

Дослідження присвячено розробці технології утилізації вапняного шламу водопідготовки з одержанням кальцієвої селітри.

Встановлено, що відходи водопідготовки за хімічним складом відрізняються від природної сировини – вапняку, який традиційно використовують для одержання кальцій нітрату. Шлам, що утворюється на стадії вапнування води містить близько 70 % кальцій карбонату, досить велику кількість заліза, що потрапляє до осаду з розчинами коагулянтів, та органічні домішки. Органічні домішки надходять з річковою водою і осаджуються в результаті коагуляції.

Процес вилучення кальцію розчином кислоти – сталій. Результати добре відтворювались на двох видах відходів різних підприємств. Це пояснюється як високою швидкістю розчинення кальцій карбонату в нітратній кислоті, так і схожим хімічним складом відходів.

До розчину потрапляють не тільки сполуки кальцію але й заліза та органічна складова шламу вапнування. Для очищення розчину запропоновано схему процесу, до якої повинні входити стадії окиснення розчину та наступного осадження заліза.

Концентрація заліза в експериментальних розчинах складала до 6 г/л. За допомогою розрахунків рівноваги осад – розчин з'ясовано, що в області низьких концентрацій нітратної кислоти залізо буде випасти в розчин, а кальцій в ньому лишатися. Зменшення концентрації проводили додаванням чистого кальцій карбонату.

Проведено кінетичні дослідження процесу осадження заліза на модельних розчинах залізо (III) нітрату. Одержано кінетичне рівняння другого порядку. Розраховано енергію активації процесу, значення якої ~ 37 кДж/моль свідчить про перебіг процесу осадження в перехідній області. Залишок містить близько 40 % заліза і може застосовуватися для одержання коагулянтів.

Застосування запропонованого методу дозволить найбільш повно використовувати відходи водопідготовки

Ключові слова: водопідготовка, вапнування, шлам, кальцій нітрат, коагулянти, розчинення, нітратна кислота, очищення,

UDC 66.061.16, 66.067.8.09

DOI: 10.15587/1729-4061.2018.141007

UTILIZATION OF LIME-SOFTENING SLUDGE TO OBTAIN CALCIUM NITRATE

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1. Introduction

The most widespread use of industrial water in the function of heat conductor and cooling agent, in heat-exchangers for obtaining technological steam and in recycling water supply requires a low value of alkalinity and hardness. Requirements to the content of hardness salts, especially carbonate salt (alkalinity) are rather high and depend on the specificity of water use [1].

The traditional and the cheapest method of reducing the carbonate hardness of water is considered its treatment

with a solution of calcium hydroxide $\text{Ca}(\text{OH})_2$, the so-called lime-softening. Lime-softening along with simultaneous coagulation is also used to dispose of liquid water treatment waste [2]. As a result of the process, the sediment is formed, namely lime-softening sludge.

Traditional units using this method of alkalinity reduction are clarifiers and sludge piles, where from the bottom part of the clarifiers "sludge" water is flown down. The designed capacity is determined taking into account a 30-year operation period. In the towns of Severodonetsk and Lisichansk, Luhansk region (Ukraine), there are several large indus-

trial enterprises which are powerful high-capacity water consumers equipped with very similar water treatment technologies. In spite of very similar technologies, each of these enterprises has its own problems related to design solutions and distinctive features of work. The sediments placed in the sludge piles have been formed for many years, from the very beginning of the operation of the enterprises, more than 30 years each. Thus, the designed capacity of the units had expired a long time ago. Bearing in mind the limitation of operation and engineering facilities, it should be noted that the filtration of these structures makes 10–25 % of the water flow. Product invading into uncovered aquifers poses a threat to the geological environment. Components of lime-softening sludge are able to leak into the environment due to increased pH in sludge piles as well as in product from it. The presence of such processes has been confirmed by other researchers [3]. This is also evidenced by the results of monitoring observations on changes in the quality state of groundwater in the location of sludge piles of Private Joint Stock Company “Severodonetsk AZOT Association” (Severodonetsk, Luhansk region, Ukraine) [4]. The chemical composition of groundwater is characterized by the following properties: dry residue 0.4–95.3 g/l, total hardness – 1.25–650.0 mmole/l, chlorides content – 60.0–46,000 mg/l, sulfates – 39–562 mg/l, nitrates – 0.002–213.0 mg/l. In comparison with the above-mentioned indicators, water has the following composition outside of the sludge piles influence: dry residue – 0.872 g/l, total hardness 9.4 mmole/l, chlorides content – 126 mg/l, sulfates – 228 mg/l, nitrates – 8.6–228 mg/l.

The presence of sludge piles creates certain threats to the geological environment associated with the filtering of the contents of the piles into the soil and its subsequent receipt into the groundwater. The geological conditions of the piles' area are primarily determined by its location within the North Donbas tectonic zone, which separates the Voronezh crystalline massif and the Donetsk folded structure. This causes a considerable fracture of the rocks of the Upper Cretaceous complex with a total thickness of 450–600 m, which is composed of marls and chalk with a content of CaCO₃ up to 97–99 %, and is blocked from the surface by low-power sandy-clay Cenozoic deposits.

