given in figures 1÷4.

As form seen from fig.1 that 5% initial concentration of mechanical particles as a part of hydrocarbonic mixes (50% oil + 50% gc.) their contents gradually decreases from 0.42 to 0.17%. at temperatures of

10÷50°C. and at 10% concentration of mechanical particles (40% oil + 60% gc.) the same situation of process is observed. that is the maintenance of mechanical particles decreases from 0.4÷0.11% at temperatures of 10÷50° C (fig.2). The further increase in concentra-

tion of mechanical particles to 15% in oil and gascondensate mix at a ratio of mix of 30% oil + 70% gc. is also observed decrease in the maintenance of mechanical particles from 0.36% to 0.12%. at temperatures from 10^0C up to 50° C (fig. 3).

Figure 1. Effect of initial concentration of mechanical impurity on efficiency of cleaning oil and gascondensate raw materials from impurity

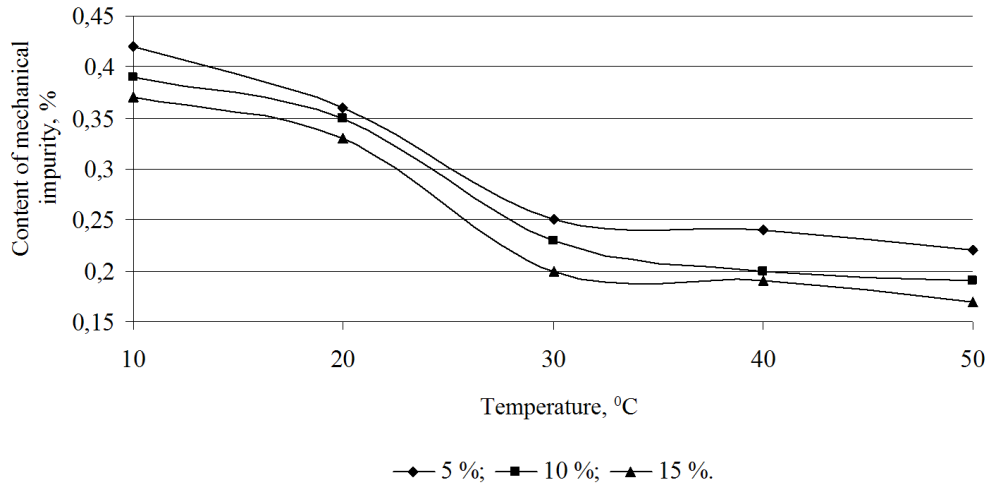*(Structure of hydrocarbonic raw materials of 50% oil + 50% gc.)*

Figure 2. Effect of initial concentration of mechanical impurity on efficiency of cleaning oil and gascondensate raw materials from impurity

(Structure of hydrocarbonic raw materials of 40% oil + 60% gc.)

This results from the fact that with increase in concentration of mechanical particles of hydrocarbonic mix. extent of cleaning of raw materials raises due to the constrained sedimentation. Speed of the constrained sedimentation will be less than a speed

calculated for a single particle as the coefficient of resistance increases due to impact of firm particles. At a ratio of components of mix of 20% oil + 80% gc. the maintenance of mechanical particles of hydrocarbonic mix changed from 0.35% to 0.10% (fig.4).
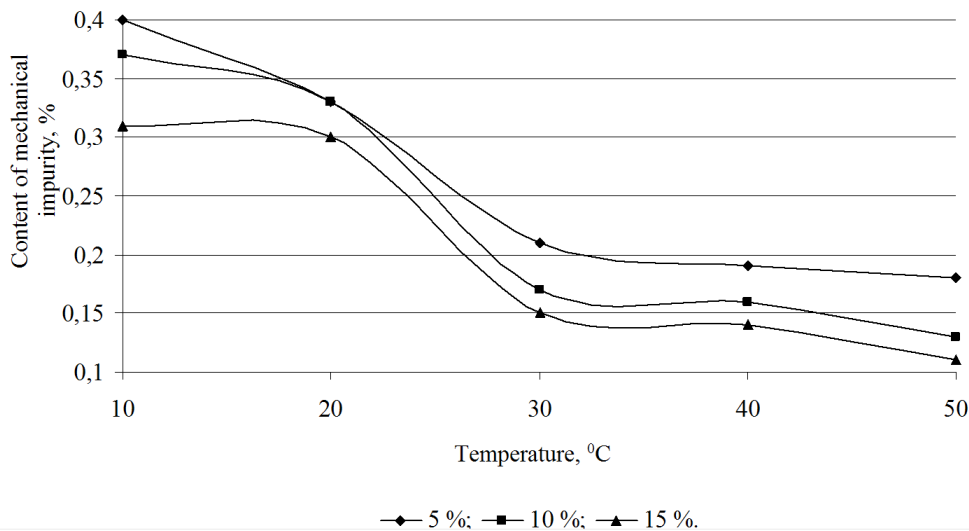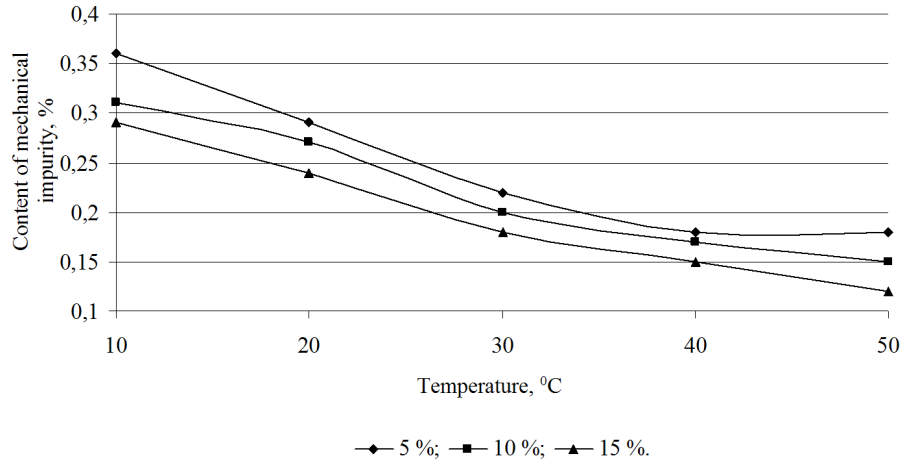
Figure 3. Effect of initial concentration of mechanical impurity on efficiency
of cleaning oil and gascondensate raw materials from impurity

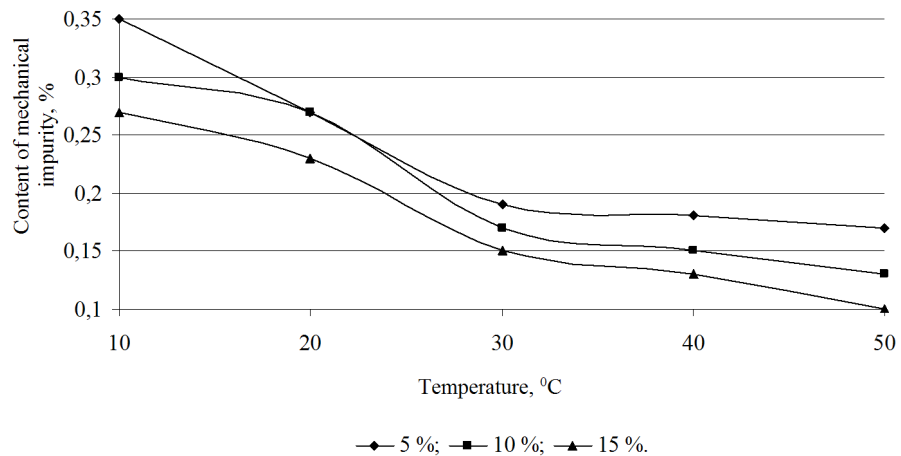*(Structure of hydrocarbonic raw materials of 30% oil + 70% gc.)*

Figure 4. Effect of initial concentration of mechanical impurity on efficiency
of cleaning oil and gascondensate raw materials from impurity

(Structure of hydrocarbonic raw materials of 20% oil + 80% gc.)

Conclusion. Thus. the pilot studies conducted on cleaning of oil and gascondensate raw materials of mechanical impurity show that positive results at the following of regime and technological parameters of a hydroclone are received: temperature – 50 °C. density – 760 kg/m³. kinematic viscosity – 890.88·10⁻³ Pa·s. and stream speed – 15 m/s. the content of mechanical impurity as a part of oil and gascondensate raw materials made – 0.069%. On the basis of the received experimental results it is possible to make a conclusion that by means of hydrocyclones possible to make effectively deep purification of oil and gascondensate mixes from mechanical impurity.

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Erkabaev Furkat,
Senior researcher,
of Laboratory of colloidal and membrane chemistry
of Institute of General and Inorganic Chemistry
of Uzbekistan Academy of Sciences
E-mail: erkabaevf@rambler.ru

Ahmedov Ulug,
Dr in chemistry, Prof.,
Head of Laboratory of colloidal and membrane chemistry
of Institute of General and Inorganic Chemistry
of Uzbekistan Academy of Sciences;

ELECTROCHEMICAL RECOVERY OF CHROMIUM IONS (VI) IN THE PRESENCE OF POLYHYDRIC ALCOHOL

Abstract: The current output of chromium is very low (15–16%) in the electrochemical reduction of chromium (VI) ions but this method is possible to purify sewage from impurities to MPC. The purpose of this work is studying the effect of polyhydric alcohols on the current of chromium in the electrochemical purification of waste solutions and wastewater.

Keywords: electrolysis, waste solution, glycerin, current density, current output.

Introduction. The reduction of ions six valent toxic chromium is carried out by various methods. They are divided into two main groups: chemical and electrochemical. It should be noted that during the electrochemical reduction of chromium ions, the current output of chromium is very low (14–16%), but the wastewater can be purified up to MPC, therefore it is advisable to purify sewage with recommended method in hard-to-reach areas, waters up to 50 m³/h, where it is difficult to regularly import chemical reagents [2–3]. In the process of recovery, most of the electricity is spent on undesirable processes, such as ion polarization, the precipitation of some impurities in the solution, and the resistance of the electrolyte. It is established that the rate of electrochemical dissolution of anodes increases with increasing current density and with a change in pH towards increasing acidity. The absolute values of the rate of dissolution of the anode range is from 1 to 10 mg/min. dm² [4].

The authors carried out experiments on the effect of polyhydric alcohols on the reduction of chromium ions [5]. The results of studies is determined the effect of various polyhydric alcohols such as glycerol, xylitol, sorbitol on the reduction of chromium (VI) ions have shown that glycerol is the best additive for increasing the degree of purification in the electrochemical reduction of six valent chromium ions from the above-mentioned polyhydric alcohols [6].

A study of the processes of complex formation of chromium (III) ions with polyhydric alcohols and sulfuric acid by the potentiometric method is devoted to the work of some authors [7; 8].

The above-mentioned authors also established by physicochemical methods of investigation the formation of a complex compound of sulfuric acid with glycerol at a ratio $H_2SO_4 : gl = 1:1$.

The elucidation of the mechanism of reduction of chromium (VI) ions during electrolysis, increasing of chromium by current and the utilization of waste

electrolytes in the electrolysis of chromium are important aspects of this study.

Recovery of chromium ions directly depends on the acidity of the solution. The acidity of the solution plays a major role in the reduction of six valent chromium to the metal from the standard electrolyte.

The purpose of this study is to increase the current of chromium in the electrolysis of waste solutions in the presence of glycerin and to determine the optimum process conditions.

Methods and materials. A model waste solution of chromium plating shop and a polyhydric alcohol-glycerin are used as the object of study. A photo colorimetric method was used to determine the content of chromium ions in solutions.

Results and discussion. To increase the chromium current and to establish the optimal conditions for the electrochemical reduction of six valent chromium in a standard electrolyte, we carried out electrolysis under the following conditions: electrolyte volume –200 ml, six valent chromium ion concentration 50 g/l, cathode-graphite, time is 1,5 hours. The concentration of chromium (VI) and chromium (III) ions were determined before and after electrolysis by the photo colorimetric method on the photo colorimeter KFK-2.

The process of reduction in a neutral medium does not occur, with an increase in the concentration of sulfuric acid to 3–4 g/l, the current output of chromium increases, further increase in the acid concentration does not affect the increase in the current of chromium (table 1).

With excess sulfuric acid in the reduction process, the solution becomes blackened, evidently due to charring of the organic reductant present.

Studies on the electrolysis of chromate-containing solutions show that during 1 hour the process of reducing the concentration of six valent chromium ions from 50 g/l to 31–32 g/l and, correspondingly, an increase in the content of trivalent chromium ions to 8–9 g/l (Table 2). Further, the process of simultaneous reduction of chromium metal from chromium (VI) and chromium (III) ions proceeds.

