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Investigation of the Conversion Process of Calcium and Magnesium Chloride Solution with Sodium Chloride

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Abstract The process of conversion of 37.14% of solutions of calcium and magnesium chlorides with sodium chlorate at 50, 75, and 90°C with the evaporation of conversion solutions was studied. The activation energies of the process and the order and rate constant of the conversion reaction were determined depending on the temperature, time and conditions of the processes. The order of the process of conversion of calcium and magnesium chlorides with sodium chlorate is equal to one. This is confirmed by the fact that the conversion rate constant, calculated from experimental data, remains almost constant for each temperature. Straight Line Dependency $lg\left(C_0 - C_\tau\right)$ from τ also indicates the first order of the process of conversion of calcium and magnesium chlorides with sodium chlorate. The conversion rate constant increases with increasing temperature. Its temperature dependence obeys the Arrhenius law. To establish the values of the conversion rate constant for different temperatures, the constants (K_0) for 37.14% solutions of calcium chloride by the Arrhenius equation and the equation for the dependence of lgK on 1/T were derived. This is confirmed by the linear graphical dependence of lgK on 1/T. The expediency of carrying out the conversion process with evaporation at a temperature of 100°C.

Keywords Conversion, Evaporation, Degree of conversion, Activation energy, Rate constant

1. Introduction

In the world, the main factor in the quality and high yield of agricultural plants is the rational use of mineral fertilizers, stimulants and pesticides. Therefore, much attention has recently been paid to the development of new, highly effective, safe types of defoliants for cotton, which effectively accelerates the processes of deleafing, the opening of mature bolls, increasing the pre-frost harvest of the first varieties, and preventing the mass reproduction of autumn generations of cotton sucking pests.

Currently, preparations for the protection of agricultural crops, defoliants and plant growth regulators are mainly imported from abroad in the form of active principles and preparative forms. For the production of magnesium chlorate defoliant (which contains 36% of the active substance in its composition) [1] at Ferganaazot JSC, the initial raw material source of bischofite (magnesium chloride) is imported from Volgograd (Russia) or Turkmenistan for foreign currency. This leads to an increase in the cost of the defoliant.

To solve this problem, employees of the Institute of General Chemistry of the Academy of Sciences of the Republic of Uzbekistan and FerPI developed a technology for obtaining a new calcium-magnesium chlorate defoliant by using it as raw material, instead of imported "bischofite", products of hydrochloric acid decomposition of dolomites m.r. "Shorsu" and "Pachkamar" [2].

The purpose of this work is to develop a technology for obtaining new defoliants of complex action, having defoliating activity, accelerating the maturation and opening of capsules based on calcium-magnesium chlorate preparation obtained from dolomites of the Navbakhor deposit [3,4,5,6,7,8].

2. Materials and Methods

To issue practical recommendations for the preparation of calcium and magnesium chlorates, the process of conversion of calcium and magnesium chlorides with sodium chlorate was studied depending on temperature and time duration. The study was carried out at temperatures of 50, 75, and 90°C and the duration of experiments was 30, 60, 90, and 120 minutes with the evaporation of conversion solutions. A 500 cm^3 round-bottom flask equipped with a stirrer was charged with 200 g of a 37% aqueous solution of calcium and magnesium chlorides obtained by hydrochloric acid decomposition of dolomites and an equivalent amount of sodium chlorate. A solution of calcium and magnesium chlorides was obtained by decomposition of local dolomites (the composition is given in Table 1.) with a 32% hydrochloric acid solution, as a result of which a solution containing37.0% of the sum of calcium and magnesium

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chlorides, its density is 1.32÷1.35 g/cm^3, pH 5.0÷5.5. Next, the flask was placed in a thermostat with a set temperature (50, 75, 90℃) and intensively mixed. Accordingly, after 30, 60, 90, and 120 minutes, the liquid phase was separated from the sediment and the corresponding chemical analysis of both phases was carried out.

The flask was placed in a thermostat with a set temperature and intensively mixed. After the required period of time, the liquid phase was separated from the sediment and an appropriate chemical analysis was performed.

Chemical analysis of the liquid and solid phases was determined by well-known methods of analytical chemistry, namely, the content of chlorate and chlorine ions was determined by volumetric permanganometric and argentometric methods [9,10,11,12], the amount of sodium by flame photometry [10,13,14,15], calcium and magnesium were determined by the volumetric complexometric method [11,16,17,18].

