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STUDY Of SOLVABILITY Of THE QUANTERNARY SYSTEM Of Naclo -Mgcl2-H2O

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Abstract

The effectiveness of the chemicals used for defoliation depends on numerous factors; the main ones include the variety of cotton, biological maturity and readiness for defoliation, power of plant development, ambient temperature, soil moisture. The process of solubility in the system sodium hypochlorite - magnesium chloride - water has been studied for the first time. On the basis of binary and six internal sections of experimental data, a diagram of the solubility of the NaClO -MgCl2-H2O system was constructed in the temperature range from -38.0 to + 60°C in order to substantiate the conditions for the synthesis of a new compound, based on the initial components, with high physiological activity. Of these, cuts I-IV were drawn from the NaClO-H2O side to the MgCI2-H2O pole, and V-VI — from the MgCI2-H2O side to the NaClO-H2O apex. On the basis of the polytherms of lateral binary systems and internal sections, a polythermal diagram of the solubility of the system magnesium chloride-sodium hypochlorite-water was constructed, on which the ice crystallization fields, MgCl2·• 12H2O, are delimited; MgCl2 • 8H2O; MgCl2 •·6H2O crystal hydrates of magnesium chloride, NaClO·• 5H2O; NaClO·• 2.5H2O crystalline hydrates of anhydrous NaClO, as well as new compounds for this system Mg(ClO3)2 and NaCl. It was found that new compounds Mg (ClO3) 2 and NaCl were formed in this system with the participation of aqueous solutions of NaClO and MgCl2, which were identified by X-ray analysis, IR spectroscopic and mass spectroscopic methods of chemical and physicochemical analysis..

Keywords: sodium hypochlorite; magnesium; chloride; water; system; solubility; sections; projection; two-component system.

Introduction

More than 20 million tons of cotton fiber are produced in the world annually. Today, the leading producers of cotton fiber are China (4 million tons per year), the United States (about 4 million tons), India (2.5 million tons), Pakistan (1.5 million tons) and Uzbekistan (1.2 million tons). These five countries account for 65% of the world's total cotton production. The remaining 35% are produced in 70 countries of the world, of which

Greece, Spain and Australia can be distinguished [1-8]. Therefore, it is relevant to have its own temporary harvesting of raw cotton, which can be carried out using defoliants.

Cotton defoliation is an agrotechnical method for preparing cotton for timely harvesting of the accumulated raw cotton crop [9]. Defoliation is the artificial removal of leaves, which is usually performed using chemicals that cause processes in plants similar to those occurring during natural aging and leaf fall [10-14].

The effectiveness of the chemicals used for defoliation depends on numerous factors; the main ones include the variety of cotton, biological maturity and readiness for defoliation, power of plant development, ambient temperature, soil moisture [15-19].

Currently, cotton growing in Uzbekistan and other Republics widely used as defoliants sodium chlorates, magnesium and sodium tricarbamidochlorate. Therefore, obtaining these defoliants on the basis of local raw materials or waste products of the chemical industry is the most important task defined in the strategy of actions for the development of the Republic of Uzbekistan [20].

As you know, during the production of caustic soda at Navoiyazot JSC, 6500-7000 t / year of sodium hypochlorite and more than 20.000 t / year of chlorine are formed. Today, this secondary raw material is not used in full. If they are processed to magnesium chlorate, it is possible to simultaneously solve two problems: the first is environmental and the second is to obtain cheap products based on the wastes of caustic soda production [21-22].

Research object and methods. In this work, the solubility in the system "sodium hypochlorite - magnesium chloride - water" in the visual polythermal method in a wide range of temperatures and concentrations is considered. IR spectroscopic analysis was performed on an Irtracer 100 spectrometer (Shimadzu, Japan) in the frequency range 400–4000 cm – 1. Samples were prepared by pressing with KBr. Magnesium Mg2+ was determined by complexometric titration [23]. The volumetric method for the determination of chlorides (Mohr's method) is based on the precipitation of chlorine with silver nitrate in the presence of an indicator of potassium chromate. [24].

2. Research method

In this work, the study of the solubility diagram of the sodium hypochlorite-magnesium chloride-water system is considered by the visual-polythermal method . The fields of ice crystallization, $MgCl_2 \cdot 12H_2O$; $MgCl_2 \cdot 8H_2O$; $MgCl_2 \cdot 6H_2O$ and anhydrous magnesium chloride, $NaClO \cdot 5H_2O$; $NaClO \cdot 2.5H_2O$, anhydrous NaClO were determined, as well as new compounds for this system $Mg(ClO_3)_2$ and NaCl, which have been identified by chemical and physicochemical methods of analysis. Mass spectroscopic analysis was performed on SRM 20 and S-115 spectrometers, mass spectrometric analysis was performed on an ICP-MS instrument, and X-ray phase analysis of the samples on a DRON-UM1 X-ray diffractometer with two Soller

slits with filtered CoKa radiation at a recording rate of 1°/min. Chemical analysis was carried out for the presence of ClO3-ion by permanganometric method, and for Na + ion by flame photometric analysis.