Table 1. – Effect of the concentration of sulfuric acid to the output current of chromium V = 200 ml; CCr = 50 g/l; I = 15 A/dm²; Cathode-graphite, τ = 1.5 hours

№ п/п	Concentration, H_2SO_4, g/l	Current output Chromium,%
1	0	0
2	0.5	1
3	1	4
4	1.5	6
5	2	9
6	2.5	10
7	3	14.5
8	4	15.5
9	5	16
10	6	16
11	7	15.9
12	8	16
13	10	16.2
14	12	16.1
15	14	16.1

Table 2. – Effect of the concentration of sulfuric acid to the output current of chromium V = 200 ml; CCr = 50 g/l; I = 15 A/dm²; Cathode-graphite

№ п/п	Time, min	Current output Chromium,%
1	0	0
2	5	3
3	10	5
4	15	6
5	20	8
6	25	10
7	30	14.5
8	35	15.5
9	40	16
10	45	16
11	50	15.9
12	55	16
13	60	16.2
14	65	16.1
15	70	16.1

It is known that polyhydric alcohols with many metals form complex compounds [9], including with trivalent chromium, reduced during electrolysis from a solution with chromium (VI) ions, which contributes to an increase in the current. By studying the effect of various concentrations of glycerin on the process of reduction of chromium (VI) ions, an optimal concentration of glycerin on the relative increase in the current yield of chromium was revealed (Fig. 1.)
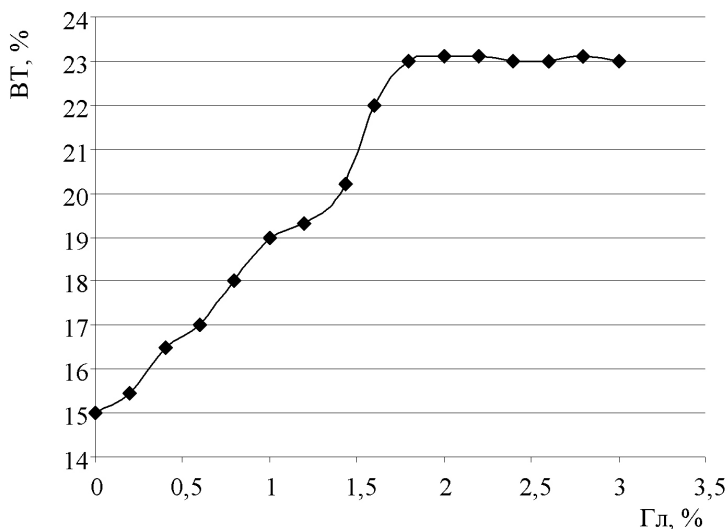
Figure 1. Effect of the amount of glycerin on the current output of chromium

The results of electrolysis in Fig. Shows that the presence of glycerol in the electrolyte up to 1–2% increases the amount of reduced metallic chromium and, correspondingly, the current output rises from 16 to 23,1%.

The obtained results of the conducted studies made is possible to determine the optimal conditions for the process. It is established that at a current density of 11–12 A/dm² the process proceeds optimally, and sulfuric acid at a concentration of about 4–5 g/l contributes to the maximum recovery of six valent chromium. It is established that within a hour, the main amount of chromium ions is recovered.

Conclusion. The results of the conducted studies show that the electrochemical reduction of chromium in the presence of glycerin, to some extent, increases the current yield of chromium (up to 23%). The use of electrochemical methods for cleaning spent solutions from six valent chromium ions, in spite of the consumption of metal and electric power, makes it possible to clean contaminated solutions up to MPC. The equipment of this method is compact, efficient, convenient to use and maintain.

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Section 5. Physics

Kattayat Sandhya,
Faculty of Engineering and Technology,
Higher Colleges of Technology, Abudhabi, UAE
E-mail: sandhyamenon24@gmail.com

Smitha Josey,
Faculty of Engineering and Technology,
Higher Colleges of Technology, Fujairah, UAE
E-mail: vivianvarsha@gmail.com

Dr. Asha J.V.,
Asst. Professor (Education),
University of Kerala, Trivandrum, INDIA
E-mail: Ashajv3@gmail.com

FLIPPED CLASSROOM MODEL IN IMPROVING UNDERGRADUATE STUDENT'S PERFORMANCE IN PHYSICS

Abstract: The purpose of this study was to assess the effectiveness flipped class room technique over traditional curriculum. Students in both cases were provided the same notes and practice sessions except students in the flipped classroom were required to watch the videos and recordings in their own pace before class and then to attend the class, where they received practice sessions covering material in each lecture followed by a question and answer/problem-solving period. In the traditional curriculum, students attended the lectures and did the same practice sessions. Evaluation of effectiveness and student performance was achieved by having students in both courses take the same exams at the end. Within a comparable group of participants in the flipped course scored significantly higher. Responses obtained in interviews with the students support the flipped classroom model.

Keywords: Flipped classroom; didactic lectures; student performance.

Introduction

In a world where the technology is gaining upper hand over the traditional methods educational instruction is also changing accordingly. The traditional classroom is normally teacher centric with explanation of a concept followed by activities such as homework and quiz. In a traditional class room there there is a warmup activity followed by discussion of previous session.This is to ensure the class is starting from the students previous knowledge. The new content is introduced after this and the method of introduction of new topic is based on the teachers judgement of the class and the topic. The method which is suitable to that content is adopted in the class by the teacher.A major role is here for the teachers expertise. The remaing session is a guided or independent practice of the content.

What is traditionally done in the class is now done at home and what is done at home can be done in the classroom. Flipped classrooms are well thought out and use both summative and formative assessment. They take time and commitment to do and this method is not a magic bullet to education; teachers still have to passionate and caring about what they are teaching and the students believe they want to help them learn. We need a strong pedagogy that drives out technology – never the other way around. Flipped Classroom is not a "predetermined" but one of many methods that are used to encourage an active learning environment. To reach success, we must be able to move outside of our normal zone of comfortness. There is a major concern for this method. Teachers may simply change their lectures to video and then have their students write papers or fill out worksheets during class. This defeats the purpose of flipping the class rooms. But if significant learning opportunities are capitalized during class time, this could truly change learning, and engage students with material outside of the classroom. Innovative teachers are "Flipping" the classroom in order to make classroom instructional time more valuable to students. This practice is best for self-motivated and directed learners. In this method teacher prepares teaching material – videos, paper work etc. and sends to the students. Students listen to instruction, discuss with peers and raise questions for the class time. In the class room there are interactive sessions and discussion about the content. It can be in any form. Some of the normal methods are problems related to the content in the video, question based sessions, experiential sessions, debate or lab work.

The 'flipped classroom' is a teaching methodology employed among any level of instruction or any discipline. With the help of online videos and simulations students learn new materials themselves prior to the discussion in the class. In the set topics teachers are giving videos links or simulations to watch before any practice or discussion in the class. This is one of their homework task. In the next meet-

ing students are discussing the topics and practicing the related materials in the class. This is in contrast to the traditional method where the students learn the materials in the class first and practice them at home in the form of homework's. These classes are unique in its implementation, practice and output. Online videos and simulations are part of both of traditional and flipped classrooms. But the implementation method is different in flipped class rooms.

Review of literature

The philosophy and methodology used to redesign the Basic Pharmaceutics II course were described in an article based on the investigation of a flipped classroom experience of first-year pharmaceutics course at the University of North Carolina. Another study intended to serve as a guide to instructors and educational programs seeking to develop, implement, and evaluate innovative and practical strategies to transform students' learning experience [1]. Students tend to prefer in-person lectures to video lectures, but prefer interactive classroom activities over lectures. Anecdotal evidence suggests that student learning is improved for the flipped compared to traditional classroom [2].

The flipped classroom, with its use of videos that engage and focus student learning, offers us a new model for case study teaching, combining active, student-centered learning with content mastery that can be applied to solving real-world problems [3].

Implementing a flipped classroom model to teach a renal pharmacotherapy module resulted in improved student performance and favorable student perceptions about the instructional approach. Some of the factors that may have contributed to students' improved scores included: student mediated contact with the course material prior to classes, benchmark and formative assessments administered during the module, and the interactive class activities [4].

Flipped classroom approaches may provide more opportunities to tailor instruction to the expertise of students, enabling more appropriate management of cognitive load [5].

A flipped classroom teaching model is introduced in Chinese schools. And this describe the challenges in the implementation of the flipped classroom teaching.The paper provides an innovative way to reform teaching in Chinese schools [6].

Integration of the flipped classroom model with online NextGenU courses can be an effective innovation in public health higher education: students achieved similar examination scores, but NextGenU/Flipped classroom students rated their course experience more highly and reported positive learning experiences and an increase in self-perceived knowledge. These results are promising and suggest that this approach warrants further consideration and research [7].

Method

The method selected in this study is mixed-method approach, experimental and pretest post-test method. The statistical methods used to check the efficiency of this method is t test p value calculation. Along with this the opinion of the students were taken in an interview format.

The course selected for the study is engineering physics of second semester engineering students. The sample selected for the study is from a population of 700 students. The course selected is intended to provide a global overview of the basic topics in physics which is the basis of any engineering field. The Learning outcomes of the course are related to the following topics where selected for the study using flipped class room technique. (1) Electricity, (2) magnetism, (3) Faradays Law, (4) Reflection, refraction (5) Electromagnetic waves. For every chapter, the teaching strategy followed three main steps: (a) Students watching the videos related to the topics at home (b) practice or discussion in the class in the next meeting (c) A conclusion. This method was followed in all topics and at the end the post test was conducted.

Students were divided into two groups: the first group was taught in the traditional way. The second group was given the flipped classroom technique. The instructors involved were well equipped and were well aware of the flipped classroom instructional technique. All of them were attended workshops or training about this technique prior to the starting of the academic year. Both the groups were experimented for a time of one academic semester. The groups were tested using the pretest to check their equivalency in their performance. Then for one academic semester the group was taught in two different methods, first group traditionally and the other using flipped classroom techniques. At the end both the groups were tested using the same posttest to check their achievement. Using statistical techniques t teat and p value the performances were compared.

Student's opinion was taken in the form of a survey. A standardized questionnaire was given to the students and their opinion was collected on the percentage of in favor, against and neutral responses were found out.

Analysis

The tests were conducted in the beginning and at the end of the academic semester. The pretest was conducted in the form of a quiz consisting of 35 multiple choice questions in different topics related to engineering physics. The average scores were compared and the equivalency of the students in their performance was verified for the initial stage. Then the students were divided in to 2 group's traditional learning group and the flipped learning group. The post test was conducted with a questionnaire of 40 question which consists of 23 multiple choice questions 7 comprehensive type questions and 10 problem solving questions. Both the groups were given the same time for solving the paper. The result for the post test is given in the table.

Table 1.

	Traditional course	Flipped course	t value p value
Number of students	86	86	3.45 0.045

It is found that the t value for the post test is 3.45. This indicates student's high performance in flipped learning environment. The low value of p at 95% confidence level shows that the result obtained is not by chance.

The results of the survey can be interpreted by taking the percentages of each response with respect to the total sample.

The survey result showed the students positive attitude towards the flipped class room.

Table 2.

Questions	favor	neutral	against
Watching videos before the class helps better understanding of the topic	68%	20%	12%
Homework's are better options than watching videos	6%	11%	83%
The time spent in watching videos is not worth	18%	20%	62%
I prefer to hear the teachers explanation and proceed with the practice than to watch the videos and coming to the class	39%	14%	47%
I need support in practicing problems after watching the videos	25%	30%	45%
I feel excited and interested in the topics given after watching the videos	68%	20%	12%
There is no use of the videos in improving my performance in the exams	19%	14%	67%
I feel more confident to solve the problems after watching the videos and attending the next day class	49%	16%	35%

Result

For an effective flipped classroom careful preparation is required from instructor's part. This method gives more importance to student's involvement. It is not a must that all students should follow the routine of watching the videos and practice the same in the next class. The less number of face-to-face lectures may demotivate the students in the beginning of this method.

The main outcomes of the study was a deeper understanding of the possibilities offered by the flipped classroom method, and student's high involvement in the tasks and lesson. The classes were student centric and students enjoyed the learning experience which incorporated more activities. The online resources prompted them to search in those areas to find the varying methods in different topics to solve the problems related to the topic even after the topic discussion. Students were trying to relate the content to daily activities and experiences. The independent working habit developed in them prompted them to do high quality work and this reflected in their other activities as well such as lab activities and home work.

Recommendations

This study can be extended to any other discipline such as chemistry, mathematics or management. This study can be conducted in a varying age group from primary to adult education. Irrespective of cultural boundaries this technique can be experimented. Flipping the class rooms can be checked with distance learning techniques.