Such geological features create conditions for the manifestation of karst processes, which is expressed in the formation of a powerful watered cracked zone in the upper part of the Cretaceous-Marlene strata. The active formation of karst suffusion sink holes in the zones of influence of industrial waste storages as well as within industrial sites of enterprises testifies to the technogenic activation of the natural-historical karst. The activation of karst processes to a greater extent is connected with the entry of a filtrate with a high pH of ~10.5 from the piles into the Cretaceous-Marlon aquifer, which is the main source of water supply in the region. The high alkalinity of water during the liming process is maintained to ensure the efficiency of further water purification on ion-exchange filters [1]. The mixing of filtrate with the waters of the chalk-marl horizon leads to a deterioration in their quality and an increase in aggressiveness with respect to the rocks that hold them.

In 2010, Private Joint Stock Company “Severodonetsk AZOT Association” had to issue a request for tender as for sludge utilization. Thus, not only ecological issues, but also certain technological difficulties require action to solve the problems of recycling waste water treatment. Taking into

consideration the fact that the majority of large industrial enterprises of the chemical complex of Ukraine were created in the 60s–70s of the last century, a similar situation may arise anywhere. Hence, the development of methods for utilizing lime-softening sludge is an extremely urgent problem.

2. Literature review and problem statement

The methods of utilization of sediments proposed in the literature can be divided into several groups, depending on the sediments' chemical content and other factors analyzed below.

1) Recycling of coagulants, which are a necessary component of the processes of water treatment and sewage treatment. Recycling is usually carried out by acid leaching of iron or aluminum compounds and subsequent separation of the mixed solution. In [5], the authors proposed to perform separation using ion-exchange resins, thus purifying the solutions to the conditional state. The authors of work [6] tried to reduce the use of fresh coagulants by adding sludge to the process of coagulation. The research [7] is very similar to the direction of using the sludge and is aimed at finding out the optimal parameters of low-temperature coagulation of spring water. Lime-softening sludge consists of a large amount of calcium carbonate, which after recycling of coagulants is still in solid waste after any of the proposed technologies.

2) Use of sediments as raw materials for construction materials, namely, bricks and cement. Typically, water treatment sludge is proposed to be used as an additional component to other types of raw materials. The paper [8] investigated the possibility of manufacturing low-porous ceramic bricks with the addition of lime-softening sludge to clay. The authors of the paper [9] proposed to add water treatment waste to the ash of rice husk to obtain bricks. A similar work [10] was performed by scientists in order to obtain light bricks.

A large number of works [11–13] is devoted to the possibility of using sludges in the production of cement. The authors of the work [11] proposed to replace part of the cement with a fired precipitate. Unfortunately, according to the results of these studies, there are not enough good technological properties of the residue. The paper [12] presents the results of experiments on the production of eco-cements using waste, including of water treatment. The residue was pre-fired for firing an organic component. According to the results of research, cement made with limestone additive had the best quality. The authors of the work resorted to the burnout of the organic component [13]. Residues in this case were used for the partial replacement of shale clay in the production of bricks.

The use of waste for the production of building materials only at first glance is feasible, since it requires changes in the technological parameters of existing industries. Replacing primary raw material with waste is problematic and does not yield the expected result. Ukraine has overcapacity in limestone production. Therefore, lime-softening sediments are unlikely to be demanded by the building materials industry as secondary raw materials.

3) The use of sediments in the natural environment for depositing into the soil in order to reduce acidity [14], or in the technogenic environment to improve sewage clarification [15].

Consequently, each of the methods of sludge utilization has certain disadvantages. In the case of using sludge for building materials, this is not enough good technological properties and the need for pre-heat treatment. In the case of coagulation recycling, there is a large amount of residues after the removal of iron and aluminum compounds. For the third group of methods – the limited use, related to the chemical properties of the waste and the environment in which they are introduced.

In the development of recycling methods, not least is the fact that the chemical composition of the water purification waste is largely different from the chemical composition of the traditional raw materials: limestone (CaCO_3 – 85–99 %; Fe_2O_3 – 0.1–1.55 %) and chalk (CaCO_3 – 83.6–99.3 %, Fe_2O_3 – 0.08–0.42 %) [16]. A special difference is the reduced content of calcium carbonate ~70 % and high iron content (up to 7–8 %) in water treatment waste.

Thus, using sludge as raw materials in the chemical industry might have a problem of iron separation. It is required by the normative quality indicators of the final product.

The most expedient way of lime-softening sludge utilization in our view should be the production of mineral salts for industrial purposes. An example of such a product can be calcium nitrate. The raw material for obtaining calcium nitrate is natural limestone. According to the quality indicators [17], the iron content in calcium nitrate should be no more than 0.05 %.

The above-mentioned methods of water treatment waste utilization have a number of disadvantages. Recycling of coagulants allows us to utilize only a small fraction of the waste, and calcium carbonate, which forms the bulk of the waste, remains unused. In the production of building materials, waste cannot completely replace the traditional raw materials, as they differ in chemical composition. And the direct use in the natural and man-made environment is very limited due to high alkalinity of waste. Consequently, the processing of calcium carbonate, which is the main part of the water treatment waste, into a commodity product that is in demand in the market, is relevant. Due to the fact that the waste contains a significant amount of iron in comparison with traditional raw materials, it is necessary to study the purification of the solution from iron and organic matter residues.

