MINISTRY OF HIGHER AND SECONDARY SPECIAL EDUCATION OF UZBEKISTAN

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RESEARCH TECHNOLOGY FOR PRODUCING MAGNESIUM OXIDE PROCESSING OF DOLOMITE SHORSU

THESIS

For the degree of Master 5A320401 - Chemical Technology inorganic substances (chemical fertilizer technology)

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TABLE OF CONTENTS

INTRODUCTION

Relevance of the theme. One of the main directions of economic development of the Republic of Uzbekistan - the development and comprehensive utilization of natural resources, the creation of competitive import-substituting products based on local raw materials[1].

Inorganic magnesium compounds used in the production of nitrogen fertilizers, fireproof materials and binding materials, feed additives, as fillers of polymeric materials, etc. As used Uzbekistan magnesium compounds are imported and mostly imported from Russia.

Ammonium nitrate is one of the main nitrogen fertilizer, produced in Uzbekistan, but its main drawback- the ability under certain conditions to be ignited subsequent detonation. This fact has caused a number of accidents and incidents related to ammonium nitrate, for example in a warehouse chemical plant in Toulouse, a series of bombings in Southeast Asia. Therefore, in some countries have banned the use of ammonium nitrate in agriculture.

According to SJSC «O'zkimyosanoat» annual costs accompanying each batch of ammonium nitrate from the factory to the field amount to about 3750 thousand dollars. Thus, the manufacturers of ammonium nitrate is a topical problem of transition to the production of fertilizer based on ammonium nitrate, preserve its agrochemical efficiency with significantly greater resistance and stability to external influences,

Studies have shown that introduction of magnesia additions, as an additional component in the manufacture of ammonium nitrate has improved nutritional properties of fertilizers, significantly increase its phase stability when using binary additives including potassium nitrate and magnesium nitrate. Also, ammonium nitrate, magnesium nitrate treatment helps to reduce or eliminate its explosive properties.

Uzbekistan does not have huge reserves of minerals magnesite, but in the country there are other magnesium-containing minerals. Because of these facts the chemical processing problem substandard (talk and dolomite), magnesite, dolomite or other magnesium-bearing materials. However, the organization of processes limited by insufficient knowledge of the physical chemistry of heterogeneous heterophase reactions and processing said feedstock.

The problem of obtaining pure magnesium oxide engaged in the twenties of the last century, several large organizations. various technology options have been worked out experimentally, but the desired result was obtained.

In the literature, few data suitable for solving a number of problems arising and required for the development of rational technology. The problem arises detailed study which seem at first glance, known reactions and chemical properties of inorganic magnesium compounds.

Objective: Development of physico-chemical principles processing dolomite deposits Shorsu to pure magnesium oxide.

Research objectives:

1. Investigation of the composition of dolomite Shorsu field.
2. The study of physical and chemical properties of dolomite Shorsu.
3. Studying the process of thermal decomposition of carbonates and magnesium hydroxide
4. Study of hydration of magnesium oxide and calcium process, precipitation of magnesium hydroxide from solutions of various acids.

Scientific novelty is to provide a physical and chemical basis for recycling dolomite Shorsu pure oxide, opening new prospects for the development directions in the magnesium oxide technology - obtaining pure magnesium oxide from dolomites chemically.

1. CHAPTER 1. LITERATURE REVIEW. CURRENT STATUS MAGNESIUM RAW MATERIALS BASE AND PRODUCTION METHODS, THE MAGNESIUM COMPOUND

1.1 The role of magnesium compounds in the industry of Uzbekistan today.

Uzbekistan has a strong mineral resource base and large prospects its increase, has real possibilities for economic recovery of the country due to the further expansion of proven reserves and mining. At present 1717 deposits revealed and about 1,000 promising manifestations of minerals, 118 kinds of minerals, of which 65 are being developed.

On the territory of Uzbekistan 1717 deposits are opened, including - 235 hydrocarbon fields, 136 - metals; 3 - coal; 55 - mining, 26 - and 30 mining and chemical - gems of raw materials; 615 - construction materials for various purposes, and 617 - fresh and mineral underground waters [2]. There is a need in the creation of domestic products based on local raw materials with the use of new approaches and technologies.

Ammonium nitrate is one of the main nitrogen fertilizer worldwide, including Uzbekistan. However, its main disadvantage is due to its oxidising properties, which under certain conditions is able to be ignited, followed by detonation. This fact has caused a number of accidents and incidents related to ammonium nitrate, for example in a warehouse chemical plant in Toulouse, a series of bombings in Southeast Asia. Therefore, in some countries have banned the use of ammonium nitrate in agriculture.

According to SJSC «O'zkimyosanoat» annual costs accompanying each batch of ammonium nitrate from the factory to the field amount to about 3750 thousand dollars. Thus, the manufacturers of ammonium nitrate is a topical problem of transition to the production of fertilizer based on ammonium nitrate, preserve its agrochemical efficiency with significantly greater resistance to external influences, stability.

Studies have shown that introduction of magnesia additions, as an additional component to the components used widely in the production of ammonium nitrate has improved nutritional properties of fertilizers, significantly increase its phase stability when using binary additives including potassium nitrate and magnesium or calcium nitrates. Also, processing of magnesium nitrate, ammonium nitrate promotes reduction or complete elimination of its explosive properties. Magnesium nitrate, in turn obtained by treating with nitric acid magnesite.

Since, in Uzbekistan little studied fields magnesite is used as an additive imported magnesite. However, Uzbekistan has huge reserves of other minerals magnesium. Extraction of their magnesium composition in the form of the active compound was the main aim of this study.

1.2 Analysis of the existing methods of active magnesium is removed from its compounds

In the 60s in the Czech Republic it was recognized as the most effective method for producing high purity hydrocarbonate magnesium oxide from magnesite substandard, which allows to obtain a product with a content of MgO 98-99%. By this method, products of thermal decomposition of dolomite magnesite or dolomite subjected to hydration. The resulting slurry of hydroxides of magnesium and calcium is subjected to 8-stage carbonation. In the first stage carbonization was carried out at 40-60 °C to complete the formation of $CaCO_3$ in the second process step is carried out under a pressure of 3-5 atm at a temperature not exceeding 25 °C to obtain a solution of $Mg(HCO_3)_2$. Hydrocarbonate solution separated from the solid phase ($CaCO_3$, SiO_2, etc.) Is decomposed under stirring by heating to a temperature above 45 °C (50 ° - 90 °C). This forms a basic magnesium carbonate $3MgCO_3$-$Mg(OH)_2$. Its thermal decomposition at 900 ° -1000 °C, a magnesium oxide. The yield is 80-85% MgO. Possibilities of use of the $CaCO_3$ slurry are dependent on the content of impurities (SiO_2, R_2O_3), and the yield of the chemical activity of MgO in the calcined magnesite[3-13].

The disadvantage of the process is a low concentration solutions (25g/l MgO), which leads to the need for very large amounts of processing solution and accordingly the use of cumbersome apparatus. This, together with high heat costs thermolysis basic magnesium carbonate makes the process energy intensive.

Firm "Rutner" (Austria) is pure magnesium oxide, magnesium chloride thermohydrolysis. Preparation of the magnesium oxide in this way there is also in the USA and Germany. In accordance with the method used by "Rutner" substandard magnesite dissolving in hydrochloric acid a magnesium chloride solution was prepared, which was purified from impurities. The purified solution was subjected to the lay processing: evaporation, the dehydration of a hydrate of magnesium chloride, magnesium chloride thermohydrolysis monohydrate, calcining magnesium oxide.

Hydrogen chloride is cooled and water is absorbed. The resulting hydrochloric acid is returned to the dissolution of magnesite[13-17].

The disadvantages of this method are high power consumption and very strong aggressiveness of fluids and gas.

Magnesium oxide is available thermal decomposition of magnesium sulfate at 1100-1200 °C, and magnesium nitrate at temperatures above 400 °C. From a thermodynamic point of view of obtaining magnesium oxide by these methods is less advantageous than thermal hydrolysis of magnesium chloride. Furthermore, well known difficulties associated with the absorption of sulfur oxides and nitrogen. However, the attempt was made to develop a technology in U.S. producing pure magnesium oxide by thermolysis of magnesium nitrate. But it turned out that by this method the obtained magnesium oxide has extremely poor sinterability[18].

Lime method for obtaining magnesium oxide abroad received widespread. As the magnesium-containing raw material is magnesium chloride solutions (sea water, salt lake brine, carnallite liquor, etc.), as well as a precipitant - hydrated lime obtained by firing limestone or dolomite. In order to improve filtration properties of magnesium hydroxide tend to reduce the rate of dissolution of calcium hydroxide. For this proposed use of coarse $Ca(OH)_2$, hydrated lime and granular even frozen granules. This method provides a magnesium oxide of the following composition (% wt.): MgO 97-98, CaO 0,6-0,8, 0,5-0,8 SiO_2, R_2O_3 0,2-0,6, Cl^- less than 0,2 [13,19-20].

The advantage of this method is an extensive resource base and the simplicity of the technology. The main drawback - the formation of calcium chloride solution. As is known, a large amount of it is formed into the soda production, and its disposal and burial is acute environmental problem. magnesium hydroxide precipitate has poor sedimentation and filtration properties and its washing consumes a large amount of water (up to 150 m^3/t). Much of the impurities contained in limestone or dolomite, goes into the final product.

The most promising precipitant $Mg(OH)_2$ is ammonia, since it is free from impurities. When choosing a magnesium-containing solution it should be noted that natural stocks soluble magnesium salts are mainly represented by magnesium chloride and sulphate. During the precipitation of magnesium hydroxide from chloride solutions have problems with disposal of ammonium chloride[21].

One of the most promising methods for the production of magnesium oxide is cyclic ammoniacal method, which consists in the following. Calcined dolomite is introduced into the ammonium salt solution, where it is at a temperature of the boiling solution and the resulting hydrated magnesium hydroxide is reacted with an ammonium salt, displacing the ammonia into the gas phase. The resulting magnesium salt solution is separated from the solid phase is precipitated there from and drive off ammonia, magnesium hydroxide, which is separated from the solution, washed and subjected to thermal decomposition. Advantages of the method - low-waste and non-waste and the possible lack of the need for large amounts of auxiliary reagents. It should be noted that the degree of use of magnesium will depend on the reactivity of magnesium oxide in the fired raw material[8-9, 22-23].

