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Section 1. Astronautics

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CONSTRUCTION OF SPECTRAL CURVES ACCORDING TO THE DATA OF THE WORLDVIEW2 SATELLITE AND ANALYSIS ON THEIR BASIS OF SPECTRAL REFLECTANCE OF SALINE SOILS

Abstract: The work presents the results of spectral analysis of soils and vegetation cover on the territories of Kura-Araks lowland with deferent salinization degree. Generalized spectral curves are constructed based on the processing of eight-channel image from the WorldView2 satellite and the selection of test sections of soils and vegetation cover on sections of different salinization degree. It is shown that the run of curves of saline soils and vegetation vary greatly in the wavelength range 660–900 nm, and the spectral reflectance of vegetation is much higher than in saline soils.

Keywords: spectral reflectance, run of spectral curves, spectral properties of soil and vegetation on saline lands.

Introduction

Analyzing the materials on soil salinization of Kura-Araks lowland, it can be noted that the history of salt accumulation in the lowland is most closely connected with the Quaternary history of the Caspian Sea. Conical and deluvial-proluvial salinization is developed within the sloping plains, and alluvial salinization — within the lowland areas. Summarizing the considerations about the sources of salts, ways of their migration, it is suggested that nowadays salt masses come with river waters due to primary weathering processes. It is also indicated that the main source of salts in Kura-Araks lowland is salts of secondary migration cycles. These are salts that accumulate under lagoon and coastal-marine concentrations, beginning from the upper Sarmatian stage till the modern coastal-marine accumulation [1; 2; 3; 4; 5; 6].

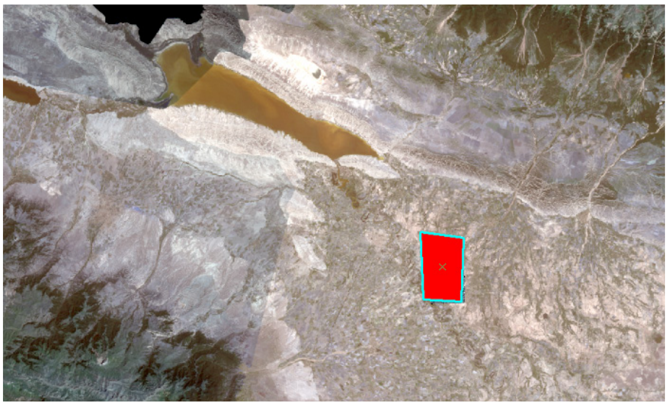

Figure1.Examined territory (red contour)

Undoubtedly, the methods of melioration measures will have fundamental differences for each genetic form of salinization, among which the most common forms in the Kura-Araks lowland are deluvial, conical and alluvial. Melioration methods in the republic are mainly developed for these salinization forms and there are sufficient research materials and design studies on them [3; 5]. Hence the interest in solving environmental monitoring tasks of soil salinization processes and their propagation by aerospace monitoring methods is fully justified.

The investigated territory is a pilot territory on one section of the Kura-Araks lowland (figure 1). The capabilities of the WorldView-2 satellite with ultra-high spatial resolution are considered in this paper. One of the main technical characteristics of the WorldView-2 satellite (it captures images with a resolution of 0.5 m in panchromatic mode and 2 m in the multispectral mode) is that apart from four traditional spectral channels (red, green, blue and near infrared-1), *WorldView-2* spectrometer includes the following additional channels: violet (or coastal blue), yellow (yellow edge), "red edge", near infrared-2 (NIR2) (figure 2) [13].

Eight spectral channels make it possible to implement three main advantages: increase of the decoding accuracy, a high level of detalization and new unique opportunities for extraction of necessary information.

Research methodology

The task of detecting the soils that become salty is one of the most important in the process of remote soil-melioration researches. The degree and type of soil salinization, the direction of salinization change of rocks, salt reserves, causes of salinization are estimated when monitoring the salt regime of irrigated soils [1,5,8]. Salinization of soils is detected by remote methods as in direct appearance of salts on soil surface, as well as in the change of reflectance of crop plants as a result of extinction of individual plants, their suppression and appearance of halophytic weeds. These phenomena change the tone and pattern of the image of saline soils massifs. Such studies were widely conducted on irrigated lands in the basins of the Amu Darya and Syr Darya [7; 9; 11].

The presence of salts in the soil in most cases helps to increase the level of light reflection by soils [15; 16; 17]. However, in real natural conditions the presence of these substances can change other properties of soils, and, consequently, indirectly influence the coloring. For example, hygroscopic salts such as magnesium and calcium chlorides cause moisture absorption and thereby contribute to the increase of soil moisture. Consequently, when such salts are present, the soil has a darker color, not a lighter one [16; 19]. The influence of carbonates, as a rule, is reduced to a linear increase of the soil reflection coefficient with the growth of salt content in soils, the area and dimensions of which are determined by the instrument resolution. Therefore, the measured indicator of soil spectral brightness is already an averaged value. A special feature of the spectral information of additional channels is the red edge channel (705–745 nm,), where, as we see in the image (figure 2), it is possible to detect the suppressed vegetation by decrease of the reflectance in this channel.

On the basis of properties of 8-channel satellite, the research methodology consisting of several stages is proposed in this work:

1. Spectral analysis of soils by a space image *WordView2*;
2. Calculation of spectral parameters and construction of spectral curves in 8 channels of the satellite;
3. Comparison of spectral curves of soils with different salinization degrees and spectral curves of vegetation that grow on saline and non-saline soils;

The spectral analysis was carried out using the software ENVI version 5.2.

A visual analysis of spectral channels with the aim of selecting the optimal combination of channels identified the following optimal combinations for selection of soils with different salinization degrees: the combination of channels: 7,5,3, and 7,3,2 provide good contrast of vegetation and soils of different types, a combination of channels 8,7,6 is very different from other combinations, as it mainly indicates the content of water in soils, and, finally, the combination of channels 8,4,1 shows the greatest contrast in soils of different salinization and humidity, as well as vegetation.

Study of spectral curves of soils and vegetation on lands with different salinization degree according to the data of WorldView-2 satellite

Fundamental researches on spectrometry were carried out by E. L. Krinov as far back as in the 1940 s. Having laid the foundation for works on the optics of landscapes, he developed the first spectrometric classification, which eventually became classical. The largest amount of experimental data was obtained on the spectral brightness in the visible range. Apart from integral reflection, the reflection maximum and minimum values are sometimes calculated, and also the inflection points of spectral curve are determined, for which purpose we calculated the first derivative $d\rho/d\lambda$ and determined wavelengths that correspond to extremum points of the function $\rho=f(\lambda)$, *where* λ — wavelength of electromagnetic spectrum (EM), ρ — spectral reflectance of Earth's surface objects [17].

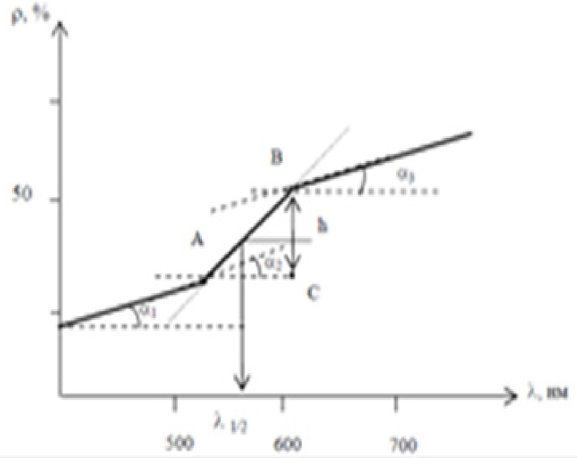

Figure 2. Base values

The system of basic indicators of soil spectral reflectance, proposed in 1995 by Orlov and co-authors, includes the following indicators (figure 2) [15; 17]:

- spectral reflectance coefficient at $\lambda=750$nm, ρ_{750};
- reflection coefficient — ρ_e;
- absolute value of the inflection located in the middle part of the spectral curve, $\Delta\rho = \rho_{650} - \rho_{480}$;
- Height of inflection;
- Location of inflection (length of wave of semi-inflection), $\lambda_{1\backslash 2}$;
- The angle of the spectral curve slope and its individual sections.

The method for diagnostics of soil cover according to remote data includes the conduct of a space survey, collection of thematic cartographic materials and conduct of selective ground-based studies, and also a multi-zone survey in three channels of visible and near infrared subspectra is performed with the aim of increasing the effectiveness of decoding. The obtained results are processed by the cluster analysis method, on the basis of which the soil map is compiled [4; 8; 9; 11; 12; 15; 17; 19].

Unlike the survey in the visible and infrared zone, this work analyzes spectral curves of 8 channel WorldView-2 satellite.

Spectral curves and histograms were constructed along the examined territory using the software package ENVI 5.2, and also spectral characteristics such as average value, maximum and minimum values, scatter of brightness values within the selected test fragments of soils with different salinization degree and vegetation were calculated. The enumerated spectral characteristics and curves for each selected test fragment are given in the table 1 and table 2. Then a comparative analysis of the obtained curves and curves from early studies was made [5; 6; 8; 9].

Tables 1 and 2 demonstrate fragments of the image, where we selected test sections with different soil salinization and sections of saline lands covered with vegetation respectively and their spectral curves, obtained using the software package ENVI 5.2. According to spectral curves, extreme points in the behavior of curves of spectral reflectance of saline soils and vegetation cover are points with wavelengths: 400 nm, 480 nm, 510 nm, 610 nm, 660 nm, 720 nm, 830 nm (Fig. 4, 5, 6, 7). The values of spectral reflectance of soils at these points differ depending on the salinization degree, humidity, salinization type and wavelength. The properties of soils were analyzed on the basis of ground-based measurements and literature sources [1; 2; 4; 8; 11; 12; 13; 14; 18].

Spectral analysis of soils with different salinization degree

Test fragments were taken on the territory of solonchaks (1, 2 fragments in table 1), solonchak soils covered with a small percentage of halophyte vegetation (fragment 3), in areas that were former cultivated, but highly saline (fragment 5), and also in soils on vegetable plots (fragment 4). Fragments of vegetation cover were taken on lands, which were long-term cultivated but subjected to salinization of one or another degree. The analysis of spectral curves of soils with different salinization degree was conducted (figure 3) and for comparison the curves were summarized in a single chart (figure 4), which shows that soils of different salinization degree vary in the values of spectral reflectance and the run of a spectral curve (Fig. 3, 4).

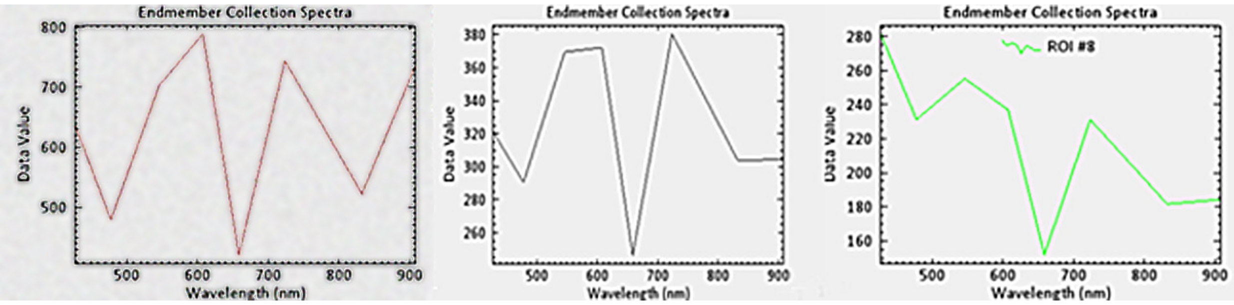

Figure 3. The run of a spectral curve of highly saline soils: long-term cultivated soils (the first) and the run of a spectral curve of low salinity, medium humus cultivated lands (the third), and the second one is the run of a spectral curve in solonchak soils (solonetz-solonchak)

Comparison of the curves (figure 5) shows:

1. All soil curves have an inflection in the range 610–720 nm at 660 nm.

2. In the visible range the run of curves is the same for all soil test fragments (table 1), there are differences in the values of spectral reflectance depending on salinization degree and soil composition. The greatest reflectance was in solonchak soils (solonetz-solonchak), according to the image in fragment 1 (table 1) the soils are white.

3. Highly saline (according to ground-based measurements 5.364%) long-term cultivated (apparently readily soluble salts under secondary salinization) soils have the greatest reflectance in comparison with all other curves (figure 1) in the range 550nm-610nm. In the picture these soils are dazzling white. Also, the curve has two inflections: the first — when passing from the red-edge zone to the near infrared 1 (NIR1) and the second one — when passing from NIR 1 to NIR2.

4. The greatest difference between soil curves of different salinization degrees is observed in the wave range from 660 nm to 900 nm. (i. e., in red edge, near infrared 1 and near infrared 2 zones). Here the soil curve with vegetable plots has the lowest reflectance (fragment 4 in table1).

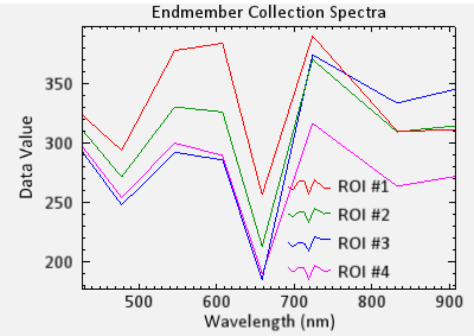

Figure 4. Generalized chart of spectral curves of soils of different salinization degrees

Thus, the run of a curve and the values of spectral reflectance on soils with different salinization degrees vary in the range of 660–90 nm (figure 4).

