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PHYSICO-CHEMICAL PRINCIPLES AND TECHNOLOGY OF PRODUCTION OF MAGNESIUM CHLORATE DEFOLIANT BASED ON LOCAL RAW MATERIALS AND SECONDARY PRODUCTS

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ABSTRACT

The process of conversion of magnesium chloride with sodium chlorate depending on the temperature and duration of time is studied. The results of carried out research have showed that for the production of magnesium chlorate, it is optimal to perform the conversion of sodium chlorate with 37.14 % aqueous solution of magnesium chloride at a molar ratio of the initial salts of 2:1 for 60 minutes at a temperature of 100°C.

Keywords: magnesium chlorate, sodium chlorate, sodium and magnesium ions, system, concentration, preparation, visual-polythermal method, temperature, solubility, conversion, reaction kinetics.

Magnesium chlorate is one of the widely used defoliant-desiccants of inorganic origin. An industrial method for producing magnesium chlorate is based on the interaction of sodium chlorate with magnesium chloride hexahydrate (bischofite) by an exchange reaction[1].

$$MgCl_2 \cdot 6H_2O + 2NaClO_3 \rightarrow Mg(ClO_3)_2 \cdot 6H_2O + 2NaCl. \qquad (1)$$

Magnesium chlorate, produced in the domestic industry (Ferganaazot JSC Uzbekistan) under the trade name Magnesium Chlorate Defoliant (CMD), contains mixtures of magnesium and sodium chlorides, which are ballast and do not have the necessary physiological activity. Chlorine and sodium ions are not completely removed from the finished product (CMD), which, at room temperature in an aqueous solution of the defoliant, upset the equilibrium of the reaction towards the formation of sodium chlorate and magnesium chloride, as a result of which the efficiency of CMD decreases[2].

In this regard, we have investigated ways to increase the concentration of the active substance and reduce the chloride content in magnesium chlorate defoliant[7].

For the physicochemical substantiation and recommendation of the technology for obtaining a concentrated liquid and solid magnesium chlorate defoliant by the conversion of magnesium chloride with sodium chlorate, first of all, knowledge of the solubility, interaction of components in aqueous systems in a wide range of temperatures and concentrations is necessary.

An analysis of the literature data shows that information on the solubility and interaction of components in the $2Na^+$, $Mg^{2+}//2Cl^-$, $2ClO^-_3 - H_2O$ reciprocal system, which justifies the process of obtaining magnesium chlorate by the conversion of magnesium chloride with sodium chlorate, is available only for a temperature of 80 °C [15].

Magnesium (Magnesium), Mg is a chemical element belonging to the II group of Mendeleev's periodic system; is included in the working - earth metals. Atomic number 12, atomic mass 24,305. Natural magnesium consists of 3 stable isotopes. 24Mg (78.60%), 25Mg (10.11%), 26Mg (11.29%). Three artificial radioactive isotopes (23Mg, 27Mg, 28Mg) were obtained. Magnesium 1808 i. At first, the British physicist took Magnesium Devi in the form of an amalgam. In 1829, the French chemist Magnius Bussy exposed magnesium chloride to potassium vapor and isolated magnesium in its metallic form. Magnesium makes up 2.35% of the Earth's crust by mass. There are more than 100 minerals of magnesium, among which dolomite, forsterite or olivine, magnesia, carnallite and others are important[16]. The serpentine mineral is formed from the leaching of olivine rocks. Its fibrous form is called asbestos. As a result of decomposition under the influence of carbon dioxide gases deep underground, the serpentinites turn into talc rocks. When Tula breaks down, it turns into magnesite ($MgCO_3$). Under the influence of $MgCl_2$ solutions, limestones turn into dolomite $MgCa(CO_3)_2$. The largest dolomite deposits in Uzbekistan are located in Samarkand region[18].