In the case of ammonium sulphate - caprolactam production waste, will be obtained magnesium sulphate solution from which, by its interaction with KCl available potassium sulfate and shenyte $K_2Mg(SO_4)_2*6H_2O$ - potassium-chlorine-free fertilizers. Abroad common method of Mannheim. About 40% of K_2SO_4 produced in the world come from this method. By existing technology K_2SO_4 obtained in muffle furnace at 500-600 °C. A disadvantage of this method are: low capacity furnace, corrosion of equipment, and as a consequence of frequent output furnaces fail, HCl gas contamination of impurities SO_2, SO_3, Cl_2, and consequently the need multistage purification, high power consumption. To address these shortcomings is proposed to carry out the process of "liquid phase" conversion with an excess of acid at a temperature of 100-120 °C in a stirred reactor. HCl gas, resulting in this case meets all requirements for acid "Ch_c" mark, which deficit is currently over 20 tones/year. Mixing potassium hydrogensulfate produced in this process with a caustic magnesite can be prepared $K_2Mg(SO_4)_2*6N_2O$. When replacing caustic to a caustic magnesite, dolomite ($MgO+CaCO_3$) available chlorine-free sustained KMg-fertilizer, containing $CaCO_3$ and hence suitable for acidic soils. Reacting potassium hydrogen with dicalcium phosphate (precipitate) is easily obtained bezhloridnoe phosphorus-potassium fertilizer. the deficit now stands at more than 20 tones/year. Mixing potassium hydrogensulfate produced in this process with a caustic magnesite can be prepared $K_2Mg(SO_4)_2*6N_2O$. When replacing caustic to a caustic magnesite, dolomite ($MgO + CaCO_3$) available chlorine-free sustained KMg-fertilizer, containing $CaCO_3$ and hence suitable for acidic soils. Reacting potassium hydrogen with dicalcium phosphate (precipitate) is easily obtained not chloride phosphorus-potassium fertilizer the deficit now stands at more than 20 tones/year. Mixing potassium hydrogensulfate produced in this process with a caustic magnesite can be prepared $K_2Mg(SO_4)_2*6N_2O$. When replacing caustic to a caustic magnesite, dolomite ($MgO+CaCO_3$) available chlorine-free sustained KMg-fertilizer, containing $CaCO_3$ and hence suitable for acidic soils. Reacting potassium hydrogen with dicalcium phosphate (precipitate) is easily obtained not chloride phosphorus-potassium fertilizer.

1.3 Thermolysis of magnesium and calcium carbonates

The equilibrium pressure of CO_2 of 0,1 MPa above mixtures of $CaCO_3$ and $MgCO_3$ + CaO + MgO, respectively, is achieved at 897 ° and 408 °C [24-26]. The heat of reaction to 298 K are respectively equal to 178 and 116.9 kJ/mole.

The initial stage of the process is characterized by the collapse of the CO_3^{2-} ion according to the scheme: $CO_3^{2-} \rightarrow CO_2 + O_2$. Adsorbed CO_2 molecules two-component solid phase ($CaCO_3$-CaO) in the vicinity of its active sites. Subsequently CO_2 molecules are desorbed and leave the crystal lattice volume. Through optical and electronic microscopy revealed two different CaO layer. Exterior - polycrystalline and inner adjacent to $CaCO_3$. The structure of the inner layer of CaO does not differ even at 20,000-fold magnification.

Electron microscopic studies thermolysis $MgCO_3$ CO_2 atmosphere showed the formation of a conglomerate of MgO crystals, the shape of which corresponds to the original carbonate.

According to various authors [27-30] limiting step $CaCO_3$ decomposition are both dissociation and diffusion of CO_2 through a layer of CaO. In the literature [30], the rate of this process is described by the equation Roginsky.

If samples used with a large mass (~ 100 g), then the rate of decomposition of $CaCO_3$ is limited by heat transfer or removal of CO_2.

Thermolysis $MgCO_3$ devoted significantly fewer jobs. They noted that the thermolysis magnesite described by the equation "compressible sphere" (Roginsky) [31-32]. The activation energy estimated at 109-234 kJ/mol [31-32] which apparently depends on the thermolysis conditions (temperature, rate of heat supply, P_{CO_2} and others). It is noted that some additives can reduce this by up to 67 kJ/mol.

It is known that pure calcium oxide crystallizes in a cubic system with unit cell parameters of 499.7 nM [33].

The presence of some impurity elements (Mn^{2+}, Mg^{2+}, Ba^{2+}, etc.), depending on the thermolysis temperature may change this value in either direction

[34]. Thermolysis temperature and time, as well as composition of the gas phase [35] have a significant effect on the kinetics of decomposition of carbonates and oxides obtained by crystallization processes. The structure, composition and dispersion of the latter influences the degree and rate of hydration.

One of the most important indicators of quality of products is thermolysis carbonates reactivity CaO and MgO (for brevity - activity). It involves determining the portion oxides which is able to react with water [21]. In the matter of assessment of the activity of CaO opinions of researchers are different. Most of them typically lead temperature which is reached when hydration. In industrial laboratories quality as determined by titration CaO acid [21]. Activity is determined MgO in lime dissolving it in 1M HCl solution at reflux and Mg^{2+} titration with Trilon B.

To determine the activity of magnesia MgO to use different methods: iodometric definition of "lemon number" etc .. This value determines the properties of the oxide such as carbonization speed bulk density, adhesiveness, etc.

Critically considering all existing methods for evaluating the activity of CaO and MgO, the authors [36] came to the conclusion that it is determined, mainly, its specific surface area. At the same time, [37,38] indicates that the reactivity due to the presence of defects and distortion in the crystal lattice.

Production Problems active CaO with high specific surface area described in detail in [39]. It indicated that during the decomposition of calcite in vacuo it reaches 100 m^2/g. This product can be called "super active". Oxide with a specific surface area of 10 m^2/g is generally considered "very active" (T thermolysis 800 ° - 850 °C). Raising the temperature to 1100 ° - 1300 °C leads to the formation of "low active" substances (0,5-0,3 m^2/g). Over 1400 °C is practically inert CaO (0,1 m^2/g).

Depending on the conditions thermolysis $MgCO_3$ in the literature are various values of the specific surface of the magnesium oxide [40]. According to [29] in the temperature range of 300 - 800 °C the specific surface area of the reaction products varies from 31 to 23 m^2/g, passing through a maximum (350

m^2/g) at 350 °C. In [41], the abnormally high values of surface of 480 - 550 m^2/g. It is also stated that at a temperature of 800 °C the specific surface area is almost independent of the expansion time.

The mechanism of decomposition of dolomite is considered in several papers [42-46], which put forward various hypotheses. The most likely mechanism is as follows. When R_{SO} > 1.7 kPa dolomite $CaMg(CO_3)_2$ is first decomposed, calcium and magnesium carbonates, the latter immediately decomposed into MgO and CO_2. When P_{CO_2}= 0.1 MPa destruction lattice $MgCO_3$ dolomite and dissociation occurs at 780-750 °C, and the thermolysis of $CaCO_3$ occurs when reaching 900 °C. When P_{CO_2}<1,7 kPa dolomite decomposition to oxide components occurs in a single stage [42] speed of the process under isothermal conditions described by "contracting sphere".

When full decomposition of dolomite formed "dolomitic lime" consisting essentially of equimolar amounts of CaO and MgO, and only when the dissociation $MgCO_3$ - so-called "caustic dolomite" - (MgO + $CaCO_3$).

The decomposition of dolomite in the air stream in the presence of various additives studied in [46-48]. It is stated that salts with anions Cl^-, NO^{3-}, CO_3^{2-} first lower temperature peak decay dolomite at 100-255 °C. In [31] it is noted that the Ea decomposition of dolomite in a CO_2 atmosphere is -188 kJ/mol, and in an atmosphere of H_2O - 112 kJ/mol.

Most detail this process is researched in [49-53]. According to [49] for thermolysis dolomite the most likely values of the activation energy of 121 kJ/mol for the first stage (a < 0.4) and 249 kJ/mol - for the second. However, in another study, the same authors give other values, accordingly 164-179 kJ/mol and 221-312 kJ/mol [50]. It emphasizes the fundamental unsuitability of the kinetic experiments under isothermal conditions, what follows seems to agree, given the industrial conditions of the thermolysis.

At the same time, Brown T. et al. [26] indicate that when using the measurement obtained more not isometric "unintelligent" kinetic parameters, vary within wide limits. The cause of these differences V.A. Logvinenko [54] explains the fact that many researchers did not take into account important parameters such as the size and distribution of particles, sample value, the conditions of Heat and Mass and others. Theoretical foundations of non-isothermal method of studying the kinetics of thermally activated processes are set out in [49-54].

To avoid limitation of the process of heat supply, research is conducted usually at a sample heating rate of 10-20 dg / min, although in practice, this rate of 2-3 deg / min [55] in shaft furnaces and 6-8 deg / min [56] in a rotating drum.

Determination of optimal conditions thermolysis dolomite in the preparation of reaction products of active papers [57-58]. However, these data are controversial. Most researchers indicate the temperature at 850 °C at a residual CO_2 content in the final product ~ 20%. Others argue for complete decarbonation dolomite at temperatures up to 1200 °C [35]. According to [57], the highest activity is reached at ~ 750 °C for caustic dolomite and ~ 950 °C in the case of dolomite lime.

The specific surface area dolomite thermolysis products are highly contradictory. Some researchers indicate a gradual reduction in its temperature increases from 500 to 1000 °C, others note the sharp increase in the same interval with a maximum at 800 °C.

The main natural carbonates are limestone consisting primarily of mineral calcite $CaCO_3$, $MgCO_3$ magnesite and dolomite $CaMg(CO_3)_2$. They all contain the impurity minerals. Depending on the ratio of $CaCO_3$:$MgCO_3$ distinguished as dolomitic limestone and dolomitic magnesite.

The most well-studied process of thermal decomposition of large pieces (> 30 mm) $CaCO_3$. The method of calculation of this process, which is limited by the heat transfer rate [55]. By this method one can calculate the time required for the complete decomposition of a piece of a predetermined size at a predetermined temperature. However, it makes no allowance recrystallization rate and the reaction product respectively produced not measured activity oxides.

Accordingly, the following can be stated. In the study of the processes of thermal decomposition of carbonates of magnesium and calcium did not pay sufficient attention to the chemical reactivity of MgO in the products formed, which is particularly important during the decomposition of the particulate material. No objective method for determining the chemical activity of MgO in the thermolysis products. Not kinetics of thermal decomposition of magnesium carbonate and calcium in non-isothermal conditions at low heating rates.

1.4 Processes of magnesium hydroxide and the formation of its particle structure

1.4.1 Hydration of calcium oxide and magnesium

The greatest number of industrial lime is converted to "hydrated lime" Ca $(OH)_2$. Using the classic reaction "wet quenching" (hydration) in this case, a so-called "milk of lime" (L:S = 4-5).

The rate and degree of hydration of CaO and MgO depend on the mineral composition of caustic lime and magnesite, conditions for their preparation, temperature, amount of water, etc.

Hydration of MgO and CaO are exothermic reactions:

$MgO\ (s) + H_2O\ (g) \rightarrow Mg(OH)_2\ (t);\ \Delta H°298 = -37{,}16\ kJ$

$CaO\ (s) + H_2O\ (g) \rightarrow Ca(OH)_2\ (t);\ \Delta H°298 = -65{,}2\ kJ$

Relative hydration mechanism of MgO and CaO in the water no consensus in the literature. Most researchers believe that the process is going on, "through the solution" mechanism, and some hold topochemical mechanism.

According to [59-60] $Ca(OH)_2$ is formed at the interface by double solid phase direct connection H_2O molecules to a solid. According to [21] on the surface of CaO to MgO formed intermediate metastable phase CaO-mH_2O and MgO-nH_2O.

The first stage "through the solution" mechanism according to [61], a process of dissolution of CaO. Its speed is limited by diffusion of Ca^{2+} from the surface layers of the grains. According to [62] formation of $Ca(OH)_2$ directly from Ca^{2+} and OH^- proposed in [63], is impossible. The second step - the formation on the surface of CaO primary product layer through crystallisation from solution.

Crystallizing $Ca(OH)_2$ according to [64] forms a colloidal system. It is noted that during colloization particles on $Ca(OH)_2$ there is a positive charge, which probably are bound at the selective adsorption of Ca^{2+} from the solution. Around the solid core OH^- - ions are condensed to form a diffuse layer of colloidal micelles, which are sealed in the process of hydration and prepared for coagulation conditions[37].