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Section 6. Chemistry

Aghayeva Kamala Kheybar,
Azerbaijan State Oil and Industry University
PhD student, the Faculty of Chemical Engineering
E-mail: agayeva-lyama@mail.ru

Baghiyev Vagif Lachin,
Azerbaijan State Oil and Industry University
Professor, Department of chemistry
and chemical materials engineering
E-mail: Vagif-bagiev@yahoo.com

CONVERSION OF ETHANOL OVER MO-W-O CATALYSTS

Abstract: In the paper investigated influence of reaction temperature and catalyst composition on activity binary molybdenum-tungsten oxide catalysts in the reaction of conversion of ethanol. The yield and distribution of ethanol conversion products depends strongly on both the reaction temperature and catalyst composition. It has been shown that molybdenum rich catalysts are active in the formation of acetic aldehyde while samples rich with tungsten are active in the ethylene formation reaction.

Keywords: ethanol, acetaldehyde, ethylene, binary catalysts, molybdenum oxide, tungsten oxide.

It is known that catalytic systems based on tungsten oxides exhibit a high activity in the oxidation reactions of various organic compounds [1–3]. However, these catalytic systems exhibit insufficient selectivity in partial oxidation reactions. From periodic literature it is known that molybdenum oxides exhibit high selectivity in soft oxidation reactions [4; 5]. In connection with this, we have studied in paper the effect of additives of molybdenum oxide on the catalytic activity of tungsten oxide in the reaction of partial oxidation of ethanol.

Experimental

Binary molybdenum-tungsten oxide catalysts of various compositions were prepared by coprecipitation from aqueous solutions of ammonium molybdate and ammonium tungstate. The obtained mixture was successively evaporated and dried at 100–120 °C, decomposed at 250 °C until the nitrogen oxides were completely separated, after that calcined at 600 °C for 10 hours. Thus, nine catalysts were synthesized with an atomic ratio of the elements from Mo: W = 1: 9 to Mo: W = 9:1. The activity of synthesized catalysts was studied in a flow unit with a tubular reactor in the temperature range 100–500 °C. The reactor was charged with 5 ml of the investigated catalyst with a grain size of 1.0–2.0 mm and its activity was studied in the ethanol oxidation reaction. Reaction of oxidation of ethanol was carried out by oxygen in the presence of water vapor. Carbon dioxide was determined on a chromatograph with a thermal conductivity detector and a 3-meter-long column filled with vaseline oil deposited on celite. Ethanol and its conversion products were determined on a chromatograph with a flame ionization detector on a 3 m column filled with a specially treated sorbent-polysorb-1.

Results and discussions

The conducted studies have shown that ethylene, acetic aldehyde, acetic acid and carbon dioxide are the products of ethanol oxidation reaction over molybdenum-tungsten oxide catalysts. The yield and distribution of ethanol conversion products depends strongly on both the reaction temperature and the atomic ratio of molybdenum to tungsten of the catalyst. As example, the effect of the reaction temperature on the yields of ethanol conversion products over catalyst Mo: W = 2:8 is shown in Fig. 1. As can be seen from Fig. 1, the reaction of ethanol conversion over studied catalyst begins at a temperature of 250 °C with the formation of 6.5% of acetic aldehyde, 3.8% of acetic acid. A further increase in the reaction temperature leads to the formation of ethylene and carbon dioxide. It can be seen from Fig. 1 that the yields of acetic aldehyde with increasing reaction temperature pass through a maximum at a temperature 350 °C (39.8%). With a further increase in the reaction temperature, the yield of acetic aldehyde decreases to 17.1% at 450 °C. Unlike acetic aldehyde, the yields of acetic acid and carbon dioxide changes in same way and increase with increasing reaction temperature and reach 12.9 and 4.5% respectively at 450 °C. The yield of ethylene with increasing reaction temperature increases strongly in the entire studied temperature range and reaches 54.3% at 450 °C. At this temperature, ethanol conversion reaches 88.8%. Based on the obtained results, it can be said that at high reaction temperatures the main product of the ethanol conversion reaction is ethylene.
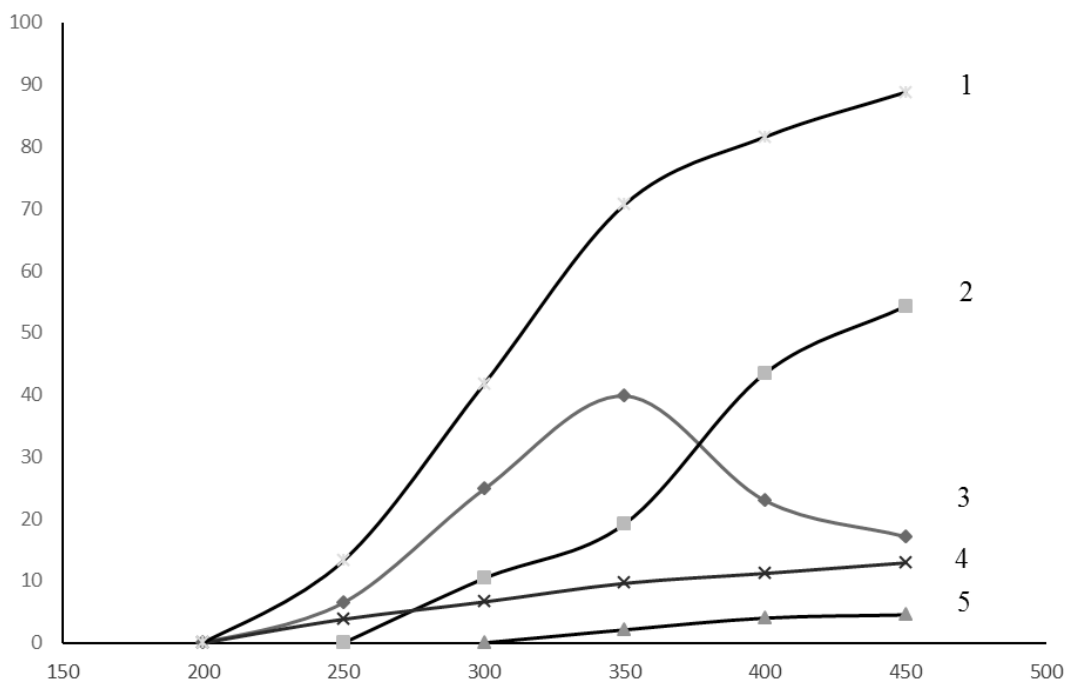

Figure 1. Influence of the temperature on activity of catalyst Mo: W = 2: 8 in the reaction of oxidation of ethanol. 1 – Conversion of ethanol, 2 – Ethylene, 3 – Acetic aldehyde, 4 – Acetic acid, 5 – Carbon dioxide

The atomic ratio of molybdenum to tungsten, strongly affects to the activity of molybdenum-tungsten oxide catalysts in the ethanol conversion reaction. In figure 2 it is shown at a temperature of 400 °C the dependence of the molybdenum-tungsten oxide catalysts activity in the reaction of ethanol conversion from their compo-sition. As can be seen from figure 2, the yield of acetic aldehyde with increasing of amount of molybdenum in the binary molybdenum-tungsten oxide catalyst first increases and on the sample Mo: W = 3:7 reaches its highest value equal to 49.8%. With a further increasing of molybdenum content in the catalyst composition, the

yield of acetic aldehyde decreases and on samples with a higher molybdenum content stabilizes at a level of about 40%. The yield of ethylene with increasing molybdenum content in the binary catalyst composition decreases from 52.9% on the sample Mo: W = 1:9 to 17.5% on the sample Mo: W =:1.
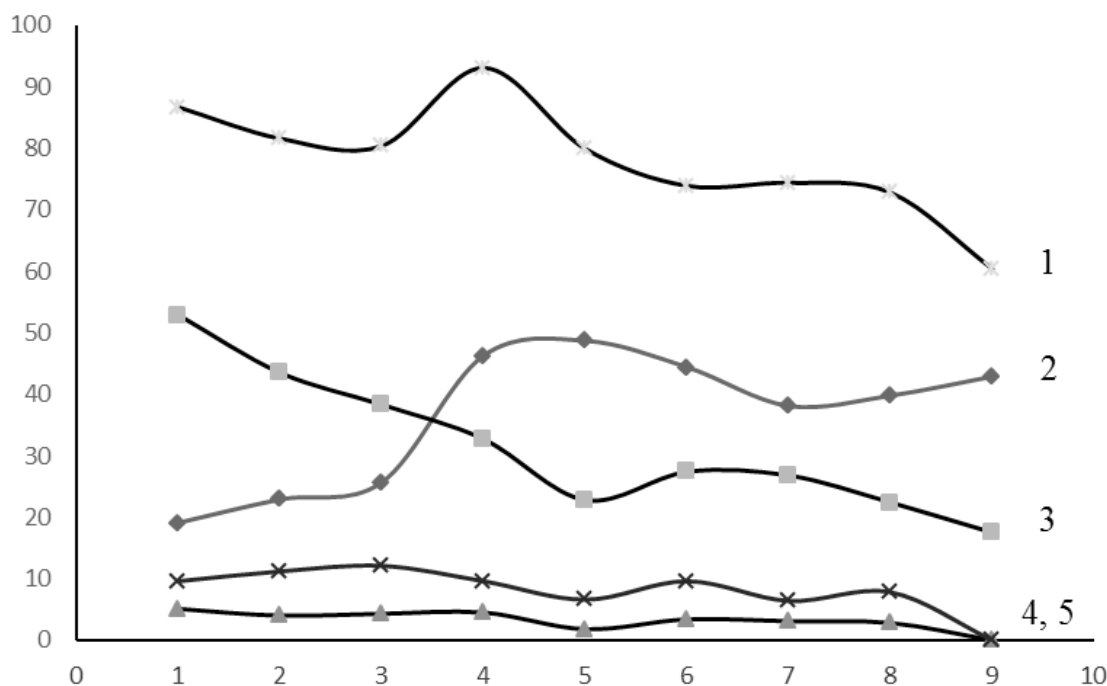

Figure 2. Dependence of the outputs of products of the reaction of ethanol conversion over Mo-W-O catalytic system. T = 400 ˚C. 1 – Conversion of ethanol, 2 – Acetic aldehyde, 3 – Ethylene, 4 – Acetic acid, 5 – Carbon dioxide

Figure 2 also shows that the yields of acetic acid and carbon dioxide are slightly dependent from the atomic ratio of molybdenum to tungsten. The yields of acetic acid and carbon dioxide at 400 °C do not exceed 12.1 and 5.1%, respectively. Thus, the reaction of ethylene formation proceeds on catalysts rich in tungsten, while the formation of acetic aldehyde proceeds on samples rich in molybdenum. From the data shown in Fig. 2, we can also say that at 400 °C the maximum conversion of ethanol over studied samples reaches up to 93.1%.

Thus, based on the carried out studies, it can be said that over molybdenum-tungsten oxide catalysts at low temperatures are dominated the dehydrogenation reaction of ethanol with the formation of acetic aldehyde, while at higher temperatures the dehydration reaction prevails with the formation of ethylene. In addition, it should be noted that molybdenum-rich catalysts are active in the formation of acetic aldehyde while samples rich with tungsten are active in the ethylene formation reaction.

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Keri Jona,
Faculty of Natural Science,
hemistry Department, University of Tirana, Albania

Mele Altin,
Faculty of Natural Science,
Chemistry Department, University of Tirana, Albania

Ylli Fatos,
Institute of Applied Nuclear Physics,
University of Tirana, Albania,

Fetallari Marjel,
Faculty of Natural Science,
Chemistry Department, University of Tirana, Albania,
E-mail: jonakeri87@gmail.com

PHYSICO-CHEMICAL CHANGES DURING THERMAL TREATMENT OF PRRENJAS CLAY

Abstract: In this work, the physical-chemical changes of Prrenjas clay were studied after its heating to 500 °C and after its freeze drying at – 196 °C. Prrenjas clay belongs to montmorillonite type, which are used in processes at high temperatures as catalyst, catalyst carriers and adsorbents. The techniques used are thermogravimetry, N_2 adsorption-desorption measurement at 77 K on Prrenjas clays for the determination of its specific surface and pore volume, and Infrared spectroscopy. The Prrenjas clay heated up under vacuum and in the presence of nitrogen shows a weight loss of around 25.5% and 22.8% at 500 °C respectively. The IK analysis shows a dehydration process of the removal of adsorbed and cation hydration water and a dehydroxylation process of the removal of structural OH groups from the surface of the clay. During freeze drying at – 196 °C partly occurs the dehydration process of mainly hydration water and the weight loss is 10.1%. The pore volume increases from 98 cm³/kg for the untreated Prrenjas clay to 103.3 cm³/kg and 118.49 cm³/kg after its heating to 500 °C under nitrogen and vacuum respectively, and to 139.01 cm³/kg after its freeze drying. The specific surface increases slightly after freeze drying from 124.2 m²/g to 126.97 m²/g, but decreases to 92.30 m²/g and 98.17 m²/g after heating it to 500 °C under nitrogen and vacuum respectively. The cationic exchange capacity is reduced from 103 meq/100 g for the untreated Prrenjas clay sample to 100.28 meq/100 g after its freeze drying, to 85.00 meq/100 g after its heating under vacuum at 500 °C and to 80.31 meq/100 g after its heating under nitrogen atmosphere at 500 °C.