Spectral analysis of vegetation cover in saline soils

The vegetation cover in saline soils is mainly herbaceous, as the survey was conducted in March and the vegetation shoots were insignificant. Table 2 shows spectral curves of the vegetation (herbaceous) cover in soils with different salinization degree and in the last line — the curve in vegetation plots of slightly saline lands.

The first line shows the curve of vegetation on solonchaks, the second curve — dense vegetation on medium saline cultivated lands, the third one — the curve of sparse vegetation on medium saline lands and the fourth curve is the vegetation cover on vegetable plots, slightly saline lands. The analysis of spectral curves in the figure 6 shows that spectral reflectance of vegetation on long-term cultivated medium saline soils is much higher than that of vegetation on cultivated non-saline, medium humus soils both in the visible range and in the infrared band.

Three curves summarized in the single chart (figure 5) show:

1. Reflectance of herbaceous vegetation cover on solonetz-solonchak, heavily saline lands in the red edge zone (705–745) is lower than that of densely cultivated vegetation and sparse vegetation on medium saline cultivated lands.

2. Run of the curve of dense cultivated vegetation in NIR1 increases and passes into a straight line in NIR2, and on the contrary, the run of the curve of sparse vegetation decreases in NIR1and passes into a monotonically increasing straight line in NIR 2.

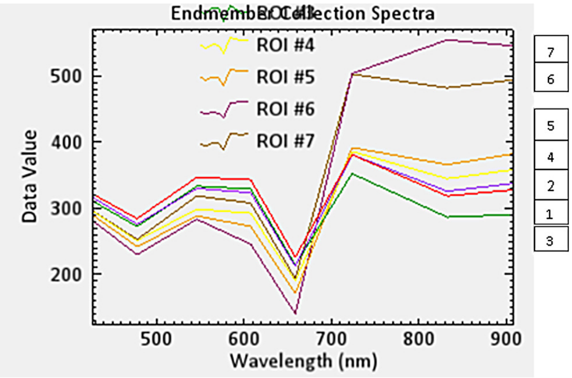

Figure 5. The run of spectral curves of herbaceous vegetation: 6 – curve on solonetz-solonchak, medium-saline soils, occasionally covered with vegetation, 7 – curve of dense herbaceous vegetation on medium saline cultivated lands, 8 – curve of sparse herbaceous vegetation on medium-saline long-cultivated lands

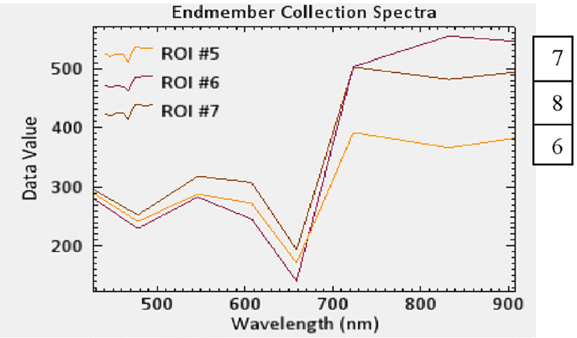

Figure 6. Spectral curves of soils and vegetation on soils of different salinization degrees, summarized in a single chart

All curves have an inflection in the interval 610 –720 nm at the point λ = 660 nm. In the section with dense vegetation (curve 7 in table 2), when passing from the red edge to NIR 1, the angle of the spectral curve slope is > 90°1.

Comparing all curves of herbaceous vegetation cover on heavily and medium saline sections and the run of vegetation curve from the section with low saline soils (curve 9 in table 2) shows that the spectral reflectance in NIR 1 and NIR 2 is higher in curve 9 and increases from NIR to NIR 2.

Conlusion

Many authors detected a spectral channel 770–880-nm (out of 13 examined ranges from 410 to 1250 nm) with the most expressed contrast of spectral brightness between open soil and vegetation cover [14; 15; 16; 17; 18; 19].

When in our researches we had the opportunity to study in detail spectral characteristics in eight spectral channels of WorldView-2 satellite, we summarized all spectral curves in a single chart (figure 6), according to which we can make the following conclusion:

1. The spectral curves of vegetation and soil with different salinization have an inflection in the range 610–720 nm at the point at λ — 660 nm;
2. The run of spectral curves in the range 410–660 nm is practically the same both in soils and vegetation on sections with different salinization degree, the only difference is in the values of spectral reflectance: it is higher in soils than in vegetation;
3. The greatest difference in the run of spectral curves in soils and vegetation on sections with different salinization degree is observed in the range 660–900 nm.
4. In the range 660–900 nm the spectral reflectance of vegetation cover is much higher than in saline soils;
5. In the red edge zone, the spectral reflectance of vegetation on solonetz-solonchak soils is less than that of vegetation on medium and low saline long-term cultivated soils;
6. The angle of curve slope of a vegetation cover on saline lands is > 90 degrees, and in saline soils it is < 90 degrees when passing from the red edge zone to the near infrared at λ= 720 nm. Hence the curve of soils decreases to NIR 1, the curve of vegetation cover increases to NIR 2.

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Table 1. – Spectral characteristics of saline soils on test sections

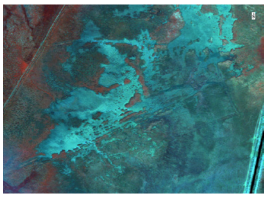
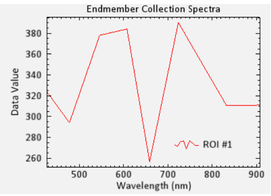
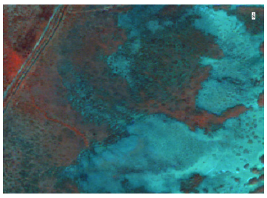
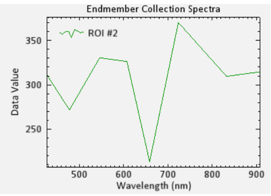
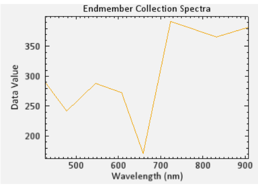
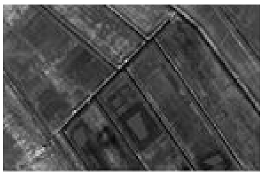
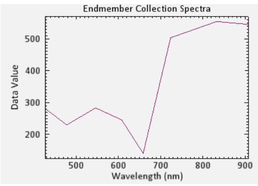
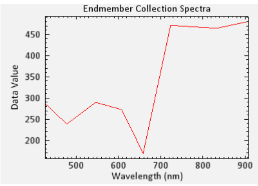
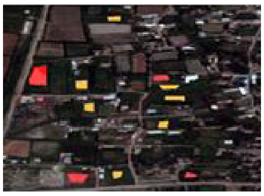
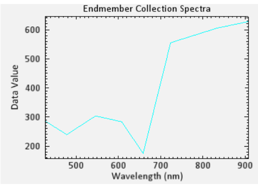
№	Test fragment	Spectral curve of test fragment	Note
1			The section is white. Sierozem-meadow strongly saline, solonetz-solonchak, the content of sodium is more than 15–20%, magnesium is more than 50%, soils salinized by a dense residue (more than 2%) [1, 8]. According to ground-based measurements, salinization is 1.78–5.364 g/l.
2			Test section is light gray. Sierozem-meadow, solonetz-solonchak, the content of sodium is > 15–20%, magnesium is > 50%, soils salinized by a dense residue (more than 2%) [1, 8]. According to ground-based measurements, salinization is 1.78–3.64 g/l.

Table 2. – Spectral characteristics of vegetation on saline soils

№	**Test fragment**	**Spectral curve of test fragment**	**Note**
6			Test section 6 is gray-brown, sierozem-meadow, solonchak-solonetz, moistened, covered with vegetation.
7			Test section 7 — plots on cultivated meddium saline lands, with dense vegetation shoots
8			Test section 8 — plots on cultivated medium saline soils, with sparse vegetation shoots
9			Test section 9 — vegetable plots on little saline lands, with vegetation shoots

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Section 2. Mathematics

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A GENERALIZATION OF FERMAT'S THEOREM ON SUM OF TWO SQUARES

Abstract: Fermat's theorem on a simple number equal to the sum of the squares of odd and even numbers is generalized to the sufficiency and higher degrees.

Keywords: sieve of Eratosthenes, prime number and sum of squares.

Among the remarkable works of Fermat is such an interesting theorem, which s almost never used: any prime number of the form $\tilde{p}=4\widehat{\mu}+1$ is the sum of squares of odd and even numbers if their sum is unambiguous and is not a square number. In symbols it looks like this [1; 2].

$$\tilde{p}=4\widehat{\mu}+1\Rightarrow\tilde{p}=(2m)^2+(2t+1)^2. \qquad (1)$$

Under the unambiguity means that for a given p, the set (m,t) is only. For example, $2^2+1^2=5$ — prime; $4^2+3^2=5^2$; $8^2+1^2=4^2+7^2=65$ — the composite numbers. Theorem (1) is necessary but insufficient. In this paper, we present the suffiiency of this theorem, i. e. made conditions when

$$\tilde{p}=4\widehat{\mu}+1\Leftrightarrow\tilde{p}=p=(2m)^2+(2t+1)^2. \qquad (2)$$

We will call $\tilde{p}$ the base prime, and p the main primes. This formulation is needed to generate prime numbers, solutions of nonlinear Diophantine equations and generalizations of Fermat's theorem to the case of higher exponents.

The reasoning is based on obtained by the method of mathematical induction the statement [3]. Any number $A(m,t,n)=(2m)^{2^n}+(2t+1)^{2^n}$, where $m=1;2;3;\ldots$, $t=0;1;2;3;\ldots$, multiples on base prime of the form $\tilde{p}=2^{n+1}\widehat{\mu}+1$.

The generalization of theorem (2) looks like this

$$\tilde{p}=2^{n+1}\widehat{\mu}+1\Leftrightarrow\tilde{p}=p=(2\widehat{m})^{2^n}+(2t+1)^{2^n}. \qquad (3)$$

Examples, if $n=1$, $m=3,t=0$, $p=2^4\cdot3^4+1^4=$ $=1297=2^2\cdot324+1$. It follows that for the condition (3) it is necessary to find the main prime numbers are right. We do this by the method of the modified sieve of Eratostene. Consider the case of $A(m,t,1)=(2m)^2+(2t+1)^2$ for a fixed t. Let $t=0$,

$A(m,0,1)=4m^2+1$. When $m=1$ that $A(1,0,1)=5$ is a mail prime. Divide m into two classes: the $\widehat{m}$ — good indexes, giving $4\widehat{m}^2+1=p$, and $\bar{m}$ are bad, giving $s=4\bar{m}^2+1$ composite number. Good $\widehat{m}(p)$ removes bad $\bar{m}$ using two arithmetic progressions (AP) if $k=0;1;2;3;\ ...$

$$\bar{m}=\begin{cases}(p+\widehat{m})+pk\\(p-\widehat{m})+pk\end{cases}. \qquad (4)$$

The index $\bar{m}$ gives a composite number $s=4\bar{m}^2+1=\tilde{p}_1\cdot\tilde{p}_2$. These basic primes are calculated according to the formula $\tilde{p}=4\widehat{\mu}+1$. They also remove bad indexes according to the formulas

$$\bar{\bar{m}}=\begin{cases}\bar{m}+\tilde{p}_1k\\(\tilde{p}_1-\bar{m})+\tilde{p}_1k\end{cases};\ \bar{\bar{m}}=\begin{cases}\bar{m}+\tilde{p}_2k\\(\tilde{p}_2-\bar{m})+\tilde{p}_2k\end{cases}. \qquad (5)$$

Set up (4, 5) is modified the sieve of Eratosthenes to identify the mail primes $4\widehat{m}^2+1=p$. Consider this method in the example. Suppose that we are given a set of indices $m=(1;2;3;4;5;6;7;8;9;10;11;12;13;14;15;16;17;18;19;20;21;22;23;24;25;26;27)$. Take $m=1$ and get $p=5$, *i.e.* $\widehat{m}=1=1$. Equation (4) make up $\bar{m}=6+5k$ and remove $\bar{m}=\{6;11;16;21;26\}$. The second AP from (4) is $\bar{m}=4+5k$. This AP removes $\bar{m}=\{4;9;14;19;24\}$. Next, take the first remote number $\bar{m}=4$, and find $s=4\cdot4^2+1=65=5\cdot13$. Then there is the bazis prime $\tilde{p}_2=13$ c $\widehat{\mu}=3$. It also removes the bad indexes. From equations (5) we have $\bar{\bar{m}}=4+13k;\bar{\bar{m}}=9+13k$, i.e. new bad number is $\bar{m}=\{17;22\}$. The following base drive $\tilde{p}=17$ with $\widehat{\mu}=4$. It coincides with the main prime $p=17$ with $\widehat{m}=2$.

If the classic sieve of Eratosthenes appeared not the remote index, this index creates a Prime number. In our sieve procedure for finding new Prime numbers is somewhat different. Suppose we have found $\widehat{m}$ and accordingly have $p=4\widehat{m}^2+1$. We must take all basis primes $\tilde{p}<p$ and their use to remove $\bar{m}$. Then make a buffer zone, a numerical piece $D(\widehat{m})=[\widehat{m},\ M(\widehat{m})]$, where in the General case

$$M(\widehat{m})=\left[0.5\cdot\left\{(p(\widehat{m}))^2-1-(2t+1)^{2^n}\right\}^{1/2^n}\right]. \qquad (6)$$

In (6) brackets $[x]$ gives the largest integer not exceeding x. After this procedure, we contend that all not deleted indices m is a good index $\widehat{m}$ in the $D(\widehat{m})$ and they give a new the main primes. This is a General rule applicable to any set of main primes $p(\widehat{m})$ and basic primes $\tilde{p}$ for any n,m,t.