Growth coagulated layer of $Ca(OH)_2$ is limited by the rate-dimensional diffusion process reactants to the interface.

According to the Ca^{2+} concentration in the liquid phase at the beginning of hydration increases dramatically (up to 2 g/l of CaO), and then decreases, which confirms the "through the solution" hydration mechanism.

Hydration of MgO characterized by an induction period [65]. During this period, the water molecules are adsorbed on the active sites of MgO particles, while the process proceeds dissolving magnesium oxide. From the resulting supersaturated solid allocated gel $Mg(OH)_2$, blocking the precursor particles. When recrystallization gel product under the influence of internal stresses hydroxide shell is destroyed, and access to the surface of H_2O molecules MgO facilitated. The third period is determined by the diffusion of the H_2O molecules through the layer formed $Mg(OH)_2$ to a portion of the unreacted MgO.

In the case of reactive MgO grinding particles predominates over their aggregation. As a result, the specific surface area $Mg(OH)_2$ is greater than the original MgO [40].

In [66] states that the rate of hydration of highly MgO Roginsky described by the equation, but deviates from it less active.

Kinetics of hydration of CaO was studied by various methods: gravity, electron microscopic, conductometric, complexometric etc. [37, 63, 67-71]. According to [67] active CaO hydration process is divided into stages and kinetic diffusion control. Indicates that this value to a <0,1-0,15 process is limited by the dissolution rate CaO. Hydration kinetics under isothermal conditions described by Erofeeva [70].

The activation energy of hydration of the "pyritical" CaO (> 1300 °C) at 25-50 °C equal to 3.8 kJ/mol, and at 75-100 °C - 85 kJ/mol [105]. According to [63] the activation energy in the range of 7-55 mm is not dependent on particle size and CaO is 42 and 31 kJ/mol, respectively, for the initial and final process step.

Process steam hydration has been little studied, especially magnesium oxide. It indicated that the reaction, at least, takes place in 2 steps: adsorption of water vapor on the surface of CaO and chemical transformation at the interface. Embryos of $Ca(OH)_2$, are formed in the old phase. According to the first stage of hydration the bin in saturated form crystallization centers of $Ca(OH)_2$, and on the second there is a growth of the reaction product layer.

A large number of studies devoted to the influence of electrolytes on the processes of hydration of calcium and magnesium oxides and their interaction [72-91].

In order to increase the degree and velocity of MgO hydration process is carried out in various electrolyte solutions [86,87]. When hydrated in solutions, e.g., $Mg(NO_3)_2$, $Mg(CH_3COO)_2$, etc., the rate of hydration is increased more than 1,5 times [72]. To enable use of low active MgO small additions of ammonium salts or a solution of HCl [73].

The acceleration process may be accomplished by hydration of CaO in solutions of sodium and calcium chlorides, HNO_3 [81]. According to [92] in concentrated salt solutions (30%) the rate of hydration is reduced by 5-6 times. Introduction SO_4^{2-}, RO_4^{3-} and other charged ions also slows down the process [61]. Some researchers believe this is due to formation of a film of $Ca(OH)_2$ around the initial oxide grains.

A large number of works devoted to the study of hydration of CaO in the presence of gypsum [93-94]. The probability of chemical interaction between CaO and $CaSO_4$ to form basic salts with almost zero [57]. When hydrated in solutions of $CaCl_2$, the formation of calcium hydroxychlorides: $2Ca(OH)_2$* $12N_2O$*$CaCl_2$ and $Ca(OH)_2$*$CaCl_2$*H_2O [37].

A significant number of studies have been devoted system MgO-Mg(Cl_2, SO_4)-H_2O. At low concentrations of $MgCl_2$ (to 5%) accelerates hydration and final product of the reaction is $Mg(OH)_2$. By increasing the $MgCl_2$ concentration, the formation of intermediate $Mg[(OH)_nCl_{2-n}]$, isomorphous with magnesium hydroxide [89]. In concentrated solutions, $MgCl_2$ and $MgSO_4$ (> 10%) produced a compound of variable composition $nMg(OH)_2$*Mg(Cl_2, SO_4)*yN_2O called magnesia cement [87-88]. According to [88], they have a specific chemical composition which could be expressed as a chemical formula.

It should be emphasized that all authors have noted the difficulties in achieving balance and the ability to crystallize as the $Mg(OH)_2$ and in metastable oxosalts for these areas.

The most systematic study of the system MgO-$MgSO_4$-H_2O was performed in [83-84]. According to [83] at concentrations of $MgSO_4$ to 5%, as in the case of $MgCl_2$, the solid solution composition [Mg(OH)1,86*(SO_4)0,7]* 0,23N_2O that contrary to the basic provisions crystallochemistry [95-96]. Most likely, these "solid solutions" are magnesium hydroxide from the solution with entrained impurity anions.

Hydroxosalts have a layered structure [89, 95]. To show stratification hydroxychloride formula (GSCh), e.g., $3Mg(OH)_2 \bullet MgCl_2 \bullet 8N_2O$ in [89] written as follows:

$$Mg_4(OH)_6(H_2O)_6 \leftrightarrow Cl_2(H_2O)_2,$$

where the left side of the main layers, right - layer. The [95] uses a simpler notation - main layers are enclosed in square brackets:

$[Mg_4(OH)_6(H_2O)_6]*Cl_2*2H_2O$

Relative to other magnesium Hydroxosalts data in the literature.

For CRP magnesium studied only qualitative changes occurring in the partial or complete removal of water by thermal decomposition [83, 97], their decomposition kinetics researched. Borned hydrooxids not associated with an increase in the solubility of $MgCl_2$ in MgO and $MgSO_4$ solutions. At room temperature a solution of $MgSO_4$, e.g., it increases to 3 g/l (in water is 0.01 g/l)

[81, 82]. In concentrated solutions with increasing supersaturation temperature $Mg(OH)_2$ reaches 17 g/l [85] achieving it time decreases significantly.

Regarding the influence of electrolytes on the mechanism of hydration processes MgO and CaO, there are several viewpoints. One of these attributes $MgCl_2$, $CaCl_2$ and other electrolytes catalytic effect, while the other involves the formation of complex compounds [73], the rate of formation and decay of which, for example, to $Ca(OH)_2$ is greater than that of $CaO*2H_2O$ [84]. According to other acceleration associated with an increase in the solubility of $Ca(OH)_2$ [37]. The latter, however, disproved data [98]. Known additives significantly increase the solubility while slowing the process. Additives alkalies, on the contrary, accelerate hydration while reducing solubility CaO.

The opinion of authors [90] the acceleration of the hydration of CaO due to a sharp increase in the degree of supersaturation of the liquid phase of the $Ca(OH)_2$ and their destabilizing effect on germs and associates hydroxide.

In our view, a violation of a causal link in this work, namely, an increase in supersaturation in these cases is the result of the acceleration of the hydration process.

Different industries requires both low-dispersion, and fumed $Ca(OH)_2$ [92].

Dispersibility of $Ca(OH)_2$ depending on the hydration conditions, and the properties of the CaO source is discussed in detail in the monograph R.Boynton[99]. More important and reliable measure physical properties of the $Ca(OH)_2$, as in the case of CaO and MgO, is the specific surface area [43]. It is known that dispersibility of $Ca(OH)_2$ affect temperature thermolysis carbonate and hydration, the ratio of W: T, mixing, electrolytes, seed crystals(Retur) [92].

Regarding the influence of salt solutions of variance $Mg(OH)_2$ is very little information. It indicates only that the products of hydration of MgO in $MgCl_2$ and $MgSO_4$ concentrated solutions and in the presence CO_3^{2-} have a low surface area due to the formation hydroxosalts[83].

In the literature there is no information about the combined influence of factors on the rate of hydration of CaO and MgO, and the resulting dispersion of hydroxides.

1.4.2 Hydration products thermolysis dolomite

Interaction dolomitic lime with water, according to some researchers, does not differ from individual hydration of CaO and MgO [93], others adhere to a different point of view [100]. Major factors determining the degree of hydration and reaction rate, while identical (temperature, time, etc.) [97-99]. It indicates that the optimal dolomitic lime hydration temperature is 80-90 °C, at 20 °C the degree of hydration is less than 65% [100].

According to [100] the activity of MgO in the calcined dolomite has maxima at temperature thermolysis 600 and 900 °C. Having explained the second maximum acceleration in the presence of MgO hydration of CaO due to a local increase in temperature. According I.E.Kazarinova portion in caustic MgO dolomite associated with residual structural links dolomite [57]. With further increase in temperature the thermolysis of these bonds are broken and MgO hydrated completely. Reduction of activity after the second peak at the decomposition temperature of more than 950 °C is a result of recrystallization MgO.

On dolomitic lime hydration process is influenced mainly anions added salts. Solutions similar chloride concentration (eq/L) affects the hydration process identical largest accelerating effect [101], and sulfate ion reduces the rate and extent of hydration of the [99-101]. Thus $CaSO_4$ promotes coagulation and crystallization of the particles of $Ca(OH)_2$, which reduces the dispersibility of the product. Specific surface hydration product at 70-80 °C for different samples dolomitic lime is 14-24 m^2/g [102]. With further increase in temperature this value decreases sharply because the recrystallization $Mg(OH)_2$ and $Ca(OH)_2$.

The presence of $CaCl_2$ in the solution increases the [103] and CO_3^{2-} - decrease dispersibility dolomitic lime hydration products. According to [40], such as dolomitic lime hydrate in water, the specific surface area increased to 65 m^2/g, and in the presence of $MgCO_3 * 3H_2O$ - only up to 22 m^2/g.

Summing up the work on the hydration of calcium and magnesium oxides can be said that, despite the very large number of studies conducted over more than a century, have not developed a mechanism of the hydration process, explaining the totality of the phenomena observed in the process. This is due to one-sided approach to the study of this process, there is no comprehensive research, confusing cause and effect relationships and insufficient regard to the provisions of the kinetics theory [104, 105]. The papers were not analyzed hydroxide composition formed without impurity anions investigated the nature and the mechanism of their capture, the joint effect of factors on the dispersibility of the resulting hydroxide, its structure.

1.4.3 Precipitation of $Mg(OH)_2$ from solutions of magnesium salts

All existing methods for producing magnesium oxide [22, 106-153] can be divided into three groups:

1. Thermal decomposition of magnesium salts;
2. Precipitation basic magnesium carbonate, followed by a thermolysis;
3. Precipitation of magnesium hydroxide from solutions of its salts with bases followed by decomposition to MgO.

Analysis methods for producing MgO shows that the most promising is ammonia. The use of ammonia to precipitate magnesium hydroxide from sulfate solutions [133-137], chloride [138-141], magnesium nitrate [142-145]. The advantage of this method is that the process for obtaining magnesium oxide can be carried out in a closed cycle, using the mother liquors to dissolve magnesium raw [146-151]. In addition, if necessary, the mother liquors $Mg(OH)_2$ (when using a sulfate solution or nitrate of magnesium) can be used as a nitrogen-magnesium fertilizer. Other advantages of the ammoniacal method compared to known methods of preparation are MgO: High purity product; ecological purity of the process; low energy consumption and ease of equipment; availability of raw materials used.