0.38% in sea water; some lakes contain 30% magnesium chloride. Magnesium is a silver-white, soft, malleable, light metal, covered with a thin layer of oxide in air, turning black. This veil protects it from further oxidation. Density of magnesium is 1740 kg/m^3, melting point is 650°, boiling point is 1105°. 2 valence in magnesium compounds. Chemically very active metal.When heated in air, it emits a dazzling white flame and forms white magnesium oxide MgO, partially bluish magnesium nitrite Mg_3N_2. Does not react with water at room temperature. When it is boiled, it slowly releases hydrogen from water. It reacts violently with water vapor at 400°. When heated, it combines with nitrogen, sulfur, halogens and other non-metals. It easily dissolves in diluted acids and releases hydrogen. Under normal conditions, it does not dissolve in aqueous solutions of alkalis. When heated to 400-500° in a hydrogen atmosphere, hydride forms MgH_2. When magnesium is heated to 500-600° with sulfur or SO_2 and H_2S, sulfide MgS is formed. Due to the fact that MgF_2 can form a protective film, fluoride is insoluble in acid. Soluble in solutions of alkaline bicarbonate and ammonium salts. All magnesium salts are colorless, bitter, soluble in water. Magnesium forms alloys with many metals[1].

Magnesium is an integral part of plant and animal organism. Some algae, foraminifera, calcareous clouds are magnesium concentrates (they contain up to 3-4% magnesium). Magnesium is part of the green pigment of plants – chlorophyll[17]. It has been found that all plant cell organelles and all living organisms contain ribosomal magnesium. Phytin is present in the form of magnesium phosphate acid salts. Human and animal body gets magnesium from food. A person needs 0.3-0.5 g of magnesium per night.If magnesium salts are not enough in the food, the normal excitability of the nervous system and muscle contraction are disturbed. When there is a lack of magnesium in cattle feed, their muscles become tight and their legs do not develop.

In industry, magnesium is obtained by electrolytic, metallothermal and coal-thermal methods, but mainly by electrolyzing a mixture of $MgCl_2$, KC1 and NaCl solutions. Dolomite is used as a raw material in the metallothermal method, and ferrosilicon or silicoaluminum is used as a reducing agent. In the carbon-thermal method, a mixture of magnesium MgO and carbon is heated in hermetic furnaces at a temperature higher than 2100°.

It is used in pyrotechnics, metallurgy, alloys, hard-to-reduce metals (vanadium, titanium, uranium, zirconium), solid cast iron production, nuclear technology, film, photography and lighting technology.

In this regard, in order to substantiate the process of conversion of magnesium chloride with sodium chlorate, the solubility of the diagonal sections $MgCl_2 – NaClO_3 – H_2O$ of the above quaternary reciprocal aqueous system was studied. The study of the solubility of physicochemical systems was carried out by the visual-polythermal method [5].

By studying the binary system "magnesium chloride - water" it was established that the polythermal solubility diagram consists of branches of ice crystallization, twelve, eight- and six-water magnesium chloride. The cryohydrate point of the system corresponds to 21.0% magnesium chloride, 79.0% water at –35.5°C. The results obtained are in good agreement with the data of other authors [3].

The system "sodium chlorate - water" was the object of research by a number of authors. Our data confirm its eutecticity[4].

Solubility in the "magnesium chloride - sodium chlorate - water" system was studied by ten internal sections. Sections I–VI are drawn from the side of magnesium chloride to the top of sodium chlorate, and sections VII–X are drawn from the side of sodium chlorate to the $MgCl_2 \cdot 6H_2O$ pole. Based on the data obtained, a polythermal solubility diagram of the $MgCl_2 – NaClO_3 – H_2O$ system was constructed at temperatures from –41.2 to 100 °C (Fig. 1).

The polythermal solubility diagram of the studied system consists of solid phase crystallization fields: ice, sodium chloride and chlorate, twelve-, eight- and six-water magnesium chloride.