Consider the example: $n=1,\ \widehat{m}=2, p=17$, $n=1,\ \ \widehat{m}=2,\ \ p=17,\ \ M(\widehat{m})=\left[0{,}5\cdot\sqrt{287}\right]=8$, $D(\widehat{m})=[2,8]$. Previous AP with $\tilde{p}=5$ and $\tilde{p}=13$ which remove bad and leave a good indexes $\widehat{m}=\{2;3;5;7;8\}$. They provide a set of the main primes in this buffer zone $p=\{17;37;105;197;257\}$. The next good index is $\widehat{m}=3$. It gives the drive $p(\widehat{3})=37$. Find $D(\widehat{3})=[2{,}18]$. Remove using (3) $\bar{m}=19+17k$ and $\bar{m}=15+17k$. On the select set there is one new $\bar{m}=15$. Base prime $\tilde{p}=29$ catches in the expansion with $m=6:4m^2+1=145=5\cdot29$. Therefore AP are $\bar{\bar{m}}=6+29k$ and $\bar{\bar{m}}=23+29k$. Removed only $\bar{m}=23$. On the interval $D(\widehat{3})=[2{,}18]$ new good $\widehat{m}=\{10;12;13;18\}$ give main primes $p=\{401;577;677;1297\}$. The number $\widehat{m}=5$ gives $p=101,\ D(5)=[5,\ 50]$ and on a given new main primes $p=\{1601;2917\}$ with $\widehat{m}=\{20;27\}$.

The following example is $n=2, t=1$, $A(m,1,2)=16m^4+81$. This gives at $\widehat{m}=1$ main prim $p=97$, $D(1)=[1{,}4]$. Two AP up in this region are $\{3+3k;\ 3+17k\}$, which leaves $\widehat{m}=\{1;2;4\}$. This gives two new main primes $p=\{337;4177\}$, with $\widehat{m}=\{2;4\}$.

The sequence of actions in the General case the following: **1.** Determined by n and t, and set $A(m,t,n)$. **2.** Find some first basic primes $\tilde{p}=2^{n+1}\widehat{\mu}+1$. **3.** Check the number $A(1,t,n)==(2)^{2^n}+(2t+1)^{2^n}$. **4.** If $A(1,t,n)=p$ is a main prime, we make 2^n AP up to a bad $\bar{m}=a_{p,h}+pk$. The initial number $a_{p,h}$ you need to be looking, $h=\{1;2;\ldots2^n\}$. For example, these numbers can find from expansions $(2\bar{m})^{2^n}+(2t+1)^{2^n}$. If $A(1,t)=\tilde{p}_1\tilde{p}_2$ then make 2^{n+1} AP to find bad $\bar{m}$. **5.** For first $A(\widehat{m},t,n)=p$ compiled buffer zone $D(\widehat{m})=[\widehat{m},M(\widehat{m})]$, where M is calculated according to the formula (6). **6.** All $\tilde{p}<(2\widehat{m})^{2^n}+(2t+1)^{2^n}$ are taken into acountin, and found 2^n AP for each base prime to be deleted $\overline{m}$ bad in a zone $D(\widehat{m})$. Not remote number is good new $\widehat{m}$ and they give a new main primes without any additional calculation. For large $\widehat{m}$, the length of zone $D(\widehat{m})$ grows proportionally with $\widehat{m}^2$, i. e. with less calculations, we get more main primes. Thus, modification of the sieve of Eratosthenes and a generalization of Fermat's theorem on sum of two squares gives a new method for fast generation of large frequency converters and solutions of linear Diophantine equations.

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Section 3. Agricultural sciences

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ZEOLITE AND PEAT INFLUENCE ON NITROGEN IN A SANDY SOIL

Abstract: Zeolite mineral and the peat may improve nitrogen to plants in the sandy soil and reduce losses to the environment.A pot experiment was conducted to determine the effect of mixing NPK with zeolite and peat on: NH_4^+, NO_3^-. The treatments evaluated were: T_1 no fertilizer 1500gr, T_2 soil +$N_{300}P_{225}K_{180}$, T_3 soil+Zeolite 6 kv/ha, T_4 soil +Zeolite 12 kv/ha, T_5 soil+Zeolite 6 kv/ha + NPK, T_6 soil+Zeolite 12 kv/ha + NPK, T_7soil+Zeolite 6 kv/ha + NPK +peat the original 5%, T_8soil+Zeolite 12 kv/ha + NPK +peat the original 5%, T_9 soil+Zeolite 6 kv/ha + NPK +peat the original10%, T_{10} soil+Zeolite 12 kv/ha + NPK + 10% peat the original.Lolium multiflora was used as the experimental plant and the experiment was realized in the green-house of the Tirana Agricultural University for a period of 7 months.Zeolitic material was take by the Munnell region.The application of peat and zeolite with NPK had the significant effect on NH_4^+, NO_3^-, use efficiency compared with NPK without additives.

Keyword: zeolite, peat, sandy soil, nitrate, ammonium.

1. Introduction

Zeolites are crystalline hydrated aluminosilicates, zeolites, as individual rocks, were discovered by the Swedish scientist Alex Frederik Cronstedt in 1756 [1, 394–399]. Zeolite addition to soil will significantly reduce water and fertilizer cost retaining water and beneficial nutrients in the root zone [2, 183–189]. A number of studies on zeolites reported improved nutrients uptake and nutrients use efficiency cultivated on acid soils [3, 3462–3467].

Increasing P availability from RP [4, 333–343], improving use of NH_4-N and NO_3-N by reducing leaching losses of exchangeable cations. Zeolites also act as slow-release fertilizer [5, 713–722], improves rice **grain yield**, N recovery and use efficiency [6, 69–76]. The attractive physical and chemical properties of natural zeolites will be used worldwide even more in the years to come in the solutions of different problems [7, 3–27]. Zeolites are, therefore, used as a promoter for better plant growth by improving the value of fertilizers; retaining valuable nitrogen and improving the quality of resulting manures and sludge [8, 183–189]. Natural zeolites have been shown to increase the soil cation exchange capacity and soil moisture, improve hydraulic conductivity, increase yields in acidified soils, and reduce plant uptake of metal contaminants in soil [9, 447–490].

2. Materials and methods

2.1 Zeolitic Material of Munella Region (Albania)

The zeolitic material used in the experiment has been sampled from the Munella region. The zeolitic material was ground to 100 mesh. A sample of from this material was analyzed for the chemical characteristics by the X-/fluorescence, in Activation Laboratories LTD, Canada. [10, 33–47]. The mineralogic study of zeolite-bearing rocks reveals authigenic cement consisting of zeolitic material and vesicles filled with zeolites, chlorite, quartz and carbonate, based on microprobe analyses, a continuous variation was observed for the Si/Al and Na+K/Na+K+Ca+Mg ratios that scatter in the range 3–3.5 and 0.01–0.18, respectively [11, 183]. Physical and chemical characterization of zeolitic material, based on methods by Collela et al. (1982), Pansini (1996), Capelleti et al. (1999), consists in: a cation exchange capacity CEC = 1.9 –2.42 meq/g and this selectivity for cations: $Zn^{2+} < Cu^{2+} < Pb^{2+}$ [12]

Table 1. – Chemical properties of the Zeolite

Quality	Unit	Value	Quality	Unit	Value
pH (H_2O, 1:5)		7.8	Na	mg kg^{-1}	75.90
$CaCO_3$	%	<0.5	Ca	mg kg^{-1}	1196
CECpot	meq/100g	6.72	Mg	mg kg^{-1}	33.60
EC (1:5)	µS/cm	91	Mn	mg kg^{-1}	ND
K	mg kg^{-1}	3.91	Fe	mg kg^{-1}	33.60

2.2 Soil and soil sampling

The studied soils that have been sampled are represented by a sandy soil (Haplic Arenosol, FAO-1988) from Lushnja District. This soil type is considered as a problematic one because of its unfavorable properties for plant growth. Total surface of Arenosols in Albania is estimated at about 10. 000 ha, this surface is in agricultural production [13, 136].Main chemical and physical characteristics of the soil under the study, before the experiment, are given in table 2.

Soil samples were taken from 0 to 30 cm soil depth from five locations, because this is the most significant soil depth to study elements in soils devoted to vegetable crops. There were 10 variants of the experimentT1 no fertilizer 1500gr, T_2 soil +$N_{300}P_{225}K_{180}$, T_3 soil+Zeolite 6 kv/ha, T_4 soil +Zeolite 12 kv/ha, T_5 soil+Zeolite 6 kv/ha + NPK, T_6 soil+Zeolite 12 kv/ha + NPK, T_7soil+Zeolite 6 kv/ha + NPK +peat the original 5%, T_8soil+Zeolite 12 kv/ha + NPK +peat the original 5%, T_9 soil+Zeolite 6 kv/ha + NPK +peat the original10%, T_{10}soil+Zeolite 12 kv/ha + NPK + 10% peat the original.

Table 2. – Chemical properties of the soil

Quality	Value
pH H_2O	8.04
pH KCl	7.56
CEC, meq/100 g	14.15
Organic matter,%	2.33
Total-N,%	0.06
NO_3^-, mg/kg	0.43
NH_4^+, mg/kg	4.04
Available-P, mg/kg	4.81
Clay,%	3.20
Haplic Arenosol (FAO 2006).	

2.3 Peat

Peat is taken in region of Fushe Krujes- Albanian city. Is taken by a depth of 0–30cm. Experimental data are given in Table 3.

Table 3. – Chemical properties of peat

Quality	Unit	Value
pH H_2O		7,44
pH KCl		6,84
CEC	meq/100gr	–
Organic matter	%	42.6
Electrical conductivity	mS/cm	0.22
N-total	%	899,35
NO_3	mg/kg	0.07
NH_4^+	mg/kg	7,30
P-avaible	mg/kg	29,425
Classification according botanical origin: Peat		

2.4 Chemical fertilizers

The application rates chemical fertilizers used in the experiment were were as follows: urea 0.045 gr/pot (300 kv/ha); superphosfate 0.199 g/pot (225 kv/ha); potassium sulphate 0.048 g/pot (180 kv/ha).

2.5 Pots

Within the experiments made in the green — house of the "Tirana Agricultural University" we used pots with a weight of 1.5 kg and dimensions: h = 13.8 cm, D = 20 cm, d = 9.15 cm.

2.6 The experiment scheme and observations

The experiment was conducted in a randomized block with four repetitions. There were 10 variants of the experiment T_1 no fertilizer 1500gr, T_2 soil +$N_{300}P_{225}K_{180}$, T_3 soil+Zeolite 6 kv/ha, T_4 soil +Zeolite 12 kv/ha, T_5 soil+Zeolite 6 kv/ha + NPK, T_6 soil+Zeolite 12 kv/ha + NPK, T_7soil+Zeolite 6 kv/ha + NPK +peat the original 5%, T_8soil+Zeolite 12 kv/ha + NPK +peat the original 5%, T_9 soil+Zeolite 6 kv/ha + NPK +peat the original10%, T_{10} soil+Zeolite 12 kv/ha + NPK + 10% peat the original.During the growing season of plants, several phenomenological and biometric measuring have been performed. The plants were cut at the maturity time, 2 cm above ground level, stored in paper containers and dried for 15 h at 60°C temperature. After that, plant material was ground, sieved and stored in the glassy vessels.

2.7 Analythical methods

The processed soil samples were analyzed for $N0_3^-$, NH_4^+. To measure NO_3^-weighed 3 gr of treatment we throw into distilled water. Interracial, centrifugation and filtering. Measure directly absorbance with wavelength spectrophotometer with 220/275nm. To measure NH_4^+,10 ml of the solution obtained treated with 4 ml reagent 1 and 4 ml reagent 2. Direct measurement of absorbance with wavelength spectrophotometer with 655nm.Analysis the contents of total nitrogen, nitrate, and ammonium are presented in mg/kg of dry matter.LSD test at p <0,05 is used to find statistical differences between treatments studied.Analyses were carried out in the Institution of Soil Study (LAME), Tirana (Albania).

3. Results and discussion

During cutting no. 2 of the experiment, we found higher contents of ammonia nitrogen in the variants with zeolite T_3 and T_4 compared with T_1control a variant without any fertilization, which means ammonia nitrogen is gradually released from zeolite and more is available for cultivated plants. A similar effect after zeolite application, although their experiments contained significantly higher zeolite amounts found in Chelischeva [14, 234–235] and Tukvadze ED [15, 223–232].