The objects of study are dolomites of the Navbakhor deposit, hydrochloric acid according to GOST 3118-77 grade “chemically pure” from KHIMPROM LLC, sodium chlorate according to GOST 12257-93 from “Farg’onaazot” JSC. During the conversion of calcium and magnesium chloride solutions with sodium chlorate, the following reactions occur:

CaCl2 + 2NaClO3 ↔ Ca(ClO3)2 + 2NaCl
MgCl2 + 2NaClO3 ↔ Mg(ClO3)2 + 2NaCl

3. Results and Discussions

Based on the data obtained, the degree of conversion of calcium-magnesium chloride with sodium chlorate and the consumption of initial components during the conversion was established (Table 2, Fig. 2).

Table 2 and Fig. 2 show that the degree of conversion significantly depends on temperature and increases with its growth. For processes of 37.14% solutions of calcium and magnesium chlorides to chlorates within 60 minutes, the degree of conversion at 323, 348, and 363 °K is 11.89; 22.36; 30.68% respectively. After 90 minutes, the degree of conversion reaches 17.66; 30.89; 38.94%, respectively, for 37.14% solutions of calcium and magnesium chloride, at temperatures of 323; 348 and 363 °K.

Table 1. Chemical composition of the dolomite sample (wt.%)

Name of the dolomite deposit	Content in % air dry matter												
	CaO	MgO	Al_2O_3	Fe_2O_3 + FeO	FeO	SiO_2	MnO	TiO_2	Na_2O	K_2O	P_2O_5	SO_3tot.	CO_2
"Navbakhor"	30,8	19,29	1,55	0,20	0,15	2,7	0,01	0,03	0,04	0,11	0,02	0,13	45,23

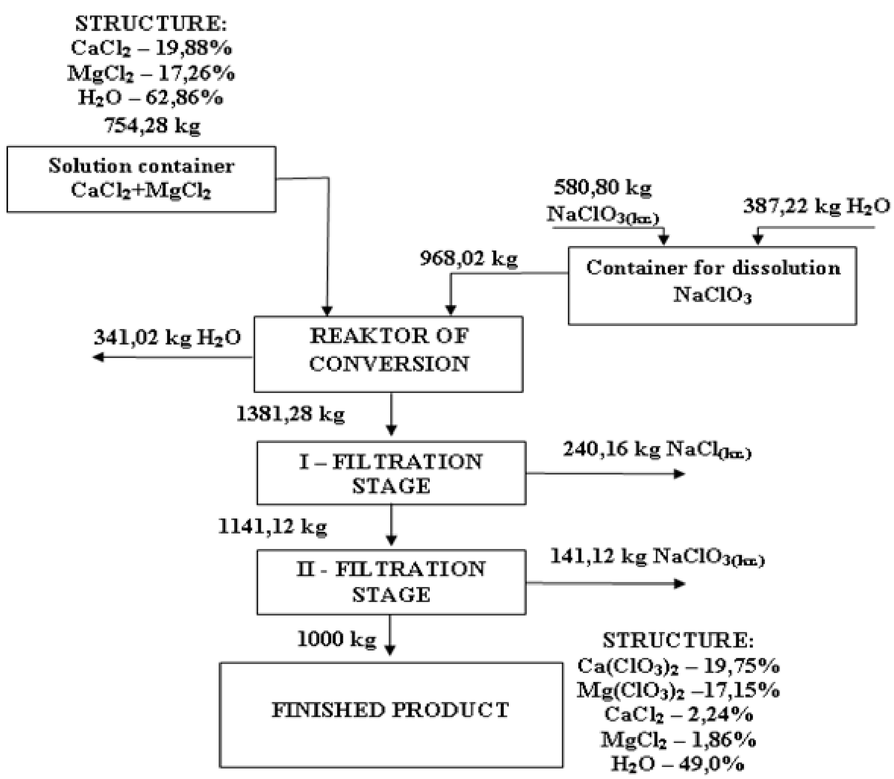

Figure 1. The material balance of obtaining 1 ton of calcium and magnesium chlorides