3. Research result

To elucidate the behavior of magnesium chloride with sodium hypochlorite in their joint presence in an aqueous solution, as well as to substantiate the process of obtaining effective defoliants based on them, the solubility in systems with the above components in a wide temperature range was studied. Therefore, for the first time, the solubility in the NaClO-MgCl2-H2O system was studied visually - by the polythermal method in a wide temperature range from minus 38.0 to plus 60 ° C.

On the diagram of solubility of the binary system magnesium chloride-water, which is an integral part of the system under study, lines of liquidus of ice, MgCl2 • 12H2O; MgCl2 • 8H2O; MgCl2 • 6H2O. The cryohydrate point of the system corresponds to 22.6% magnesium chloride, 77.4% water at a temperature of -33.7 ° C.

On the polythermal diagram of the solubility of the NaClO-H2O system in the temperature range from –16.5 to 60 ° C, we have established the branches of ice crystallization, NaClO • 5H2O, NaClO • 2.5H2O; and anhydrous NaClO intersecting at the eutectic point lying within 19.2% sodium hypochlorite at a temperature of -16.5 ° C.

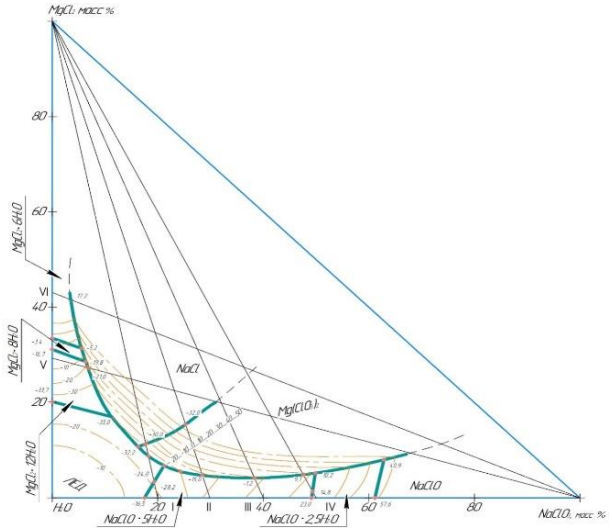

Fig. 1 Diagram of the solubility of the magnesium chloride-sodium hypochlorite-water system

The system magnesium chloride - sodium hypochlorite - water was studied from minus 38.0 to plus 60oC using six internal sections. Of these, cuts I-IV were drawn from the NaClO-H2O side to the MgCl2-H2O pole, and V-VI — from the MgCl2-H2O side to the NaClO-H2O apex. On the basis of the polytherms of lateral binary systems and internal sections, a polythermal diagram of the solubility of the system magnesium chloride-sodium hypochlorite-water was constructed, on which the ice crystallization fields, MgCl2 • 12H2O, are delimited; MgCl2 • 8H2O; MgCl2 • 6H2O crystal hydrates of magnesium chloride, NaClO •

5H2O; NaClO • 2.5H2O Crystalline hydrates of anhydrous NaClO, as well as new compounds for this system Mg(ClO3)2 and NaCl (Fig. 1).

These fields converge at seven invariant triple points of coexistence of three different solid phases. For these points, the compositions of the equilibrium solution and the corresponding crystallization temperatures were determined (Table 1).

Solubility isotherms are plotted on the polythermal diagram at every temperature of 10°C. A projection of the polythermal solubility curve on the lateral water sides of the system was constructed. The crystallization field of the Mg(ClO3)2 and NaCl compound formed by the interaction of the initial components occupies a significant part of the diagram. From the occupied area of crystallization, one can judge that this compound of Mg(ClO3)2 and NaCl is slightly soluble in this system relative to its other components [23].