Precipitation as the process consists of several stages: formation of a supersaturated solution, solid phase nucleation, crystal growth, aging of the system, the decomposition system of the solid phase separation from the mother liquor. These processes take place almost simultaneously. Each subsequent stage starts with some delay from previous [154-157].

As is known, the crystallization kinetics may be represented by the curves of type "concentration - time". Typically, the first portion of the curve is gentle and corresponds to a period of induction (the formation of crystal nuclei). Ends of the induction period can be recorded by various methods: chemical, conductometric, potentiometric and optical. It is shown that the main parameters of nucleation does not depend on the method of investigation.

Crystal growth is defined by two processes: diffusion "building" particles (submicrocrystal or molecules) to the surface of the growing crystal and introducing them into the crystal lattice structure. The mechanism of the crystal growth process is highly dependent on the supersaturation. With significant supersaturation crystal growth is mainly determined by the diffusion of [158].

In [160] of the crystal growth of the magnesium hydroxide. It is found that when supersaturation ratio <3 decrease in the concentration of the supersaturated solution obeys first order equation, and the crystal growth is limited by the surface reaction on the interface.

Chemical vapor deposition reactions usually occur at high supersaturation far from equilibrium. This creates the conditions for the formation of unstable precipitation with high surface due to the imperfections of their structures, which contributes to a further irreversible structural changes accompanied by precipitation and transition system "pellet-stock solution" in a more stable state [164].

According to the classification proposed by Wasserman I.M. [156], the system is divided into two types: a system with constant composition and precipitation systems with variable composition sediments. In the first type occurs only basic reaction. Interfacial reactions of nature capable of changing the composition of the deposit does not occur. In systems of the second type, along with the main reaction proceed secondary reactions interaction between system phases: neutralization, hydrolysis, metabolism or synthesis.

Magnesium hydroxide precipitate relates to systems of the first type - its main processes of aging are dehydration and structure [162-164]. At the same time Shoikhet B.A. in the study of aging magnesium hydroxide, calcium hydroxide precipitated from ocean water, I have found that during the incubation suspensions $Mg(OH)_2$ without stirring for 5-10 days of its filtration properties are deteriorated. According to the author in this case proceeds particulate grinding process caused by a secondary chemical reaction with the mother liquor sludge [155]. However, the author does not result in any evidence to support the secondary chemical reaction in the system.

Physical views of aging are aggregation and recrystallization. There are two types of recrystallization - a collective (Ostwald) and structural.

Ostwald recrystallization is a consequence of differences in particle solubility, other than its size. The latter is described Ostwald-Freundlich equation.

It is known that the deposition process is influenced by various factors sachets: nature of the mixed reagents, pH precipitation process, the molar ratio of the reactants, the feed rate of the precipitant, the intensity and duration of stirring a slurry, the concentration of the initial reactants.

Influence of the nature of the magnesium-containing solution [$MgSO_4$, $MgCl_2$, $Mg(NO_3)_2$] for the degree of precipitation (respectively 0.84; 0.85; 0.92) and a specific cake resistance to filtration ($R * 10^{-3}$ cm / sec, respectively 16, 3000, 9000) shown in [136]. The process was conducted without mixing. Zooming precipitation pH promotes growth of the particles in the basal plane [167]. The particles precipitated in the range of pH 10,5-12,5 flake form had a high specific surface and a large diameter to thickness ratio. The relatively low pH precipitation (less than 8.5) favors the growth of the particles along the axis "c", which leads to crystal formation unit structure with a low specific surface area. According to [168] magnesium hydroxide particles precipitated from a solution of $Mg(NO_3)_2$ potassium hydroxide (pH end deposition - 12.1) consist of plates and "needles" with dimensions significantly smaller than the particle size of precipitated ammonia solution (pH end deposition - 10); in the latter case the plates have a well defined block structure and have a lower specific surface area (100 and 45 m^2/g, respectively). [169] was found that by adding a magnesium-containing base in solution most of the particles $Mg(OH)_2$ is thick and solid plate with sharply defined edges. The apparent density of the deposit in this case is 1,93 g/cm^3. When the reverse order of deposition pellet has an apparent density of 1.36 g/cm3. Particles thus have the form of gelatinous formations easily changing its shape by mechanical action. in the latter case the plates have a well defined block structure and have a lower specific surface area (100 and 45 m^2/g, respectively). [169] was found that by adding a magnesium-containing base in solution most of the particles $Mg(OH)_2$ is thick and solid plate with sharply defined edges. The apparent density of the deposit in this case is 1.93 g/cm^3. When the reverse order of deposition pellet has an apparent density of 1.36 g/cm^3. Particles thus have the form of gelatinous formations easily changing its shape by mechanical action in the latter case the plates have a well defined block structure and have a lower specific surface area (100 and 45 m^2/g, respectively) [169] was found that by adding a magnesium-containing base in solution most of the particles $Mg(OH)_2$ is thick and solid plate with sharply defined edges. The apparent density of the deposit in this case is 1.93 g/cm^3. When the reverse order of deposition pellet has an apparent density of 1.36 g/cm^3. Particles thus have the form of gelatinous formations easily changing its shape by mechanical action. When the reverse order of deposition pellet has an apparent density of 1.36 g/cm^3. Particles thus have the form of gelatinous formations easily changing its shape by mechanical action. When the reverse order of deposition pellet has an apparent density of 1.36 g/cm^3. Particles thus have the form of gelatinous formations easily changing its shape by mechanical action.

Excess precipitant decreases solubility precipitate and cause decomposition of basic salts (in case of their formation) during the precipitation of metal hydroxides [154]. Shoikhet B.A. [170] during deposition $Mg(OH)_2$ solutions of $MgCl_2$ (360-400 g/l) recommends the use of excess NH_4OH 40-45% against stechiometric. The authors [135-137, 146] is considered optimal when deposited $Mg(OH)_2$ of $MgSO_4$ solution, 30% excess aqueous ammonia in the [145] proposes to use 20% excess ammonia to precipitate $Mg(OH)_2$ of mixed solution of magnesium and ammonium nitrates. When choosing an excess of the precipitant, researchers took into account only one criterion - the degree of precipitation.

It is known [155] that dispersibility rain depends essentially on the rotational speed stirrer. In [136] established that filtration cake resistance of $Mg(OH)_2$ obtained by reacting solutions H_3N $MgSO_4$ and reduced with stirring at 9-11 times as compared with the precipitate obtained in the absence of stirring. Quantitative data on the intensity of stirring in the given work are not available.

A significant influence on the properties and structure of the precipitation rate has pouring precipitant. The dramatic improvement in filtration properties precipitate was observed with increasing duration of pouring the base from 0.5 to 2 hours. A further increase in the duration of feeding the precipitator virtually no effect on sediment filter coefficient [163]. It should be noted, however, that the work there is no data on the volume of the mixed reagents and mixing intensity, which makes it impossible for the practical use of the results.

In [135] established that with increasing concentration degree of the deposition solution $MgSO_4$ $Mg(OH)_2$ is reduced. Loss of Mg^{2+} with the mother liquor per unit weight of $Mg(OH)_2$ remain unchanged. With increasing concentration of magnesium sulphate solution from 0,1 to 2 mol/l value of the specific resistance to filtration of sludge decreases 21 times. The authors of [136] attribute this to the fact that at high concentrations is an intensive aggregation of the particles, while the individual particle size decreases.

Storage duration slurry after feeding the precipitator (H_3N solution) was given in the 30 min, stirring was absent.

Temperature effect on the degree of sedimentation and filtration resistance precipitate $Mg(OH)_2$ obtained by reacting solutions of $MgSO_4$ and H_3N reviewed in [136]. It is found that with increasing temperature, the induction period of the deposition process is reduced, increasing supersaturation removal rate of $Mg(OH)_2$ and the amount of resistivity precipitate filtered. Recently, according to the authors, due to the formation of a large number of nuclei and the decrease in the average particle size. To obtain a well filterable sediment authors selected temperature 30-40 °C. Shoikhet B.A. [155] during deposition $Mg(OH)_2$ from solutions of magnesium chloride with aqueous ammonia believed that the degree of precipitation of magnesium hydroxide increases with process temperature and recommended temperature 60 °C.

According to Chaly B.P. [166] when applying H_3N solution instead of NaOH, hydroxides of Al, Cr, Fe(III) contaminated with more basic salts. When depositing the magnesium hydroxide from a solution of $Mg(NO_3)_2$ potassium hydroxide - on the contrary, precipitates contain 2-7 times the amount of nitrate ion, than in the case of H_3N solution. The contents of sulfate ion in the preparation of magnesium hydroxide from the solution by $MgSO_4$ capacity increases from 0.05 to 0.15% in the third deposition [170]. In papers unfortunately not reported in any form anions present in the precipitated magnesium hydroxide.

It is known that urea additive changes the crystal habit NaCl [171]. We establish that the presence of urea larger crystals are obtained K_2SO_4 [172]. In connection with the above, it is of interest to study the influence of additives on urea crystallization process of $Mg(OH)_2$ precipitate and properties. Selecting said additive due to the fact that the latter during the crystallization process and not lost in the mother liquor composition may act as a component of a complex nitrogen-magnesium fertilizer [174-176].

Of particular interest is the work T.Sirosaki [177] who investigated the formation process of $Mg(OH)_2$ with the structure of brucite when deposited from its salts solution (Cl^-,NO_3^-, SO_4^{2-}). Using electron microscopy and X-ray analysis it showed that the intermediate material is a hydrated magnesium hydroxide

$Mg(OH)_2$*nN_2O representing a package consisting of layers of 2D crystals thickness of 1 - 3 unit cells with layers of water molecules. With water from the layers displaced over time. Anions of organic acids (citric) stabilized magnesium solution, penetrating the interlayer. A typical during precipitation of magnesium hydroxide is that a large amount of precipitate is formed which is filtered and surprisingly easy represents translucent mass states.

1.5 Conclusion of the first head

As indicated above, the country requires pure magnesium oxide produced by rational technology using local raw materials. At the same time there is an urgent need to engage in chemical processing of dolomite. However, the organization of their processing technology to obtain pure oxide and other magnesium compounds constrained by insufficient knowledge of the reactions of inorganic magnesium compounds. There is a problem of development of physical and chemical bases of processing of dolomite, which, according to the literature review, it is necessary to solve the following tasks:

1. To study the kinetics of thermolysis of magnesium carbonate and calcium in non-isothermal conditions at low temperature rising rates.
2. To determine the optimum conditions of thermal decomposition of the magnesium carbonate pieces with dimensions of less than 40 mm in order to obtain maximum activity with MgO.
3. To investigate the kinetics of the thermal decomposition of $Mg(OH)_2$ and to ascertain the role of the impurity anions magnesium salts in the process.
4. It is necessary to establish the physical and chemical laws of formation of magnesium hydroxide with desired dispersion, the structure and chemical composition during hydration its oxides and its precipitation from solutions of ammonia nitrate. To do this:

a. elucidate the mechanism of hydrated magnesium oxides, and calcium, to determine joint effect of factors on the dispersibility of the resulting calcium hydroxide caustic investigate hydration processes dolomite and dolomitic lime;

b. examine the kinetics of precipitation of $Mg(OH)_2$ and magnesium hydroxide aging system - the mother liquor.