3. The aim and objectives of the study

The aim of the work is to develop a method for utilizing lime-softening sludge to obtain calcium nitrate of air quality.

To achieve this aim, the following objectives were set:

- to develop a waste dissolution regime that would prevent excessive gas production and allow for sustainable results;
- to develop a method for cleaning solutions from iron compounds;
- to determine the mechanism and kinetic characteristics of the process of deposition of iron compounds from solutions.

4. Material and methods

4.1. Dissolution of lime-softening sludge

The general water treatment technology of the enterprises of the chemical and refining industry is quite

similar, and at the stage of the lime-softening process, it supposes the use of lime solution and coagulants, i. e. iron and/or aluminum sulfates, so sediments apart from calcium carbonate also contain products of hydrolysis of these salts.

Sediments formed during the entire operation time consist of lime-softening and coagulation products – CaCO_3 , $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, $\text{Fe}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$ and organic compounds.

Soluble organic compounds usually present in water are humic and fulvic acids. They are a mixture of high molecular compounds that contain various functional groups in their composition. Fulvic acids are derivatives of humic acids, soluble in alkalis and acids, they are lighter in color than humic ones and better soluble in water. The chemical composition of fulvic acids can be presented by the molecular formula $\text{C}_{14}\text{H}_{19}\text{O}_{12}\text{N}$. With ions of calcium, barium and trivalent cations in alkaline medium ($\text{pH} > 10$), fulvic acids are sedimented [19]. When interacting with oxidants that can form atomic oxygen (hydrogen peroxide or ozone), fulvic acids in the acid environment are oxidized to complete destruction. Lime-softening sludge by chemical composition is similar to the compositions of such natural formations like limestone, chalk, brucite, anhydrite, limonite, gibbsite, etc. The above noted natural formations are used as raw materials for the chemical, metallurgical, building and other industries [20], but the content of the waste components differs from natural minerals.

For research, lime-softening sludge taken from the water treatment shop of the Private Joint Stock Company “Severodonetsk AZOT Association” and PJSC “LINIK” has been used, the average chemical content of which is given in Table 1.

Table 1

Composition of lime-softening sludge

“Severodonetsk AZOT Association”					
Component	$\text{CaCO}_3 + \text{Ca}(\text{OH})_2$	$\text{Mg}(\text{OH})_2$	$\text{Fe}(\text{OH})_3$	$\text{Al}(\text{OH})_3$	SiO_2
%, weight	74.96	19.20	2.26	1.66	1.92
PJSC “LINIK”					
Component	$\text{CaCO}_3 + \text{Ca}(\text{OH})_2$	$\text{Mg}(\text{OH})_2$	$\text{Fe}(\text{OH})_3$	$\text{Al}(\text{OH})_3$	SiO_2
%, weight	77.47	20.35	1.17	-	1.01

For conducting experiments on the dissolution of lime-softening sludge, 30 % (weight) nitric acid has been used; it has been prepared by diluting the nitric acid (production of “Severodonetsk Azot Association”) with distilled water.

Before the dissolution, the lime-softening sludge has been dried to remove moisture. Then it was put into a flask containing 340 ml of nitric acid (stoichiometric amount according to the reaction (1)) by portions (equal to 6 g). The portion size has been determined experimentally, to prevent the excess gas formation that occurs due to the allocation of carbon (IV) oxide. Exposure time between adding portions made 10 minutes. After exposing each portion, samples of the solution have been taken where calcium and iron content has been analyzed.



After finishing exposure of the total waste amount, the solution has been exposed for 2 hours at room temperature,

then it has been heated to 60–90 °C to remove the residual carbon (IV) oxide from the solution. After cooling, the solution has been filtered and iron and calcium content has been analyzed. The content of Fe³⁺ ions in the solution has been analyzed by the complex metric method, which is based on the formation of a colored complex with sulfate-salicylic acid. The content of Ca²⁺ ions has been analyzed by the complex metric method in the presence of Eriochrome black indicator T.

After chemical analysis, the oxidation of the solutions has been performed by hydrogen peroxide (32 % weight) for 60 minutes. After oxidation, the solution has been boiled for 15 minutes to destruct a residual hydrogen peroxide amount. Then after cooling to a temperature of -30 °C, the amount of calcium carbonate calculated according to the reaction (1) has been added to the solution to remove the excess acid as well as iron compounds. The final composition of the solution has been analyzed for the calcium and iron content.

4.2. Research of the kinetics of iron precipitation from the solution

The most optimal way to remove iron from the acidic solution of calcium nitrate is the hydrolysis of its soluble salt by increasing its pH. PH increase has been carried out by adding calcium carbonate. In this case, removal of iron in the precipitate can be described by the reaction (12). The reaction (13) is carried out after the dissolution of the waste, which is described by the reactions (1)–(12) given below.

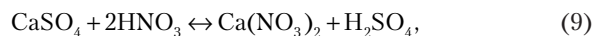
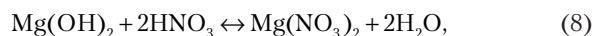
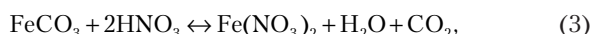
Experiments have been performed on the investigation of the kinetics of iron precipitation from the solution. To study the kinetics of the deironing process, we use a solution of iron (III) nitrate, which was prepared from the reagent Fe(NO₃)₃·7H₂O (chemically pure) and calcium carbonate (pure).

