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## ХІМІЯ. ХІМТЕХНОЛОГІЯ

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# RESEARCH OF CALCIUM OXIDE HYDRATION IN CALCIUM NITRATE SOLUTIONS

*М.А. Олійник*, *А.Б. Шестозуб*. **Дослідження процесу гідратації оксиду кальцію в розчинах кальцій нітрату.** Мінеральні добрива – це один з важливих чинників інтенсифікації сільського господарства і збільшення кількості продуктів харчування. Обсяги виробництва і внутрішнього споживання мінеральних добрив в Україні свідчать про те, що використання азотних добрив тільки наближається до необхідної науково обгрунтованої кількості. Одним з найпоширеніших штучних мінеральних добрив є кальцієва селітра. ***Мета:*** Метою роботи є дослідження і теоретичне обгрунтування процесів, які відбуваються при приготуванні суспензій гідроксиду кальцію $Ca(OH)_2$ в розчинах кальцій нітрату $Ca(NO_3)_2$. ***Матеріли і методи:*** В роботі використано технічний оксид кальцію (негашене вапно) ДСТУ Б В.2.7-90-99, розчини кальцієвої селітри концентрацій 15, 20, 25, 30, 35 і 40 % $Ca(NO_3)_2$. Вміст вапна при приготуванні суспензії у розчині змінювали (в перерахунку на оксид кальцію CaO) від 150 г/дм$^3$ до максимально можливого. Кожний із цих розчинів насичували при температурі 40 °C вапном до максимально можливої концентрації. Придатними для використання в наступних експериментах і в технології отримання кальцієвої селітри вважалися ті розчини (суспензії), які протягом 12 годин не втрачали своєї рухливості (транспортабельності). ***Результати:*** Результати експериментів показують, що при збільшенні концентрації нітрату кальцію у розчині в діапазоні 15…40 % кількість вапна, яку можна ввести в цей розчин без втрати ним транспортабельності, зменшується. Подальше збільшення вище вказаної кількості вапна в розчинах зазначеної концентрації призводить до його загуснення, втрати рухливості (транспортабельності). Розрахунки показали, що за присутності кальцієвої селітри розчинність $Ca(OH)_2$ зменшується приблизно на порядок, що може привести до формування на поверхні оксиду кальцію CaO твердої фази $Ca(OH)_2$, яка також може утворювати водневі зв'язки з компонентами розчину. Оскільки ймовірність утворення в розчині водневих зв'язків велика, то існує можливість утворення кластерів.

*Ключові слова:* кальцій нітрат, вапно, гідратація, концентрація, суспензія.

*M.A. Oliynyk*, *A.B. Shestozub*. **Research of calcium oxide hydration in calcium nitrate solutions.** Mineral fertilizers are one of the important factors of agriculture intensification and increasing of food products quantity. The volume of fertilizers production and its domestic consumption in Ukraine indicate that nitrogen fertilizer using only comes nearer to the required number of science-based. One of the most widespread artificial fertilizers is the calcium nitrate. ***Aim:*** The aim is to study and theoretically substantiate the processes occurring in the preparation of suspensions of calcium hydroxide $Ca(OH)_2$ in solution of calcium nitrate $Ca(NO_3)_2$. ***Materials and Methods:*** The technical calcium oxide (quicklime) DSTU BV.2.7-90-99, solutions of calcium nitrate of 15, 20, 25, 30, 35 and 40 % $Ca(NO_3)_2$ concentrations were used in the work. The content of lime in the preparation of a suspension in the solution changed (in terms of calcium oxide CaO) from 150 g/dm$^3$ to the maximum possible. Each of these solutions saturated at 40 °C in lime to maximum concentration. Suitable for use in these experiments and in the technology of calcium nitrate obtaining are considered the solutions (suspensions) that within 12 hours did not lose their mobility (transportability). ***Results:*** The experimental results show that increasing of the concentration of calcium nitrate in solution within the range 15...40 %, the amount of lime that you can put into the solution without loss of transportability decreases. Further increasing of lime quantity in solutions concentrations causes to its solidifying, loss of mobility (transportability). Calculations showed that in the presence of calcium nitrate the solubility of $Ca(OH)_2$ is reduced nearly by order that can lead to the formation of calcium oxide CaO the solid phase $Ca(OH)_2$ on the surface, which also can form hydrogen bonds with the components of the solution. As the probability of formation of hydrogen bonds in solutions is high, there is a possibility of formation of clusters.