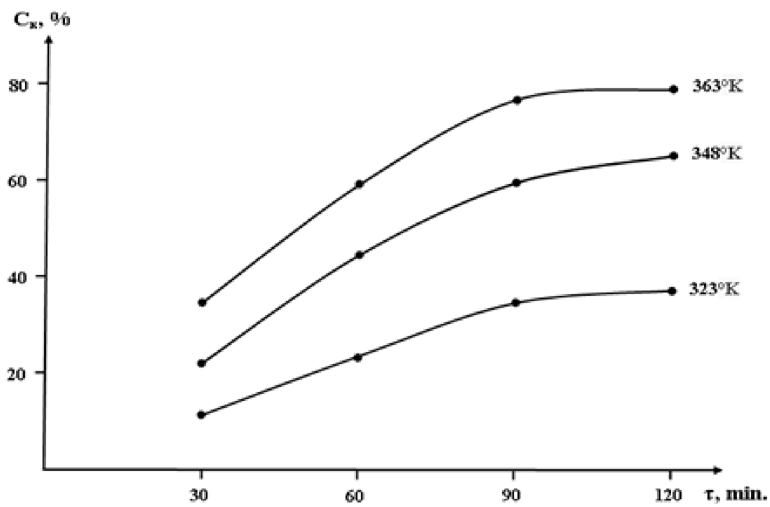

Figure 2. Dependence of the degree of conversion of calcium and magnesium chloride with sodium chlorate on the temperature and duration of the process with the evaporation of conversion solutions

Table 2. Dependence of the rate constant and the degree of conversion on the temperature and duration of the process in the conversion of calcium chloride solutions from evaporation

Temperature, OK	Time, (τ), minute	The content of calcium and magnesium chlorates in the liquid phase, %	Degree of conversion, (Sk)%	rate constant, K·10-2, τ-1	lgK	$\lg(C_0 - C_\tau)$	Activation energy, (E), kcal/mol
For a 37.14% solution of calcium and magnesium chlorides							
323	thirty	5.96	11.12	0.00013427754	-3.871996624	1.802363174	5133.63136
	60	11.89	23.13	0.00313269802	-2.504081467	1.756636108	
	90	17.66	34.31	0.00326342781	-2.48632599	1.713826424	
	120	19.17	36.95	0.0026954918	-2.569361985	1.700963178	
	Average			0.00152329928	-2.8579415165	1.743447221	
348	thirty	11.78	22.0	0.00027817448	-3.555682715	1.760573254	5133.63136
	60	22.36	44.38	0.00058155328	-3.23541049	1.672467313	
	90	30.89	59.72	0.006545276	-2.184072035	1.585573519	
	120	34.81	65.13	0.00580373075	-2.236292744	1.538950562	
	Average			0.00330218362	-2.802864496	1.639391162	
363	thirty	17.59	34.27	0.00043711794	-3.359401369	1.714413592	5133.63136
	60	30.68	59.11	0.00972726242	-2.012009368	1.58793549	
	90	38.94	76.54	0.00915134017	-2.038515301	1.483729899	
	120	39.27	79.00	0.00695429857	-2.157746668	1.478999132	
	Average			0.00656750477	-2.3919181765	1.56626952825	

In the case of a conversion process with evaporation, the data have the following meanings: for 323; 348 and 363 °K after 60 minutes the degree of conversion is 11.89; 22.36; 30.68% for 37.14% solutions of calcium-magnesium chlorides, respectively. A subsequent increase in the duration of the conversion practically does not lead to an increase in the degree of conversion of calcium and magnesium chlorides with sodium chlorate. At 363 °K and an experiment duration of 120 minutes, the degree of conversion was 79.0%, respectively. At this temperature, increasing the duration of the experiment from 90 to 120 minutes leads to an increase in the degree of conversion by only 2.46%.

The reaction order of the conversion process was determined using the first-order kinetic equation:

$$K = 2{,}303 / \tau lgC_0 / (C_0 - C_\tau) \quad [19,20] \qquad (1)$$

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

According to the obtained data, the order of the conversion reaction of calcium and magnesium chlorides with sodium chlorate is equal to one. This is confirmed by the fact that the conversion rate constant calculated by equation (2) based on experimental data remains practically constant for each temperature (Table 2). In addition, the linear dependence $\lg(C_0 - C_\tau)$ on τ also indicates the first order of the process of conversion of calcium and magnesium chlorides with sodium chlorate (Fig. 3). The conversion rate constant increases with increasing temperature (Table 2). Its dependence on temperature obeys the Arrhenius law. This is confirmed by the rectilinear graphical dependence of lgK on 1/T.