The kinetic curves have been obtained in isothermal conditions at temperatures of 30, 40, 50 and 60 °C. In a flask equipped with an electric stirrer, 150 ml of iron (III) nitrate solution was placed. The flask was placed in a water thermostat until the temperature reached 30, 40, 50 or 60 °C. Then 2 g of calcium carbonate was introduced into the solution with stirring. Mixing was carried out using a stirrer at a speed of 300 rpm. Samples of the solution were collected at the same time interval (30 s) and separated from the precipitates by filtration. Then the concentration of iron was analyzed by the above-mentioned method.

5. Research results of the process of obtaining a solution of calcium nitrate

Nitric acid, which has been taken for the experimental research allows us to conduct a fairly complete separation of lime-softening sludge that is formed during the industrial water treatment in order to obtain calcium nitrate and residues that can be further treated or used in accordance with existing technologies [5]. It is easy to demonstrate by performing equilibrium calculations of the dissolution process of the sediment-solution system [20].

Here is the scheme of chemical reactions of dissolution of sludge components by nitric acid:



The formation of acid salts, i.e. calcium and iron hydrocarbons occurs in conditions of excess acid by the reactions (2) and (4). For the coagulation process, iron (II) sulfate, which precipitates as Fe(OH)₂ is often used. In the sludge storage process, Fe(OH)₂ is gradually oxidized to Fe(OH)₃. However, the possibility of incomplete oxidation exists, therefore, the equilibrium of the reactions (5) and (6) should be taken into account.

The reactions (7) and (8) describe the dissolution of the excess lime solution, which in addition to Ca(OH)₂, also contains Mg(OH)₂ and is also included in the lime sludge. The lime solution is made from quicklime of natural origin, which usually contains Mg(OH)₂ impurities. The reaction (9) occurs with the component of the CaSO₄ solution formed due to contact of the coagulant FeSO₄ or Al₂(SO₄)₃ with calcium salts. Aluminum sulfate is more expensive and effective coagulant than iron sulfate. The reaction (10) runs with the precipitate that was obtained using aluminum sulfate as a coagulant.

Calculations were made on solubility values and dissociation constants of products, which are formed in conditions of low concentration of acid, which occurs as it is consumed at the end of the dissolution process.

The equilibrium salt concentration that is formed during the reactions (1)–(10) has been calculated by the equation and is given as:

$$C = \sqrt{K_{sp}/\alpha}, \quad (11)$$

Taking into account that sludge components are metal carbonates and hydroxides, the calculations are carried out according to dissociation constants of carbonic acid ($K_1=4.5 \cdot 10^{-7}$; $K_2=4.8 \cdot 10^{-11}$), water ($K_w=10^{-14}$) and the solubility values of metal hydroxides and carbonates, which are components of waste.

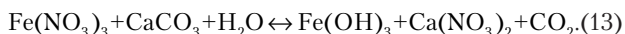
$$\alpha = K_1 \cdot K_2 / \left([H^+]^2 + K_1 \cdot K_2 + K_1 [H^+] \right),$$

$$\alpha = K_a / \left(K_a + [H^+] \right). \quad (12)$$

The results of calculations and reference data are shown in Table 3.

Considering that the dissolution of calcium carbonate in the calcium nitrate process is carried out in nitric acid of 30 % concentration, the dissolution of iron compounds is also possible, but during the reaction of calcium carbonate dissolution, the acid concentration will decrease. This definitely will cause iron salts hydrolysis. The calculated equilibrium concentration points to this fact.

After oxidizing the solution by hydrogen peroxide, iron is transformed from Fe²⁺ to Fe³⁺. Iron (III) hydroxide precipitation by calcium carbonate occurs by the reaction and is written as:



Initial pH of iron (III) hydroxide precipitation based on reference data makes 2–3 [17], and hence the concentration of nitric acid should be in the range of 0.01–0.001 mole/l.

According to the results of calculations (Table 2), an effective calcium carbonate dissolution in such conditions, in contrast to iron compounds, is still possible.

Table 2

Calculation results of solubility of sludge components in low-concentration nitric acid