*Keywords*: calcium nitrate, lime, hydration, concentration, suspension.

**Introduction**. Mineral fertilizers are one of the important factors of agriculture intensification and increasing of food products quantity. The volume of fertilizers production and its domestic consumption in Ukraine indicate that nitrogen fertilizer using only comes nearer to the required number of science-based.

One of the most widespread artificial fertilizers is the calcium nitrate. It is widely used, particularly as the basis of anti-ice mixes and corrosion inhibitors; as an additive in building mixtures; as the components of emulsion explosives, accumulating solutions in refrigeration and others.

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The chemical industry, including the production of mineral fertilizers is the branch which requires high material and energy expenses at a time when a major development trends now is resource saving. The actual is development of energy saving technologies of calcium nitrate production containing additional nutrients, primarily through improvement of prior preparation processes of calcium material acid treatment. Apart from entering into a ground the main nutrients (NPK), entering the Ca-compounds increases mobile forms of calcium, increases the microbiological and enzymatic activity of soil [1]. Using of calcium nitrate solution as a component of emulsion explosives reaches 15...30 % of the total mass [2]. Because of the wide scope of application a number of demands put forward this product: reduction of insoluble substances, enrichment solution of calcium nitrate and granular product with additional nutrients and reduce water absorption and caking, others.

In this regard, various approaches designed to improve the quality of calcium nitrate in solution and in granulated form, including the approach of pure calcium obtaining [3]. Chvertka [4] proposed decrease of suspended particles in calcium nitrate solution by flotation, and Obrestad [5] — treatment by flocculants.

In turn, Oliynyk [6] proposed energy-saving technology of calcium nitrate obtaining while increasing the concentration of lime in the initial suspension and the introduction of additional nutrients.

Note that a significant impact on quality of calcium saltpetre solution, including its contents, is method of introducing of initial reagents [7].

In modern calcium nitrate manufacturing various types of calcium processed with aqueous solutions of nitric acid suspended in the reaction system. When using quicklime the formation of different intermediate calcium compounds happened that will affect the suspension, and at the critical concentrations will lead to its thickening.

**The aim** is to study and theoretically substantiate the processes occurring in the preparation of suspensions of calcium hydroxide $Ca(OH)_2$ in solution of calcium nitrate $Ca(NO_3)_2$.

**Materials and Methods.** The technical calcium oxide (quicklime) DSTU BV.2.7-90-99, solutions of calcium nitrate of 15, 20, 25, 30, 35 and 40 % $Ca(NO_3)_2$ concentrations were used in the work. The content of lime in the preparation of a suspension in the solution changed (in terms of calcium oxide CaO) from 150 g/dm$^3$ to the maximum possible.

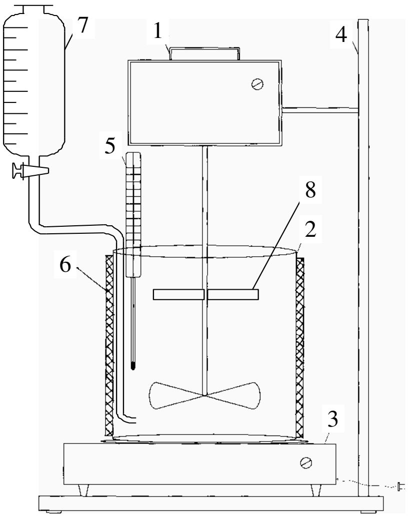

*Fig. 1. Scheme of laboratory facility for the preparation of hydroxide suspensions: 1 — electric mixer with paddle; 2 — reactor; 3 — electric oven; 4 — tripod; 5 — thermometer; 6 — thermal insulation; 7 — graduated tank of nitric acid; 8 — additional paddles*

Laboratory studies conducted on the installation, schematically shown in Fig. 1. Installation consists of cool reactor (working volume 1.75 dm$^3$) made of stainless steel grade 12Kh18N10T, electric motor with the paddle mixer and the possibility of speed control that mounted on a tripod of electric oven to maintain the temperature in the reactor.