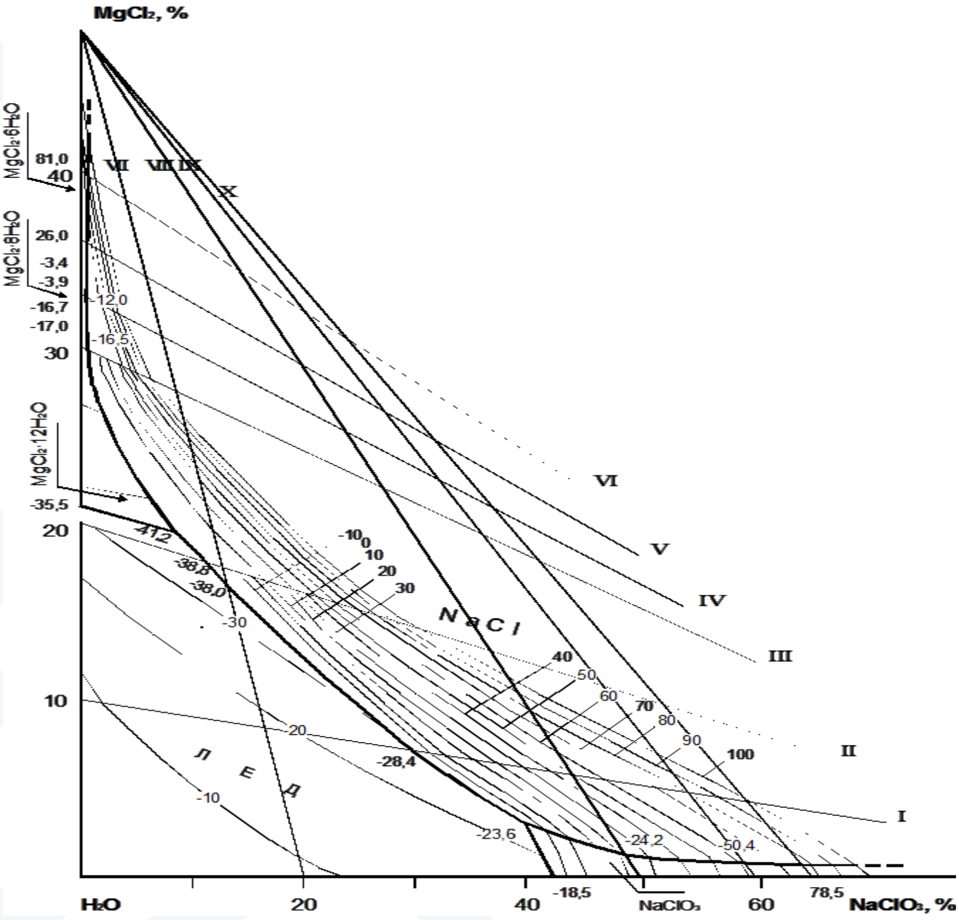

Fig 1. Polythermal solubility diagram of the system "magnesium chloride - sodium chlorate - water"

The fields converge at four triple invariant nodal points of the joint existence of three different solid phases. Their characteristics are presented in table 1.

Table 1. Double and triple points of the system "magnesium chloride - sodium chlorate - water"

Liquid phase composition, %			**Freezing temperature.,°C**	**solid phase**
$MgCl_2$	**$NaClO_3$**	**H_2O**		
39,60	0,40	60,00	81,5	$MgCl_2 \cdot 6H_2O$ + NaCl
36,80	0,50	62,70	26,6	Same
35,60	–	64,40	−3,5	$MgCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 8H_2O$
34,70	0,50	64,80	−3,8	$MgCl_2 \cdot 6H_2O$ + $MgCl_2 \cdot 8H_2O$ + NaCl
32,70	0,70	66,60	−11,9	$MgCl_2 \cdot 8H_2O$ + NaCl
32,30	–	67,70	−16,3	$MgCl_2 \cdot 12H_2O$ + $MgCl_2 \cdot 8H_2O$
31,90	0,90	67,20	−16,8	$MgCl_2 \cdot 12H_2O$ + $MgCl_2 \cdot 8H_2O$ + NaCl
30,00	1,0	69,00	−17,3	$MgCl_2 \cdot 12H_2O$ + NaCl
21,90	–	78,10	−35,5	Ice + $MgCl_2 \cdot 12H_2O$
19,70	8,90	71,40	−41,5	Ice + $MgCl_2 \cdot 12H_2O$ + NaCl
11,20	18,00	70,80	−38,4	Лед + NaCl
16,70	13,50	69,80	−37,0	Same
7,30	29,30	63,40	−28,2	Same
3,20	39,40	57,40	−23,5	Ice + $NaClO_3$ + NaCl
–	41,80	58,20	−18,3	Лед + $NaClO_3$
1,20	48,60	50,20	24,4	$NaClO_3$ + NaCl
0,80	59,30	39,90	60,5	Same
0,40	64,40	35,20	78,8	Same
				Same

The polythermal state diagram shows isothermal solubility curves every 10°C in the temperature range of –30°C –100°C. The projections of the system on the sides "magnesium chloride - water" and "sodium chlorate - water" are built.