2. CHAPTER 2. DESCRIPTION THE STARTING MATERIALS AND METHODS OF RESEARCH

2.1 Characteristics of dolomite

Natural mineral - Dolomite is a rock-forming minerals of sedimentary carbonate rocks. Mineral and rock named after the French mineralogist and chemist D.Dolomo, the first to discover them in the Alps in northern Italy.

Dolomite - natural magnesium containing material, which consists of calcium and magnesium carbonates and impurities imparting color. The composition of dolomite is not homogeneous. component content ranges depends on the field and the level of occurrence of the natural raw material layers.

Dolomites - are natural, affordable, abundant mineral. Color is usually white or gray, but can be any other color - yellow, red, pink and other, occasionally is colorless and translucent. Dolomite is scratched with a knife, and not too heavy. It does not melt and crack. In cold HCl it dissolves slowly, and heated - faster.

Natural dolomites (density 2-2,86 gr/cm^3, hardness 3,5-4), in addition to the basic mineral dolomite $CaMg(CO_3)_2$ contain impurities of quartz, calcite, gypsum, clays, and others, giving the rock different colors.

Dolomite is a natural stone properties: high strength, an interesting pattern, allowing to create an unusual composition. Color dolomite goes well with almost all the construction and natural materials. Made of dolomite wall tiles is an absolutely natural material and has filtering properties, it has a positive effect on the climate in the room decorated by her. Dolomite is suitable for finishing both outside and indoors[178].

In the construction of dry mixtures with dolomite filler, are considered the best and refer to mixtures of the highest class, have the best technological properties. Another dolomite filler is often found in the composition of paint products, rubber products, linoleum, sealants, mastics, and so on.

Pure dolomite is an excellent raw material for the extraction of magnesium metal, used mainly in the production of lightweight alloys. From dolomite prepared magnesium salts used in medicine. In the building materials industry dolomite used for the manufacture of special types of cement[178].

Dolomite is used in metallurgy (as a raw material for refractories, and as flux) for the manufacture of glass and glaze white magnesia; in construction (as facing, crushed stone and gravel, raw materials for the production of binders), in agriculture (to neutralize acidic soils). Dolomite is used for the production of mineral wool insulation products. Dolomite used in the glass industry, MgO contain at least 18%, SiO_2 of not more than 5%, Al_2O_3 is not more than 0,4%.

Dolomite deposits exist in Uzbekistan, particularly in Tashkent, Bukhara, Samarkand, Navoi, Ferghana, Namangan and Kashkadarya regions.

The field "Dzharkak" dolomite reserves constitute 92475 thousand m^3 (the layer №692475 thousand m^3), "Karmana" stocks dolomite C_2 constitute 11,75 million m^3 "Irlik» (CaO - 31,40; MgO – 20,16; CO_2 – 47,16) stocks of carbonate rocks C_2 - 18 mln m^3. Growth of stocks is not limited to, "Muruntau» (CaO - 32,61; MgO – 22,20; CO_2 – 45,26) stocks dolomite C_2 constitute 75 mln m^3. Perspectives on the flanks are not limited to, "Besapan» (CaO - 32,2; MgO – 20,8, CO_2 – 45,6). reserves dolomite C_2 - 72 million m^3 is practically unlimited.

One of the fields is a dolomite mine "Shorsu" in the Ferghana Valley. Sufficiently high content of basic components consisting of dolomite: CaO - 29,5-31,5%; MgO- 16-18%; Fe_2O_3 - 0,17%.

Used for laboratory experiments dolomite of Shorsu represented pieces of various shapes and sizes. The total weight, in addition to large pieces were a lot of small pieces, as well as part of the dolomite powder. Color samples were light gray and pale pink.

The study, first of all, began to sample analyzes.

The chemical composition of dolomite m "Shorsu" given in Table 1.

Table 1

The chemical composition of dolomite Shorsu sample (wt.%)

Content in% of air dry substance												
CaO	MgO	Al_2O_3	Fe_2O_3 + FeO	FeO	SiO_2	MnO	TiO_2	Na_2O	K_2O	P_2O_5	SO_3 total	CO_2
31.48	19,17	0.32	0.29	0.25	2.87	0.01	0.02	0.05	0.15	0.03	0.3	45.0

Dolomite "Shorsu" except chemical analysis, was subjected to physical and chemical analysis methods.

These X-ray analysis confirms the results of the chemical analysis of the high content of calcium and magnesium carbonate in the raw material (Fig. 1).

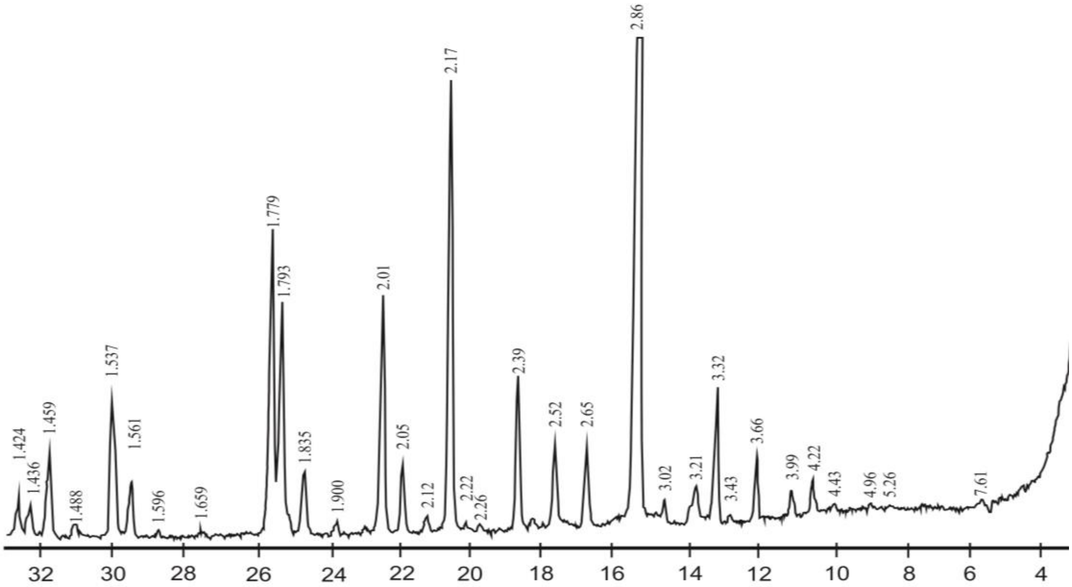

Figure 1. XRD pattern of dolomite "Shorsu"

The X-ray diffraction samples identified all reflections of dolomite (0,410; 0,368; 0,288; 0,143 ...) nm and a reflection of quartz (0,424; 0,334; 0,222; 0,218; 0,181 ...) nm low intensity[179].

There have been a low-intensity lines of calcite (0,303; 0,190 ...) nm and clay minerals (0,761; 0,321 ...) nm [180].

Derivatograms sample analysis dolomite "Shorsu" given in Table 2.

Table 2

Derivatografic data thermolysis dolomite "Shorsu"

Temperature effect interval, °C	peak effect, FROM	Mass loss, %	The total mass loss,%	Nature thermoeffect	The resulting compound
70-160	150	0.77	0.77	endothermic	removal of the adsorbed water
160-350	310	1.59	2.38	endothermic	removing bound water
350-522	410	0.40	2.78	endothermic	disintegration of dolomite $CaCO_3$, $MgCO_3$
522-742	711	3.57	6.35	endothermic	dissociation of $MgCO_3$
742-820	770	6.59	13.94	endothermic	dissociation $CaCO_3$
820-918	890	32.54	46.48	endothermic	dissociation $CaCO_3$

On heating a sample of dolomite curve detected four endothermic effect at 150, 310, 410, 890°C, and two exothermic effect at 711 and 770 °C.

The first three endothermic effect occur in the temperature interval 70-160, 160-350, 350-522 °C and the weight loss is 0.77, 1.59, 0.40% respectively. The next two exothermic effect is also accompanied by a decrease in weight. In the temperature range of 522-742; 742-820 °C the mass loss was 3.57% and 6.59% respectively[179]. Character last endothermic effect caused by decomposition of heavy calcium carbonate to form magnesium oxide. Weight reduction temperature in the range 820-918 °C in the TG curve was 32.54%. Total weight loss in the range 70-918 °C was 46.48%.

Based on the studied properties are given initial data for designing exhaust aperture size, wall angles, the guide arrangement of trays, unloading devices and devices enabling unloading process.

For this purpose, studies have been conducted to study the technological parameters such as particle size distribution, moisture content, density, bulk density, natural angle of repose, fluidity dolomite "Shorsu" (Table. 3, Tab. 4).

TABLE 3

Grain size distribution of dolomite m "Shorsu"

Graininess%					
10 <5mm	-5 ÷ +3 mm	-3 ÷ +2 mm	-2 ÷ 1 mm	-1 ÷ 0.5 mm	>0.5 mm
23.8	11.0	8.5	14.9	6.6	35.2

TABLE 4

The change of physical and mechanical properties of dolomite m "Shorsu" depending on humidity

Technological indicators	Humidity%		
	1.0 - 1.5	2.0 - 2.2	2.4 - 2.5
Density (Wed), g/cm3	2.74	2.80	2.83
Bulk density, g/cm3	1.23	1.26	1.31
natural angle repose, degrees	39.6	41.1	42.2
Fluidity, s	15.0	18.0	20.0

Among the parameters allowing to evaluate the mobility of the particles of particulate material, the angle of repose provides its free surface. The smaller the angle of repose, the higher mobility particles have a granular medium. Furthermore, the magnitude of the slope angle allow to choose the right size storage circuit to determine a free bulk material on the support element of the conveying installation.

Bulk density characterizes mobility of dolomite particles and granular material is required to determine the main parameters of its movement into the storage container, and the expiration of the mode through the discharge device hoppers, silos, feeders[180]. Determination of the bulk density dolomite necessary for determining the main dimensions bins, conveying performance and metering devices, calculate the pressure exerted by the bulk material on the walls of blood vessels and valves.

A melt flow index of granular and powdered chemicals is one of the important indicators of their physical properties that determine their quality. From the value of this parameter depends on the velocity of the precipitation product silos, bins, feeders, bucket elevators, etc. Therefore, when designing the appropriate transport, manufacturing and warehouse equipment is always necessary to know the turnover rate and related products.

Study dolomite particle size distribution "Shorsu" has shown that it is presented in the granulometric class> 0.5 mm, respectively, where yield is 35.2 and 38.4%.

It is found that with increasing humidity dolomite from 1.5 to 2.5% of the value of density, bulk density, natural angle of repose and fluidity are increased respectively from 2.74-2.85 g/cm^3; from 1.23 to 1.31 g/cm^3; from 38.7 to 42.2 degrees and from 14.0 to 20.0 seconds[181].

Thus, the specimen "Shorsu" dolomite deposits has satisfactory physical and mechanical properties.

2.2 Research of the kinetics of processes

Studies carried out by an isothermal method. The substances used as starting reactants mark "Ch$_c$" or recrystallized salt mark "Ch$_c$". The establishment of equilibrium is determined by a constant ion concentration in the liquid phase and the coefficient of refraction of the liquid phase. Identification of solids carried by chemical and thermal analyzes. The stirring system was performed in a two necked glass flasks with stirrers[182].

When studying the process of hydration tests carried out with oxides of calcium and magnesium "h" stamps, as well as their technical analogs ("lime" CaO and "magnesium" - MgO). Inactive form CaO obtained by decomposition of chemically precipitated $CaCO_3$ at 1300 °C for 7 hours. The sulfate and chloride electrolytes for hydration oxides were prepared "Ch$_C$" from their respective salt marks.