Reaction No.	Sludge component	Solubility product K _{SP} [21]	K _a , reaction product	[H ⁺], mole/l	α	C, mole/l
1	CaCO ₃	3.8·10 ⁻⁹	4.8·10 ⁻¹¹	0.01	2.16·10 ⁻¹³	132.64
				0.001	2.16·10 ⁻¹¹	13.27
				0.0001	2.15·10 ⁻⁹	1.33
				0.00001	2.067·10 ⁻⁷	0.14
2	CaCO ₃	3.8·10 ⁻⁹	4.5·10 ⁻⁷	0.01	0.000045	0.0092
				0.001	0.00045	0.0029
				0.0001	0.0045	0.0009
				0.00001	0.045	0.0003
3	FeCO ₃	3.47·10 ⁻¹¹	4.8·10 ⁻¹¹	0.01	2.16·10 ⁻¹³	12.67
				0.001	2.159·10 ⁻¹¹	1.27
				0.0001	2.15·10 ⁻⁹	0.13
				0.00001	2.067·10 ⁻⁷	0.01
4	FeCO ₃	3.47·10 ⁻¹¹	4.5·10 ⁻⁷	0.01	4.5·10 ⁻⁵	0.0009
				0.001	4.5·10 ⁻⁴	0.0003
				0.0001	4.5·10 ⁻³	0.00009
5	Fe(OH) ₂	8·10 ⁻¹⁶	1·10 ⁻¹⁴	0.01	10 ⁻¹²	0.03
				0.001	10 ⁻¹¹	0.009
				0.0001	10 ⁻¹⁰	0.003
6	Fe(OH) ₃	1·10 ⁻¹⁷	1·10 ⁻¹⁴	0.01	10 ⁻¹²	0.003
				0.001	10 ⁻¹¹	0.001
				0.0001	10 ⁻¹⁰	0.0003
7	Ca(OH) ₂	5.5·10 ⁻⁶	1·10 ⁻¹⁴	0.01	10 ⁻¹²	2345*
				0.001	10 ⁻¹¹	741.5*
				0.0001	10 ⁻¹⁰	234.5*
8	Mg(OH) ₂	7.1·10 ⁻¹²	1·10 ⁻¹⁴	0.01	10 ⁻¹²	2.65
				0.001	10 ⁻¹¹	0.84
				0.0001	10 ⁻¹⁰	0.26
9	CaSO ₄	2.5·10 ⁻⁵	1.2·10 ⁻²	0.01	1.2	0.005
				0.001	12	0.0014
				0.0001	120	0.0005
10	Al(OH) ₃	1·10 ⁻³²	1·10 ⁻¹⁴	0.01	10 ⁻¹²	10 ⁻¹⁰
				0.001	10 ⁻¹¹	10 ⁻¹⁰
				0.0001	10 ⁻¹⁰	10 ⁻¹¹

Note: * – the calculated values of the concentration of calcium salts are limited by their solubility in the temperature range of studies

The results of chemical analyzes of the processes of dissolution of water treatment waste are illustrated in Fig. 1, 2.

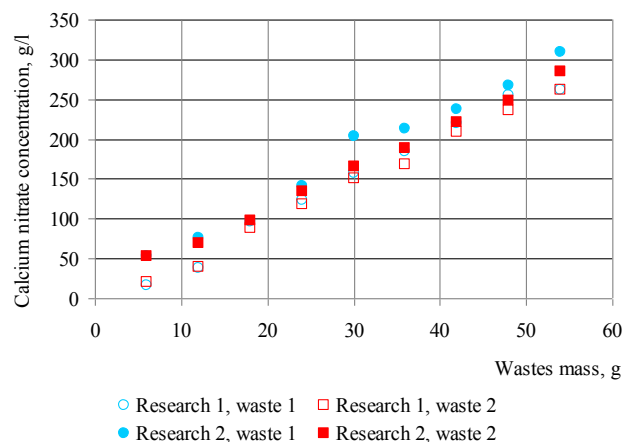


Fig. 1. Increase of calcium nitrate concentration in the waste dissolution process

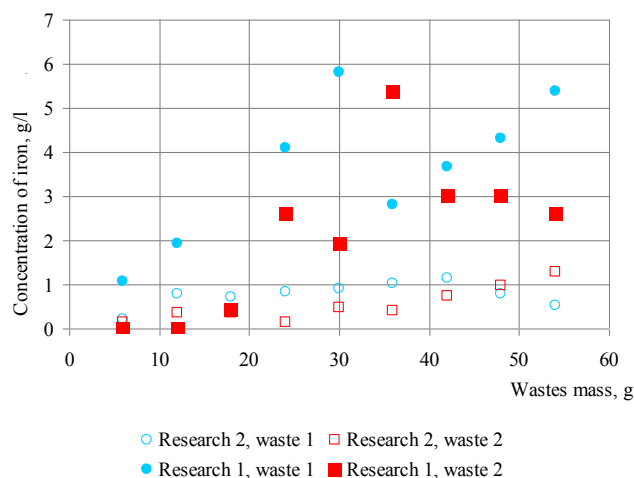


Fig. 2. Changes in the concentration of iron in the solution in the lime-softening process

The concentration of calcium nitrate in the solution continuously increases with practically constant speed, calcium carbonate dissolves almost completely (>97 %).

The concentration of iron in the solution changes stochastically, this is due to several reasons:

- the rate of dissolution of iron compounds;
- the size of dissolved particles.

After filtering, the solution has a fairly intense yellow-brown color, which is due to the presence of iron salts and soluble fulvic acids. The solution also contained the residual amount of nitric acid, the concentration of which made 18–20 g/l. After adding 20 ml of hydrogen peroxide solution (32 % mass), holding it for an hour and the subsequent 15 minute-boiling, the solutions significantly lightened. After cooling the solution to remove the residual acid and to precipitate iron, calcium-carbonate has been added, the amount of the latter has been calculated by the value of the residual acid concentration and by reaction (13). After filtration from the precipitate, the solutions obtained had a concentration as shown in Table 3.

Table 3

Chemical composition of solutions of calcium nitrate after cleaning of iron

Component	Concentration, g/l			
	Solutions obtained from sludge of "Severodonetsk AZOT Association" (waste 1)		Solutions obtained from sludge of PJSC "LINIK" (waste 2)	
	Research 1	Research 2	Research 1	Research 2
Ca(NO ₃) ₂	336	353	434	455
Fe ₂ O ₃	0.1	0.3	0.1	0.3
pH	3.8	2.6	3.5	2.9

The results of kinetic researches of iron precipitation from the solution are illustrated by kinetic curves in Fig. 3.