TABLE I DOUBLE AND TRIPLE NODAL POINTS OF THE MAGNESIUM CHLORIDE-SODIUM HYPOCHLORITE-WATER SYSTEM

Liquidphasecomposition, %			Crystal temperature. ^0C	Solidphase
NaClO	$MgCl_2$	H_2O		
1	2	3	4	5
19.2	-	80.8	-16.5	Ice+ $NaClO·5H_2O$
20.0	2.3	77.7	-23.2	Ice + $NaClO·5H_2O$
20.2	8.9	70.9	-26.0	Ice + $NaClO·5H_2O$+ $Mg(ClO_3)_2$
18.0	9.6	72.4	-27.0	Ice + $Mg(ClO_3)_2$
16.0	11.2	72.8	-32.2	Ice + $Mg(ClO_3)_{2+}$ NaCl
17.8	12.0	71.0	-30.0	$Mg(ClO_3)_{2+}$ NaCl
24.5	16.5	59.0	30.0	$Mg(ClO_3)_{2+}$ NaCl
7.8	5.8	86.6	-15.0	$NaClO·5H_2O$+ $Mg(ClO_3)_2$
38.0	4.9	57.1	-1.2	$NaClO·5H_2O$+ $Mg(ClO_3)_2$
47.2	5.9	46.9	9.1	$NaClO·5H_2O$+ $Mg(ClO_3)_2$
49.6	8.0	42.4	10.8	$NaClO·5H_2O$ +$NaClO·2.5H_2O$+ $Mg(ClO_3)_2$
49.2	2.5	48.3	14.8	$NaClO·5H_2O$ +$NaClO·2.5H_2O$
48.8	-	51.2	23.0	$NaClO·5H_2O$ +$NaClO·2.5H_2O_2$
60.8	-	39.2	57.5	$NaClO·2.5H_2O$ +NaClO·+ $Mg(ClO_3)_2$

62.8	9.2	28.0	47.9	$NaClO{\cdot}2.5H_2O$ +NaClO·
-	20.8	79.2	-33.6	Ice +$MgCl_2{\cdot}12H_2O$
11.0	17.6	71.4	-38.0	Ice + $MgCl_2{\cdot}12H_2O$+ NaCl
6.0	28.0	66.0	-21.0	$MgCl_2{\cdot}12H_2O$+ NaCl
5.9	31.6	66.5	-19.8	$MgCl_2{\cdot}12H_2O$+ $MgCl_2{\cdot}8H_2O$+ NaCl
-	32.0	68.0	-16.7	$MgCl_2{\cdot}12H_2O$ +$MgCl_2{\cdot}8H_2O$
-	34.4	65.6	-3.4	$MgCl_2{\cdot}8H_2O$+ $MgCl_2{\cdot}6H_2O$
5.1	32.4	62.5	-5.2	$MgCl_2{\cdot}8H_2O$+ $MgCl_2{\cdot}6H_2O$+ NaCl
3.1	43.2	53.7	61.2	$MgCl_2{\cdot}6H_2O$+ NaCl

Table 1 shows the double and triple nodal points of the magnesium chloride-sodium hypochlorite-water system. As can be seen from the table in the system is six triple invariant points and four different solid phases.

The crystallization field of the Mg(ClO3)2 and NaCl compound formed by the interaction of the initial components occupies a significant part of the diagram. From the occupied area of crystallization, one can judge that this compound of Mg(ClO3)2 and NaCl is slightly soluble in this system relative to its other components [23].

Thus, the results of studying the heterogeneous equilibrium in the system of magnesium chloride - sodium hypochlorite - water made it possible to establish the temperature and concentration limits of the release of the compound Mg(ClO3)2 and NaCl using the identified chemical and IR spectroscopic and X-ray analysis, mass spectroscopic methods of physicochemical analysis, which are shown in Fig. 2.

Chemical analysis of the solid phase isolated from the assumed crystallization region of the compound Mg(ClO3)2 and NaCl gave the following results: Found, wt%: Mg2+ - 11.11; ClO3- -55.76; Na+ - 19.50; Cl— 10.37 and H2O-3.2% For Mg(ClO3)2, calculated, wt%: Mg2+ - 11.14; ClO3- - 55.79; Na+ - 19.60; Cl—10.47 and H2O-3.0%.

IR spectroscopy is one of the methods used for the qualitative determination of the structure and identification of new compounds. In this regard, the IR spectra of Mg(ClO3)2 and NaCl and its constituent components were studied to clarify the types of chemical bonds, the place and method of coordination of the initial NaClO and MgCl2 molecules, as well as the isolated compound