Keywords: Prrenjas clay, surface, thermal treatment, dehydration, dehydroxylation.

Introduction

The Prrenjas clay is a natural mineral found in Prrenjas, southeast of Albania and is studied regarding its chemical composition, mineralogical content and cation exchange capacity towards Pb^{2+} cations from Jozja *et. al.* [1], who came at the conclusion that it is an Fe-rich montmorillonite type of clay, mixed with 10% illite and 12% of other phases

(chlorite, kaolinite, antigorite, halloysite), so belonging to the smectite group.

Clay minerals with smectite content have been studied for changes of the chemical-physical properties of their surfaces during different treatments and in summary books on clay minerals of which the two most recent and most quoted are "Handbook of clay science" 2nd edition by F. Bergaya, G. Lagaly and "Development in Clay Science " 2006, from F. Bergaya. Typical changes in the chemical composition of the smectites are suitable followed by IK spectroscopy and the interpretation of spectra, often complex of their own is described in the literature by Madejova [2] and Tomić *et. al.* [3]. The changes during thermal treatment of clays that also belong to the smectite type are described from Zivica *et al.* [4], Jasimm *et al.* [5], Sennour *et al.* [6], Manjot Toor *et.*

al. [7; 8], and the reported changes appear to depend on the mineral content in each case.

In this work are studied by infrared spectroscopy the chemical changes of the Prrenjas clay and the changes in its surface properties pore volume, specific surface and cation exchange capacity after the heating at 500 °C or after its freeze drying at 77 K.

Materials and methods

Prrenjas clay is collected in Prrenjas area at the coordinates 41.067; 20.552, about 20 cm under the surface and washed by decantation The chemical composition and the diffractometry analysis of its averaged sample shows that it is an aluminum silicate with smectite structure 2:1, with 2 tetrahedral SiO_2 and one octahedral Al_2O_3 layers with high content of iron and magnesium and small content of Ca, K and Na as following:

Table 1.

$SiO_{2\%}$	$Al_2O_{3\%}$	$Fe_2O_{3\%}$	CaO%	MgO%	$Na_2O\%$	$K_2O\%$	$TiO_2\%$	MnO%
53.41	15.12	17.01	2.85	10.56	0.13	0.63	0.19	0.18

Those clay data and its washing procedure are given in details from Murtaj *et. al.* [9]. After washing the clay samples were dried over night at 105 °C under atmospheric pressure. Blue methylene (chloride of tetramethylthionines) > 99% pure is the product of Alpha Aesar.
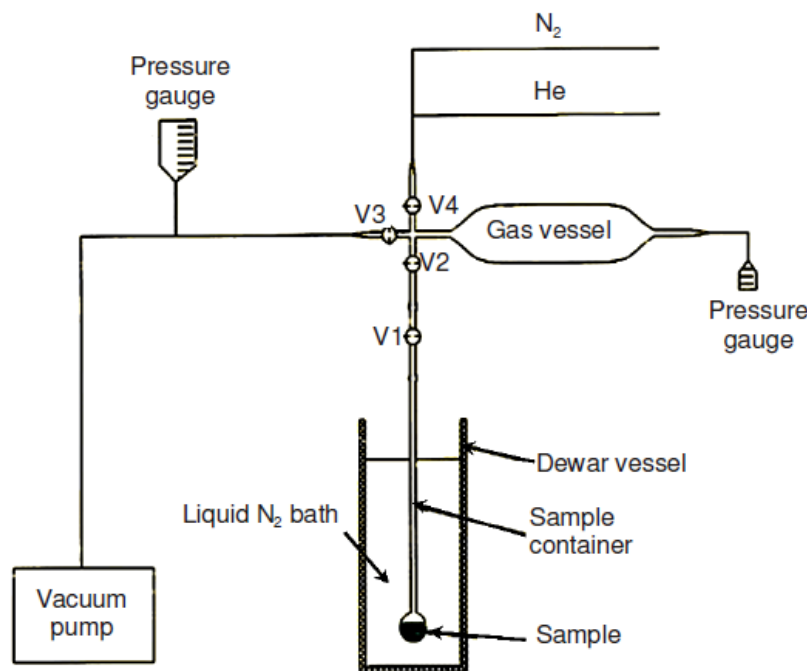

Figure 1. Apparatus for gaseous N_2 adsorption-desorption measurement at 77 K on Prrenjas clay

Adsorption-desorption measurements of gaseous N_2 on clay samples at 77K

Same apparatus shown in figure 1 is used for the adsorption-desorption measurement of N_2 on Prrenjas clay samples at 77 K, for their thermogravimetric analysis during heating up to 500 °C under vacuum and nitrogen atmosphere, and for their weight change during the freeze drying process. It is made out of glass equipped with a vacuum pump reaching pressures as low as 5 Pa.

The construction of this apparatus and the procedure for measuring the adsorption-desorption isotherms of N_2, on the Prrenjas clay samples at the temperature 77 K is explained in detail elsewhere [9]. The sample mass used for measurement was around 0.5 g and determined by an analytical balance (Bell Engineering) with an accuracy ± 0.1 mg.

Weight loss measurement during freeze drying process

For the freeze drying of the clay sample, the sample vessel of the apparatus shown in the figure 1 was immersed in a Dewar filled with liquid nitrogen at 77K. It was evacuated at 5 Pa over 26 hours until constant weight and a gravimetric analysis of the sample was performed by measuring its weight in the analytical balance after different time periods.

Thermogravimetric analysis

Thermogravimetric analysis of the Prrenjas clay samples by heating them from 20 °C to 500 °C under vacuum or under nitrogen atmosphere were performed in the apparatus of figure 1, by replacing the Dewar vessel with an tubular oven in which the temperature was measured by a NiCr-Ni thermocouple and adjusted at ± 3 °C by using an automatic controller connected with the thermocouple and with the current supply of the oven. The sample was weighted after increasing the temperature in 50 degrees steps and so the thermogravimetric curves were constructed.

Determination of the cation exchange capacity of Prrenjas clay by blue methylene method – 0.500 g of Prrenjas clay dried over night at 105 °C/5 Pa were mixed with 100 mL of distilled water in an Erlenmeyer flask of 200 mL. The obtained suspension is titrated with a 12.5 mM solution of blue methylene under stirring. The blue methylene is exchanged against other clay interlayer cations and so removed from water. The titration continues until the blue methylene is not fully from the clay. To evidence this fact, a round-shaped glass rod is dipped to the bottom of the flask and taken out, in order to get on the tip of it some clay particles that has adsorbed blue methylene. Then the tip of the rod is contacted with a filter paper and the trace that it leaves is observed. The end of the titration is achieved when the trace left by the rod is a blue circle of clay particle and around it a colorless crown, known as "halopoint". The cation – exchange capacity (CEC) of the clay expressed as miliequivalents (meq) per 100 g of dry clay is calculated using the following formula:

CEC = 100/D*C*NMB (meq/100g) where:

C – volume of blue methylene solution added to the suspension until reaching "halopoint" in liters,

D – weight of dried clay,

NMB = A/319.9 (A-weight of dry blue methylene used for the preparation of 1 liter water solution, and 319.9 g/mol – molar mass of blue-methylene).

Fourier Transform Infrared (FTIR) Spectroscopy analysis

Infrared analysis of the Prrenjas clay samples were performed in a Nicolet 6700 FTIR of the producer Thermo Scientific equipped with an Attenuated Total Reflectance (ATR) device. The samples were analyzed as dried powder form by applying them on the ATR crystal. The measurements were performed in the Institute of Applied Nuclear Physics, University of Tirana.

Results and discussions

The weight loss of smectite clays during their thermal treatment in the range from 20 ºC to 500 ºC occurs because of the dehydration and dehydroxylation processes [2]. This phenomena is evidenced in this work for the case of Prrenjas clay and the associated properties changes as well.

The process of dehydration and dehydroxylation is evidenced in the changes in the infrared (IR) spectrums of untreated and treated Prrenjas clays from 4000–400 cm^{-1} given in the figure 2. It is shown from Jozja et.al. 2003 that Prrenjas clay is an hydrated aluminum silicate and belongs to montmorillonite type of the smectite group with a 2:1 layered silicate structure, meaning two tetrahedral sheets sandwiching one octahedral sheet. The tetrahedra contain mostly Si (IV) as the central atom, while the octahedral sites are occupied mostly by Al (III), Fe (III) or Mg (II). The IR spectrum of the untreated Prrenjas clay is very similar to this of nontronite, an Fe-rich dioctahedral smectite clay, with Fe (III) prevailing in the octahedral positions. This can be assumed based on the appearance of the IR bands at 3565 cm-1 belonging to OH stretching in the FeFeOH group, at 818 cm-1 belonging to the Fe$_2$OH bending band and at 672 cm-1 belonging to the out of plane Fe–O vibration, which are reported from Madejova 2003 to be characteristic for nontronite. Those OH bands are present in the untreated and freeze dried Prrenjas clay samples but disappear after heating the clay up to 500 °C evidencing the dehydroxylation happening in this temperature.
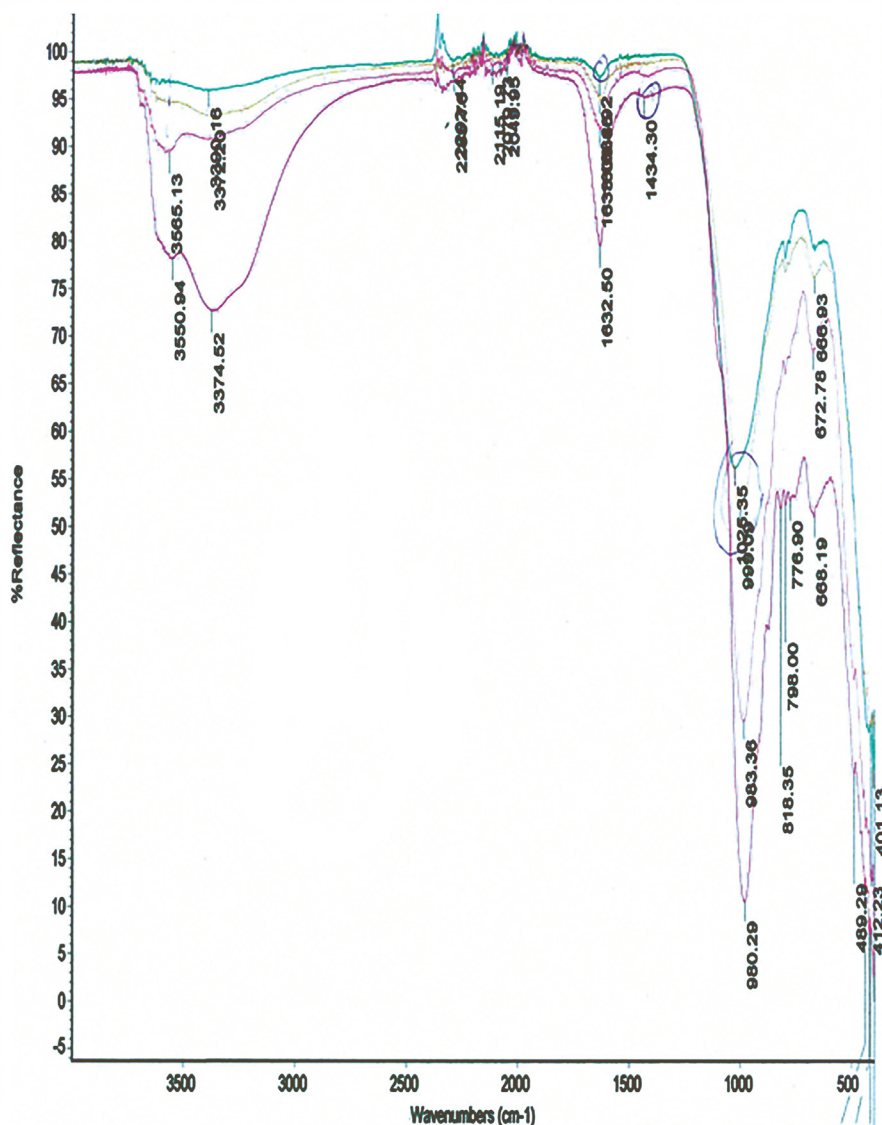

Figure 2. Infrared spectra of Prrenjas clay samples as untreated (red), after freeze-drying (purple), after heating at 500 ˚C under nitrogen (blue) and after heating at 500 ˚C under vacuum (green)

The band in the 1632.5 cm^{-1} belongs to H-O-H bending vibrations of water molecules adsorbed on montmorillonite, which diminishes drastically when compared to the freeze-dried or heated to 500 °C showing the degree of dehydration. The spectrum of the untreated and freeze dried Prrenjas clay shows a range of overlapping bands from 3550 cm^{-1} to 3695 cm^{-1} due to the OH stretching vibrations of the tructural OH groups bonded to octahedral central atoms ordered as following; Fe-Mg-OH at 3550 cm^{-1}, Al-Fe-OH at 3564 cm^{-1}, Al-Mg-OH at 3592 cm^{-1}, Al-Al-OH at 3617– – 3653 cm^{-1}, Al-Mg-OH at 3695 cm^{-1}. A broad band of hydration water is present at 3375 cm^{-1} due to the overlapping asymmetric and symmetric (H–O–H) stretching vibrations of hydrogen bonded water. A shoulder near 3260 cm^{-1} was ascribed to an overtone of the bending mode of cation hydration water. The OH structural stretching bands almost disappears after heating the clay to 500 °C, so evidencing the dehydroxylation process occurring at this temperature.