According to the data obtained, most of the polythermal solubility diagram of the "magnesium chloride - sodium chlorate - water" system is occupied by the crystallization field of one of the conversion products - sodium chloride, which indicates its low solubility relative to other components of the system.

As a result of the conversion of magnesium chloride with sodium chlorate in the liquid phase, magnesium chlorate is formed, the crystallization field of which, due to its good solubility in the studied temperature and concentration ranges, is absent on the solubility diagram of the $MgCl_2 – NaClO_3 – H_2O$ system.

An analysis of the solubility diagram of the studied system shows that with an increase in temperature and concentration of the initial components in the liquid phase, an expansion of the sodium chloride crystallization field is observed. This indicates that with increasing temperature, the conversion of magnesium chloride with sodium chlorate in an aqueous medium proceeds easily and more completely. The results obtained show the expediency of carrying out the conversion process at 90–100°C. At these temperatures, the minimum concentration of sodium chlorate in the liquid phase, which causes the conversion of magnesium chloride with the formation of sodium chloride and magnesium chlorate, is 0.15–0.17%. With the aim of issuing practical recommendations for obtaining magnesium chlorate defoliant, the process of conversion of magnesium chloride with sodium chlorate was studied depending on temperature and time duration. The study was carried out at temperatures of 50, 75, 100 °C and duration of experiments 15, 30, 45, 60, 90, 120 minutes. A 250 cm^3 round bottom flask equipped with a stirrer was charged with 100 g of a 37.14% aqueous solution of magnesium chloride and an equivalent amount of sodium chlorate. The flask was placed in a thermostat with a given temperature and vigorously stirred. After the required period of time, the liquid phase was separated from the precipitate and the corresponding chemical analysis was carried out. On the basis of the data obtained, the degree of conversion of magnesium chloride with sodium chlorate and the consumption of initial components during conversion were established (Figs. 2 and 3).

From fig. 2 it can be seen that the degree of conversion significantly depends on the temperature and increases with its growth. Within 45 minutes, the degree of conversion at a temperature of 323, 348 and 373 K is 40.1, respectively; 49.9 and 62.9%. After 60 minutes, the degree of conversion is reached to 48.7; 60.8 and 71.98%, respectively, at temperatures of 323; 348 and 373 K. A subsequent increase in the duration of the conversion practically does not lead to an increase in the degree of conversion of magnesium chloride with sodium chlorate. At a temperature of 373 K and an experiment duration of 120 minutes, the degree of conversion was 72.3%. At this temperature, an increase in the duration of the experiment from 60 to 120 minutes leads to an increase in the degree of conversion by only 0.32%.This, apparently, is explained by the fact that during the first 60 minutes of conversion, a sufficient amount of sodium chloride is formed according to reaction (2), which subsequently negatively affects the course of this reaction in an aqueous medium.

$$MgCl_2 + 2NaClO_3 = Mg(ClO_3)_2 + 2NaCl. \qquad (2)$$

An analysis of the kinetic curves for the consumption of magnesium chloride and sodium chlorate per 100 g of a 37.14% solution of magnesium chloride in the conversion process at 323–373 K indicates that the amount of consumed initial components increases in the first 60 minutes (Fig.3), and after 60 minutes is practically unchanged. An increase in temperature from 50 to 100°C. leads to an increase in the consumption of magnesium chloride and sodium chlorate during conversion.

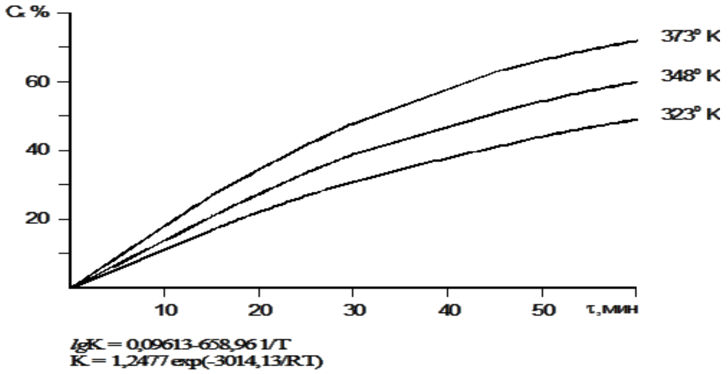

Fig 2. Dependence of the degree of conversion of magnesium chloride with sodium chlorate on temperature and time duration