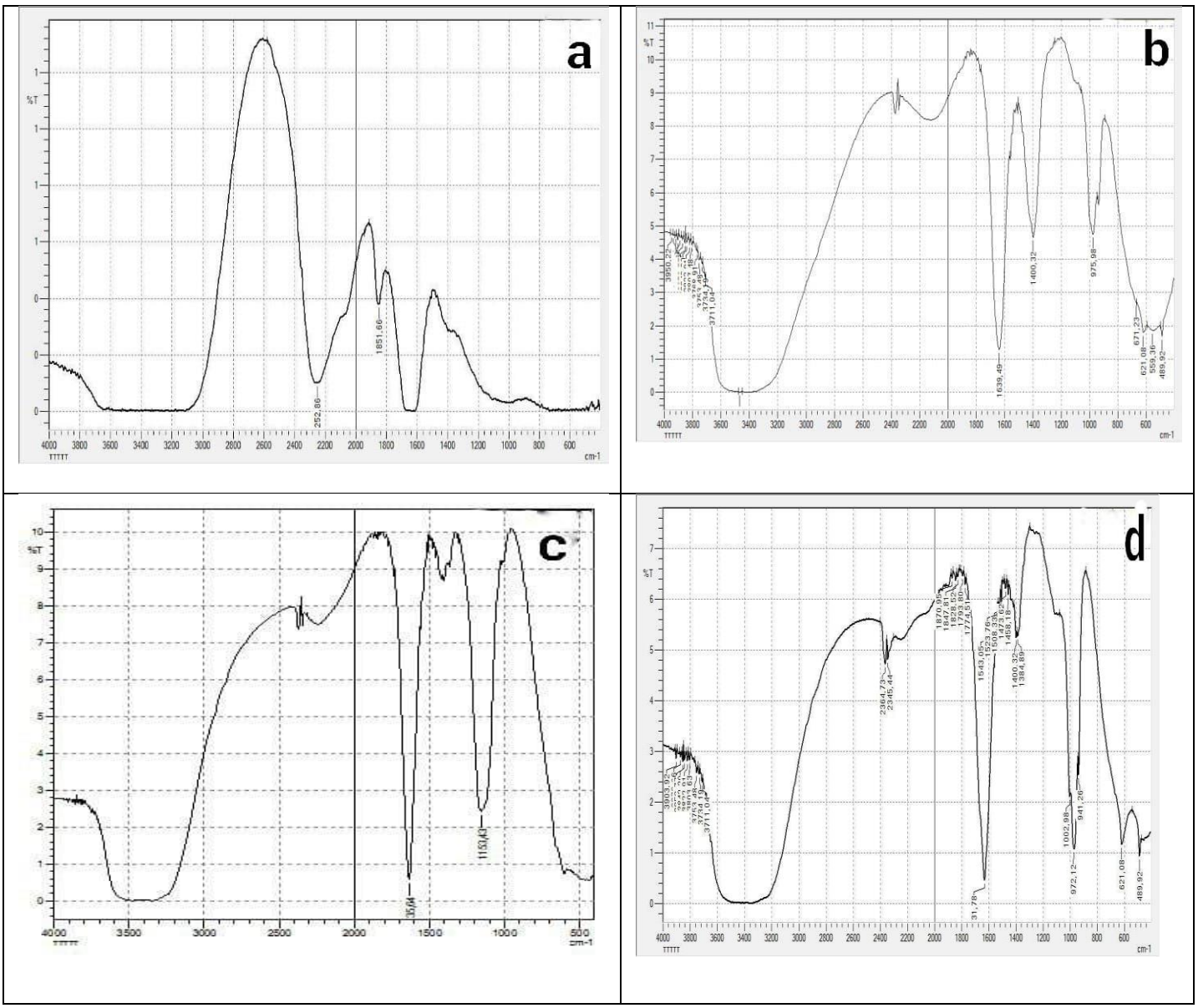

Fig. 2 IR spectra of Mg(ClO3)2 (d) and NaCl (c), its constituent components NaClO (b) and MgCl2 (a)

In the IR spectra of bishafite (MgCl2 • 6H2O), absorption bands are observed in the region of 3000-3600 cm-1, which belong to the - O - H group of crystallization water. Gentle bands in the spectra indicate that in the region of 3200-2800 cm-1 there are usually absorption bands related to the symmetrically stretching and deformation vibrations of chlorides, in our case MgCl2, at 1600-1660 cm-1 there are bands of deformation vibration H-O-H groups (Fig.2a).

In the spectra of sodium hypochlorite in the region of 3600-3000 cm-1, gentle bands are observed, which refer to crystallization water. Deformation vibrations of the same group appear in the area of 1633 cm-1 (Fig. 2b). The 1400 cm-1 bands can be attributed to antisymmetric stretching vibrations of sodium chloride. In the spectrum there are still intense bands at 935-950 cm-1 and this refers to symmetric stretching vibrations of [ClO4] - ions, its bending vibration is 489 cm-1, at 681 cm-1 it is antisymmetric bending

vibration. The characteristic bands for NaClO are observed in the region of 3630 cm-1, symmetric stretching vibrations of [ClO] - ions and its antisymmetric stretching vibrations are observed at 671-700 cm-1.