An interesting band is at 1434.30 cm^{-1} which belongs to vibrations of the CO_3^{2-}, related to some $CaCO_3$ content of the clay. This band is shown in the freeze dried clay spectrum but it disappears in the thermally treated clay spectrums because at 500 °C we have its removal as CO_2.

The most intense band is found in the 980–1040 cm^{-1}, which is attributed to the stretching vibration of the Si-O bond of the tetrahedral layers. It shows an upwards deviation of band from the untreated clay 980 cm^{-1} to the freeze dried clay at 983 cm^{-1}, heated clay at 500 °C under vacuum at 999 cm^{-1}, to heated clay at 500 °C under nitrogen at 1025 cm^{-1}. The less water is present in the clay the more is the upward deviation of the band, so showing a strong interaction of water with the oxygen atoms in the surface of the layers (oxygen of Si-O bond), resulting in high stability of inter-layer water in the clay. This fact is evidenced by the IR spectrum of freeze dried clay, which shows that in this process only the adsorbed water hydrating the inter-layer cations is removed, so the Si-O band does not deviate much.

After heating of the clay at 500 °C under vacuum, the pore volume results higher than the clay pore volume after heating under nitrogen atmosphere (see Table 1), so readsorbed inter-layer water is more in the first case and the deviation of the Si-O band from that of the untreated clay is less.
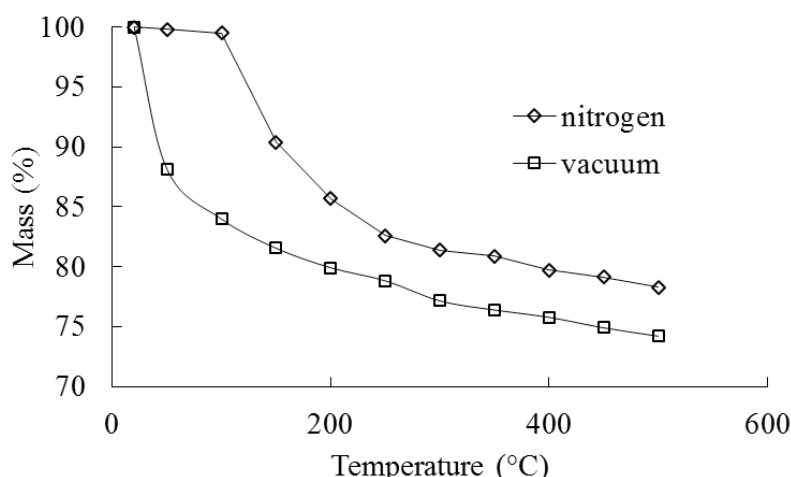

Figure 3. Change in weight of Prrenjas clay during heating from 20° C to 500° C under nitrogen atmosphere and under vacuum

Figure 3 shows the thermogravimetric analysis of the Prrenjas clay samples when heated from 20 ºC to 500 ºC under nitrogen atmosphere and under vacuum of 5 Pa. The form of the curves is similar and can be separated in two parts. From 20 ºC to 300 ºC there is an exponential decrease of the sample weight

losing around 20% of the initial weight. From 300 ºC until 500 ºC takes place a linear weight loss of the sample weight with increasing temperature. From the thermogravimetric curves constructed during the thermal activation of Prrenjas clay in the presence of nitrogen it results that the total amount of weight removed from the clay is 22.4% where 17.8% leaves at the interval 20–300 °C. From the thermogravimetric curves constructed during the thermal activation of the Prrenjas clay under vacuum it results that the total amount of weight removed from the clay is 25.5% where 20.7% leaves at the interval 20–300 °C. In the figure 4 is shown the weight loss of the Prrenjas clay sample with the time during its freeze drying process at the temperature 77 K and pressure 5 Pa. After 23 hours the sample weight doesn't change showing a loss of around 10%. During this process only partial dehydration of the clay sample takes place.
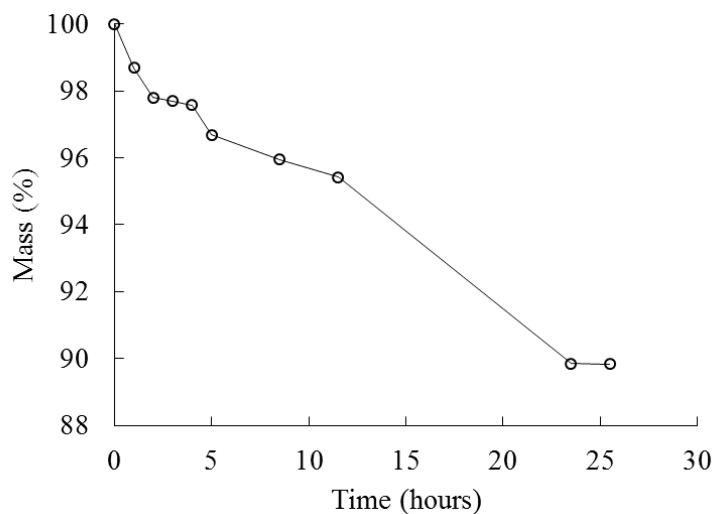

Figure 4. Change in weight during the freeze drying process of Prrenjas clay sample
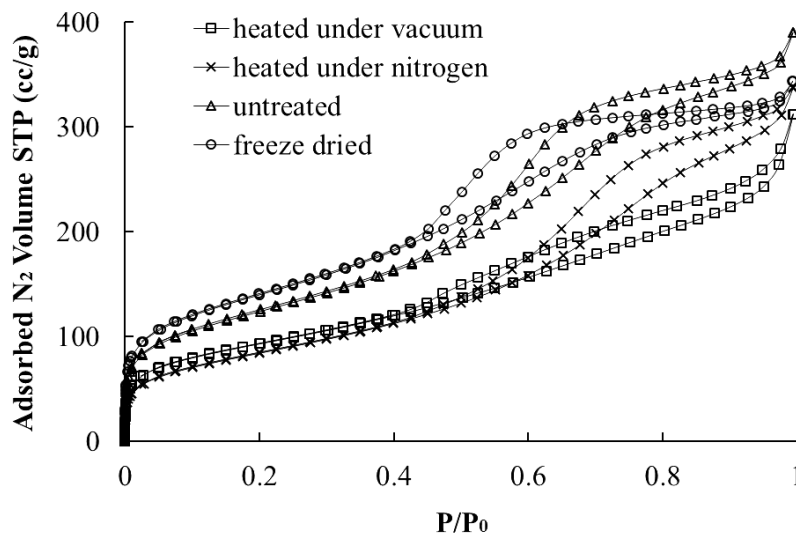

Figure 5. Adsorption – desorption isotherms of gaseous N_2 at temperature 77 K on the Prrenjas clay samples untreated and after its freeze drying, after heating to 500 ˚C under nitrogen atmosphere and after heating to 500 ˚C under vacuum

In the figure 5 are shown the adsorption-desorption isotherms of gaseous N_2 on Prrenjas clay samples as untreated, after freeze drying, after heating to 500 °C under vacuum and after heating to

500 °C under nitrogen. The specific surface and the pore volume of the samples have been determined using the BET equation [10] and the Gurwitch rule [11].

Table 1. Specific surface, pore volume and CEC of Prrenjas clay samples untreated, after freeze-drying it and after heating it up to 500 °C under nitrogen or under vacuum

Samples	Specific surface (m^2/g)	Pores volume (cm^3/kg)	CEC $(meq/100\,g)$
Untreated	124.22	98.04	103.12
Freeze-dried	126.97	139.01	100.28
Heated up 500 °C under nitrogen	92.30	103.37	80.31
Heated up 500 °C under vacuum	98.17	118.49	85.00

Clay porosity is closely related to the amount of water they contain. During dehydration, at first is removed the water of the interlayers and the water of the mesopores. While water vapor pressure decreases, the hydration state of the interlayer space changes step by step from a three-layer structure to a double-layer structure and then to a single-layer structure. So the pore volume and specific surface decreases. In the table 1 it is shown that the untreated Prrenjas clay sample has a Specific surface of 124.22 m²/g and a pore volume of 98.04 cm³/kg. When freeze dried it increases very little the specific surface and increases significantly the pore volume to 139.01 cm³/kg, because some hydration water is sublimed and the structure of the clay is preserved. When heated up to 500 °C new pores are created, but also the specific surface is decreased to 98.1 m²/g or 92.3 m²/g.

In table 1 the values of CEC for the four Prrenjas clay samples are given. CEC decreases slightly after freeze drying of the clay sample (from 103.12 meq/100 g to 100.28 meq/100 g) and significantly after heating the sample up to 500 °C under nitrogen or under vacuum 80.3 meq/100 g or 85 meq/100 g respectively. The decrease of CEC after heating in the clays is known as the Hofman-Klemen effect [12]. This effect refers to the reduction of the negative loading of the layer, the cation-exchange capacity and the increase of the loading octahedron layer with small cations such as Li $^+$, Mg^{2+}, Cu^{2+} during thermal treatment. The explanation of this effect is that the heating causes these small cations to migrate from their interlayer position to the layer structure where they became non-exchangeable.

Conclusions

The Prrenjas clay has a high content of montmorillonite type mineral and shows interesting properties as high CEC, specific surface and pore volume. For its uses in applications at temperatures up to 500 °C the physical – chemical changes during heating until that temperature were studied.

The main chemical changes happening during heating were evidenced by FTIR spectroscopy and thermogravimetry, showing that dehydration and dehydroxylation of the Prrenjas clay occurs. The weight loss of the Prrenjas clay at 500 °C is around 25%.

The surface properties, surface area, pore volume and CEC of Prrenjas clay changes after heating at this temperature. The surface area is reduced from 124.22 m²/g to 98.1 m²/g or 92.3 m²/g the pore volume is increased from 98.04 cm³/kg to 118.49 cm³/kg or 103.37 cm³/kg, and the CEC is reduced from 103.12 meq/100 g to 85 meq/100 g or 80.3 meq/100 g, depending if heating is performed under vacuum or under nitrogen atmosphere respectively.

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Orazbaeva Aysara Askarovna,

Narkhodzhayev A.Kh.,

Zakirov B. S.,

Kucharov B.Kh.

Institute of the general and inorganic chemistry AS RUz,

Tashkent, Uzbekistan,

E-mail: aysara8305@gmail.com

INTERACTION OF MONOETANOLAMINE FORMIC ACID WITH COPPER ACETATE MONOHYDRATE

Abstract: The ternary system of $COOH \cdot NH_2C_2H_4OH \cdot (CH_3COO)_2Cu \cdot H_2O \cdot$ was studied in this article. There were determined viscosity, density, refractive index and pH. It is shown that compounds with a molar ratio of components monoethanolamine formic acid: copper acetate monohydrate, equal 1:1 are formed in from molar solutions.

Keywords: physical and chemical analysis, X-ray phase analysis, thermal analysis, index of refraction, density, viscosity, pH of the medium, isomolecular series, copper acetate, monoethanolamine formic acid.

Introduction

For physical and chemical justification of process of receiving protectant on the basis of acetic and formic acids, monoethanolamine, copper carbonic, cuprous oxide, one – and two-replaced monoethanolamine acetic acid is necessary to carry out research on studying of their solubility in difficult systems. In literary data there are some sources on solubility in individual systems with the presence of the above components.

Methods and materials

Threefold system acetic acid-monoethanolamine-water was studied by isomolecular method [1] it was established that compound with acetic acid in the ratio of 1:1 are in solid state, and at a ratio of 1:2 is in liquid state. Identity of the formed compound has been proved by chemical, X-ray phase and thermal analysis methods.