To determine the kinetic characteristics of the investigated process, the processing of experimental data has been carried out using kinetic equations of the 1st and 2nd order.

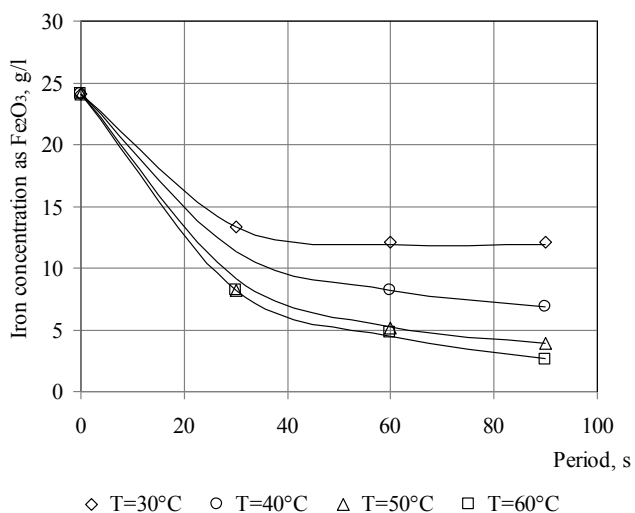


Fig. 3. Changes in iron concentration in the solution over time at different temperatures

To determine the observed reaction order as well as the specific reaction rate, the data have been processed in the coordinates of the dependences $\ln C - \tau$, $1/C - \tau$, where C is the concentration of iron nitrate, mol/l; τ – time from the reagents contact, s. The choice of the kinetic equation has been made on the basis of comparison of the approximation validity coefficients R^2 . The results of the curves processing and the determined rate constants for different concentrations are given in Table 4.

Table 4

The values of the rate constant and approximation validity at different temperatures

T, °C	k ₁	R ²	k ₂	R ²
30	0.007	0.715	0.055	0.889
40	0.011	0.735	0.093	0.821
50	0.014	0.799	0.153	0.953
60	0.017	0.964	0.207	0.859

By the values of the second-order reaction rate constants, the activation energy of the process, which has made

37 kJ/mole has been calculated. This indicates the process flow in the transition zone, where both the rates of chemical reaction and diffusion have comparable values. The calculation was carried out in the logarithmic coordinates of the Arrhenius equation (14):

$$\ln K = \ln K_0 - E_a/RT. \tag{14}$$

The calculation results are shown in Fig. 4.

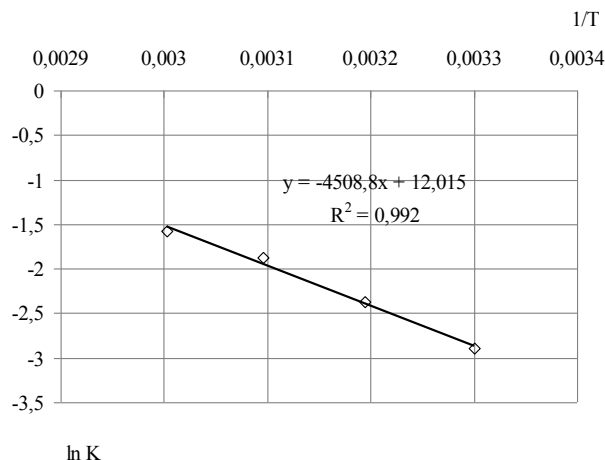


Fig. 4. Calculation according to the Arrhenius equation

Thus, the rate of the process can be described by the equation (15):

$$-dC/d\tau = 165215 \cdot e^{-4508.8/T} \cdot C^2, \tag{15}$$

where $165215 = e^{12.015}$ is the value of the pre-exponential multiplier calculated from the Arrhenius equation;

$$4508.8 = E_a/R,$$

where E_a is the value of the activation energy (J/mole), R is the universal gas constant.

The sediment obtained from the waste had a yellow-brown color and gelatinous structure, was poorly filtered. The content of ferrum (III) hydroxide in these sediments is 40–42.5 %.

6. Discussion of the results of the study of the process of obtaining the calcium nitrate solution

An increase in the concentration of calcium nitrate in the process of dissolving two investigated wastes is almost identical, which is caused by very much rapid dissolution of calcium carbonate in nitric acid and indicates the sustainability of the process. Since the calcium carbonate content in the waste is almost the same 74.96 and 77.47 % by weight, very similar results were obtained.

The concentration of iron in the solution increases first, and then, as nitric acid is consumed, decreases, which is explained by the partial hydrolysis of iron salts. The value of iron concentration in the final solution varies from 0.5 to 5 g/l. The difference in the rate of iron accumulation in the solution may be due to the difference in the crystalline structure of sludge, and some difference in its chemical composition.

The dark brown color of waste solutions is associated with the presence not only iron salts, but also fulvic acids, capable of forming colored complexes with iron compounds. Hydrogen peroxide in acidic medium destroys fulvic acids, which is observed as the formation of a lighter color of the solution.