The reaction order of the conversion process was determined using the first-order kinetic equation similarly to the work of the authors of.

$$К = 2{,}303/\tau \cdot \lg C_0 / (C_0 – C_\tau), \qquad (3)$$

where C_0 and C_τ are the concentrations of magnesium (or sodium) chloride, respectively, at the initial stage of conversion and over the elapsed time interval (τ), K is the conversion rate constant.

According to the obtained data, the order of the process of conversion of magnesium chloride with sodium chlorate is equal to one. This is confirmed by the fact that the conversion rate constant calculated by equation (2) on the basis of experimental data remains almost constant for each temperature (Table 2). In addition, the linear dependence of $\lg(C_0 – C\tau)$ on τ also indicates the first order of the process of conversion of magnesium chloride with sodium chlorate (Fig. 4). The conversion rate constant increases with increasing temperature (Table 2). Its dependence on temperature obeys the Arrhenius law. This is confirmed by the rectilinear graphical dependence of lg K on 1/T (Fig. 4).

Table 2. Rate constant of conversion of magnesium chloride with sodium chlorate

τ, minutes	**Rate constant, К·10⁻² minutes**			**E, kDj/ mole**
	50 °C	**75 °C**	**100 °C**	
16	1,154	1,590	2,144	12,622
32	1,165	1,590	2,104	–
48	1,139	1,581	2,204	–
64	1,113	1,561	2,121	–
Average	1,142	1,580	2,143	

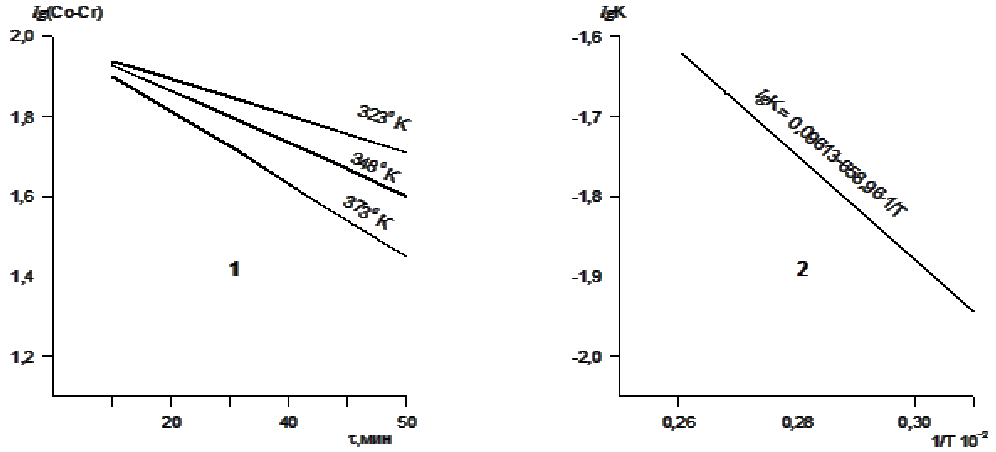

Fig 4. Addiction $lg(C_o – C_τ)$ от τ и lg K от 1/T (2)[8]

In order to establish the values of the conversion rate constant for various temperatures, the constants (K_o) were calculated for the Arrhenius equation:

$$K=K_o e^{E/RT} \quad (3)$$

and an equation for the dependence of lg K on 1/T was derived.

Let's transform more complex functions into linear ones. After taking the logarithm of equations (3), we obtain[9]:

$$\lg K=\lg K_o - E/2.303•1.987 \cdot 1/T \quad (4)$$

In order to shorten the notation, we introduce new notation:

$$\lg K=η;\ \lg K_o=ą\ ;b= E/2.303•1.987=E/4{,}575;1/T=ξ \quad (5)$$

We get:

$$η= ą – в•ξ. \quad (6)$$

Compositional relationship:

$$b_{2,1}= η_2–η_1/ξ_1 – ξ_2;b_{3,2}= η_3–η_2/ξ_2 – ξ_3;b_{3,} = η_3–η_1/ξ_1 – ξ_3 \quad (7)$$

and by calculating the individual values of b on the basis of experimental data (table 2), we find the average value of b.