When studying system of $COOH \cdot NH_2C_2H_4OH \cdot (CH_3COO)_2Cu \cdot H_2O$ researchers established that at interaction of formic acid with monoethanolamine at water solutions in molar ratios of formic acid: monoethanolamine (6:1); (6:2); (1.5:1) and (1:1) four complex compounds are formed in a liquid state [2] whose identity was proved by various methods of the chemical and physicochemical analysis. From the provided literary data it is known that the physical and chemical systems offered in our researches demand study in depth. In addition, chemism of interaction of monoethanolamine formic acid with copper acetate monohydrate isn't considered.

Hence, for physical and chemical justification of process of receiving seed disinfectant on the basis of the monoethanolamine formic acid and copper acetate monohydrate solubility in system of $COOH \cdot NH_2C_2H_4OH \cdot (CH_3COO)_2Cu \cdot H_2O$ by method of isomolecular series has been studied.

Results and discussion

Isotherms of solubility of this system on index of refraction, density, viscosity and pH at 20 °C are characterized by the inflection providing to 20.0%; 65.0% of monoethanolamine formic acid (fig. 1.), i. e. to a molar ratio of monoethanolamine formic acid: copper acetate monohydrate equal to 1:1. Appearance of one additional one essential bend on a curve of an isotherm confirms formation of the novel compound forming while interaction of the monoethanolamine formic acid with copper acetate monohydrate. On isotherms

of index of refraction at 20 °C 3 branches of crystallization are accurately overlooked. The first branch corresponds to area of solution of copper acetate monohydrate, the second is the formed complex salt $HCOOH \cdot NH_2C_2H_4OH \cdot (CH_3COO)_2Cu \cdot H_2O$ and the third is the monoethanolamine formic acid.
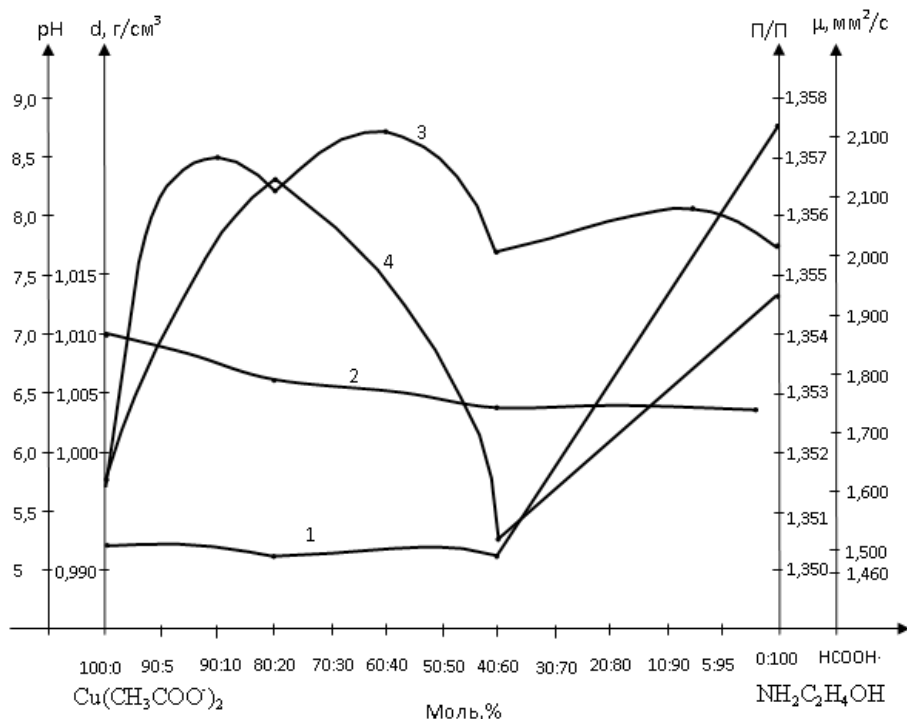
Figure1. Line chart "structure – property" of system of $COOH \cdot NH_2C_2H_4OH \cdot (CH_3COO)_2Cu \cdot H_2O$ 1 – pH; 2 – density; 3 – index of refraction; 4 – viscosity

On isotherms of density and pH indicating points of a bend are not expressed so characteristically.

Compound of monoethanolamine formic acid with copper acetate monohydrate has been obtained while interaction of monoethanolamine formic acid with crystal copper acetate monohydrate, taken in the ratios revealed when studying this system (fig. 1.) by method of isomolecular series.

In a solid state it was recovered that one complex salt of the monoethanolamine formic acid with copper acetate monohydrate in the ratio of 1:1.

Table 1.

	HCOOH	**$NH_2C_2H_4OH$**	**$(CH_3COO)_2Cu$**
It was found, mass%:	15.91	21.14	62.95.
For structure of 1:1 it was calculated, mass%	15.9	21.15	62.93

As X-ray phase analysis showed that the received compound on the basis of a monoethanolamine formic acid and copper acetate monohydrate is characterized by own values of interplanar spaces that confirms their identity (fig. 2).

The synthesized compounds on the basis of the monoethanolamine formic acid and copper acetate monohydrate in a ratio of monoethanolamine formic acid: copper acetate monohydrate equal to 1:1 it is dissolved well in water at (0 °C): 0–10.24; 20–15.0; 40–17.5, and 50–19% but it are dissolved poorly in organic solvents (toluene, benzene). Whereas, good solubility of these compounds is observed in ethyl alcohol, in acetone solubility [worsen] slightly.

On a curve of heating of a derivatogramm of the received compound (1:1) there are observed

two endothermic effects at 102, 183 °C and five exothermic effects at 283; 342; 396; 460; 720 °C (fig. 3).

The first endothermic effects can be explained by salt melting, the second (at 183 °C) correspond-

ing to decomposition of substance with loss of weight to 2.86%. However, character of the following endothermic effects at 283; 342; 396; 460 and 720 °C connected with continuation of decomposition and burning of products of a thermolysis.
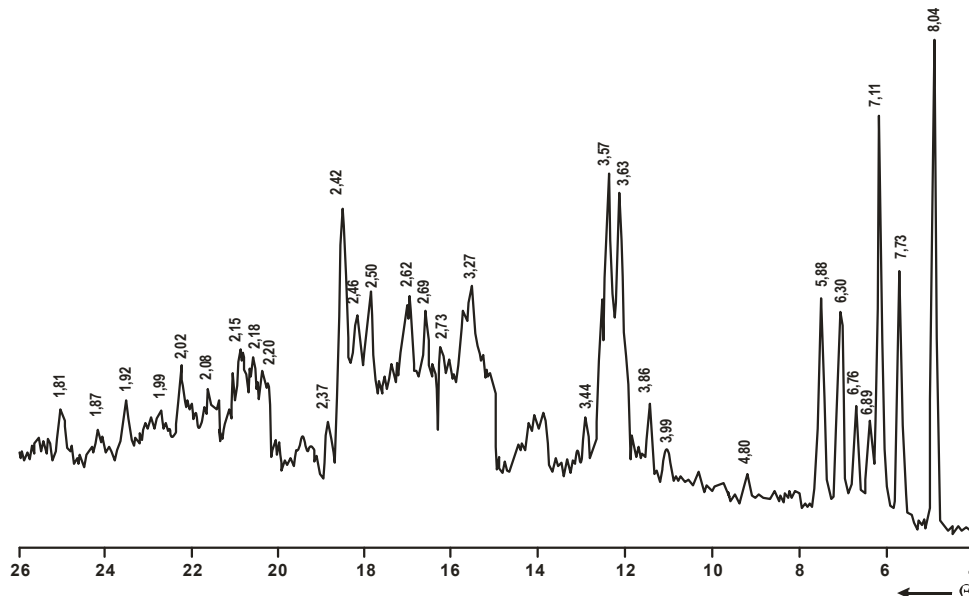

Figure 2. Roentgenogram of the monoethanolamine formic acid and copper acetate monohydrate
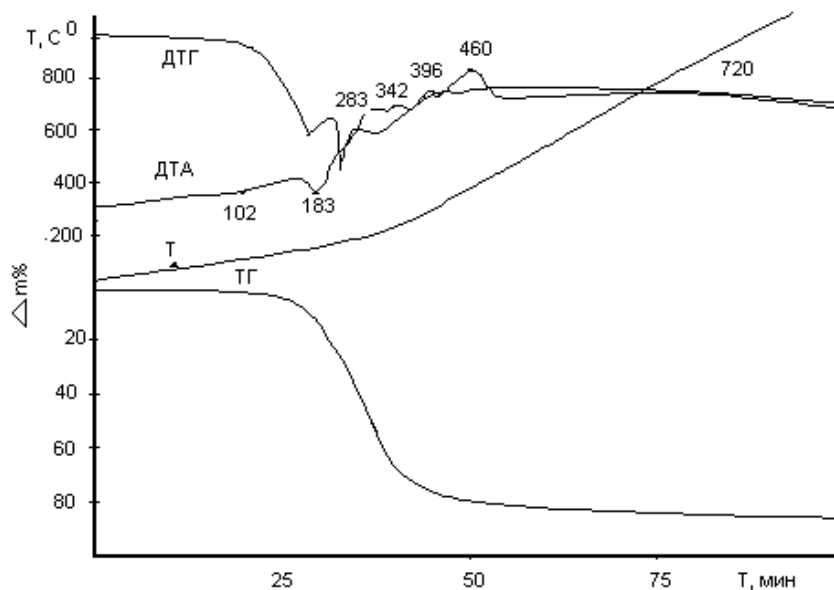

Figure 3. Thermogravimetry curve of monoethanolamine formic acid with copper acetate monohydrate.

Conclusion. Thus, the threefold system of COOH·NH$_2$C$_2$H$_4$OH·(CH$_3$COO)$_2$Cu·H$_2$O has been explored. Viscosity, density, index of refraction and pH has been measured. It is shown that compounds with a molar ratio of components of monoethanolamine formic acid: copper acetate monohydrate, equal to 1:1 in isomolecular solutions are formed.

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Tojiev Rustam,
Bobokulova Oygul,
Mirzalulov Kholtura,
Tashkent chemical technological institute
E-mail: bobokulova79@mail.ru

USE DISTILLER LIQUID FOR CLEARING OF LEACHS OF LAKES KARAUMBET AND BARSAKELMES FROM SULFATES

Abstract: Clearing processes leachs of lakes Karaumbet and Barsakelmes from sulphates with use of a withdrawal of manufacture soda ash – distiller liquids are investigated. Influence of duration of process, temperatures and norms of distiller liquids on structure changes leach and degree of sedimentation of sulphates is revealed**.**

Keywords: leach, bischofite, distiller liquid, sodium chloride, magnesium chloride, ions of sulfate.

Introduction. Priority problem of development of economy of Uzbekistan is development and release import substitution production on the basis of local mineral resources. One of such products is bischofite or magnesium chloride.

Magnesium chloride is used in chemical, easy, a power industry, in building, medicine, metallurgy and other branches of a national economy. Unfortunately, for the present moment manufacture bischofite in Republic is absent. The requirement for it is satisfied only at the expense of import that is connected with huge expenses of currency.

Therefore development of raw sources of salts of magnesium and carrying out of researches on their involving in industrial production are an actual problem.

The work purpose is influence studying distiller liquids – a withdrawal of soda factory on a chemical compound and degree desulfanation leachs of lakes Karaumbet and Barsakelmes, as most comprehensible sources of raw materials for manufacture bischofite and located in Republic Karakalpakstan.

The basic components leachs of salt mines of Karaumbet and Barsakelmes are cations of sodium, magnesium, anions of chlorine and sulphates [1–3]. Calcium, iron practically are absent. Salt contents in leach makes 30–40%. In leach of lakes Karaumbet contents NaCl fluctuates from 16.8 to 22.7%; $MgSO_4$ – from 5.2 to 8.3%, $MgCl_2$ – from 6.2 to 8.3%. Leach of deposits Barsakelmes contains from 18.8 to 29.0% NaCl, from 1.8 to 4.7% $MgSO_4$ and from 1.2 to 7.1% $MgCl_2$. Total salt contents of leach Karaumbet approximately in 1.2 times above, than leach of Barsakelmes, but thus contents NaCl on 4–5% more low.

Presence at structure leach sulphate of ions interferes with its direct use for allocation of magnesium chloride. Therefore, one of use ways leach for reception bischofite is disposal of sulphates.

Objects and methods: Researches on desulfanation leach of lakes Karaumbet and Barsakelmes spent with distiller liquid.

In work used of lakes Karaumbet, Barsakelmes and distiller liquid of UE «Kungrad soda factory» which structure is resulted in table 1.

Norm distiller liquid counted proceeding from parity SO_4^{2-}/Ca^{2+}. Chemical and mineralogical structure of leach, distiller liquid and products of desulfanation established known methods of the chemical analysis [4–6].