For calculations of industrial equipment, one needs knowledge about the kinetics of the process. We obtained a kinetic equation of the 2nd order, which quite accurately (accuracy of approximation $R^2=0.821-0.953$) describes the process of iron precipitation from a nitrate solution using calcium carbonate.

In order to test the equation (15), a solution of calcium nitrate was obtained from the lime-softening sludge of Severodonetsk "AZOT". The concentration of iron (III) nitrate in it was 14 g/l. After adding calcium carbonate and exposing for 2 minutes, the concentration of the solution, which was 0.6 g/l iron (III) nitrate, was determined. This correlates well with the value $C=0.5$ g/l calculated by the equation (15).

The process of processing lime-softening sludge according to the following scheme, shown in Fig. 5 is proposed.

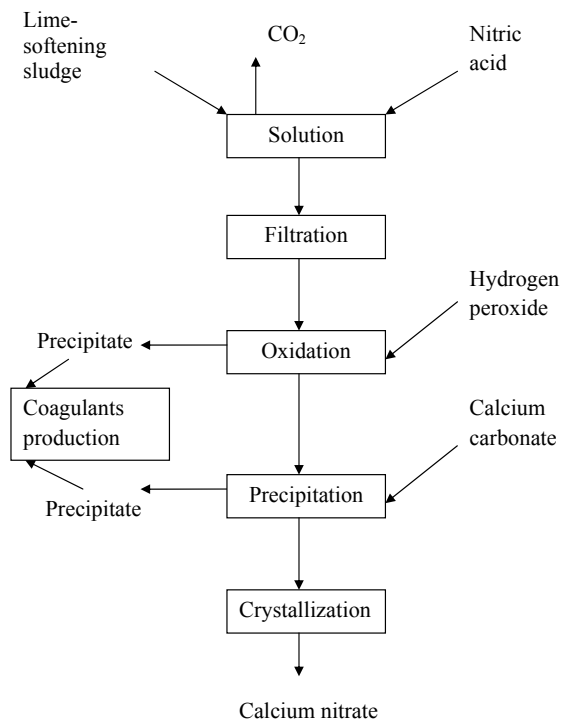


Fig. 5. Scheme of processing lime-softening sludge

The technological scheme should include the following technological steps:

- dissolution of waste in nitric acid;
- filtration of insoluble sediment containing insoluble organics, silicates and aluminum hydroxide;

- further the solution enters the oxidation of soluble fulvic acids and iron compounds;
- after oxidation, boiling of the solution is provided for the destruction of the hydrogen peroxide residue;
- from the oxidized solution, iron is removed by precipitation of calcium carbonate by reducing the acidity of the solution and hydrolysis of iron salts.

Calcium nitrate obtained as a result of crystallization can be used as a mineral fertilizer or chemical reagent for the preparation of other calcium salts. In addition to calcium nitrate, one can obtain chemically deposited calcium carbonate, i. e. a polymer filler, which is also in demand on the market. The residue after dissolving the waste and cleaning the solution contains about 40 % iron and can be used to recycle coagulants by the method proposed in [5].

The limitation of the research is insufficient information on the organic component of lime-softening sludge. The sludge has been accumulated for many years, hence the concentration and qualitative composition of this component may have changed.

In order to improve the technology of utilization, the study of the process of oxidation of the waste solution is required. There is also the dependence of the process efficiency on individual factors. To develop technological equipment, it is necessary to study the filtration properties of sediments and the dependence of these properties on the precipitation conditions.

7. Conclusions

1. Dissolution of waste in nitric acid occurs at a constant rate, almost identical for the two types of waste used. The degree of dissolution of calcium carbonate was more than 97 %. The concentration of calcium nitrate in solutions was 350–450 g/l. Adding waste to acid in portions not exceeding 10 % of the total amount allows avoiding excess gas formation.

2. Precipitation of iron from the solution of waste was accomplished by increasing the pH of the solution to the values of 2.6–3.8, which causes the hydrolysis of iron salts. PH increase was carried out by neutralizing the excess acid with calcium carbonate. The final concentration of iron in the solution did not exceed 0.3 g/l.

3. We found that the process of iron deposition is very accurately described by the second-order kinetic equation. The activation energy of the process is determined. The value of about 37 kJ/mole indicates the process flow in the transition area, where the rates of chemical reaction and diffusion have comparable values.

In general, the waste processing method can be carried out according to the proposed principal technological scheme. The method allows obtaining calcium nitrate, a mineral fertilizer, which is in market demand.

References

1. MWH's Water Treatment: Principles and Design / Crittenden J. C., Trussell R. R., Hand D. W., Howe K. J., Tchobanoglous G. John Wiley & Sons, Inc., 2012. doi: <https://doi.org/10.1002/9781118131473>
2. Combining coagulation, softening and flocculation to dispose reverse osmosis retentates / Ordóñez R., Moral A., Hermosilla D., Blanco Á. // Journal of Industrial and Engineering Chemistry. 2012. Vol. 18, Issue 3. P. 926-933. doi: <https://doi.org/10.1016/j.jiec.2011.08.004>