The study was conducted as follows. In the reactor 2 was loaded with 1 dm$^3$ calcium nitrate indicated above. Each of these solutions saturated at 40 °C in lime to maximum concentration. Suitable for use in these experiments and in the technology of calcium nitrate obtaining are considered the solutions (suspensions) that within 12 hours did not lose their mobility (transportability).

**Results and Discussion**. The experimental results show that increasing of the concentration of calcium nitrate in solution within the range 15...40%, the amount of lime that you can put into the solution without loss of transportability decreases. Further increasing of lime quantity in solutions concentrations causes to its solidifying, loss of mobility (transportability). So, for a 15 %-solution of calcium nitrate $Ca(NO_3)_2$, the maximum possible concentration of lime in terms of calcium oxide is 350 g/dm$^3$, for 20 %-solution — 320 g/dm$^3$, for 25 %-solution —

295 g/dm$^3$, for 30 %-solution — 275 g/dm$^3$, for 35 %-solution — 240 g/dm$^3$, and for 40 %-solution — 200 g/dm$^3$, respectively (Fig. 2).

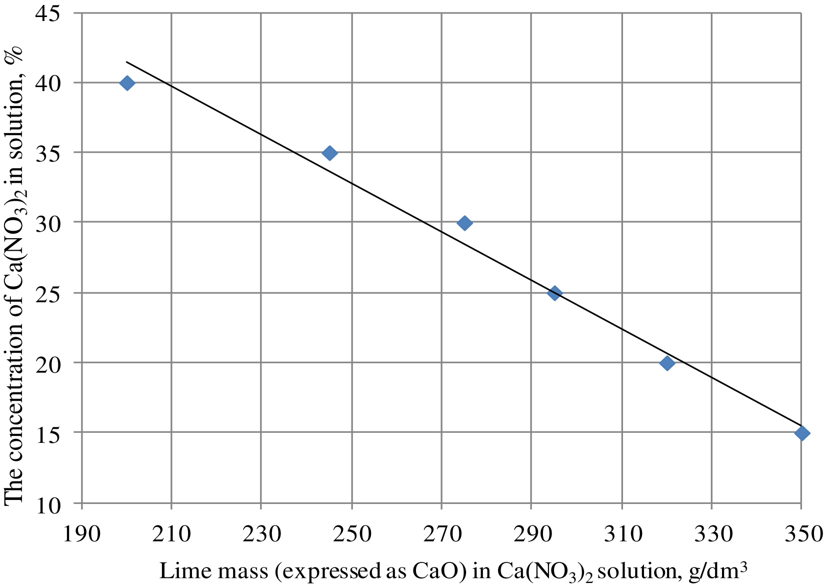

*Fig. 2. Dependence of lime concentration in the transport solution on $Ca(NO_3)_2$ concentration*

These lime concentrations can vary from deviation ±3 g/dm$^3$. Further increasing of lime quantity in solutions concentrations causes to its solidifying, loss of mobility (transportability). It is formed viscous gel-like mass, which is not subject of transportation with pipelines. Experimentally it was found that the dynamic viscosity of the obtained suspension shall not exceed 1.0...1.1 Pa·s. Increasing the viscosity of the suspension leads to difficulties in pumping and transportation with pipelines, and in some cases prevents these processes.

In subsequent studies used the 35 %-solution of calcium nitrate $Ca(NO_3)_2$ and determines the degree of conversion (hydration) of calcium oxide CaO therein.