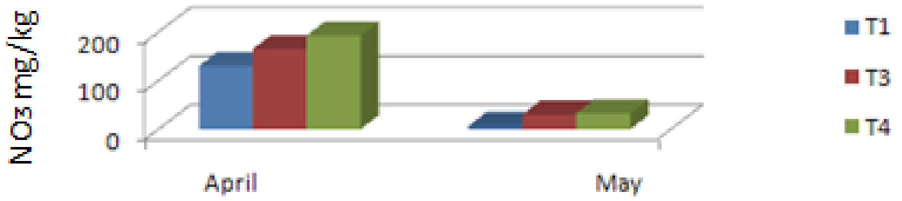

Figure 1. T1 –controll, T3-soil+Zeolite 6 kv/ha, T4-soil +Zeolite 12 kv/ha

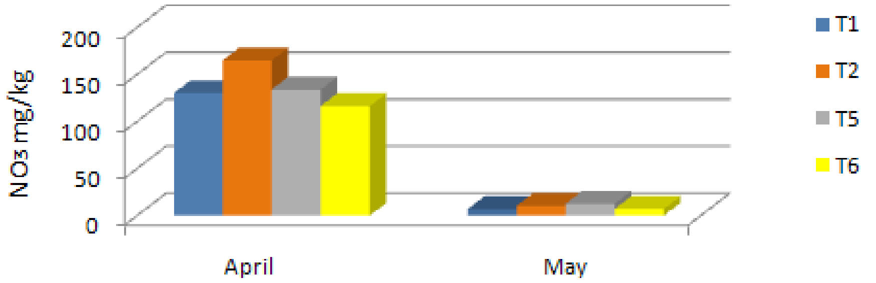

Figure 2. T_1 –controll, T_2-soil +NPK, T_5-soil+Zeolite 6 kv/ha + NPK, T_6-soil+Zeolite 12 kv/ha + NPK.

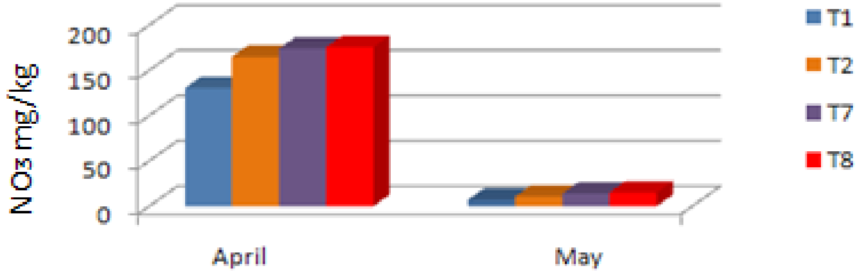

Figure 3. T_1 –controll, T_2-soil +NPK , T7-soil+Zeolite 6 kv/ha + NPK +peat the original 5%, T8-soil+Zeolite 12 kv/ha + NPK +peat the original 5%

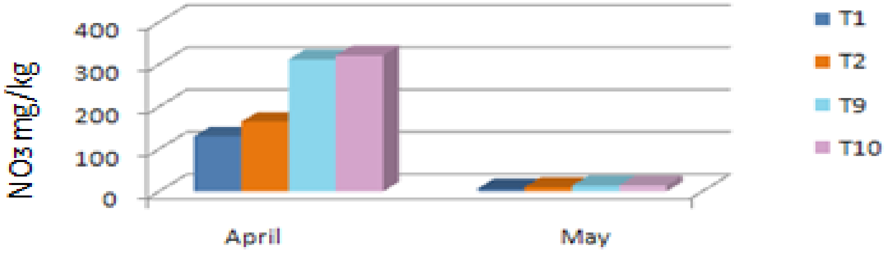

Figure 4. T_1 –controll, T_2-soil +NPK, T_9-soil+Zeolite 6 kv/ha + NPK +peat the original 10%, T_{10} soil+Zeolite 12 kv/ha + NPK + 10% peat the original

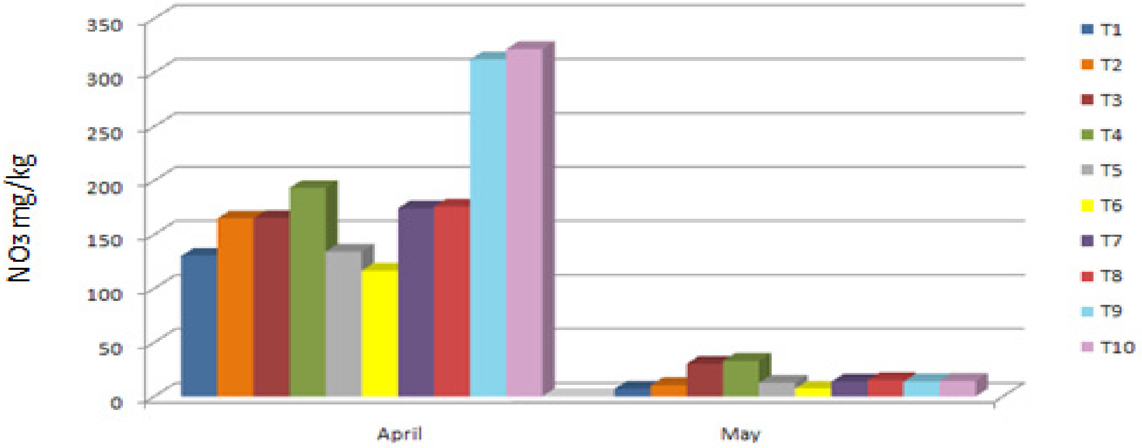

Figure 5. T_1 no fertilizer 1500gr, T_2 soil +$N_{300}P_{225}K_{180}$, T_3 soil+Zeolite 6 kv/ha, T_4 soil +Zeolite 12 kv/ha, T_5 soil+Zeolite 6 kv/ha + NPK, T_6 soil+Zeolite 12 kv/ha + NPK, T_7soil+Zeolite 6 kv/ha + NPK +peat the original 5%, T_8soil+Zeolite 12 kv/ha + NPK +peat the original 5%, T_9 soil+Zeolite 6 kv/ha + NPK +peat the original10%, T_{10} soil+Zeolite 12 kv/ha + NPK + 10% peat the original

Application of 2 t of zeolite in heavy soils increased the hydrolysable nitrogen content twice, and when they used 4 and 6 t of zeolite, it increased by 4 and 5 times, respectively Sopkova [16, 145–149] and Ming DW [17, 619–654] and Rehakova M [18, 260–264], and Uher A [19, 46–52] suggested that fertilizer with the addition of zeolite became a 'slow-releasing fertilizer', although [20, 149–154] debated the use of the term in relation to zeolite.Similar results were obtained by [21, 106–112] in their experiments there was an observed decrease of the N-NO3-in the soil only to the level of 41%–48% after the zeolite application compared with the nitrate nitrogen content in the control variant.T_5, T_6 compared to $T_2$and T_1 in fig 2.The same results are also found at Ippolito [22, 1721–1731].

T_7, T_8, T_9, T_{10} compared to $T_2$and T_1 in fig 3 and fig 4.The higher soil available NO_3^- compared with NPK alone (T_2) as presented in Fig.3 was because of the presence of zeolite, this is possible because of the clinoptilolite zeolite's ion exchange system which enables absorption of anions such as NO_3^- and phosphates [23].

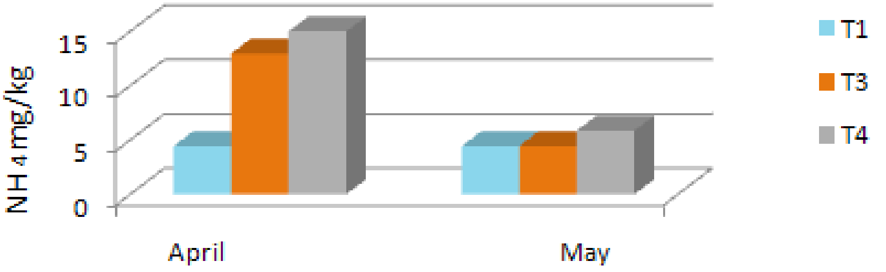

Figure 6. T1 –controll, T3-soil+Zeolite 6 kv/ha, T4-soil +Zeolite 12 kv/ha

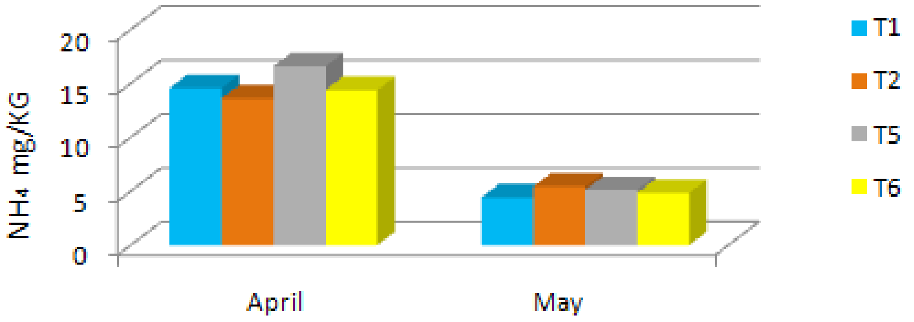

Figure 7. T_1 –controll, T_2-soil +NPK, T_5-soil+Zeolite 6 kv/ha + NPK, T_6-soil+Zeolite 12 kv/ha + NPK

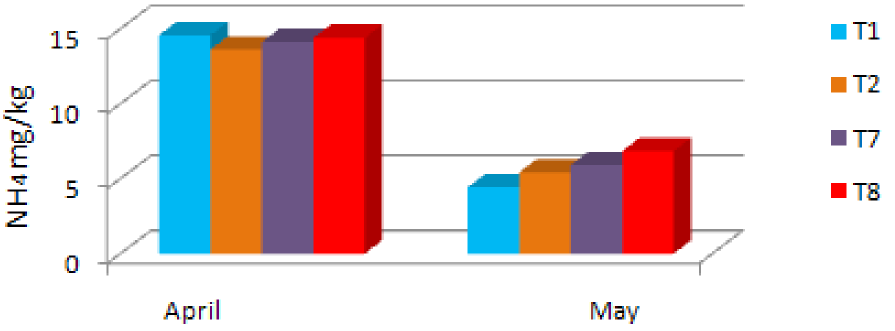

Figure 8.T_1 –controll, T_2-soil +NPK , T7-soil+Zeolite 6 kv/ha + NPK +peat the original 5%, T8-soil+Zeolite 12 kv/ha + NPK +peat the original 5%

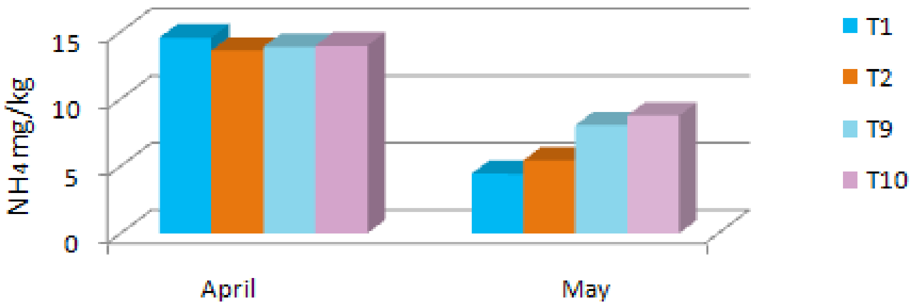

Figure 9. T$_1$ –controll, T$_2$-soil +NPK, T$_9$-soil+Zeolite 6 kv/ha + NPK +peat the original 10%, T$_{10}$ soil+Zeolite 12 kv/ha + NPK + 10% peat the original

T$_7$, T$_8$ compared to T$_2$ and T$_1$ in the fig 8.T$_9$, T$_{10}$ compared to T$_2$ and T$_1$ in the fig 9, NH4 was significantly higher in the NPK with zeolite and peat treatments (T$_7$, T$_8$, T$_9$, T$_{10}$) than in NPK without additives (T2) and soil alone (T1)no fertilizer. The higher concentration of soil exchangeable NH4 in T$_7$, T$_8$, T$_9$, T$_{10}$ were partly due to increasing the pH of the soil as mineralization of organic N to NH4 is enhanced by the higher pH [24,157–164].It is also possible that some of the NH4 released during NPK hydrolysis were adsorbed onto the exchange surface of zeolite (T$_3$, T$_4$, T$_5$, T$_6$) and humic substances of peat (T$_7$, T$_8$, T$_9$, T$_{10}$).

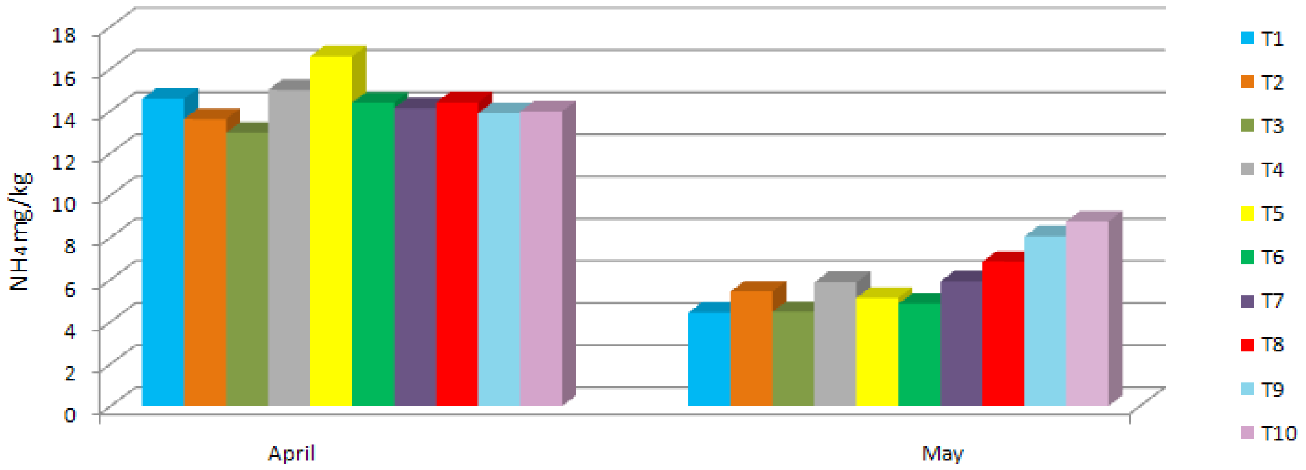

Figure 10. T$_1$ no fertilizer 1500gr, T$_2$ soil +N$_{300}$P$_{225}$K$_{180}$, T$_3$ soil+Zeolite 6 kv/ha, T$_4$ soil +Zeolite 12 kv/ha, T$_5$ soil+Zeolite 6 kv/ha + NPK, T$_6$ soil+Zeolite 12 kv/ha + NPK, T$_7$soil+Zeolite 6 kv/ha + NPK +peat the original 5%, T$_8$soil+Zeolite 12 kv/ha + NPK +peat the original 5%, T$_9$ soil+Zeolite 6 kv/ha + NPK +peat the original10%, T$_{10}$ soil+Zeolite 12 kv/ha + NPK + 10% peat the original

According to Kithome, NH$_4$ retained by zeolite is generally released slowly because of the CEC of this zeolite and nitrification in the soil [25, 622–629].