The calculation of the average value ą is found by the formula:

$$ą = Ση + b\cdot Σξ/3. \quad (8).$$

Подставляя рассчитанные величины ą и b в уравнение (5), будем иметь:

$$η = 0{,}096130 – 658{,}96\cdot ξ; \quad (9)$$

$$lgK = 0{,}09613 – 658{,}96\cdot 1/T. \quad (10)$$

Znachenie kajushcheysya energii activatsii (E), vychislennoe po formula E = b•4.575, sostavilo 3014.73 cal/mol, ili 12.622 kDj/mol. Substavlyaya vychislennoe znachenie a v lgKo = a, I get:

$$lgK_o = 0{,}09631.$$

Hence Ko = 1.2477.

After substituting the values of K_o and E, the empirical Arrhenius equation (3) takes the form:

$$К=1,2477 \exp(-3014,73/RT). \qquad (11)$$

Based on equations (8) and (9), the rate constants of the conversion reaction for various temperatures in the range of 323–373 K every 10 K and the temperature coefficient of the conversion rate were calculated (Table 3).

According to the data obtained, the temperature coefficient of the conversion rate with an increase in temperature by 10 K in the range of 323–373 K increases by a factor of 1.22–1.146.

Table 3 Rate constant and temperature coefficient of conversion rate at various temperatures

Temperature, °C	Conversion rate constant, K•10–2 min-1	Temperature coefficient of conversion rate, (γ)
50	1,142	–
60	1,310	1,146
70	1,496	1,142
80	1,696	1,134
90	1,909	1,126
100	2,143	1,122

Thus, it follows from the results of the studies that it is optimal to obtain magnesium chlorate by converting sodium chlorate with a 37.14% aqueous solution of magnesium chloride at a molar ratio of the initial salts of 2:1 for 60 minutes at a temperature of 100 °C.

REFERENCES

1 Bafoev, A. X., Rajabboev, A. I., Niyozov, S. A., Bakhshilloev, N. K., & Mahmudov, R. A. (2022). Significance And Classification of Mineral Fertilizers. Texas Journal of Engineering and Technology, 5, 1-5.

2 R.A. Makhmudov, K.Kh. Majidov, M.M. Usmanova, Sh.M. Ulashov, & S.A.Niyozov. (2021). Characteristics Of Catalpa Plant As Raw Material For Oil Extraction. The American Journal of Engineering and Technology, 3(03),70–75. https://doi.org/10.37547/tajet/Volume03Issue03-11