The hydration of calcium and magnesium oxides was performed with vigorous stirring in thermostatically controlled glass reactor, the temperature is maintained to within ± 0,5 °C.

The solutions were warmed to prior experiments the calculated temperature. The process is mainly carried out at a weight ratio "liquid:solid" (L:S) equal to 15.

After a certain time, the resulting slurry of hydroxides was filtered on a Buchner funnel and washed with acetone to stop oxide hydration[182-184].

The degree of hydration of CaO and MgO calculated by chemical analysis found experimentally as a fraction amount of water of hydration to its theoretically possible in a number of $Ca(OH)_2$ - (25%) or $Mg(OH)_2$ - (31%).

2.3 Chemical analysis methods and instrument

Chemical analysis of the solids and solution were carried out in accordance with procedures and conditions set forth in the literature [182-186].

Contents of calcium and magnesium ions was determined trilonometric loss on ignition - weigh sample in a muffle furnace at 950 - 1000 °C to constant weight.

free ammonia content was determined by direct titration involving ammonia and - formalin method [184].

Sedimentation analysis of oxides and hydroxides of magnesium and calcium was carried out on [185]. The dispersion medium in the case of oxides served ethyl alcohol, and for $Mg(OH)_2$ - distilled water saturated with magnesium hydroxide.

Carbon dioxide in the starting raw material dolomite was determined by treating the sample with hydrochloric acid, followed by absorption of CO_2 with a solution of potassium hydroxide [107].

In order to characterize the physicochemical properties of dolomite, and the intermediates formed during the decomposition of dolomite, as well as during the conversion of the calcium chloride solution and magnesium with sodium chlorate physicochemical methods for the determination of moisture were used, repose angle, density, viscosity, pH and crystallization temperature.

Moisture in solid samples was determined by drying to constant weight at a temperature of 80-105 °C for 3 hours [108].

The angle of repose, bulk density, flowability, strength and density of raw dolomite samples was determined by the method of [109,110].

Density dolomite samples, solutions, and the pulp was determined with the pycnometer universal capillary stopper in microsection. Values taken as the average of three measurements. The relative error was 0.02% [111].

Viscosity - IWF capillary viscosimeter with a capillary diameter of 1.16 mm (error not greater than 2% rel.). The temperature in the oven was maintained within ± 0,1°C. With each sample produced five-six measurements and the average of them was taken as the viscosity of the test solution. Accuracy of results ± 0.0001 · 10-1 m^2/s [112].

Measurement of pH of solutions formed during decomposition and conversion of dolomite solutions of calcium and magnesium chlorides and chlorates of calcium and magnesium were performed at pH - meter «FE-20 METTLER
TOLEDO»[113].

The temperature of the crystallization solutions were determined using a thermometer with an accuracy of ± 0,1 °C.

XRD dolomite samples and solid phases, isolated from the system was performed on DRON - 3.0 with filtered copper radiation at 40 kV voltage, power toka20 mA, counter disk speed of movement - 2 deg/min. Values-spacings found by the directory according to the angle of reflection [116,117], and the intensity of the diffraction lines was evaluated by scale.

Differential thermal analysis of samples dolomite and solid phases, isolated systems in the study was carried out on «Paylik-Paylik-Erday» [118,119] derivatograph system at a rate of 9-10 K/min and 0.1 g lifting sensitivity galvanometers When T - 900 TG - 200, DTA 1/10. Recording was carried out under atmospheric conditions. Holder served corundum crucible diameter of 7 mm without cover. We used as reference Al_2O_3.

2.4 Conclusions of the second head

The results of the chemical, physico-chemical and physical-mechanical methods of analysis dolomite "Shorsu". According to the chemical analysis of the dolomite it has the following chemical composition (wt%.): CaO - 31,48; MgO - 19,17; CO_2 - 45.0; SiO_2 - 2,87; Fe_2O_3 + FeO - 0,29; Al_2O_3 - 0,32; TiO_2 - 0,02;

MnO - 0,01; Na_2O - 0,05; K_2O - 0,15; P_2O_5 - 0,03; SO_3 total. - 0.30.

X-ray diffraction and thermal analysis methods dolomite were confirmed by chemical analysis of the high content of the raw material calcium and magnesium carbonates. On the X-ray diffraction reflections are identified all the crystals of dolomite and quartz. Derivatograms dolomite sample are characterized by having a number of effects. The first three endothermic effect occur in the temperature range 92-410 °C and the weight loss is 2,39-5,93%, respectively. The next two exothermic effect is also accompanied by a decrease in weight. In the temperature range 504-870 °C the mass loss is 20,29-26,43% respectively. Character last endothermic effect caused by decomposition of heavy calcium carbonate to form magnesium oxide. Total weight loss in the range 60-918 °C is 44,74-46,48%.

It is found that with increasing humidity dolomite from 1.5 to 2.5% of the value of density, bulk density, natural angle of repose and fluidity are increased respectively from 2.74-2.85 g/cm^3; from 1.23 to 1.31 g/cm^3; from 38.7 to 42.2 degrees and from 14.0 to 20.0 seconds.

Thus, a sample of dolomite has satisfactory physical and mechanical properties.

3. CHAPTER 3. STUDY OF EXPANSION DOLOMITE AND DETERMINE THE OPTIMUM PARAMETERS TO EXTRACT THE ACTIVE MAGNESIUM OXIDE

In the laboratory, "Technology of Mineral Fertilizer" Department "Chemical Technology" Fergana Polytechnic Institute series of laboratory experiments on magnesium extraction were carried out in a separate dolomite chemically pure component by firing and quenching method, and a chemical method.

3.1 Removing the magnesium compounds dolomite "Shorsu" firing method

3.1.1 Investigation of the composition of half-burnt dolomite "Shorsu" and its hydration products

Dolomite pieces put in a porcelain cup and placed the cup in a muffle furnace. Installed in the controller 700 °C and heating included. Once the temperature of 700 °C was calcined reached within 1 hour. Removed several pieces of dolomite for analysis.

The analysis results are shown in Table №1.

Table №1

№	**Component name**	**After calcination for 1 hour at a temperature**	
		700-750 °C	**1100 °C**
1.	Mass fraction of magnesium in terms of MgO,%	19.5	26.68
2.	The mass fraction of calcium in terms of CaO,%	36.4	31.54
3.	Mass fraction of residue insoluble in acid,%	3.34	21.5
4.	Mass fraction oxide (III) R_2O_3,%	0.92	0.36
5.	Mass fraction of carbonates, CO_3^{2-},%	26.06	1.3
6.	Mass fraction of sulfate, SO_4^{2-},%	9.79	6.46

Calcined dolomite crushed in a mortar to a powder, water extinguished: weighed 100g. and stirred with 130 cm^3 of distilled water. When slaking calcined dolomite mixture self warmed to a temperature of 30-35 °C.

The resulting mixture is well mixed and left for 17-18 hours. The mixture after standing separated into two layers: the precipitate and the clear liquid in the ratio of 8:1.

The liquid was drained and sampled. The sample was dried at a temperature of 100-105 °C and completed analysis.

The results are shown in Table №2.

Table №2

№	Component name	The amount of component
1.	Mass fraction of magnesium in terms of MgO	23.7
2.	The mass fraction of calcium in terms of CaO	39.48
3.	Mass fraction of residue insoluble in acid	11.05
4.	Mass fraction oxide (III) R_2O_3	0.23

3.1.2 The research of the calcined dolomite "Shorsu" and its hydration products

Dolomite pieces of various shapes and sizes 1,5-3,4 1,8-4,2 cm × mass 204.0 c. placed in the cups and placed in a muffle furnace heated to 650-700 °C firing. Set the temperature control to 1000 °C and heating was continued. 5 through firing hours at a temperature of 1000-1100 °C disconnected heating muffle furnace and left to cool the sample.

After cooling, the sample is weighed, the weight of the calcined sample was 104.0 g., Indicating a virtually complete removal of CO_2.

Perform analysis of calcined dolomite. The results are shown in Table 3 №.

Table №3

№	**Component name,%**	**The amount of component**
1	The mass fraction of calcium, calculated as CaO,%	48.38
2	Mass fraction of magnesium, calculated as MgO,%	30,05

Part of dolomite crushed, the second part left in pieces.

The first glass put calcined dolomite pieces weighing 50.0 g. and filled with distilled water at room temperature in an amount of 50.0 g. The first few minutes of calcined dolomite pieces retain their shape, signs quench the reaction, the familiar lime slaking, were observed. After 20-30 minutes dolomite pieces began to increase in size, swell, and then loosened and disintegrate. The liquid temperature in the beaker rose to 40-50 °C and continued to grow. The consistency of a loose mass acquired form slurry, which was observed in the mass reflux. Bulk temperature in the beaker rose above 100 °C. The mixture has become kind of a loose fluffy mass. In a glass added another 50.0 grams. water and stirred. After cooling and settling in the first glass was formed in the lower part is very light precipitate (almost white). At the bottom were visible dark particles. Precipitate a mild agile, easily mixed with a glass rod. When defending not compacted.

Concurrently with the first experience of the second glass made 70.8 t. crushed calcined dolomite and 100 grams. water and mixed well with a glass rod. Signs of extinction occurred almost immediately. Temperature of the mixture rose above 100 °C, boiling of the mixture was observed. Similarly to the first experience I gained weight loose pasty consistency. The glass of water was added 2 times, the first time 100 c. and 5 minutes later another 146.0 grams. After cooling and settling in the second mass of glass is also divided into two layers.

The precipitate formed in the second glass after standing is not compacted, easily agitated. The clear solution was decanted. The precipitate was analyzed for calcium and magnesium. The results are shown in Table №4.

Table №4

№	Component name,%	The amount of component
1	The mass fraction of calcium, calculated as CaO,%	42.73
2	Mass fraction of magnesium, calculated as MgO,%	25.75

3.1.3 Study ended hydrated dolomite calcine

We spent quenching water new batch of calcined dolomite, the method described in paragraph 3.1.2. To do this, it takes 100 grams. calcined dolomite and 1000 grams. water. After cooling and settling glass with quicklime mixture placed in a water bath at 20-23 °C to avoid temperature rise above 26 °C and the transition bicarbonates in form of insoluble carbonates. The mixture was stirred in a beaker and the mixture is applied to the liquid carbon dioxide. Carbonization was carried out for 7 hours. In the process of settling the mixture was separated into two layers: transparent liquid and precipitate. The precipitate is dense, easily agitated.

The precipitate was separated by filtration through filter paper. Analysis Performed precipitate and filtrate for calcium and magnesium. The results are shown in Table №5.

Table №5

№	Component name,%	Filtrate	Deposit
1.	The mass fraction of calcium, calculated as CaO,%	0.05	40.18
2.	Mass fraction of magnesium, calculated as MgO,%	0.01	19.16

3.1.4 Study composition calcined at different temperatures and the intensity of dolomite and products of their hydration

Dolomite pieces were placed in molds from refractory bricks are not heated muffle furnace, the heating regulator set at 800 °C and 1,000 °C. Calcination at 800 °C was carried out for 6 hours. Calcination at 1000 °C was carried out for 3 hours. After cooling, the calcined dolomite performed an analysis on the content of calcium and magnesium, and compared with the results of the firing in the prior experiments. The results are shown in Table №6.