A similar finding was reported by Ahmed who evaluated the effect of zeolite and TSP on acid soils [26, 394–399]. The findings in this study suggest that retention of NH_4^+ may be due to the effect of zeolite, which is noted for NH$_4$+ releasing slowly as well as protecting it from excessive nitrification in soil [27, 839–845]. In another study, Huang and Petrovic [28, 1190–1194] found significant retention of NH_4^+ and $NO_3^-$when a sandy soil was amended with zeolite. This was attributed to increased soil surface area and CEC [28, 1190–1194]. The ability of T$_7$ and T$_8$ to cause significant accumulation of exchangeable NH_4^+ and available NO_3^- was partly due to the retention property of zeolite as explained by Ferguson and Pepper [29, 231–234].

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Section 4. Technical sciences

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DEVELOPMENT OF SPECIAL SUCKER ROD PLUNGER PUMP

Abstract: Special design change has been made to reduce wear in the pair "cylinder-plunger", that's an additional component (centering element) and packing unit have been installed.

As a result of such design change, the alignment of the plunger and cylinder of the pump is provided, which reduces wear of these components, oil leakage through annular gap between cylinder and plunger of the pump, and also coefficient of the pump feeding.

The given offer has practical value, as it increases durability of the given pump.

Keywords: filtration, development, bottom hole pressure, functional dependence, position, reservoir, discharge, reduce.

In the sucker rod pumps one of the main reasons of the refuse of the work of plunger is that the chromium-plated coating of its surface is subjected to wear [1]. Practice proves that the biggest wear in the plungers is met at the distance of 10÷15 sm from its ends and mainly the wearing place unilaterally along the diameter, as well as along the length [2; 3].

In the conditions of exploitation of the particles of mechanical mixtures, mainly sand particles entering in the annular gap between the plunger and cylinder of the pump moving there unilaterally press the plunger to the interval wall of the cylinder and as a result of it, powerful friction takes place because of the increase of normally compressing force and increase of the wearing the plunger and cylinder of the pump and in reverse extended excentric annular zone, consumption of hydroabrasive mixture increases, and also as a result of absence of alignment in the connection of the plunger and extending rod and compressing of the plunger in the lower and upper final points in the cylinder is one of the main factor making condition for wear of the plunger and cylinder [8; 9].

For partial liquidation of abovementioned factors influencing on the wear of the pair plunger+ cylinder, sucker rod pump having plunger of special type has been offered [4; 5].

The difference of the considered sucker rod pump from the existing pumps is the transfer the force into the cylinder, occurring in the extending rod in radial derection accepting it. In fig.1 sucker rod pump supplied with the plunger of special type has been shown.

Sucker rod pump consists of cylinder 1, plunger 2, discharge valve 3, suction valve 4, extending rod 5, alignment element 6 and packing unit 7.

As it is seen from the figure, extending rod was connected with the end of the lower part of the plunger. But alignment extending rod has state type along the diameter then its lower part as the bush is smaller than the upper part that enters the plunger. Annulus packer is installed into the lower part of the bush, which sets against the upper part of the lateral section. In the upper part of the alignment there is internal facet. The alignment has possivility to make some movement relatively to the plunger up and down, which is limited, in the movement up it sets against the ledge in the extending rod and moving down it sets against the ledge in the lower part inside the plunger.

Work principle of sucker rod with the offered design of plunger is described below. In the process of suction, that's in the movement of the plunger 2 up, discharge valve 3, installed on the plunger is closed under the pressure influence created by the fluid column inside the tubing column. As a result of the pressure in the alignment 6, getting displacement in the direction down proportionally to it, presses packing unit 7 to the upper lateral section of the plunger. As a result packing unit causes lateral deformation and forms leakage fro0m the tubing reversely into the pump cylinder. Let's mention that in the construction with the restriction of beforehand installed to the displacement of the alignment, pressing of the packing unit is adjusted. The purpose of the forming of internal facet in the upper end of the alignment 6 is to direct particles of mechanical mixtures sticked in the internal wall of the cylinder inside the plunger selecting them and to provide more effective work of the packer 7.

In the movement of the plunger down, that's in the process of discharge as a result of increasing the pressure in the space under the plunger discharge valve opens and suction valve closes. At this time pressure in the space over the alignment is considered.

As a result of friction it is separated from the plunger and gets displacement up. It gives an opportunity to restore its initial position of the packer. This, the condition for reduce the friction force to the minimum is formed, which creates obstacle to the free drop of the plunger.

It is necessary to mention that in the movement down, as a result of moment formed relatively to the force in the upper point directed up hydraulic resistance in radial direction, pressing of the plunger to the cylinder is eliminated. In the movement of the plunger in the direction down the force, connected with lateral deformation of the extended rod and a result of these forces, pressing the plunger to the cylinder is eliminated.

Thus, in the offered sucker rod pump, at the expense of the wear in the contact of plunger and cylinder and reduce of volume losses of the fluids, as a result of inverse leakage into the cylinder makes possible to significant increase of the service term and productively in compareson with corresponding indices of series production.

Analysis of the work of the offered sucker rod pump has been carried out. As it was mentioned the purpose of the presented construction is the supply of alignment of the area (surface) reduce of the wear in the considered pairs. 10 pumps of R and T type with 44 mm conditional diameter have been tested to determine work ability of sucker rod pump and its efficiency.

Before the test corresponding sizes of plunger and cylinder of the pumps marked for comparison with indicator micrometer and nutrometer. Have been taken sizes were mentioned along plunger length in equal distances from each other on lateral sections in 12 places, but on the cylinder on six places. Based on arithmetic mean value of the obtained sizes, their diameters has been determined and the size of the gap between the plunger and cylinder has been accepted as difference of the diameters of the cylinder and plunger. After the lifting of sucker rod pumps out of the wells their conditions were examined, sizes of plunger and cylinder have been taken. Degree of wear of each pump has been determined on the basis of it.

In table 1, information about technical indices and about the wear of sucker rod pumps have been given. As it is seen from the table, in all cases indices of the tested pumps are higher than corresponding indices of mass pumps. The results show that in the tested pumps arithmetic mean wear is 21% less than in the compared mass pumps.

For clearness wear epure of mass produced and offered plungers operating in well N2275 has been shown in figure 2.

In figure 2 a wear along the plunger diameter has been shown, but in figure 2b wear of the special type has been shown. As it is seen from this figure, wear intensity for time unit of special type plunger is much lower and wear along the surface of plunger takes place uniformly. As it is from epure, at the end parts of the offered plunger wear quantity is sharply lower Abovementioned can be explained fig the facts that in the process of pump work in up and down movement of special type plunger its alignment with cylinder is provided and reverse leakage of fluid through annular gap reduces.

Let's mention, in carrying out of the tests no constructive blunder has been observed in the plunger and after the lifting out of the well it is useful for the secondary exploitation.

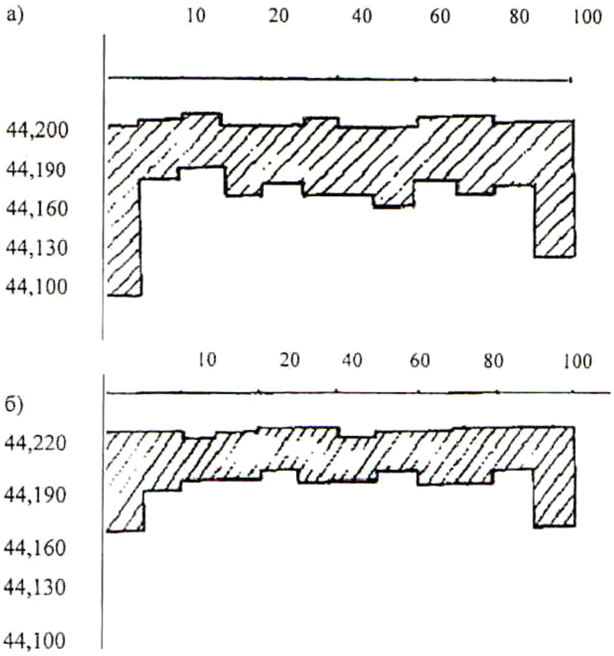

Figure 1. 1–cylinder, 2–plunger, 3–discharge valve, 4–suction valve, 5–extending rod, 6–alignment element, 7–packing unit

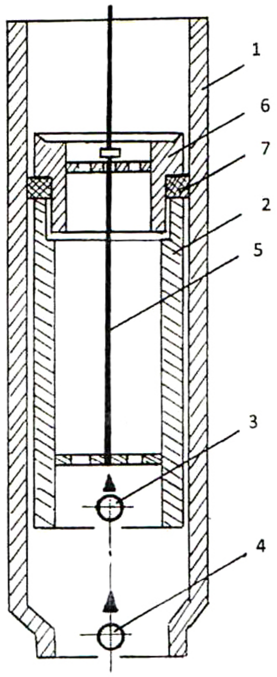

Figure 2. Epure of plunger wear of sucker rod pump of R type with 44 mm conditional diameter

a) Epure of mass produced plunger wear;
b) Epure of special type plunger

Table 1. – Comparative wear indices of special type and mass produced plungers

N-of well	Mass pumps					Tested pumps				
	Average diameter of plunger, mm		Durability of pump work, day	Plunger wear, mkm	Intensity of plunger wear, mkm/day	Average diameter of plunger, mm		Durability of pump work, day	Plunger wear, mkm	Intensity of plunger wear, mkm/day
	Before lowering into the well	After lifting out of the well				Before lowering into the well	After lifting out of the well			
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*
936	44.200	44.130	24	70	2.196	44.130	43.050	40	80	2.000
2657	44.300	44.200	43	130	3.023	44.330	44.192	66	138	2.090

1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*
2538	44.210	44.985	150	225	1.500	44.210	43.963	190	247	1.300
6068	44.400	44.290	59	110	1.865	44.400	44.134	64	86	1.344
655	44.220	44.127	30	93	3.100	44.220	44.205	46	115	2.500
3332	44.280	44.180	79	100	1.266	44.280	44.220	60	60	1.000
2270	44.220	44.185	10	35	3.500	44.220	44.109	37	111	3.000
2430	44.280	44.137	55	143	2.600	44.280	44.097	76	183	2.407
2195	44.350	44.307	34	43	1.265	44.350	44.283	73	67	1.089
1191	44.215	44.143	38	72	1.895	44.215	44.132	55	83	1.509

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ENRICHMENT OF COPPER — MOLUBDENIUM ORES BLOWING AGENT BASED ON RECYCLED PRODUCTS OF ORGANIC PRODUCTION

Abstract: This article about of flotation color and precious metals used are known surface active substance (SAS) — foaming agents on the basis of local secondary material cubes in enrichment separation copper-molybdenum ores Almalyk Mining Metallurgical Plant (MMP) of Uzbekistan tests were carried out blowing agent samples (HA-1, HA-2).

Keywords: metallurgical plants, foaming agents, surfactants, ores, copper, blowing agent, flotation, potassium butyl xanthate.

Currently, the mining and metallurgical plants of the republic for the flotation of non-ferrous and precious metals used are known surface active substance (SAS) — foaming agents, as potassium butyl xanthate (BPC) and the T-92 reagent.

We have developed a technology for production of SAS on the basis of local secondary raw materials and oil and fat chemical plants of Uzbekistan [1].

We suggest an intensication of the process of enrichment of ores by flotation with collecting agents and foaming agents on the basis of local secondary produkta — cubes in enrichment separation copper-molybdenum ores Almalyk Mining Metallurgical Plant (MMP) of Uzbekistan tests were carried out blowing agent samples (NA-1, NA-2)at the current ore deposit "Kalmakyr" entering the processing on the copper concentrator. The chemical composition of the ore is show in table № 1 distillation process refinery cotton oil acid soap stock (NA-1). Heir synthesis was performed in the laboratory, selected key ratios of the starting components, and Now, there are the synthesis conditions (temperature, time, concentration). In our pilot plant collected by the developed optimal formulation of new surfactants (NA-1) has been achieved experimental batches of surfactant — flotation reagents, which were tested as somostoyatelno, so in combination with conventional reagents [2].