3. Evaluation of the impact of lime softening waste disposal in natural environments / Blaisi N. I., Roessler J., Cheng W., Townsend T., Al-Abed S. R. // *Waste Management*. 2015. Vol. 43. P. 524–532. doi: <https://doi.org/10.1016/j.wasman.2015.06.015>
4. Waste disposal sites. Department of Ecology and Natural Resources of Luhansk Oblast State Administration. URL: <http://www.eco-lugansk.gov.ua/2013-12-12-00-50-06-3/2013-12-12-00-50-06-3/mvv>
5. Petruzzelli D. Coagulants removal and recovery from water clarifier sludge // *Water Research*. 2000. Vol. 34, Issue 7. P. 2177–2182. doi: [https://doi.org/10.1016/s0043-1354\(99\)00357-7](https://doi.org/10.1016/s0043-1354(99)00357-7)
6. Evaluation of reusing alum sludge for the coagulation of industrial wastewater containing mixed anionic surfactants / Jangkorn S., Kuhakaew S., Theantanoo S., Klinla-or H., Sriwiriyarat T. // *Journal of Environmental Sciences*. 2011. Vol. 23, Issue 4. P. 587–594. doi: [https://doi.org/10.1016/s1001-0742\(10\)60451-2](https://doi.org/10.1016/s1001-0742(10)60451-2)
7. Coagulation efficiency and flocs characteristics of recycling sludge during treatment of low temperature and micro-polluted water / Zhou Z., Yang Y., Li X., Gao W., Liang H., Li G. // *Journal of Environmental Sciences*. 2012. Vol. 24, Issue 6. P. 1014–1020. doi: [https://doi.org/10.1016/s1001-0742\(11\)60866-8](https://doi.org/10.1016/s1001-0742(11)60866-8)
8. Zhang L. Production of bricks from waste materials – A review // *Construction and Building Materials*. 2013. Vol. 47. P. 643–655. doi: <https://doi.org/10.1016/j.conbuildmat.2013.05.043>
9. Utilization of water treatment plant sludge in structural ceramics bricks / Benlalla A., Elmoussaouiti M., Dahhou M., Assafi M. // *Applied Clay Science*. 2015. Vol. 118. P. 171–177. doi: <https://doi.org/10.1016/j.clay.2015.09.012>
10. Lightweight bricks manufactured from water treatment sludge and rice husks / Chiang K.-Y., Chou P.-H., Hua C.-R., Chien K.-L., Cheeseman C. // *Journal of Hazardous Materials*. 2009. Vol. 171, Issue 1-3. P. 76–82. doi: <https://doi.org/10.1016/j.jhazmat.2009.05.144>
11. Energy-efficient thermal treatment of sewage sludge for its application in blended cements / Pavlík Z., Fořt J., Záleská M., Pavlíková M., Trník A., Medved I. et. al. // *Journal of Cleaner Production*. 2016. Vol. 112. P. 409–419. doi: <https://doi.org/10.1016/j.jclepro.2015.09.072>
12. Lin K. L., Chiang K. Y., Lin C. Y. Hydration characteristics of waste sludge ash that is reused in eco-cement clinkers // *Cement and Concrete Research*. 2005. Vol. 35, Issue 6. P. 1074–1081. doi: <https://doi.org/10.1016/j.cemconres.2004.11.014>
13. Mageed A. A., Rizk S. A., Abu-Ali M. H. Utilization of water treatment plants sludge ash in brick making // *Journal of Engineering Sciences Assiut University*. 2011. Vol. 39, Issue 1. P. 195–206.
14. Effect of water treatment additives on lime softening residual trace chemical composition – Implications for disposal and re-use / Cheng W., Roessler J., Blaisi N. I., Townsend T. G. // *Journal of Environmental Management*. 2014. Vol. 145. P. 240–248. doi: <https://doi.org/10.1016/j.jenvman.2014.07.004>
15. Co-treatment of reject water from sludge dewatering and supernatant from sludge lime stabilization process for nutrient removal: A cost-effective approach / Hu D., Zhou Z., Niu T., Wei H., Dou W., Jiang L.-M., Lv Y. // *Separation and Purification Technology*. 2017. Vol. 172. P. 357–365. doi: <https://doi.org/10.1016/j.seppur.2016.08.032>
16. *Industrial Minerals and Their Uses: A Handbook & Formulary* / A. Peter (Ed.). William Andrew Inc., 1996. 647 p.
17. Calcium nitrate. It's properties, production and application in agriculture / Beglov B., Namazov S., Dodahodzaev A., Yuldashev S., Ibragimov G. MeKchnat, Tashkent, 2001.
18. Calcium Nitrate Market by Application (Wastewater Treatment Chemicals, Fertilizers, Concrete Manufacturing, Explosives and Others) – Global Industry Perspective, Comprehensive Analysis, Size, Share, Growth, Segment, Trends and Forecast, 2015–2021. URL: <https://www.zionmarketresearch.com/report/calcium-nitrate-market>
19. Rodríguez F. J., Núñez L. A. Characterization of aquatic humic substances // *Water and Environment Journal*. 2011. Vol. 25, Issue 2. P. 163–170. doi: <https://doi.org/10.1111/j.1747-6593.2009.00205.x>
20. *Handbook of Green Analytical Chemistry* / M. de la Guardia, S. Garrigues (Eds.). Wiley, 2012. 566 p. doi: <https://doi.org/10.1002/9781119940722>
21. Harvey D. *Modern Analytical Chemistry*. 1st ed. McGraw-Hill Companies, Boston, 2000. 816 p.