Particular importance for the stage of preparation of suspensions in experimental studies is interaction time of reagents, which determines the degree of slaking of calcium oxide in 35 %-solution of calcium nitrate, productivity and size of equipment. Significant impact on the degree of conversion of calcium oxide has the intensity of mixing. The dependence of the degree of conversion of calcium oxide from Reynolds criterion Re and interaction time is shown in Fig. 3.

Thickening of suspension formed by adding calcium oxide in calcium nitrate solution of variable concentration is happening with different amounts of calcium oxide in solution. Moreover, increasing the concentration of calcium nitrate leads to a decrease of calcium oxide at which the thickening suspension happen. The experimental results are shown in Table 1.

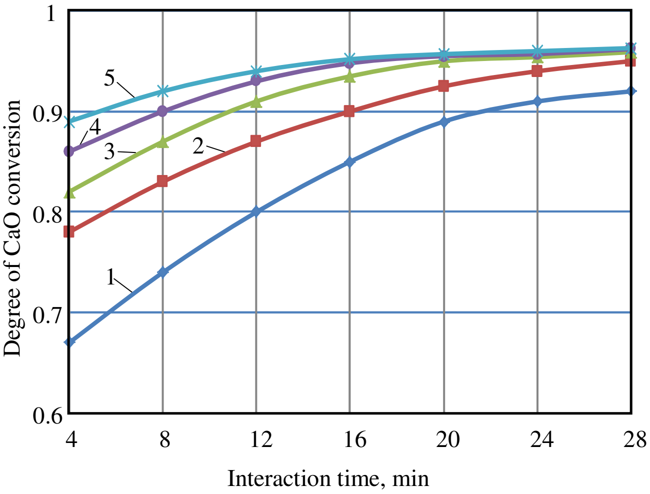

*Fig. 3. The dependence of the degree of CaO conversion on the intensity of mixing and interaction time: 1 — Re = 1000; 2 — Re = 4000; 3 — Re = 7000; 4 — Re = 10000; 5 — Re = 13000*

*Table 1*

*The properties of the suspension at critical concentration of calcium oxide CaO*

| Components and some parameters of suspension | Values | | | | | |
|---|---|---|---|---|---|---|
| The concentration of the initial solution $Ca(NO_3)_2$, % | 15.0 | 20.0 | 25.0 | 30.0 | 35.0 | 40 |
| The concentration of the initial solution $Ca(NO_3)_2$, mol/dm$^3$ | 0.998 | 1.418 | 1.845 | 2.302 | 2.796 | 3.330 |
| The density of the of the initial solution of Ca $(NO_3)_2$, g/dm$^3$ | 1119.3 | 1163.6 | 1211.0 | 1259.0 | 1311.0 | 1366.0 |
| Critical lime content expressed as CaO with thickening of the suspension, g/dm$^3$ | 350.0 | 300.0 | 295.0 | 275.0 | 243.0 | 200.0 |
| Critical lime content expressed as CaO with thickening of the suspension, mol/dm$^3$ | 6.24 | 5.35 | 5.26 | 4.90 | 4.33 | 3.57 |
| Water mass in the initial solution of $Ca(NO_3)_2$, g | 951.4 | 930.9 | 908.3 | 881.3 | 852.2 | 819.6 |
| The mass of water required for complete hydration of CaO to $Ca(OH)_2$, g | 112.5 | 96.4 | 94.8 | 88.4 | 78.1 | 64.3 |
| Water mass remaining after hydration of CaO, g | 838.9 | 834.5 | 813.5 | 792.9 | 774.1 | 755.3 |

Table 1 shows that the water mass required for complete hydration of calcium oxide CaO by the reactions

$$CaO + H_2O = Ca(OH)_2 \tag{1}$$

or

$$CaO + Ca^{2+} + H_2O = 2CaOH^+ \tag{2}$$

significantly less than the water mass which is present in suspension. So, impossible explain the thickening process by water flow in accordance with reactions (1) and (2). Thus there are other processes that are likely to occur at scheme outlined below.