Table 1. – Chemical contents leachs of likes Karaumbet, Barsakelmes and distiller liquid

| The name	Ionic structure, weights %					Salt structure, weights %			
	Na^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	$MgCl_2$	$NaCl$	$CaCl_2$	$MgSO_4$
Leach of lake Karaumbet	8.01	3.25	0.02	17.53	6.66	6.28	20.37	0.05	8.33
Leach of lake Karaumbet after summer corfs	8.40	5.70	0.06	25.94	4.25	17.41	21.37	0.20	5.41
Leach of lake Barsakelmes	9.06	1.64	0.01	17.07	2.34	4.13	23.05	0.03	2.54
Distiller liquid	2.18	0.007	3.03	8.74	0.03	0.00	5.54	8.41	0.04

Researches on desulfanation leachs of lakes Karaumbet and Barsakelmes with distiller liquid spent on the laboratory installation consisting of a glass reactor, placed in the thermostat, and supplied with a mixer. Speed of rotation of the electric motor of a mixer regulated a rheostat.

Influence of duration of process, temperatures and norms of distiller liquid on a chemical compound and degree desulfanation of leachs is studied.

Results of researches of influence of duration of process and temperature on ionic and a chemical compound, on degree desulfanation of leach are presented in table 2.

The analysis of data of table 2 shows, that with increase in duration of process from 5 till 20 minutes at temperature 20 °C degree desulfanation considerably raises. Through 5 mines it makes 58.37%, and through 20 mines reaches 88.59% and through 30 mines makes 89.80%. The further increase in duration process till 180 minutes does not lead to essential increase in degree desulfanation. This results from the fact that reaction of interaction SO_4^2 – anions and Ca^{2+} – cations occurs within 20 minutes and thus about 90% of ions SO_4^2 – and Ca^2 + react with formation of dehydrate calcium sulphate on reaction:

$$CaCl_2 + Na_2SO_4 (MgSO_4) + nH_2O =$$
$$= CaSO_4 \cdot 2H_2O + 2NaCl (MgCl_2 \cdot 6 H_2O).$$
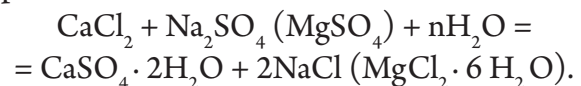
The part dehydrate calcium sulphate remains in a brine because of its small solubility and consequently degree desulfanation does not exceed 90% at duration of process desulfanation 30–60 minutes.

With increase in temperature degree desulfanation slightly decreases. At temperature 20, 40 and 60 C degree desulfanation of leach makes through 5 mines – 58.9; 54.13 and 50.88%, through 30 mines – 89.80; 84.50 and 78.27% and through 60 mines – 90.33; 85.40 and 79.21%, accordingly.

Table 2. – Influence of duration of process and temperature on structure and degree desulfanation leachs of lakes Karaumbet at norm distiller liquid 100%

Time, mines	Ionic structure l. f., weights %					Salt structure l. f., weights %				$\gamma_{SO_4^{2-}}$, % отн.
	Na^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	$MgCl_2$	$NaCl$	$CaCl_2$	$MgSO_4$	
1	2	3	4	5	6	7	8	9	10	11
Temperature of desulfanation 20 °C										
5	5.67	2.33	0.40	15.24	0.96	8.27	14.43	1.12	1.20	58.37
10	5.72	2.35	0.22	15.36	0.52	8.79	14.55	0.60	0.65	77.85
15	5.74	2.36	0.14	15.41	0.34	8.99	14.60	0.40	0.42	85.49
20	5.75	2.36	0.11	15.43	0.27	9.08	14.62	0.32	0.33	88.59
30	5.75	2.36	0.10	15.44	0.24	9.11	14.62	0.28	0.30	89.80
60	5.75	2.36	0.10	15.44	0.23	9.13	14.63	0.27	0.28	90.33

1	2	3	4	5	6	7	8	9	10	11
180	5.75	2.36	0.09	15.45	0.22	9.14	14.63	0.26	0.27	90.81
Temperature of desulfanation 40° C										
5	5.67	2.33	0.44	15.22	104	8.18	14.41	1.21	1.30	54.93
10	5.71	2.35	0.25	15.34	0.60	8.69	14.53	0.71	0.76	74.07
15	5.73	2.35	0.19	15.38	0.46	8.85	14.56	0.54	0.58	80.27
20	5.73	2.35	0.17	15.40	0.40	8.93	14.58	0.46	0.49	83.08
30	5.74	2.36	0.15	15.41	0.36	8.97	14.59	0.43	0.45	84.50
60	5.74	2.36	0.14	15.41	0.34	8.99	14.60	0.40	0.43	85.40
180	5.74	2.36	0.14	15.42	0.33	9.01	14.60	0.38	0.41	86.07
Temperature of desulfanation 60° C										
5	5.66	2.32	0.47	15.19	1.13	8.08	14.39	1.32	1.42	50.88
10	5.68	2.33	0.37	15.26	0.87	8.38	14.46	1.02	1.09	62.36
15	5.70	2.34	0.29	15.32	0.69	8.59	14.50	0.80	0.86	70.45
20	5.71	2.35	0.25	15.34	0.60	8.70	14.53	0.69	0.74	74.46
30	5.72	2.35	0.21	15.37	0.51	8.80	14.55	0.59	0.63	78.27
60	5.72	2.35	0.20	15.37	0.49	8.83	14.56	0.57	0.61	79.21
180	5.72	2.35	0.20	15.38	0.47	8.84	14.56	0.55	0.59	79.79

Apparently from the table, with increase in duration of process the contents of ions of calcium in a liquid phase decreases. At 20 C in 5, 30 and 60 minutes the contents of ions of calcium in a liquid phase makes 0.40; 0.10 and 0.10% accordingly, and at temperature 60 C decrease till 0.47; 0.21 and 0.20%, accordingly. This results from the fact that with temperature increase solubility dehydrate sulphate of calcium increases and, accordingly, its contents in a liquid phase increases.

Table 3. – Norm of influence distiller liquid on structure and degree desulfanation of leach of lakes Karaumbet and Barsakelmes at temperature 20 ℃ and durations of process of 30 minutes.

Norm, ratio.%	Ionic structure ж. ф., weights %					Salt structure ж. ф., weights %				$\gamma_{SO_4^{2-}}$, % отн.
	Na^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	$MgCl_2$	NaCl	$CaCl_2$	$MgSO_4$	
1	2	3	4	5	6	7	8	9	10	11
Leach of like Karaumbet										
75	5.80	1.99	0.15	14.36	1.37	6.51	14.75	0.40	1.71	67.10
90	5.65	1.80	0.13	14.21	1.24	6.69	14.20	0.36	1.22	80.00
100	5.43	1.77	0.12	13.86	0.29	6.72	13.82	0.34	0.36	92.30
105	5.36	1.73	0.15	13.75	0.18	6.66	13.63	0.43	0.23	95.00
110	5.29	1.69	0.21	13.64	0.14	6.54	13.44	0.58	0.18	96.00
Leach of likes Karaumbet after flight corfs										
75	6.15	4.18	0.30	23.82	1.46	14.94	15.64	0.84	1.83	51.06
90	5.85	3.97	0.21	23.53	0.76	14.35	14.88	0.58	1.53	61.27

1	2	3	4	5	6	7	8	9	10	11
100	5.66	3.84	0.13	23.35	0.30	14.75	14.40	0.35	0.37	89.28
105	5.56	3.78	0.15	23.26	0.22	14.60	14.14	0.42	0.28	91.84
110	5.48	3.72	0.19	23.18	0.20	14.39	13.94	0.54	0.24	92.69
Leach of like Barsakelmes										
75	7.55	1.37	0.26	19.68	1.25	4.13	19.20	0.73	1.56	50.03
90	7.31	1.32	0.06	20.11	0.41	4.77	18.59	0.18	0.51	83.14
100	7.15	1.29	0.10	20.37	0.24	4.82	18.19	0.28	0.30	89.80
105	7.08	1.28	0.13	20.50	0.19	4.83	18.01	0.36	0.24	91.60
110	7.00	1.27	0.17	20.63	0.17	4.81	17.80	0.46	0.21	92.50
125	6.79	1.23	0.28	20.99	0.13	4.68	17.29	0.78	0.17	93.84
150	6.47	1.17	0.46	21.55	0.09	4.51	16.46	1.27	0.11	95.56

Optimum conditions of process desulfanation leach of lake Karaumbet with distiller liquid are duration of process of 20–30 mines and temperature 20–30 °C. Results of researches of influence of norm of ions of calcium and process temperature desulfanation of leach of lake Karaumbet on ionic and salt structure of a liquid phase, and also degree desulfanation of are presented in tables 3–5.

Optimum conditions of process desulfanation leach of lake Karaumbet with distiller liquid are duration of process of 20–30 mines and temperature 20–30 °C. Results of researches of influence of norm of ions of calcium and process temperature desulfanation leach of lakes Karaumbet on ionic and salt structure of a liquid phase, and also degree desulfonation are presented in tables 3–5.

Table 4. – Norm of influence distiller liquid on structure and degree desulfanation leachs of lakes Karaumbet and Barsakelmes at temperature 40 ˚C and durations of process of 30 minutes

Norm, ratio.%	Ionic structure ж. ф., weights %					Salt structure ж. ф., weights %				$\gamma_{SO_4^{2-}}$, % отн.
	Na^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	$MgCl_2$	NaCl	$CaCl_2$	$MgSO_4$	
1	2	3	4	5	6	7	8	9	10	11
Leach of like Karaumbet										
75	5.77	1.98	0.25	14.29	1.60	6.24	14.69	0.68	2.01	61.24
90	5.55	1.81	0.24	14.00	0.97	6.35	14.12	0.66	0.94	73.49
100	5.41	1.76	0.23	13.80	0.55	6.42	13.75	0.65	0.68	85.14
105	5.34	1.72	0.25	13.70	0.42	6.39	13.57	0.71	0.53	88.34
110	5.26	1.68	0.31	13.58	0.38	6.27	13.39	0.86	0.48	89.19
Leach of like Karaumbet after summer corfs										
75	6.12	4.15	0.33	23.70	1.25	14.68	14.00	1.42	2.01	46.56
90	5.76	3.97	0.25	23.41	0.65	14.21	14.26	0.69	1.71	55.87
100	5.52	3.94	0.19	23.23	0.25	15.13	13.80	0.66	0.40	81.47
105	5.12	3.76	0.20	23.14	0.18	14.51	13.55	0.71	0.30	83.81
110	4.97	3.70	0.24	23.08	0.17	14.30	13.36	0.91	0.26	84.58
Leach of like Barsakelmes										
75	7.41	1.36	0.43	19.58	1.6	3.53	19.58	1.16	2.27	46.32
90	7.27	1.31	0.10	20.01	0.52	4.56	18.96	0.20	0.73	77.00

1	2	3	4	5	6	7	8	9	10	11
100	7.11	1.28	0.16	20.27	0.24	4.80	18.92	0.44	0.43	83.14
105	7.04	1.27	0.21	20.40	0.21	4.71	18.37	0.57	0.34	84.81
110	6.99	1.26	0.28	20.53	0.16	4.70	18.15	0.73	0.30	85.64

The analysis of data of table 3 shows, that at desulfanation with norm increase distiller liquid from 75% to 100% degree desulfanation raises on 39.9%, and with the further increase in norm from 100 to 150% degree desulfanation increases only on 5.76%. Besides, the norm increase distiller liquid more than 100% leads to appreciable increase in the contents of ions calcium in a liquid phase leach, i. e. the contents of calcium chloride increases.

The same law of change of degree desulfanation and contents of ions Ca^{2+} depending on norm distiller liquid and temperatures remains in results of experiments with leachs of lakes Karaumbet and Barsaqelmes.

Apparently from tables 3–5 with temperature increase degree desulfanation at the expense of increase in solubility of calcium sulphate monotonously decreases.