The essence and novelty of the proposed formulation and use of surfactant is technology that is used in their production local nedifitsitnoe organic feed. According to the proposed technology provided a anionic surfactant (NA-1), which in quality is a substitute for scarce reagents collector BPC (US price of 1820 USD per 1t.) And a blowing reagent T-92 (the price of US $ 640 per 1t.).

We suggest an intensification of the process of enrichment of ores by flotation with collecting agents and foaming agents on the basis of local secondary podukta — bottoms distillation process cotton soap stock fatty acids (HA-1).

Table 1 – Chemical content of ores

content,%										Sulfides of ores,%
Си	Mo	CaO	MgO	Fe	S	$Si0_2$	$A1_2O_3$	Аи	Ag	
0,41	0,004	1,62	1,59	5,8	3,0	56,4	13,12	0,5	3,5	94,73

Samples blowing agent HA-1, HA-2 is a liquid of dark brown color, without odor, which are readily soluble in water.

To determine the foaming properties of the experiments in the open cycle data set of reactants (Table № 2) compared to the standard T-92 blowing agent, blowing agent at a rate of 30,0 g/t, as well as mixtures of blowing agents: AT-1–15,0 g/t + t 92 –15,0 g/t and NA-2 –15,0 g/t + t 92 –15,0 g/t, according to the regime adopted in the factory:

Table 2

№ experiments	Product	Exit,%	Copper,%		The flow rate of the blowing agent, the entrance	Conditions for experiments
			P	E		
Flowing agent T-92						
I	Flotation concentrate № 1	3,98	7,380	72,78	T-92–30,0	Content:
	Flotation concentrate № 2	4,05	1,350	13,55		
	Black concentrate	8,03	4,340	86,33		
	Waste	91,97	0,060	13,67		
	Ores	100,0	0,404	100,0		
Flowing agent NA-1						
II	Flotation concentrate № 1	3,0	8,980	66,87	NA-1-30,0	kst — 25,0 g/t
	Flotation concentrate № 2	2,61	1,790	11,60		
	Black concentrate	5,61	5,635	78,47		
	Waste	94,39	0,092	21,53		
	Ores	100,0	0,403	100,0		
III	Flotation concentrate № 1	2,43	10,330	62,07	Mixture: NA-1-15,0 +T-92–15,0	
	Flotation concentrate № 2	5, П	1,880	23,76		
	Black concentrate	7,54	4,600	85,83		
	Waste	92,46	0,062	14,17		
	Ores	100,0	0,404	100,0		
Flowing agent NA-2						
IV	Flotation concentrate № 1	1,60	12,160	48,39	NA-2-30,0	
	Flotation concentrate № 2	3,56	3,430	30,37		
	Black concentrate	5,16	6,140	78,76		
	Waste	94,84	0,090	21,24		
	Ores	100,0	0,402	100,0		
V	Flotation concentrate № 1	2,81.	8,850	61,68	Mixture: NA-2-15,0 +T-92–15,0	
	Flotation concentrate № 2	4,05	2,280	22,90		
	Black concentrate	6,86	4,970	84,58		
	Waste	93,14	0,067	15,42		
	Ores	100,0	0,403	100,0		

Fineness of grinding ore: + 0,21 mm — 5,0%,
– 0,071 Mm — 60,5%;
– PH 10,8ed;
– Xanthate consumption — 25,0 g/t;
– Consumption of spindle oil — 7,0 g/t.

The results of the experiments, as well as the visual monitoring of the process of flotation showed that these agents have a foaming capability close to the standard, compared with the known T-92. At a flow rate of blowing agent 30,0 g/t, in the experiment with HA-1-foaming weaker and rougher concentrate output below 2,42% or less copper recovery in the concentrate to blister 7,86%, compared to an experiment conducted with T-92 reagent.

In the experiment where a mixture of blowing agents taken NA-1–15,0 g/t + T 92–15,0 g/t — concentrate primary lower yield (1,55%), and copper extraction below respectively — to 591%, in comparison with experiment with only one t-92–30,0 g/t. Front flotation biased towards the control of flotation: Exit the main concentrate — 2,43%, the control of the concentrate — 5.11%, copper recovery in the control of flotation concentrate was — 23,76%.

The foaming agent HA-2 has lower foaming ability than HA-1. Results of the experiments showed the feasibility of conducting further experimental tests based on blowing agent CO ANC for the flotation of copper-molybdenum ores processed in the factory [3].

The foaming agent HA-2 has lower foaming ability than HA-1. Results of the experiments showed the feasibility of conducting further experimental tests based on blowing agent CO ANC for the flotation of copper-molybdenum ores processed in the factory.

Conclusion: Thus foaming NA-1 and NA-2 are recommended as blowing agents to further improve and implement the process in the flotation beneficiation of non-ferrous and precious metals.

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MODIFICATION OF CERAMIC MASS ON THE BASIS OF LOESS-LOAMS WITH APPLICATION OF CONGLOMERATE OIL-SLOW MIXTURE FOR ESTABLISHMENT OF ENERGY EFFICIENT TECHNOLOGY OF OBTAINING LIGHTWEIGHT AGGREGATE

Abstract: The results of studies on obtaining the lightweight aggregate were presented. In scientific experimental research, loess-like loams, sand and oil sludge from various deposits are used. The introduction of oil sludge into the composition of ceramic masses allows reducing energy costs by 20–25%.

Keywords: lightweight aggregate, conglomerate mixture, loess-loam, heat conductivity, technology.

Nowadays a distinctive feature of developed countries is the rational consumption of resources. Energy and resource saving in technologies of production of building materials, efficient use of production waste is a priority area of the Republic of Kazakhstan.

In developed countries, energy efficiency policies promote the growth of competitiveness of the economy and production, the development of science and technology, new modern technologies, innovations.

Energy saving in the industrial sector means obtaining the same economic result, but the lowest cost energy or obtaining higher performance at the expense of the smaller or the amount of energy per unit of production [1].

This means reducing energy consumption and at the same time saving money [2].

Currently, one of the promising building materials is lightweight fillers, which are used as fillers in lightweight, structural and other types of concrete, and also as a heat-insulating material.

From the point of view of increasing energy efficiency in the production of building materials, oil sludge is of the greatest interest.

Every year a large amount of oil wastes is stored and transported to the dumps, the volume of which reaches thousands of tons.

These indicators are growing every year. Oil companies use a part of oil sludge, burning them in special installations, as oil sludge belongs to the category of flammable and combustible materials [3].

Such indicators of oil sludge, as combustibility and flammability, provide for the content of valuable hydrocarbon compounds in them as oil, paraffin, resins, asphaltenes.

Therefore, oil sludge should be considered not as a waste, but as a valuable energy-releasing and additionally modifying additive for other sectors of the economy [4].

The authors [5] investigated the possibility of using oily waste in the production of expanded clay.

It was found that the pore-forming additive from the oil waste improves the performance of the keramzit samples: the swelling coefficient increases 1.1 times, and the swelling interval is wider by 20 °C than the conventional additive.

The authors developed the technology of lightweight fillers using waste automotive oils (waste oil products) in compositions with quartz sand.

An additive in the amount of 1% of used oils in the composition with quartz sand allowed to increase swelling clay raw material, to increase mechanical strength and to lower the temperature of firing aggregates.

Technologies are known where the authors propose to use construction waste in the production of light aggregates for concrete [7; 8]. As a result of research, lightweight aggregates with improved properties were obtained.

The purpose of our study is to investigate the possibility of obtaining a lightweight aggregate based on non-expanding loess-like loams in fine sand and oil sludge compositions.

The main raw materials are: loess-like loam of the Chagansky and Kyzylorda deposits.

As a pore-forming, corrective additive was used oil sludge LLP Zhaykmunay, JSC PetroKazakhstan Kumkol Resources. The fine grained sand of the "Cretaceous Hills" deposit (Uralsk) and sand barren sand of the Kyzylorda deposit was used as reinforcing additives.

The studied chemical compositions of the loess-like loam are presented in Table 1.

Table 1. – Chemical composition of loam of Kyzylorda and Chagan deposits

Name of raw materials	Oxide content, mass%												
	SiO_2	Al_2O_3	TiO_2	CaO	MgO	Fe_2O_3	P_2O_5	F	SO_3	CO_2	Na_2O	K_2O	p. l.
Loam of Kyzylorda deposit	52,58	12,25	–	12,0	2,13	5,10	–	–	2,57	–	3,60	–	9,78
Loam of Chagansky deposit	55,1	14,3	–	13,2	3,1	7,3	–	–	2,8	–	–	2,6	11,43

To prepare a conglomerate mixture, the oil slimes were pre-mixed thoroughly in a propeller-type laboratory mixer. After cross-linking, the oil sludge has the following characteristics: conventional viscosity at 80 °C — 2.1 Pa·s; Density at 20 °C, — 950–960 kg/m^3; The content of petroleum products is 34.0–37.9% by weight, water is 27–36.2% by weight, mechanical impurities are 4.0–4.5% by weight.

The next stage in obtaining conglomerate oil sludge mixture is the joint mixing of oil sludge with fine-grained sand in certain proportions. The resulting conglomerate, after mixing, acquires flow ability and creates favorable conditions for subsequent mixing with loess-like loam.

After the preparation of the raw material the components are dosed for preparing ceramic masses. Component ceramic compositions are presented in Table 2.

Table 2. – Component ceramic compositions

Composition number	Component, mass%	
	Loam of Chagansky deposit	Conglomerate mixture in the composition fine-grained sand (Cretaceous hills) and oil sludge of Zhaikmunai LLP
1	95	5
2	90	10
3	85	15
	Loam of Kyzylorda deposit	Conglomerate mixture in sand composition (Kyzylorda deposit) and oil sludge of PetroKazakhstan Kumkol Resources JSC
4	95	5
5	90	10
6	85	15

From the prepared ceramic mass by the method of plastic molding, granules with a diameter of 10–20 mm were formed.

The molded granules were dried in a drying oven at a temperature of 80–90 °C to a residual moisture content of 7–8%.

The dried granules were heat-treated at a temperature of 350–370 ° C in an electric muffle furnace and fired in a rotary kiln RSR120–1000/13 according to a specially designed regimen. The firing temperature was between 1100–1200 ° C.

Burned granules were tested for determine the physical mechanical properties. The results of the experimental studies are presented in Table 3.

Table 3. – Physical and mechanical properties of the samples under study

Composition number	Firing temperature °C	Bulk density, kg/m^3	Crushing strength in a cylinder, MPa	Heat conductivity coefficient, W/m*K
1	1150–1160	675	4,4	0,1
2		662	4,3	
3		654	4	0,07
4		540	5,1	0,1
5		470	4,5	0,07
6		451	4,3	

Conclusions and the results.

As the results of experimental studies show, with an increase in the content of the conglomerate mixture from 5 to 15%, the changes in the physical and mechanical properties of the samples obey the following regularities:

– the bulk density gradually decreases from 675 to 451 kg/m^3;

– the strength of the samples when squeezed in the cylinder is higher in the formulations where it has the lowest content of the conglomerate mixture;

– the thermal conductivity of the samples also changes in the direction of decrease. At the same time, the thermal conductivity is lower in the compositions, where the content of the conglomerate mixture is the highest.

A distinctive feature of the developed technological solutions is that to obtain a lightweight aggregate, weakly-loess loess-like loams that promote the expansion of the raw material base for the production of lightweight aggregates are used as the main raw material.

In addition, the use of oil sludge in the technology production of lightweight aggregates as an energy-releasing component reduces energy costs by 20–25%.

Environmental effect is achieved by using the waste oil industry in the production of finished products in demand.

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AMMONIUM NITRATE WITH BENTONITE CLAYS ADDITIVE FROM UZBEKISTAN

Abstract: The samples of nonpacking AN obtained by bentonite in NH4NO3 melt subsequent prilling bentonite clay's melt have been prepared. It has been that bentonite additives in NH_4NO_3 melt containing 1% of humidity at AN:BG = 100: (1–1.5) roses strength of AN granules in 1.5–2.0 fold while the packing reduces in 2–3 times in comparison to saltpetre containing magnesite. Furthermore, the granules hold 50 and more cycles of $20 \leftrightarrows 50$ ° C heat-cool. When cooling the melt with bentonite it was revealed that absence of III phase and presence of direct transition of IV→II that differs from pure NH_4NO_3 leading to stable behaviour of AN at variations in temperature (25–55° C) without destruction of granules. This phenomenon is important during the storage and handling of products.

Keywords: ammonium nitrate, bentonite clay, melt, granulation, nonpacking, strength, packing, thermo stability, porosity, blotting capacity, polymorphic transition, density and viscosity.

Introduction

The majority nutritious for plants are nitrogen, phosphorus and potassium. Namely these three elements provide the growth of farming industry. In Uzbekistan there are JSC "Maxam-Chirchik", "Navoiazot" and "Ferganaazot" produce nitrogen fertilizers which assortment consist of ammonium nitrate (AN), urea and ammonium sulphate. In addition, three JSC such as "Ammophos-Maxam", "Samarkandkimyo" and "Kokand superphosphate zavod" produce phosphorus containing fertilizers namely ammophos, suprephos-NS, ammonium sulphate-phosphate, PS-Agro, feed ammonium phosphate, nitro calcium phosphate, simple and enriched superphosphate. Unitary enterprise (UE) "Dehkanbad potassium fertilizer plant" lets out just potassium chloride. In 2015 nitrogen industry produced 942.72 thousand tonnes of nitric fertilizers in amount of 100% in form 1646.66 thousand tonnes of AN, 586.66 thousand tonnes of carbamide and 192.65 thousand tonnes of ammonium sulphate.