Table №6

№	Component name,%	Temperature / Time firing				
		700-750 °C / 1 hour	1100 °C / 1 hour	1000-1100 °C / 5 hours	800 °C / 6 hours	1000-1100 °C / 3 hours
1.	The mass fraction of calcium, calculated as CaO,%	36.4	31.54	48.38	56.21	56.2
2.	Mass fraction of magnesium, calculated as MgO,%	19.5	26.68	30,05	30.1	25.1

After firing performed dolomite quenching the hot water in the ratio S:L = 1: 5. Dolomite slices put into jars and filled it with pre-heated to 90-95 °C with hot water. In the process of quenching the hot mass remains 85-90 °C. Moreover, if water is poured into dolomite portions, then the introduction of the first portion of water boiling occurs. If all the water to make immediately, then the mass remains hot, but not boiling is observed noticeable. During the quenching the mixture was stirred constantly by bubbling air. After standing in a glass formed two layers. Bottom layer - mobile, easy mixing the precipitate. Top layer - transparent liquid. The liquid was drained carefully. Performed sediment analysis for calcium and magnesium. The results are shown in Table №7.

Table №7

№	Component name,%	The amount of component
1.	The mass fraction of calcium, calculated as CaO,%	45.37
2.	Mass fraction of magnesium, calculated as MgO,%	26.92

3.1.5 Mixing the calcined dolomite aqueous magnesium chloride

To investigate the possibility of obtaining active compounds from magnesium dolomite was conducted calcining dolomite at temperatures of 650 ... 900 °C in increments of 50 °C. The starting dolomite rock was crushed and placed in a chamber oven, kept at a predetermined temperature. The resulting binder shuts aqueous magnesium chloride density 1.2 g/cm^3.

CaO and MgO content was determined by the results of thermal analysis differentsilno binder obtained by the stoichiometric equation reaction by calculating the amount of undecomposed breed. The results are shown in Table №8.

Table №8

Firing temperature, °C	MgO,%	CaO%
650	3.2	0
700	6	1
750	11.7	6.5
800	19.6	12.2
850	32.6	43.7
900	39.3	57.8

The results indicate that with increasing firing temperature in the binder content of active magnesium oxide increases.

3.1.6 Effect of additives on the structure of calcined dolomite

As shown in the first chapter in the preparation of active compounds of magnesium dolomite, foreign scientists use-intensifiers calcination additive for complete decarbonation magnesium component species. As an additive-intensifier has been selected NaCl, as the most effective.

It was designed and implemented by two-factor experiment to establish the general laws of influence of firing temperature and to determine optimal dosages additive-intensifier. Significant factors were selected:

X - firing temperature of 500 to 700 °C;

Y - the amount of additive of from 1 to 3% by weight dolomite.

Intervals of varying the firing temperature was chosen based on the earlier experiments.

For the experiment the initial dolomite rock salt together with pulverized, the resulting mixture was granulated, the granules for 2 hours maintained a box furnace at given temperatures. Sintered pellets were ground, the resulting material is shut water. The experimental results are shown in Table №9.

Table №9

Firing temperature, °C	**Additive%**	**The content of MgO,%**
500	*1*	*14.1*
500	*2*	*20.5*
500	*3*	*23.2*
600	*3*	*32.2*
700	*3*	*34*
700	*2*	*33.7*
700	*1*	*33*
600	*1*	*24.1*
600	*2*	*30.1*

3.2 Preparation of magnesium oxide from dolomite "Shorsu" chemical method

One area of processing minerals containing magnesium is a chemical method that consists in dissolving dolomite with nitric acid and further chemical deposition target components. The method of chemical separation of magnesium and calcium based on the similarities and differences between chemical and physical properties of calcium and magnesium. Since carbonates and hydroxides of magnesium and calcium are not soluble in water, the impact on the solution of magnesium nitrate and calcium alkaline solutions does not lead to the separation of elements. It is necessary to turn to precipitate water-insoluble magnesium and calcium compounds. When exposed to a solution of magnesium nitrate solution and calcium sulphate formed by the exchange reaction and precipitates of calcium sulfate.

The process of producing MgO occurs in several stages:

- Dolomite dissolution in nitric acid.
- Filtration reacted mixture.
- Calcium precipitation.
- Branch precipitate calcium sulfate and drying.
- Precipitation of iron impurities.
- Precipitation of magnesium.
- Branch magnesium carbonate and drying.
- Calcining magnesium carbonate to obtain magnesium oxide.
- Using the final filtrate.

3.2.1 Dolomite dissolution in nitric acid.

Dissolution of dolomite with nitric acid proceeds in the following main reactions

$$MgCO_3 + 2HNO_3 = Mg(NO_3)_2 + H_2O + CO_2 \uparrow$$

$$CaCO_3 + 2HNO_3 = Ca(NO_3)_2 + H_2O + CO_2 \uparrow$$

The glass poured into 56% nitric acid in it in small portions with constant stirring, was added crushed dolomite. When making the first portions of the dolomite signs of ongoing reaction observed in 30-40 seconds. It starts to separate carbon dioxide. Upon further introduction of dolomite gas is released more rapidly and formed a brown foam. The foam volume greater than the volume of nitric acid for experiment taken three or four times, depending on the weight of another portion of dolomite. In the early dissolution of the foam settles quickly, for 20-30 seconds. After making 50-60% of the estimated amount of dolomite formed more stable foam. If you make a large portion of the foam is formed so much that it can not repay, even with vigorous agitation and the foam spills over the edge of the glass. After making the last portion of dolomite and foam settling determined by universal indicator paper pH = 3-4. Under the control of pH in the glass is further made dolomite until pH = 5-6. Dissolution lasted for 6 hours, a lot of time it takes the foam subsidence. As a result, the glass formed sufficiently thick mixture was dark brown, on the bottom glass settled particles not dissolved.

3.2.2 Filtration reacted mixture dolomite.

Filtration reacted mixture is carried out with the aim of separating impurities not soluble in nitric acid.

Filtration led to the application of a vacuum, so as filtration under its own weight was almost impossible. Filtration proceeded slowly for 4 hours. The filter cake was left of the smaller pieces of gray-brown (undissolved particles of dolomite), colorless crystals from transparent to milky white different sizes (from sand to a pea size), and very thin brown precipitate was similar to the clay. The filter cake was washed with three portions of hot distilled water, the washings were collected in the filtrate.

We received the filtrate straw yellow color. The composition of the filtrate are mainly water-soluble calcium nitrates and magnesium, and small amounts of iron salts that give the solution a yellow color.

3.2.3 Precipitation of calcium and separating the precipitate from the solution.

Calcium can be precipitated from solution in the form of a sulfate solution of a water soluble sulfate such as sodium sulfate.

The process proceeds by reaction of

$$Ca(NO_3)_2 + (NH_4)_2SO_4 = CaSO_4 \downarrow + 2\ NH_4NO_3$$

Prepared ammonium sulphate solution at a concentration close to a saturated solution - 19%.

The beaker with the solution of calcium nitrate and magnesium nitrate under stirring have estimated the amount of sodium sulphate solution. The solution first became cloudy, then became opaque white. After mixing the solution was left alone. Over time, fluid in the upper part of the cup is clarified and becomes transparent. The settling of sediment fastest runs in the first 15 minutes and then slows down and lightened for 16 hours about a third of the contents of the glass. The precipitate during this time does not become dense and easy to stir until smooth.

Filtration of the suspension were vacuum using a Buchner funnel through filter paper. Filtration proceeded quite easily, and the filtrate ceased to flow into the receiving flask an hour. The filter formed semi soft pasty mass purely white. While stirring with a glass rod the upper layer of sludge in the receiving flask was again drain the filtrate. No precipitate began to vigorously stirred, the precipitate on the steel surface gently press the flat part of the trowel. By sediment fairly well become separated liquid. The precipitate became markedly dehydrated. After 15-20 minutes, the filter was formed quite a dense mass. After the filtrate ceased to be allocated have finished filtration and the precipitate was transferred to a drying oven, with the temperature kept 100-110ºS.

Drying calcium sulfate was run for 6 hours. After drying, calcium sulfate remained white and became solid. Composition of the precipitate is shown in Table №10.

Table 10

№	**Component name**	**Results, %**
1	The mass fraction of calcium in terms of CaO	30.5
2	The mass fraction of calcium calculated as $CaSO_4 \times 2H_2O$	95.8
3	Mass fraction of magnesium in terms of MgO	1.35
4	Water content	0.05
5	Mass fraction of iron in terms of Fe_2O_3	0.04

Filtration in the receiving flask was going to pale yellow filtrate. The solution is mainly present in the magnesium nitrate and a small amount of impurities imparting color solution.

3.2.4 Precipitation of iron impurities from the solution.

Iron impurities attached to the end of magnesium carbonate hydroxide or yellow tint. Free from impurities iron by using sodium hydroxide solution. The beaker with the filtrate obtained after the precipitation and separation of calcium sulphate, with stirring, small portions of sodium hydroxide solution was introduced. In this solution turned intensely yellow. The solution was allowed to stand for two hours, while the bottom of the glass formed yellow precipitate. The solution was filtered. The filtrate became almost colorless.

3.2.5 Magnesium precipitation from solution.

The magnesium can be precipitated from solution in the form of carbonate or hydroxide. In this experiment, magnesium was precipitated as carbonate sodium carbonate solution.

The reaction proceeds according to the equation:

$$Mg(NO_3)_2 + Na_2CO_3 = MgCO_3 \downarrow + 2NaNO_3$$

The beaker with the filtrate obtained after the precipitation and separation of the iron compounds when made by stirring the calculated amount of 20% sodium carbonate solution. Contents of the glass was milky white immediately. Contents of the beaker was left alone for 16 hours. After holding sediment settles poorly and in the upper part of the glass hardly clarified.

3.2.6 Branch magnesium carbonate and drying.

Branch magnesium carbonate precipitate was conducted through filter paper using a vacuum. Filtration of the precipitate takes place slowly, considerably slower than in the calcium sulfate precipitate separation. The filtrate enters the receiving flask dropwise. After closure of the filtrate compartment, the filter cake remains sufficiently moist and soft. Get dry enough to precipitate out.

The precipitate was transferred to a funnel with a filter paper and a bit dry. The precipitate is then transferred to an oven and dried at a temperature 100-110 ºC for 12 hours. After drying with magnesium carbonate was obtained as a light solid pieces which are easily pulverized in a mortar into a powder.

If the precipitation of magnesium carbonate to conduct without iron precipitation, ready magnesium carbonate has a greyish-yellow.

3.2.7 Calcining magnesium carbonate to obtain magnesium oxide.

The dried magnesium carbonate was placed in a muffle furnace. Predetermined temperature of 450 °C. Calcination was continued for 4 hours. The calcined product was crushed in a mortar.

Ready magnesium oxide, white powder with low gray shade. The resulting product was analyzed and made into a table №11.

Table 11

№	Indicator	Results, %
1	Mass fraction of magnesium in terms of MgO	69.6
2	The mass fraction of calcium in terms of CaO	5.6
3	Mass fraction of sulfate	1.8
4	Mass fraction of nitrates	0.16
5	Mass fraction of iron in terms of Fe_2O_3	0.02
6	Water content	0.12
7	Mass fraction of substances not soluble in nitric acid	UTS

3.2.8 Using the final filtrate and feedstock flow.

From the filtrate remaining after separation of magnesium carbonate can receive various liquid fertilizers, in which the composition may be administered required amount phosphor and potassium-containing components.