3 Hujakulova, D. J., Sh M. Ulashov, and D. K. Gulomova. "TECHNOLOGY OF DEODORIZATION OF SOYABEAN OIL." Galaxy International Interdisciplinary Research Journal 9.12 (2021): 171-174.
4 Shodiev Z. O., Shodiev S., Shodiev A. Z. THEORETICAL BASIS OF EFFECTIVE SEPARATION OF COTTON FROM AIR FLOW //Современные инструментальные системы, информационные технологии и инновации. – 2021. – С. 12-15.
5 Ниёзов , С., Шарипов, Ш., Бердиев, У. ., Махмудов , Р. ., & Шодиев , А. . (2022). ТРУЩИНЫ, ВЫПУСКАЮЩИЕСЯ ПРИ ПРОИЗВОДСТВЕ ХЛОРИДА КАЛИЯ ИЗ СИЛЬВИНИТОВОЙ РУДЫ. Journal of Integrated Education and Research, 1(4), 440–444. Retrieved from https://ojs.rmasav.com/index.php/ojs/article/view/302
6 Ниёзов С.А., Шарипов Ш.Ж., Бердиев У.Р., & Шодиев А.З. (2022). ВЛИЯНИЕ НИТРАТ И НИТРИТОВ НА ОРГАНИЗМ. Journal of Integrated Education and Research, 1(4), 409–411. Retrieved from https://ojs.rmasav.com/index.php/ojs/article/view/301
7 Amanovich, M. R., Obitovich, M. S., Rakhmatilloyevich, T. H., & Oybekovich, S. Z. (2021). The use of biological active additives (BAA) in the production of flour confectionery products. The American Journal of Engineering and Technology, 3(05), 134-138.
8 Mahmudov Rafik Amonovich, Shukrullayev Javohir Oybek ugli, Ereshboyev Husniddin Fazliddinovich, & Adizova Muqaddas Odil kizi. (2022). Improvement of Technology of Gypsum Production Raw Materials and Products in Production. Texas Journal of Multidisciplinary Studies, 6, 182–184. Retrieved from https://zienjournals.com/index.php/tjm/article/view/1059
9 Фатиллоев, Ш. Ф., Ш. Б. Мажидова, and Ч. К. Хайруллаев. "ВЛИЯНИЕ ДОБАВОК АЗОТНОКИСЛОТНОГО РАЗЛОЖЕНИЯ ФОСФОРИТОВ ЦЕНТРАЛЬНОГО КЫЗИЛКУМА НА ГИГРОСКОПИЧЕСКИЕ СВОЙСТВА АММИАЧНОЙ СЕЛИТРЫ." Gospodarka i Innowacje. 22 (2022): 553-556.
10 Kazakovich, Khayrullayev Chorikul, Fatilloyev Shamshod Fayzullo o'g'li, Dehkonova Nargiza, and Jabborova Aziza. "STUDY OF THE POSSIBILITY OF USE OF LOCAL PHOSPHORITES AND SEMI-PRODUCTS OF THE PRODUCTION OF COMPOUND FERTILIZERS AS ADDITIVE TO AMMONIA NITRETRE." EPRA International Journal of Research and Development (IJRD) 7, no. 4 (2022): 49-52.
11 Фатиллоев, Шамшод Файзулло Угли, Бехзод Мавлон Угли Аслонов, and Алишер Камилович Ниёзов. "ИЗУЧЕНИЕ МЕХАНИЧЕСКИХ СВОЙСТВ КОЖИ ОБРАБОТАННЫМИ ПОЛИМЕРНЫМИ КОМПОЗИЦИЯМИ." Universum: технические науки 11-4 (80) (2020): 49-51.

12 Komilovna, H. M. U., Yormatova, D. Y., Tursunova, D. X., Kamolova, Z. M., & Teshayeva, M. S. (2021). Properties of the Soya Flour. Annals of the Romanian Society for Cell Biology, 9042-9046.

13 Narzullaeva, A. M., Khujakulov, K. R., Tursunova, D. H., & Teshaeva, M. S. (2020). Study of the Influence of the type of the catalyst on the technological process of hydration of higher fatty acids into alcohols, optimal parameters of the process, the industry of use of higher alcohols. International Journal of Advanced Research in Science, Engineering and Technology, 7(11), 15954-8.

14 Тешаева, М. Ш. К., Жураев, А. О., Исматов, С. Ш., & Камолова, З. М. К. (2018). Добавки для получения полимерных материалов и их переработки. Вопросы науки и образования, (1 (13)), 18-20.

15 Komilovna, H. M. U., Yormatova, D. Y., Tursunova, D. X., Kamolova, Z. M., & Teshayeva, M. S. (2021). Properties of the Soya Flour. Annals of the Romanian Society for Cell Biology, 9042-9046.

16 Камолова З. М. Қ. ЧАРМ МАҲСУЛОТЛАРИНИ ЁҒЛАШДА ҚЎЛЛАНИЛАДИГАН КОМПОЗИЦИЯЛАР ВА УЛАРНИНГ ТАҲЛИЛИ //Oriental renaissance: Innovative, educational, natural and social sciences. – 2022. – Т. 2. – №. 6. – С. 148-153.

17 Хужакулова, Д. Ж., & Мажидов, К. Х. (2019). Новые способы технологии дезодорации масел. ТЕХНИКА И ТЕХНОЛОГИЯ ПИЩЕВЫХ ПРОИЗВОДСТВ, 112.

18 Khujakulova D. J., Salimova Z. B. CHEMICAL INDUSTRY PRODUCTS TO INCREASE AGRICULTURAL PRODUCTIVITY AND PRODUCTION.

19 Shodiyev Z. O., Shodiyev A. Z. Mathematical modeling of the motion of a piece of cotton in a separator tube. – 2020.