Ionization of calcium hydroxide $Ca(OH)_2$ contained in the solution is as follows:

$$Ca(OH)_2 \xleftrightarrow{K_2} CaOH^+ + OH^- \xleftrightarrow{K_1} Ca^{2+} + 2OH^-, \tag{3}$$

$$K_2 = \frac{[CaOH^+]\cdot[OH^-]}{[Ca(OH)_2]} \approx 1 \text{ (strong alkali)}, \ K_1 = \frac{[Ca^{2+}]\cdot[OH^-]}{[CaOH^+]} = 5\cdot10^{-2}.$$

According to the scheme the material balance of calcium compounds can be represented by marking $C$ as the total concentration of calcium compounds in the solution, as follows:

$$C = [Ca(OH)_2] + [CaOH^+] + [Ca^{2+}].$$

To calculate the equilibrium concentration of $[CaOH^+]$ in solution let make use of expressions for $K_1$ and $K_2$ taking $K_2 = 1$. Then $[Ca(OH)_2]$ and $[Ca^{2+}]$ can be expressed via $[CaOH^+]$, and the material balance will take the following form:

$$C = \frac{[CaOH^+]\cdot[OH^-]}{K_2} + [CaOH^+] + \frac{K_1[CaOH^+]}{[OH^-]}.$$

Solving the equation with respect to $[CaOH^+]$, we obtain the expression

$$\frac{[CaOH^+]}{S} = \frac{K_1[OH^-]}{[OH^-]^2 + K_1[OH^-] + K_1K_2},$$

where $S$ — solubility value, which will allow calculate the relative concentration of $[CaOH^+]$ when concentration of $[OH^-]$ changing.

Similarly equation for calculation of equilibrium concentrations of $[Ca(OH)_2]$ and $[Ca^{2+}]$ have been obtained

$$\frac{[Ca(OH)_2]}{S} = \frac{[OH^-]^2}{[OH^-]^2 + K_1[OH^-] + K_1K_2},$$

$$\frac{[Ca^{2+}]}{S}=\frac{K_1K_2}{[OH^-]^2+K_1[OH^-]+K_1K_2}\ .$$

Fig. 4 shows the distribution of forms of existence of calcium compounds from solution pH when thickening.

As shown in Fig. 4, hydration of calcium oxide CaO is going partially according to reaction

$$CaO + Ca^{2+} + H_2O = 2CaOH^+. \qquad (4)$$

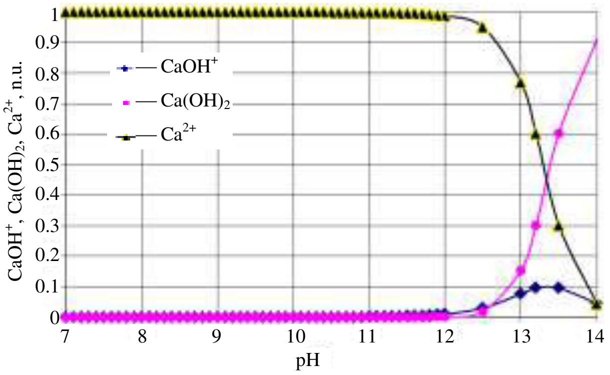

*Fig. 4. Distribution of forms of existence of calcium compounds from solution pH upon reaching the thickening*

This forms $CaOH^+$ ion in which oxygen is in a state of unfilled orbitals that should promote the formation of hydrogen bonds and occur the clusters (Fig. 5); thus, solution become capsulate and as a result, suspension is thickening.

During calculations were conducted the values of basicity coefficients not taken into account, since for large values of ionic strength for a rough approximation you can accept their values as constant.