If the precipitating calcium and magnesium to apply sodium sulfate and sodium hydroxide, the final filtrate contains sodium nitrate, and a small amount of calcium ion, magnesium sulfates. Sodium nitrate can distinguish, this filtrate was concentrated to a damp salt, it was separated by filtration and dried. feed rate at 1,000 kg is given in Table №12.

Table №12

№	Raw materials	Consumption, kg
1.	Dolomite	6653.4
2.	Nitric acid	13551.6
3.	Ammonium sulfate	3917.5
4.	ammonium carbonate	2803.7
5.	25% ammonia water	419.2
6.	Water	37530.2

3.3 Conclusions of the third chapter

From the test results should be:

- On standing the mixture after quenching significant separation of the mixture composition was observed.
- Calcining removes carbon dioxide, magnesium and calcium in the form of oxides proceeds.
- Qualitative firing achieved at temperatures above 700-750 °C. The firing time in the laboratory for at least 3 hours.
- While stirring with water magnesium and calcium oxides are transformed into the form of hydroxides, flows quenching process.
- On standing the mixture after quench at various temperatures and appreciable settling slurry distribution layers is not observed.
- carbonization process under laboratory conditions was carried out at atmospheric pressure, consequently unable to obtain the individual components in the form of soluble bicarbonate.
- Calciners methods do not allow to obtain the desired results - obtaining magnesium and calcium compounds from dolomite separately.
- Dolomite chemical method is possible to obtain a sufficiently pure magnesium compounds - carbonate, hydroxide, oxide.
- A byproduct of preparation of magnesium compounds is calcium sulfate.
- Caudal filtrates after the separation of magnesium compounds can be used for preparation of various forms of liquid fertilizers.
- solid waste produced in the chemical method, non-toxic, since chemically inert.
- A disadvantage of chemical methods is the high cost of chemicals used - nitric acid, ammonium sulfate, ammonium carbonate.

4. CHAPTER 4. DESIGN TECHNOLOGY FOR PRODUCING MAGNESIUM OXIDE OF DOLOMITE SHORSU

4.1 The technology for producing pure magnesium oxide from the semi burnt dolomite nitric acid ammonia method

Results of research and technological research served physico-chemical basis for the development concept flowsheet producing magnesium oxide.

Schematic diagram of the preparation of the magnesium oxide in this manner is shown in references. Dolomite with a particle size of not more than 40 mm, subjected to thermal decomposition in an oven with a rotating drum under optimum conditions (p.1.3). The resulting semi Burnt dolomite after grinding to -0.20 mm sent to the step for the magnesium nitrate solution.

Received from the furnaces and cooled milled semi burnt dolomite is dissolved in nitric acid. In this case reactions occur:

$$MgO + 2HNO_3 = Mg(NO_3)_2 + H_2O$$

$$CaCO_3 + 2HNO_3 = Ca(NO_3)_2 + CO_2 + H_2O$$

$$Fe_2O_3 + 6HNO_3 = 2Fe(NO_3)_3 + 3H_2O$$

$$Al_2O_3 + 6HNO_3 = 2Al(NO_3)_3 + 3H_2O$$

Also, soluble calcium sulfate contained in the feedstock. To happened boiling solution, the reaction is carried out in a cascade agitators and a water jacket, and the dosing of the semi burnt dolomite is performed gradually, ie, in each stage of the cascade, except the last. Nitric acid is introduced entirely into the first stage of the cascade with an excess of 5% from stoichiometry.

To avoid the possible crystallization of the magnesium nitrate solution process is carried out so that its concentration in solution was obtained of approximately 40%. To obtain a solution with a concentration of the initial 60% nitric acid is diluted to a concentration of 39-40% precipitation washings with washing steps.

After the reaction solution with a temperature of 80-85 °C is filtered to separate the insoluble residue from the acid, which is washed with hot water (90 °) and is directed to waste.

The washing water is sent pas diluting nitric acid.

Freed from the insoluble residue a solution fed to the precipitation step of iron and aluminum ions. Precipitation of magnesium hydroxide slurry being prepared from it by a pitch and water washing of the precipitate of hydroxides of iron and aluminum. The process is carried out in a cascade of devices with low-speed agitators, steam jackets at a temperature not lower than 85 °C. To prevent the precipitate $MgOHNO_3$ slurry of magnesium hydroxide is dosed into each stage of the cascade, so that in the end the solution was pH 6.0-6.5 (no greater than 7).

From the stage apparatus hydroxides of iron and aluminum in the slurry of magnesium nitrate solution fed into the settler.

The thickened slurry is filtered and clarified solution, having a control filtering and cooled in shell and tube heat exchanger to 65-60 °C, is fed to the precipitation step of $CaCO_3$.

The washed filter cake was hydroxides of iron and aluminum is sent to the warehouse.

Precipitation of $CaCO_3$ from a solution of magnesium nitrate being 26 % solution of ammonium carbonate at 55-60 °C in two cascaded devices with a stirrer and a residence time of 0.5 hours. The excess of ammonium carbonate in the solution should be 3-5 g/l.

Preparation of ammonium carbonate organized as described in [187]. The scrubber is packed with irrigated with water and the circulating solution in the lower portion is fed ammonia gas and a gas containing CO_2.

In the deposition process the following reactions:

$Ca(NO_3)_2 + (NH_4)_2CO_3 = 2NH_4NO_3 + CaCO_3$

$CaSO_4 + (NH_4)_2SO_3 = (NH_4)_2SO_4 + CaCO_3$

The resulting calcium carbonate is crystallized in the form of aragonite [188].

Separation of the slurry is carried out using a thickener and a filter. The washed precipitate $CaCO_3$ on the filter is dried at 140 °C in a drum dryer due to the heat of combustion of natural gas. The dried product corresponding to the purity mark "clean", is sealed and sent to the finished products of slide. The wash water is sent to the dilution of the nitric acid. The filtrate was pumped to stage precipitation of magnesium hydroxide.

Precipitation of magnesium hydroxide is conducted in a cascade of devices with turbine agitators, steam jackets 25 % ammonia water. Temperature in reactors 50-55 °C. Ammonia water is introduced into the 2-fold excess in the 1st machine. The residence time of the slurry in the stage 2 hours.

Ammonia water Ammonia water absorption is obtained in the column with bubble trays and heat exchangers.

Separation of the slurry is carried out using a thickener and filter. The precipitate is washed on the filter by displacing and further subjected to 3-stage countercurrent washing by dilution.

The residence time is $Mg(OH)_2$ in 1.5 hours repulpatorah washings are sent: a part for dilution with nitric acid, and the other part - by ammonia absorption. The air is sucked from the vacuum pump filter, washed by ammonia in a scrubber filter air.

The washed precipitate magnesium hydroxide partially directed to the deposition of iron and aluminum ions, and the bulk of it enters the rotary kiln to dehydration, which is carried out at 1100 °C. The result is a product comprising at least 99% MgO.

The flue gases coming from the furnace into a scrubber, irrigated with water in which they are cleaned of oxide and hydroxide, magnesium dust, and from possible impurities NH_3 and NO_2. Cleaned gases are emitted into the atmosphere. The heated scrubbing 95-97 °C until water is used for washing the magnesium hydroxide as part of it, after filtration - washing of the precipitate of hydroxides of iron and aluminum.

The filtered mother liquor of magnesium hydroxide containing ammonia, ammonium nitrate and magnesium is sent for reprocessing.

4.1.1 The use of by-products

The mother liquor can be used in the production of ammonium nitrate. To the filtered mother liquor of magnesium hydroxide containing ammonia, ammonium nitrate and magnesium is heated in a shell and tube heat exchanger to 100 °C, and the gas-liquid mixture enters the apparatus IOT production of ammonium nitrate.

Since the mother liquor ratio of Mg^{2+}:NH^{4+} is greater than the standard ammonium nitrate, about half of the total quantity of nitrate to be obtained from the fresh ammonia and of 60% nitric acid. Due supplying UNT apparatus in the mother liquor with a high content of water, the solution flowing out of it, is obtained at a concentration lower than it should be according to regulations technological management ammonium nitrate. Therefore, the solution should be concentrated to a concentration of 90% in the additional evaporator unit.

The washed filter cake hydroxides of iron and aluminum coagulants can be obtained.

$$2\ Fe(OH)_3 + 3H_2SO_4 + 3H_2O = Fe_2(SO_4)_3 * 9H_2O$$

$$2\ Al(OH)_3 + 3H_2SO_4 + 12H_2O = A1_2(SO_4)_3 * 18H_2O$$

This will require a mixer fitted with a water jacket.

Acid-insoluble residue which was washed on the filter with hot water (90 °) and is directed to the dump, can be used as a grout filler.

4.2 Comparative technical and economic analysis methods of producing pure magnesium oxide

Table 7.3.

Technical and economic indicators methods for producing magnesium oxide

The name of indicators	**Measure**	**Production method**	
		A method of company "Rutner"	**Nitric acid ammonia**
Costs per 1 ton of magnesium oxide			
Materials			
$MgCl_2$ solution (29%)	m^3	6.5	0
Dolomite	Tonnes	0	3

Energy consumption			
Natural gas	m^3	-	270
Steam	Gcal	9.3	6.8
Water	m^3	-	98
Electric power	kWh	870	120
Byproducts			
$CaCO_3$	tonnes	-	1.5-1.6
Coagulant	tonnes	-	0.2
Yield MgO	%	99	91
The line	Thousand. t / year	25	20-23

Semi burnt magnesite proposed process nitric acid ammonia method. Advantages of this method are: low waste, low energy consumption.

In this case, the additional products are a coagulant for wastewater treatment and pure calcium carbonate which can be used as filler.

The method has reserves in improving productivity and reducing energy costs. It is possible to realize through the use of precipitants for preparing solutions of 40-50% solutions of ammonium nitrate and water instead of using part of the mother liquor $Mg(OH)_2$ for the production of liquid nitrogen and nitrogen-magnesium fertilizer.

5. CONCLUSIONS

1) As a result of systematic studies of reactions of thermal decomposition of magnesium carbonate and calcium magnesium compounds, the hydration of magnesium and calcium oxide, hydroxide precipitation by ammonia of magnesium from the solution, the interaction of oxide and magnesium hydroxide with salt solutions developed physicochemical principles processing dolomite deposits "Shorsu" on pure oxide, that will allow to develop the production of magnesium compounds and to solve important national economic problems.

2) The mechanism of the hydration reaction of magnesium and calcium oxide, based on the theory of acid-base catalysis and theory of crystallization from solutions and allowing to predict the influence of electrolytes on the reaction rate and the resulting dispersion of hydroxides.

3) Results of the experiments on the deposition of magnesium hydroxide of ammonia nitrate solutions allow to choose the process conditions with a given degree and deposition with desired properties of magnesium hydroxide.

4) Based on the research results and calculations compiled schematic diagram low- complex processing dolomite nitric acid-ammonia method. In the proposed scheme, other than pure magnesium oxide, simultaneously turns $CaCO_3$ mark "clean" and coagulant.

5) Comparative analysis of the feasibility of obtaining pure magnesium oxide by methods of the company "Rutner" and proposed in this work showed that for obtaining magnesium oxide from dolomite is preferable to use nitric acid ammonia method.

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