Ammonium nitrate is all-round fertilizer that uses effectively on all type of soils at introduction under various crops. It can be introduced as basal dose and additional fertilizing. However, this fertilizer has two severe drawbacks such as packing during the storage and high explosion hazard [1–3].

Introduction modifying additives to AN improves its consumer properties. One of the best additive eliminating AN packing is magnesia. Today our manufactures use caustic magnesite MgO and brusite $Mg(OH)_2$ as additives for AN, bought from abroad that leads to increase prime prise. In terms of large-tonnes of AN it is necessary to replace both magnesite and brusite to local raw materials to save currency. For that, bentonite clay can be available rather reserves are quite more. By the way, there has been the approximately 200 deposits and developments of bentonite clays with reserves more than 2 billion tonnes in Uzbekistan [4].

Materials and methods

The composition and physic-mechanical properties of bentonite from Azkamar, Kattakurgan, Lagon and Navbakhor (brand PPD – carbonate and polygorsite, as well as PBG – alkaline-earth), which worked out, are summarized in table 1 and 2. In order to obtain modified AN it was used AN brand "pure" as the main component. Moreover, granular NH_4NO_3 and industrial product, AN containing 34.6% of N and 0.28% of MgO were used for comparison.

Table 1. – Chemical composition of initial bentonite clays from various fields

Components	**Content, weight%**				
	Azkamar	**Kattakurgan**	**Lagon**	**Navbahor**	
				Brand PPD	**Brand PBG**
SiO_2	50,34	57,89	49.73	46.06	72.23
Al_2O_3	15,21	16,71	14.74	8.78	8.82
Fe_2O_3	5,67	5,19	5.57	3.0	3.93
CaO	4,76	1,12	2.26	12.2	1.26
MgO	2,3	2,9	4.45	4.33	1.81
CO_2	3,41	< 0,2	2.97	9.35	0.20
K_2O	2,36	3,92	4.75	1.05	1.33
Na_2O	2,31	1,68	2.15	0.75	1.12
SO_3	1,48	< 0,10	0.57	1.39	1.10
P_2O_5	0,13	0,14	0.1	0.77	0.50
H_2O	5,42	6,17	3.80	6.0	4.37

Table 2. – Physic-mechanical behaviours of bentonite clays from different deposits

Properties	**Показатели**			
	Azkamar	**Kattakurgan**	**Lagon**	**Navbahor, brand PPD**
1	***2***	***3***	***4***	***5***
Humidity, %	2.23	2.15	2.38	1.62
Free density, г/см^3	0.796	0.641	0.792	0.620
Density with compaction, г/см^3	1.193	0.946	1.074	0.916
Angle of slope, degree.	26°53′	20°33′	17°25′	24°50′

1	2	3	4	5
Friability, sec.	18.33	17.42	14.17	16.27
Hygroscopic point, %	37.5	38.0	38.0	38.5
Moisture capacity, %	6.91	7.14	6.21	8.26
PH of 10% suspension	7.46	7.33	7.38	7.40

In current study there has been that composition and properties of nonpacking AN obtained based on bentonite clay (BC) and melt of AN with weight ratios AN: BC from 100:0.5 to 100:3.0. Control on quality of AN obtained with bentonite was conducted as follows: nitrogen content, strength, caking, thermal resistance of granules was determined recurrent cycles of heat-cool at 20⇆50 °C, thermal stability was defined by buffer action, porosity, blotting capacity, and polymorphic transmission of NH$_4$NO$_3$. During the exploration it was studied that effect of bentonite on rheological properties of AN melt. Nitrogen content in product was determined by Kjeldal, ammonia distillation in alkaline condition with Devard's melt subsequent titration [5].

Strength of granule according to [6], but packing by express technique [7]. Measure of granule porosity was defined by volumetric method to [1]. Blotting capacity of granule in towards to liquid fuel (solar oil) was determined on granular porous AN brand "pure", according to TU 6-03-372-74. Density of nitrate-bentonite slurry was found by picnometric, and viscosity by efflux method. The polymorphic transformation of AN was defined in a range of heat-cool temperature from 25 to 175 °C – from 175 to 25 °C on equipment NETSCH STA 409 PC/PG by fixing their caloriferic effect. The thermal resistance of granule for recurrent cycles of heat-cool at a range of 20⇆50 °C was determined by [8].

Table 2 shows that bentonites containing 1.62–2.38% of humidity have density such as 0.796 g/cm^3 for Azkamar, 0.641 g/cm^3 for Kattakurgan, 0.792 g/cm^3 for Lagon and 1.21 g/cm^3 Navbahor PPD. Angle of natural slip of bentonite clay is 17–26 degree. However, their flowability is steady, and spreaded without difficulty. Limiting moisture capacity is 6.21–8.26%, but much higher humidity the raw loses its friability. As the main clayey mineral in bentonite are montmorillonite, kaolinite, polygorsite illite and chlorite. Besides, these minerals there are calcite, quartz, potassium spar, baryte, and so on. Composition and properties of bentonite clays allow forecasting possibility to use them as AN's modifier. Preparatory to introduction of them into AN melt the additives were milled till size 40 micro and dried till 1.0 % of humidity. For preparation of operative embodiments certain amount of pure NH$_4$NO$_3$ was melted at 175 °C. Following that, weighed portion of bentonite was fed into the melt. Obtained bentonite-nitrate melt was held in 3 minutes after that it was granulated by prilling way.

Results and discussion

It is revealed that additive from any type of bentonite reduces packing of AN. The more of amount of bentonite the higher strength, thermal resistance of granules grow and the less packing of ones. In fact, that nonpacking AN with less 34% of N possesses sufficient strength of 1.90–3.85 MPa and can hold 50 and more cycles of heat-cool. The packing of AN with ratio of AN:BG = 100: (1–1.5) is less in 2-3 times (table 3) than AN with magnesite (4.67 kg/cm^2). In that case, AN added Navbahor bentonite has the most strength 2.50–2.94 MPa.

It has been established that granule strength of pure NH4NO3 without additives constitutes 1.36 MPa, while that of AN with magnesia makes 1.58 MPa. The granule strength of pure NH4NO3 has already after 10 thermal cycles destructed at 5%, but after 80 ones destructed completely. In terms of the granules with magnesia has crushed after cycles while since 100 cycles it has destructed in full. Whereas, AN containing bentonite with 2.0% of humidity retains its wholeness since 50 thermal cycles. After all, the degradation of granules starts just since 60 cycles.

Also it is seen from table 3 that porosity of pure NH4NO3 and AN with magnesia constitute 22.0 and 9.10% respectively. But addition of Azkamar bentonite in NH4NO3 melt from 1 to 3 g in towards to 100 g of NH4NO3 makes to reduction the porosity granule from 7.71 to 6.85% using Navbahor bentonite (brand PPD), from 7.92 to 7.01% Kattakurgan bentonite from 7.73 to 6.89% and from 7.84 to 6.93% Lagon bentonite. Depending the upon ratio AN:BC blotting capacity of solar oil by AN granules oscillates in a range 2.88–3.77; 3.06–3.90; 2.97–3.81 and 3.02–3.92 g of fuel in towards to 100 g of product, respectively Azkamar, Navbahor, Kattakurgan and Lagon. However, this figure for pure NH_4NO_3 was 4.82 g while AN containing 0.28% of MgO was 4.33 g. In fact, that above mentioned confirms reasons growth of the strength of fertilizers' granule.

Table 3. – Impact of initial bentonite'moisture and its amount on granule strength, as well as AN packing

Weight ratio of AN: BC	**N, %**	**Strength of granule, MPa**	**Packing, kg/cm^2**	*** Porosity of granule, %**	*** Blotting capacity of granule, g**
With Navbahor bentonite (PPD)					
100: 0.5	34.29	2.01	2.28	no determined	no determined
100: 1.0	34.10	2.50	2.17	7.92	3.90
100: 1.5	33.92	2.94	1.95	no determined	no determined
100: 2.0	33.71	3.15	1.51	7.44	3.22
100: 2.5	33.63	3.30	1.35	no determined	no determined
100: 3.0	33.45	3.51	1.69	7.01	3.06
With Azkamar bentonite					
100: 0.5	34.29	1.90	1.89	no determined	no determined
100: 1.0	34.12	2.30	1.67	7.71	3.77
100: 1.5	33.94	2.52	1.52	no determined	no determined
100: 2.0	33.75	2.74	1.35	7.28	3.09
100: 2.5	33.56	2.95	1.28	no determined	no determined
100: 3.0	33.42	3.12	1.44	6.85	2.88
With Lagon bentonite					
100: 0.5	34.30	2.14	2.09	no determined	no determined
100: 1.0	34.11	2.14	1.77	7.84	3.92
100: 1.5	33.95	2.54	1.69	no determined	no determined
100: 2.0	33.78	2.82	1.41	7.40	3.26
100: 2.5	33.60	3.34	1.33	no determined	no determined
100: 3.0	33.46	3.85	1.59	6.93	3.02
With Kattakurgan bentonite					
100: 0.5	34.28	1.96	2.74	no determined	no determined
100: 1.0	34.14	2.20	2.25	7.73	3.81
100: 1.5	33.96	2.50	1.98	no determined	no determined
100: 2.0	33.77	2.74	1.74	7.30	3.17
100: 2.5	33.61	3.21	1.52	no determined	no determined
100: 3.0	33.44	3.60	1.87	6.89	2.97
NH_4NO_3 "pure"	34.96	1.58	5.62	22.0	4.82
AN with 0.28% of MgO	34.6	1.32	4.67	9.10	4.33

** with additive of Navbahor bentonite brand PPD*

Thermal explores conducted in a range of heat-cool from 25 to 175 ° C – from 175 to 25 ° C presented (table 4) that melting NH_4NO_3 (without additives) passes through the transformation IV→III; III→II; II→I and I→melt. In case, polymorphis transition IV→III is 46 ° C, III→II – 85 ° C, II→I – 126 ° C, while phase transition under I→melt is 169 ° C. Because of polymorphic transition IV→III leads to large deformation of crystal lattice. Moreover, for AN with bentonite additives 4 consequent modification transitions observed typical to NH4NO3, but differenced on temperature transition and ratio AN : BC. So, the temperature transition IV→III, III→II, II→I and I→melt changed 56.1; 91.1; 133.6 and 174.2 ° C, respectively when AN : BC = 1:0.5 whereas at AN : BC = 1 : 2.5 it was 58.7; 92.3; 134.1 and 170.3 ° C using Azkamar bentonite. As seen of them that additive of bentonite reduces considerably melting point and crystallization of NH_4NO_3. Similar pattern can be observed and the rest type of bentonites. In that case, they differenced each other on value indicated figure.

Table 4. – Modification transition temperature based on melt of AN and Azkamar and Kattakurgan bentonites

Weight of AN: BC	Peak value on the curve								
	IV→III	III→II	II→I	I→плав	плав→I	I→II	II→III	III→IV	II→IV
	Heat from 25 to 175° C				Cool from 175 to 25° C				
NH_4NO_3	46	85	126	169	169	125	48	30	–
With Azkamar bentonite									
100: 0.5	56.1	91.1	133.6	174.2	167.4	122.2	–	–	49.3
100: 1.0	58.2	92.0	133.7	173.4	167.0	122.2	–	–	49.9
100: 1.5	59.0	92.6	133.9	172.3	166.5	122.4	–	–	50.1
100: 2.0	58.3	93.0	134.0	171.1	166.2	122.6	–	–	50.4
100: 2.5	58.7	92.3	134.1	170.3	166.0	123.0	–	–	50.6
With Kattakurgan bentonite									
100: 0.5	55.6	90.8	133.4	174.0	167.4	122.2	–	–	49.8
100: 1.0	56.0	91.4	133.5	173.2	167.2	122.3	–	–	50.1
100: 1.5	56.5	92.1	133.6	172.0	166.9	122.6	–	–	50.3
100: 2.0	57.2	92.5	133.7	170.3	168.2	123.0	–	–	50.5
100: 2.5	57.7	93.1	133.9	169.1	167.8	123.2	–	–	50.6

It has been revealed the value of polymorphic transition observed during the cool is lower than heat. When cooling melt of pure NH_4NO_3 melt transition melt→I; I→II; II→III и III→IV takes place at 169; 125; 48 and 30 ° C respectively. At that time cooling AN with bentonite modification transition occurs through melt→I; I→II; II→IV. As result, III phase does not generate, that is transition II→IV passes III phase that provides lesser deformation of crystal lattice, as well as sufficient strength. Following that, bentonite additive stabilizes IV modification during the storage and application of AN at temperature fluctuation till +51° C dramatic volume change of its crystals connected with modification transition will not takes place.

Therefore, increase in temperature monotonous reduces in both density and viscosity of AN melt independently from amount of bentonite. In studied ranges ratio AN : BC (100 : 0.5-3.0) and temperature (165–185° C) density and viscosity of all bentonite-nitrate melts (1.437–1.65 kg/cm^3 and 4.88–9.14 cps respectively) differenced slightly on viscosity of AN containing magnesia (1.433–1.454 kg/cm^3 and 4.85–5.91 cps) and is quite acceptable for prilling.

Thus, bentonite clays on elimination of AN packing can change completely imported additives namely brusite and magnesite. The AN modified by bentonite exceeds industrial AN (State standard 2-85) on physic-mechanical figures. As bentonite clay is inexpensive and available that provides economic expediency for AN manufacture.