Thus, based on the data of IR spectroscopic studies, it can be concluded that the [ClO]- ion under the action of external factors is converted into [ClO4] - and Cl- (NaCl) ions.

In the IR spectra for chlorate [ClO3] - ions, absorption bands related to crystallization water are observed. Bands belonging to symmetric stretching vibrations (MgCl2) belong to the regions of 3200-3500 cm-1 in the IR spectrum and to the Raman spectrum. The bending vibration of H2O molecules appears at 1631 cm-1, weak intense bands at 1400-1384 cm-1 refer to NaCl. Intense bands at 1003 cm-1 can also be attributed to [ClO3] - ions, at 972 cm-1 and 941 cm-1 it is characteristic to Mg(ClO4)2. The absorption bands at 621 cm -1 are related to antisymmetric stretching vibrations of magnesium chlorate (Fig. 2d).

The crystalline material was used to prepare tablets for X-ray phase analysis. The X-ray diffraction pattern of the material is shown in Fig. 3., and X-ray phase analysis on a DRON-UM1 diffractometer. The phase composition was identified in accordance with the ASTM card index.

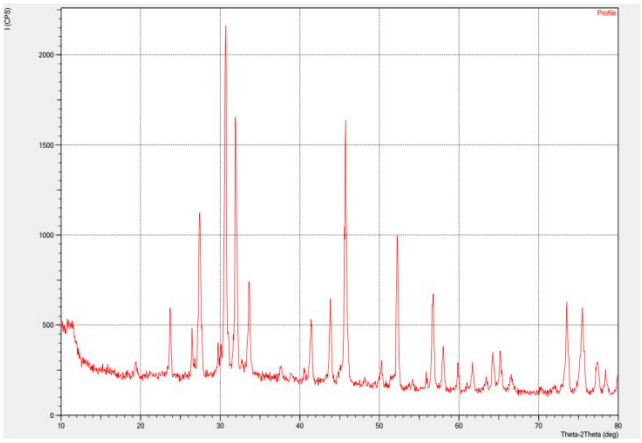

Fig. 3. X-ray diffraction pattern Mg (ClO3) 2

X-ray diffraction studies (Fig. 3) of magnesium chlorate showed that comparing the X-ray diffraction data, it is easy to see that all reflections in the diffractogram of a compound are, as a rule, characterized by intrinsic angles of reflection, a set of interplanar distances. This indicates the individuality of magnesium chlorate and its crystal lattice.

TABLE I Results of mass spectroscopic analysis of raw materials (sodium hypochlorite and bischofite) and magnesium chlorate

№	**Mass, %**	**1**	**2**	**3**
Геол №		**NaClO**	**$MgCl_2$**	**$Mg(ClO_3)_2$**
Na *	**0,004-11%**	>5500000	400	120000

Mg *	**0,004-11%**	21950	>15000000	74000
Al *	**0,002-20%**	3280	1180	1000
P	**1,0-4000**	1500	4500	470
K *	**0,008-30%**	800	555000	4700
Ca *	**0,005-28%**	19500	272500	1500
Sc	**0,10-4000**	37,5	32,5	1,90
Ti *	**0,0006-9%**	70	50	53,0
Cr	**1,0-4000**	1400	2500	22,0
Mn	**0,002-10%**	402,5	392,5	14,0
Fe *	**0,006-30%**	1250	490	530
B *	**0,10-4000**	40,0	4250	20,0

As can be seen from table 2, the feedstock and magnesium chlorate in the solubility diagram fully correspond to the system magnesium chloride-sodium hypochlorite-water.

4. Discussion and Conclusion

Thus, on the basis of the solubility polytherm of the magnesium chloride-sodium hypochlorite-water system, it was studied in the first, from minus 38.0 to plus 60oC using six internal sections. On the basis of the polytherms of lateral binary systems and internal sections, a polythermal diagram of the solubility of the system magnesium chloride-sodium hypochlorite-water was constructed, on which the ice crystallization fields, MgCl2 • 12H2O, are delimited; MgCl2 • 8H2O; MgCl2 • 6H2O crystal hydrates of magnesium chloride, NaClO • 5H2O; NaClO • 2.5H2O crystalline hydrates of anhydrous NaClO, as well as new compounds for this system Mg(ClO3)2 and NaCl. It was found that in this system, with the participation of aqueous solutions of NaClO and MgCl2, new compounds Mg(ClO3)2 and NaCl were formed for this system, which were identified by IR spectroscopic methods of chemical and physicochemical analysis.

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