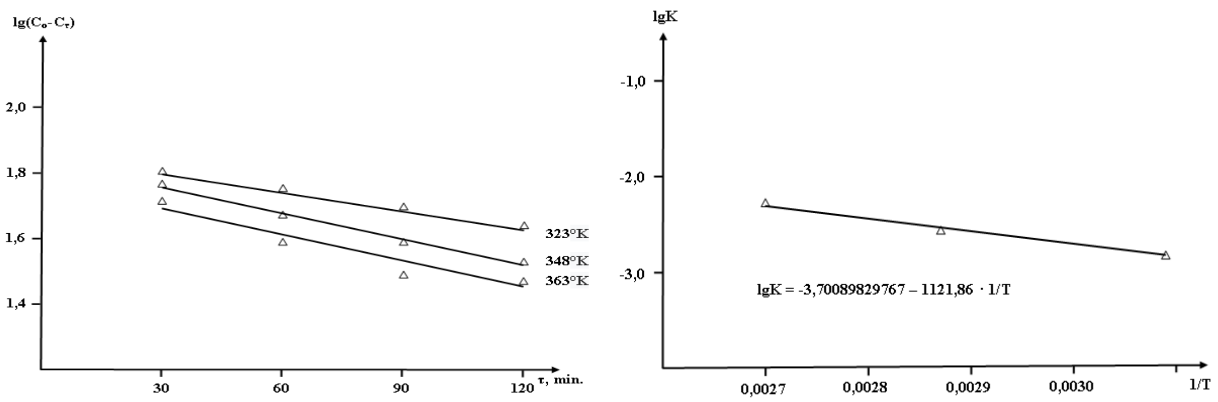

Figure 3. Dependence of lg ($C_0 - C_\tau$) on τ for conversion processes of 37.14% solutions of calcium and magnesium chlorides with sodium chlorate, as well as the dependence of lgK on 1/T

To establish the values of the conversion rate constant for various temperatures, the constants (K_0) were calculated for 37.14% solutions of calcium chloride and magnesium using the Arrhenius equation.

$$K = K_0 e^{E/RT} \qquad (2)$$

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

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

$$lgK = lgK_0 - E / 2{,}303 \cdot 1{,}987 \cdot 1/T \qquad (3)$$

To shorten the notation, we introduce a new notation

$$lgK = \eta;$$
$$lgK_0 = a; \qquad (4)$$
$$b = E / 2{,}303 \cdot 1{,}987 = E / 4{,}184; \; 1/T = \xi$$

We get:

$$\eta = a \text{ -} b \cdot \xi \qquad (5)$$

Making relationships:

$$b_{2,1} = \eta_2 - \eta_1 / \xi_1 \quad \xi_2;$$
$$b_{3,2} = \eta_3 - \eta_2 / \xi_2 \quad \xi_3;$$
$$b_{3,4} = \eta_3 - \eta_1 / \xi_1 \quad \xi_3;$$
$$b_{4,1} = \eta_4 - \eta_1 / \xi_1 \quad \xi_4$$

and by calculating the individual values of "b" based on experimental data, we find the average value of "b".

The calculation of the average value "a" is found by the formula:

$$a = \Sigma\eta + b\Sigma\xi / 4 \qquad (6)$$

For a process using 37.14% calcium and magnesium chlorides with evaporation, the data have the following values. Substituting the calculated values "a" and "b" into equation (5) we will have:

$$\eta = -3{,}70089829767 - 1121{,}86\,\xi \qquad (7)$$

$$lgK = -3{,}70089829767 - 1121{,}86\,(1/T) \qquad (8)$$

The value of the apparent activation energy (E), calculated by the formula E=b·4.576, was 5133.63136 cal/mol. Substituting the calculated value "a" into lgK0=a we get:

$$lg\,K_0 = -3{,}70089829767.$$

From here $K_0 = 1{,}991e^{-7}$ or $K_0 = 0{,}1991 \cdot 10^{-3}$

After substituting the values of K0 and E, the empirical Arrhenius equation (3) takes the form

$$K = 0{,}1991 \cdot 10^{-3} \cdot exp(1121{,}86 / T) \qquad (9)$$

When carrying out the conversion with evaporation after the calculations, the following equation was derived:

$$\lg K = -3{,}70089829767 - 1121{,}86 \cdot \frac{1}{T} \qquad (10)$$

4. Conclusions

Thus, from the results of the studies it follows that to obtain a defoliant with an optimal content of the active substance, it is recommended to carry out the conversion of 37.14% solutions of calcium and magnesium chloride with sodium chlorate at a molar ratio of components 1:2 for 60 minutes at 363 °K with evaporation, as a result of which 41.0% solutions of calcium-magnesium chlorate defoliant can be obtained.

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