Conclusion

Finally, there have been investigated the physic-mechanical properties of (disperse composition, moisture, apparent density, angle slope, fluidity, pH, hygroscopicity, moisture capacity) Uzbek bentonite. Furthermore, it was studied that preparation process of nonpacking AN with bentonite in the NH_4NO_3 melt (99,85 % solution) at 175 °C before its granulation by prilling way. In that case, the amount of additive was changed from 0.5 to 3.0 g in towards to 100 g of NH_4NO_3. Also the composition and properties were determined. In order to obtain nonpacking AN, which possess sufficient strength (1.90–3.85 MPa) hold 50 and more cycles of heat-cool (20⇆50 °C), while humidity of bentonite should be no more 1–2%. To compare the strength of pure AN makes 1.36 MPa while AN with magnesia is 1.64MPa. The packing AN with ratio AN: BC = 100 : 1÷1.5 that is less by 2–3 times than AN with magnesia (4.67 kg/cm^2). When studying polymorphic transition in cycle heat-cool (from 25 to 175 – from 175 to 25 °C) it was shown that with cooling melt of AN with bentonite transition melt→I; I→II и II→IV takes place subsequently. Accordint to III phase does not form because of polymorphic transition IV→II passes III phase that provides lesser deformation of crystal lattice and the largest strength of granules. A base of the above mentioned rheological properties (density and viscosity) of bentonite-nitrate melts were defined. The result obtained can be available for granulation by prilling.

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Section 5. Chemistry

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SYNTHESES ON THE BASIS OF MORPHOLINE WITH EPICHLOROHYDRIN

Abstract: The spontaneous polymerization of morpholine has been investigated with epichlorohydrin. It is shown that by mixing the morpholine with epichlorohydrin in bulk in the environment in various organic solvents, at temperatures from 10 to 50 °C the chemical reaction, which is accompanied by formation of water-soluble high-molecular product. Determined reaction orders by monomer and the total energy of activation for this reaction.

Keywords: spontaneous, polymerization, solvent, reaction order, monomer, activation energy.

The synthesis of compounds with morpholine fragments and search in this series of new biologically active substances are actual problem of modern organic synthesis. A morpholine derivatives possess antimicrobial, analgesic activity and provided psychotropic properties. They are synthetic analgesics, anticonvulsants and antituberculous, some of which have found application in medicine, pharmaceutics, organic synthesis, petrochemical and other ortaclar national economy [1, 25–26; 2, 26–28]. In this regard, expanding the range of derivatives of morpholine is of great theoretical and practical interest.

We have found that in the interaction of morpholine (MF) with epichlorohydrin (ECG) as the mass, and among various organic solvents in the temperature range from 20 to 50 °C the chemical reaction, which is accompanied by formation of water-soluble high molecular weight product [3, 26].

It has been determined experimentally that the radical inhibitors — 2,2,6,6-tetramethylpiperidine-1-oxyl, hydroquinone and oxygen in the air does not have a significant inhibiting effect, i. e. exclude the radical nature of the process.

The study of kinetic regularities of the spontaneous polymerization of morpholine with epichlorohydrin has been carried out with the gravimetric method. To study the effect of nature of solvents on the reaction of polymerization of morpholine with epichlorohydrin, the process has been carried out in solvents medium with different dielectric constant (benzene, acetone, ethanol, dimethylformamide).

Increase in the dielectric constant of these solvents from 2.33 to 36.7 accelerates the process of spontaneous polymerization, while the highest rate was observed in the medium of dimethylformamide (Fig.1).

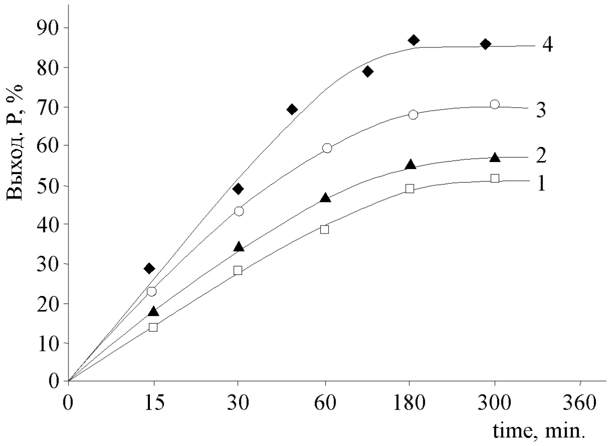


Figure 1. The dependence of the yield of oligomer in the interaction of morpholine with epichlorohydrin at the ratio of 1:1 in different solvents: 1–benzene; 2–acetone; 3–ethanol; 4–dimethylformamide at 50 °C

Increase in the velocity of process of spontaneous polymerization with increasing medium polarity, apparently, can be explained by the acceleration of the salt formation in the polar medium, which is the limiting stage of the process. The polymerization reaction in the three studied systems proceeds homophase, and in benzene heterophase. To study the kinetic features of the reaction of spontaneous polymerization ethanol has been chosen asolven. Kinetic measurements of spontaneous polymerization in the solvent at different temperatures of 30–50 °C has been carried out (Fig. 2).

The figure shows that as the temperature increases, the rate of the investigated reaction increases. However, the reaction at high temperatures did not consider it necessary, as can occur secondary reactions, which negatively reflected in the fundamental reactions.

From the temperature dependence of the reaction rate at 30–50 OS the value of the effective activation energy of the process, which is of 56.2 kJ/mol, which is close to the value of the activation energy of the reaction of quaternization in Menshutkin reactions, has been determined.

IR-spectal analysis has been conducted to identify the structure of the synthesized product based on morpholine with ECG. In the IR spectra of the synthesized product, the signals of the stretching vibrations C–Cl bonds (1270 cm^{-1}) relating to-CH_2Cl group of the epichlorohydrin, as well as deformation fluctuations of the NH group (1545 cm^{-1}) morpholine completely disappear and develop absorption bands in the region 3350–3250 cm^{-1}, characteristic of quaternary ammonium groups.

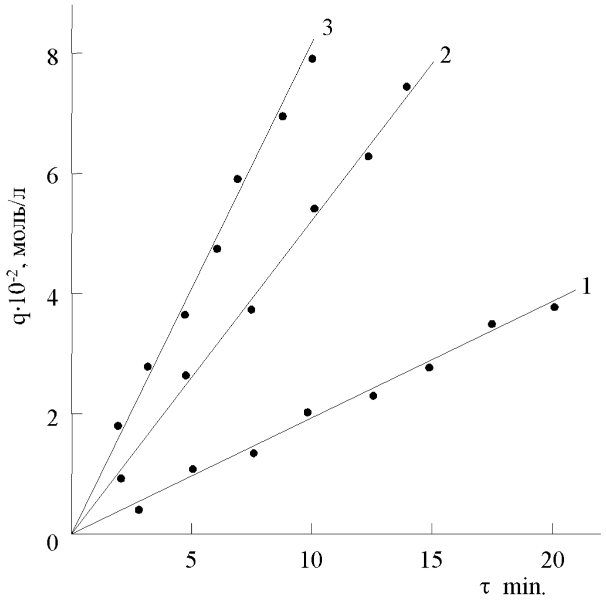
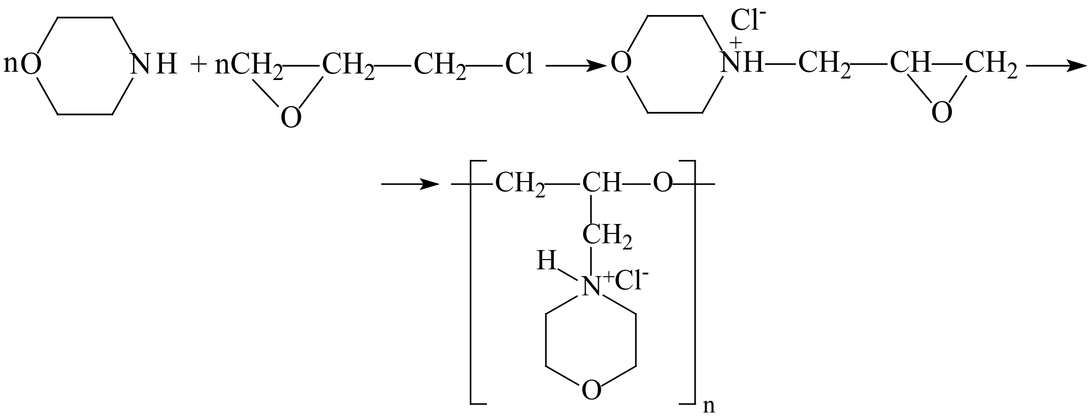


Figure 2. The dependence of the spontaneous polymerization reaction of morpholine with epichlorohydrin on the temperature, °C: 1–30; 2–40; 3–50. [Morpholine]= [Epichlorohydrin]=1:1 mol/l; [Hydroquinone]= $1\cdot10^{-4}$ mol/L

The simultaneous formation of new intense bands of absorption at 1511 cm^{-1} related to asymmetric stretching vibrations of an ether –C-O-C bonds, which are absent in the spectrum of the ECH. This testifies that the reaction is accompanied with the disclosure epoxygroups (1250, 930–850 cm^{-1}) of epichlorohydrin in the process of spontaneous polymerization.

Based on the results of IR-spectral studies and literature data the structure of synthesized polymers can be described as following:



The results of experimental studies and IR spectral analysis show that the necessary phase discovered spontaneous polymerization process is the Menshutkin reaction, i. e. the reaction of quaternization of MF with epichlorohydrin with formation of quaternary salt, which is involved in the polymerization.

So, spontaneous polymerization of morpholine with ECH consists of the reaction of quaternization and polymerization. Study of the reaction of quaternization separately failed, as the resulting salts are involved in the instant polymerization.

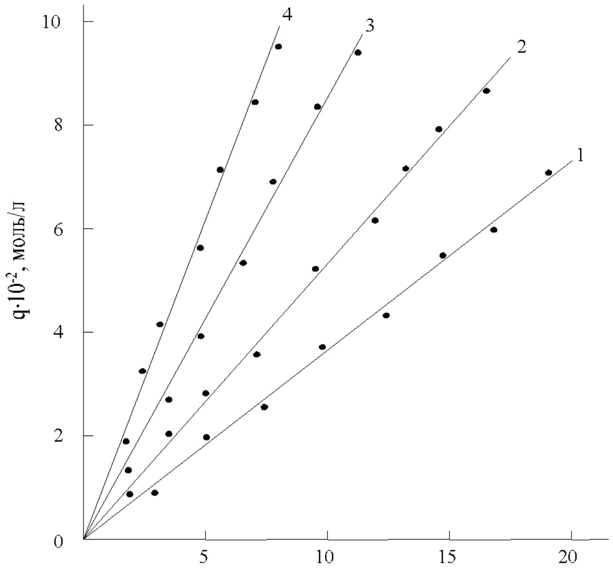


Figure 3. The dependence of the spontaneous polymerization reaction of MF with ECH on the concentration of morpholine, mol/l: 1–0,25; 2–0,5; 3–0,75; 4–1,0. [ECH]=1.0 mol/l [Inh]= 1·10–4 mol/l. Temperature of 50°C

To study the influence of the concentration of initial reagents on the polymerization process shows that the rate of reaction increases along with increasing concentration of morpholine and the ECH. The reaction order for the concentration of morpholine is 1.1, and the concentration of the ECH is 0.9 (Fig. 3, 4).

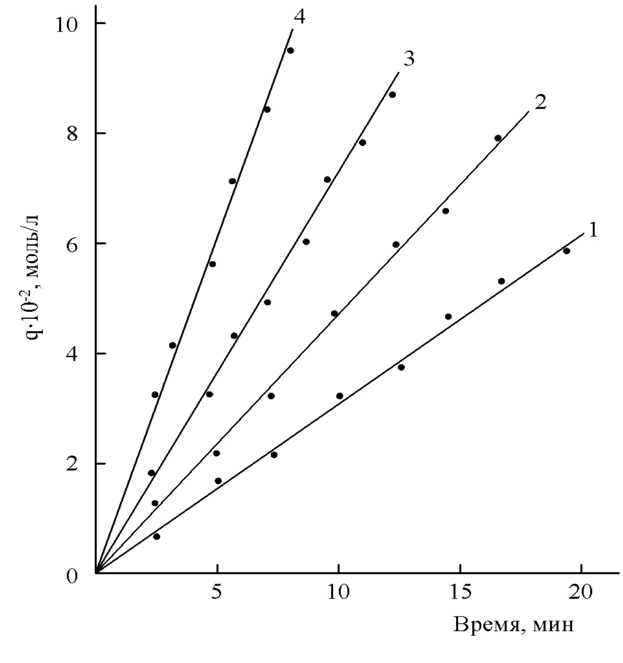


Figure 4. The dependence of the spontaneous polymerization reaction of MF with ECH from ECH concentration, mol/l: 1–0,25; 2–0,5; 3–0,75; 4–1,0. [MF]=1.0 mol/l [Inh]= 1·10–4 mol/l. Temperature of 50°C

The synthesis of polymers on the basis of tetrahydro-1,4-oxazine with 3-chlorine-1,2-epoxypropane the mass was performed as following: to 1 mol of 3-chloro-1,2-epoxypropane and 1% hydroquinone (on total mass of the original reagents) is added with stirring 1 mole of tetrahydro-1,4-oxazine. The reaction mixture is heated to 50 °C for 3 hours. After some time the reaction product is precipitated by sulphuric ether. The yield is 90–92%. The synthesized polymer is a powder of white or light pink.

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