Solubility values $S$ can be defined using the solubility constant $K_{sp}$ $[Ca(OH)_2] = 5.47\cdot10^{-6}$. Calculations are performed without considering the degree of hydration of calcium oxide CaO and activity coefficients, taking an extra concentration $C$ as the molar concentration of $Ca(NO_3)_2$ in solution:

$$K_{sp} = [Ca^{2+}]\cdot[OH^-]^2 = 5.47\cdot10^{-6}.$$

Material balance of $Ca(OH)_2$ solution:

$$Ca(OH)_2 \leftrightarrow Ca^{2+} + 2OH^-, \qquad (5)$$

$$[OH^-] = 2S;\ [Ca^{2+}] = S + C, \qquad (6)$$

$$K_{sp} = (S + C)\cdot(2S)^2. \qquad (7)$$

According the value of $C$ given in Table 1, calculate the value of $S$, which are suitable for determining the relative concentration of $Ca(OH)_2$ using Eq. (5)...(7).

Calculations showed that in the presence of calcium nitrate the solubility of $Ca(OH)_2$ is reduced nearly by order that can lead to the formation of calcium oxide CaO the solid phase $Ca(OH)_2$ on the surface, which also can form hydrogen bonds with the components of the solution. As the probability of formation of hydrogen bonds in solutions is high, there is a possibility of formation of clusters (Fig. 6).

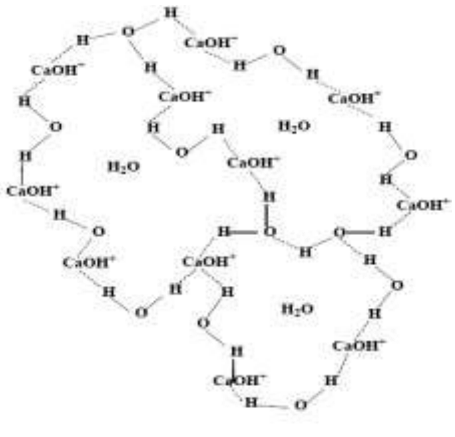

*Fig. 5. Formation of clusters through hydrogen bonds*

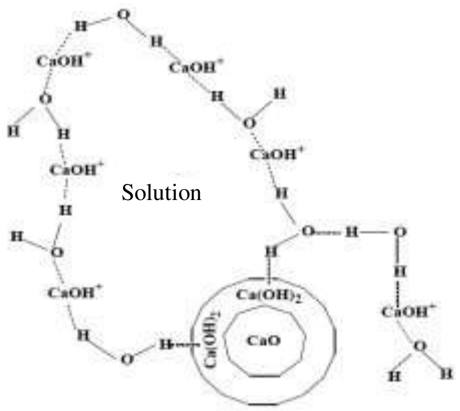

*Fig. 6. The formation of $Ca(OH)_2$ membrane and clusters around CaO grain through hydrogen bonds*

**Conclusions**. A number of experiments was held aimed at research and theoretical study of processes occurring in the preparation of suspensions of calcium hydroxide $Ca(OH)_2$ in solution of calcium nitrate $Ca(NO_3)_2$. Experimentally determined the highest possible content of lime in a solution of calcium nitrate and the possibility of increasing the critical concentration of calcium oxide CaO for thickening of slurry. Theoretically grounded the calcium oxide hydration process and mechanism of slurry thickening.