Table 5. – Norm of influence distiller liquid on structure and degree desulfonation leachs of lakes Karaumbet and Barsakelmes at temperature 60 ˚C and durations of process of 30 minutes

Norm, ratio%	Ionic structure ж. ф., weights %					Salt structure ж. ф., weights %				$\gamma_{SO_4^{2-}}$, % отн.
	Na^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	$MgCl_2$	NaCl	$CaCl_2$	$MgSO_4$	
1	2	3	4	5	6	7	8	9	10	11
Leach of like Karaumbet										
75	5.75	1.97	0.35	14.23	1.86	5.95	14.62	0.98	2.32	54.91
100	5.38	1.75	0.36	13.72	0.85	6.09	13.68	0.99	1.06	76.93
105	5.31	1.71	0.37	13.63	0.70	6.08	13.50	1.03	0.88	80.34
110	5.24	1.67	0.41	13.52	0.64	5.99	13.32	1.15	0.80	81.83
Leach of like Karaumbet after summer corfs										
75	4.32	2.27	0.34	18.26	1.20	7.36	13.61	0.96	1.95	47.64
90	5.66	2.28	0.28	18.36	0.50	7.63	13.92	0.78	1.65	57.17
100	4.37	2.29	0.26	18.45	0.53	8.38	13.75	0.71	0.76	77.84
105	4.37	2.29	0.27	18.48	0.46	8.48	13.77	0.74	0.63	81.30
110	4.37	2.30	0.31	18.49	0.41	8.60	13.78	0.85	0.58	82.45
Leach of like Barsakelmes										
75	5.65	2.30	0.78	15.11	1.33	7.38	14.67	2.04	2.06	47.11
90	5.62	2.31	0.61	15.18	1.10	7.82	14.74	1.14	1.56	62.36
100	5.60	2.32	0.48	15.24	0.80	8.11	14.80	1.24	1.24	65.23
105	5.61	2.33	0.41	15.26	0.70	8.32	14.82	1.07	1.03	69.00
110	5.62	2.33	0.35	15.29	0.67	8.44	14.84	0.91	0.88	72.47

The conclusion. The carried out researches have shown basic possibility of use distiller liquid UE «Kungrad soda factory» for desulfanation leachs of lakes Karaumbet and Barsakelmes. Optimum conditions of process desulfonation leachs of lakes Karaumbet and Barsakelmes are temperature 20–30 °C, norm of distiller liquid 100–105%, durations of process of 30 minutes. Thus the contents of sulphates in

desulfanation leach makes 0.29–0.85%, and calcium of 0.12–0.15%. For reception of purer solutions pre- liminary desulfanation leach it is necessary to subject to deep clearing of sulphates and calcium.

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Shukurov Jamshid Sultonovich,
Candidate of Science (PhD) in Technics
E-mail: kumush1984@mail.ru

Askarova Mamura Komilovna,
Candidate of Science (PhD) in Chemistry

Tukhtaev Saiydiaxral,
Doctor of Science, academician,
Institute of General and Inorganic Chemistry
of the Academy of Sciences
of the Republic of Uzbekistan

THE SOLUBILITY OF COMPONENTS IN THE SYSTEM $NaClO_3 \cdot CO(NH_2)_2$ – C_2H_5OH–H_2O

Abstract: We studied the solubility of components in the system $NaClO_3 \cdot CO(NH_2)_2 - C_2H_5OH - H_2O$ visual – polythermal method in a wide temperature range. On the phase diagram delimited fields of crystallization: ice, urea, monourea of chlorate of sodium, two water and one aqueous ethanol. In the system under study is no formation of new chemical compounds. The system is simple atonicescom type.

Keywords: defoliant, monourea of chlorate of sodium, mutual system, the crystallization temperature, ethanol.

Introduction. The development of highly efficient and mild on plants of domestic products is an important problem of intensification of agriculture in our Republic.

For pre-harvest removal of leaves, cotton, seed crops, beans, potatoes, sunflower seeds and rice are used special substances – defoliants, causing defoliation of plants. Timely use of defoliants provides as an accelerator of fruit ripening food plants for pre-harvest removal of foliage of potatoes and other vegetable and melon crops, drying of seeds of sunflower, rice, lupine, beans, soybean, planting of sugar beet and etc. [1–4] for the preparation of plants to mechanical harvesting of the accumulated harvest.

With the aim of physico – chemical substantiation of the process of obtaining effective, "soft" acting defoliant on the basis of monourea of chlorate of sodium and ethanol [5], we studied the interaction of the above components in the system $NaClO_3 \cdot CO(NH_2)_2 - C_2H_5OH - H_2O$.

As starting substances used $NaClO_3 \cdot CO(NH_2)_2$ synthesized by introducing a melt of urea sodium chlorate in a molar ratio of 1:1. After the formation of a homogeneous melt of the components cooled isolated crystals of the compound $NaClO_3 \cdot CO(NH_2)_2$. System $NaClO_3 \cdot CO(NH_2)_2 - H_2O$ studied in the temperature range from complete freezing to –33,0° C and 100° C (Fig. 1).

Polythermal diagram it is characterized by the presence of the three branches of crystallization: ice $CO(NH_2)_2$ and $NaClO_3 \cdot CO(NH_2)_2$, which intersect at two double points. The first of them corresponds to joint crystallization of ice and $CO(NH_2)_2$ at a temperature of –33,0° C and concentration 61,0% $NaClO_3 \cdot CO(NH_2)_2$, 39,0% H_2O. Second double point meets the joint crystallization of $CO(NH_2)_2$ and $NaClO_3 \cdot CO(NH_2)_2$ at a temperature of 37,2° C, concentration of 67,5% $NaClO_3 \cdot CO(NH_2)_2$, 32,5% H_2O.

The study of the solubility of the binary system ethanol – water showed that the chart delineates four branches of crystallization: ice, $C_2H_5OH \cdot 2H_2O$, $C_2H_5OH \cdot H_2O$, and C_2H_5OH. Our results for this system agree well with the known published materials [6].
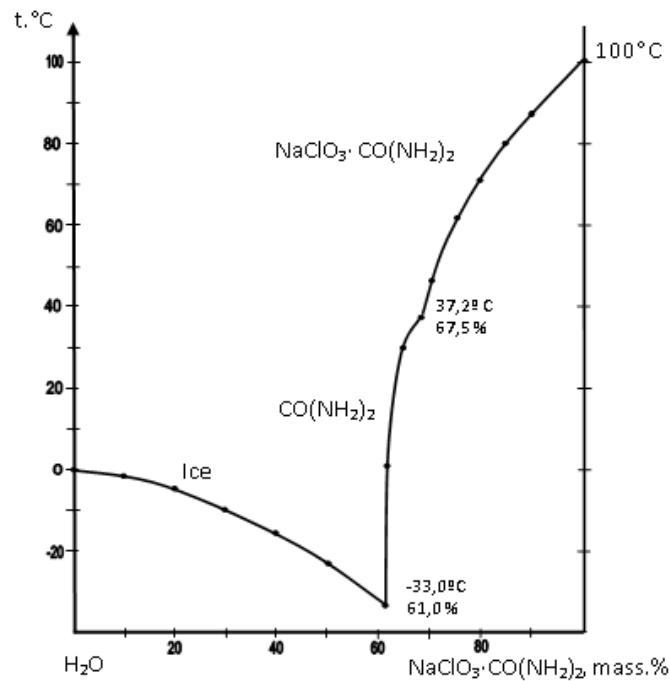

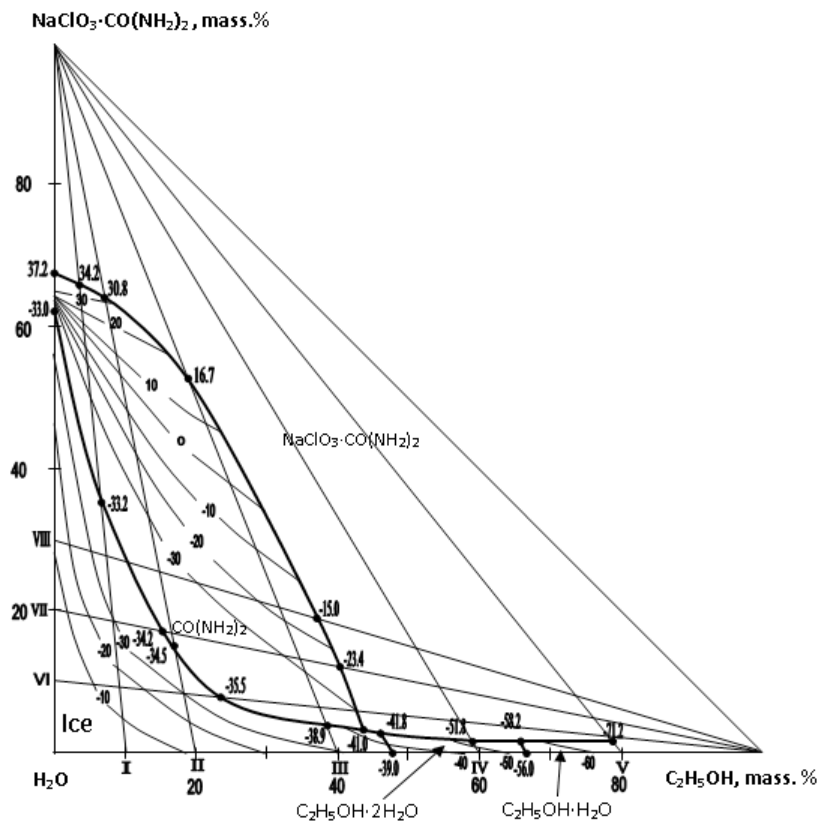Figure 1. Solubility diagram of the system $NaClO_3 \cdot CO(NH_2)_2 - H_2O$

Figure 2. Polythermal solubility diagram of the components in the system

System $NaClO_3 \cdot CO(NH_2)_2 - C_2H_5OH - H_2O$ studied the visual – polythermal method with the help of eight internal cross section. The I–V breakdown investigated by $C_2H_5OH - H_2O$ to the top of $NaClO_3 \cdot CO(NH_2)_2$, VI–VIII sections from the $NaClO_3 \cdot CO(NH_2)_2 - H_2O$ to the top of C_2H_5OH. Based on polytherm binary systems and internal sections built polythermal solubility diagram from –71,2 to 37,2 °C (Fig.2).

$NaClO_3 \cdot CO(NH_2)_2 - C_2H_5OH - H_2O$

On the phase diagram of the system state demarcated the field of crystallization of ice, urea, monourea of chlorate of sodium, two water and one ethanol aqueous ethanol.

These crystallization fields converge in three triple nonvariant points in the system that have the compositions of equilibrium solutions and corresponding crystallization temperature (table 1).

Table 1. – Double and triple point system NaClO · CO (NH₂)₂ – C₂H₅OH – H₂O

The composition of the liquid phase%			T_{cr}. °C	Solid phase
$NaClO_3 \cdot CO(NH_2)_2$	C_2H_5OH	H_2O		
67.5	–	32.5	37.2	$NaClO_3 \cdot CO(NH_2)_2 + CO(NH_2)_2$
66.2	3.7	30.1	34.2	
64.1	7.2	28.7	30.8	
52.8	18.8	28.4	16.7	
19.2	27.2	53.6	–15.0	
12.0	40.3	47.7	–23.4	
5.8	42.8	51.4	–33.5	
2.8	44.1	53.1	–41.0	Ice + $NaClO_3 \cdot CO(NH_2)_2 + CO(NH_2)_2$
61.0	–	39.0	–33.0	Ice + $CO(NH_2)_2$
34.9	6.8	58.3	–33.2	
27.2	9.8	63.0	–33.6	
16.8	15.8	67.4	–34.2	
14.6	17.2	68.2	–34.5	
7.8	23.8	68.4	–35.5	
3.9	38.5	57.6	–38.9	
–	47.8	52.2	–39.0	Ice + $C_2H_5OH \cdot 2H_2O$
2.6	46.2	51.2	–41.8	Ice + NaClO3·CO(NH2)2+ C2H5OH·2H2O
1.8	59.2	39.0	–51.8	$NaClO_3 \cdot CO(NH_2)_2 + C_2H_5OH \cdot 2H_2O$
1.4	66.2	32.4	–58.2	$NaClO_3 \cdot CO(NH_2)_2 + C_2H_5OH \cdot 2H_2O + C_2H_5OH \cdot H_2O$
–	67.0	33.0	–56.0	$C_2H_5OH \cdot 2H_2O + C_2H_5OH \cdot H_2O$
0.8	79.1	20.1	–71.2	

On the polythermal solubility diagram of every 10ºC isotherm applied. Built the projection of the polythermal solubility curves on the corresponding side of the waterside of the system. In the system of $NaClO_3 \cdot CO(NH_2)_2 - C_2H_5OH - H_2O$ the formation of the new connection fails.

In the studied temperature and concentration, range in the system is observed salting-out the effects of the components on each other. With increasing concentration of ethanol in the system, it salting-out effect on monourea of chlorate of sodium increases.

In the temperature range $-41.0 \div 37.2\,°C$, there is a joint crystallization of monourea of chlorate of sodium with urea. Urea, together crystallization with ice at temperatures $-33.0 \div -41.0\,°C$. the Two aqueous ethanol crystallization together with ice in the temperature range $-39,0 \div -41,8\,°C$ and in the temperature range $-56,0 \div -58,2\,°C$ together with one water ethanol.

The results of the studied systems indicate the possibility of obtaining a defoliant by joint dissolution of the original components.

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