### Література

1. Лазарев, В.И. Влияние кальцийсодержащих соединений на микробиологическую активность и физико-химические свойства почвы / В.И. Лазарев, Н.Н. Трутаева // Достижения науки и техники АПК. — 2006. — № 10. — С. 7–9.
2. Пат. 41672 Україна, МПК С06В 31/00. Емульсійна вибухова речовина «Україніт-ПП-2Б» / Купрін О.В., Іщенко М.І., Савченко М.В., Купрін В.П.; патентовласник ТОВ «ІСТ-ФОРТ». — № u200902994; заявл. 30.03.2009; надр. 25.05.2009, Бюл. № 10.
3. Пат. 2239601 Российская Федерация, МПК C01F 11/36, C05C 5/04. Способ получения очищенного раствора нитрата кальция / Сеземин В.А., Абрамов О.Б., Захарова О.М.; патентообладатель ООО «Научно-инженерный центр». — № 2003133785/15; заявл. 20.11.2003; опубл. 10.11.2004.
4. Дослідження причин появи та методів зниження зважених часток в кальцієвій селітрі вітчизняного виробництва / Н.В. Чвертка, А.Б. Шестозуб, А.О. Багно та ін. // Зб. матеріалів 4-ї Української науково-техн. конф. «Сучасні проблеми технології неорганічних речовин», 14–16 жовтня 2008 р., Дніпродзержинськ, Україна. — Дніпродзержинськ: ДДТУ, 2008. — С. 149−150.
5. Пат. 220612 Польща, МПК C01F 11/36, C01F 11/38. Sposób oczyszczania roztworów lub stopów azotanu wapnia, oraz roztwór/stop azotanu wapnia / Obrestad T., Mutsaers P., Wallestad I.; YARA INTERNATIONAL ASA. — № 387815; заявл. 16.04.2009; надр. 30.11.2015.
6. Предпосылки создания энергосберегающей технологии производства модифицированной кальциевой селитры / Н.А. Олийнык, А.Б. Шестозуб, Н.Д. Волошин и др. // Мат-лы XVII Междунар. заоч. науч.-практ. конф. «Технические науки — от теории к практике», 23 января 2013 г., Новосибирск, РФ. — Новосибирск: Изд. «СибАК», 2013. — Ч. 2. — С. 46–54.
7. Олійник, М.А. Дослідження впливу способу введення сировини на якість розчину кальцієвої селітри / М.А. Олійник, А.Б. Шестозуб, М.В. Зайцев // Зб. тез доповідей 5-ї Всеукраїнської наукової конференції студентів, аспірантів і молодих учених «Хімічні проблеми сьогодення», 14–17 березня, 2011 р., Донецьк, Україна. — Донецьк: Ноулідж, 2011. — С. 139.

### References

1. Lazarev, V.I., & Trutaeva, N.N. (2006). Effect of calcium-containing compounds on microbial activity and physico-chemical properties of the soil. *Achievements of Science and Technology of AIC*, 10, 7–9.
2. “IST-FORT” LLC. (2009). *“Ukrainit-PP-2B” Emulsion Explosive*. Ukraine Patent: UA 41672.
3. “Nauchno-Inzhenerniy Tsentr” LLC. (2004). *Purified calcium nitrate solution preparation method*. Russian Federation Patent: RU 2239601.
4. Chvertka, N.V., Shestozub, A.B., Bagno, A.O., Voloshin, M.D., & Aleksanov, O.P. (2008). Study on reasons and methods to reduce the suspended particles of the domestically produced Calcium Nitrate. In *Proceedings of the 4th Ukrainian Scientific and Technical Conference on Modern Problems in Technology of Nonorganic Substances* (pp. 149−150). Dniprodzerzhynsk: Dniprodzerzhynsk State Technical University.
5. Yara International ASA. (2015). *Sposób oczyszczania roztworów lub stopów azotanu wapnia, oraz roztwór/stop azotanu wapnia*. Polish Patent: PL 220612.
6. Olinyk, N., Shestozub, A., Voloshin, N., Aleksanov, O., & Bagno, A. (2013). Background energy power generation modified calcium nitrate. In *Proceedings of the 17th International Scientific and Practical Conference “Engineering: From Theory to Practice”* (Vol. 2, pp. 46–54). Novosibirsk: SibAK.
7. Oliynyk, M.A., Shestozub, A.B., & Zaitsev, M.V. (2011). Study of the effect of route of administration of the raw materials on the quality of Calcium Nitrate solution. In *Proceedings of the 5th All-Ukrainian Scientific Conference of Students, Aspirants, and Young Scientists “Today’s Chemical Problems”* (p. 139). Donetsk: Knowledge.

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