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Physicochemical Foundations of the Technology of Obtaining High-Purity Manganese Nitrate Hexahydrate

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Abstract

Effect of the parameters of crystallization process and the preparation of the initial raw material on the quality of manganese nitrate hexahydrate was investigated. The optimal parameters of crystallization process were revealed. Results of the investigation of the effect of metal manganese leaching on the purification from admixtures of calcium and chloride ions are presented. A low-waste technology of the production of high-purity manganese nitrate hexahydrate is proposed.

Key words: manganese nitrate hexahydrate, crystallization, leaching, admixtures

INTRODUCTION

Currently, manganese nitrate is usually prepared by the reaction of metal manganese or manganese carbonate with dilute nitric acid [1, 2]. As the result of the interaction of these components, a solution of manganese nitrate is formed which is then subjected to evaporation and crystallization [3–5].

The analysis of the current state of manganese nitrate production and quality in Russia demonstrated that the manufactured product does not have the purity required for obtaining manganese dioxide used in the production of high quality capacitors. Existing technological solutions do not provide obtaining high quality manganese nitrate, they are multi-stage, energy intensive requiring thus for further improvement.

The crystallization of salts from contaminated solutions represents a reliable and efficient method for the treatment of crystalline products [6, 7]. The crystallization results in the displacement of most of the impurities from the solid to a solution. However, this process is often accompanied by a co-crystallization of isomorphous impurities, adsorption of dissolved substances onto the faces of the crystals and

by an occlusal capture of trace impurities by the main crystallizing substance. The distribution of trace impurities due to the crystallization from the solution depends on the following factors: the nature of macro- and microcomponents, the solvent composition, final crystallization temperature, pH, the presence of a complexing agent, *etc.* [8–10].

In connection of the above mentioned and in view of the absence of a theory concerning the laws of some processes, for developing and improving the technology of obtaining manganese nitrate hexahydrate with high purity we conducted experimental studies of the main processes of the technology: leaching the contaminants from the feedstock, purifying the solutions of manganese nitrate impurities, manganese nitrate hexahydrate crystallization, purifying the crystallizate.

EXPERIMENTAL

The chemical composition of the raw material (metal manganese), solutions, and the final product were analyzed by a light emission spectrometry technique using an Optima3000

atomic emission spectrometer with coupled plasma ionization (PerkinElmer, USA) and by means of chemical analysis (State Standard GOST 8269.1-97). The study of leaching the materials and purifying the solutions from impurities was carried out using a reactor with a programmed mode of mixing and measuring the pH of the medium. For the investigation of the crystallization process of manganese nitrate we used a set-up consisting of LT-30 LIOP cryostat with programmable cooling, a crystallizer with a cooling jacket, vertical WiseStir HT50DX rotary stirrer with digital control and thermometer. The filming of crystal growth was carried out using a thin-layer optical cell by means of MBS-9 optical microscope and MYscope 560MCCD digital camera. The statistical analysis of experimental data and photo image processing was carried out by means of a computer using Table Curve, MYscope Photo software packages. The level of the solution evaporation and the yield of the finished product were determined *via* direct measuring the precipitate mass and solving the material balance equation.

RESULTS AND DISCUSSION

It is known that the conditions for the creation of supersaturation have a significant impact on the size, shape and purity of crystals [8]. In this regard, we investigated the stability of solutions under supercooling.

As the object of investigation we have chosen a technical solution of manganese nitrate, obtained by reaction of metal manganese with dilute nitric acid, as well as a solution prepared from purified reactive purity manganese nitrate hexahydrate. According to spectrometric data, the technical manganese nitrate solution contained the following impurities, %: Fe 0.0345, Cd 0.0006, Cu 0.0101, Pb 0.0102, Zn 0.0071, Co 0.0009, Ca 0.0541, and Ni 0.0011.

In order to determine the stability of manganese nitrate solutions in the experiments we measured the value of the maximum supersaturation and exposure, wherewith the mass crystallization began. The studies performed resulted in obtaining data concerning the effect of different factors on the stability of the solutions under investigation. The effect of stir-

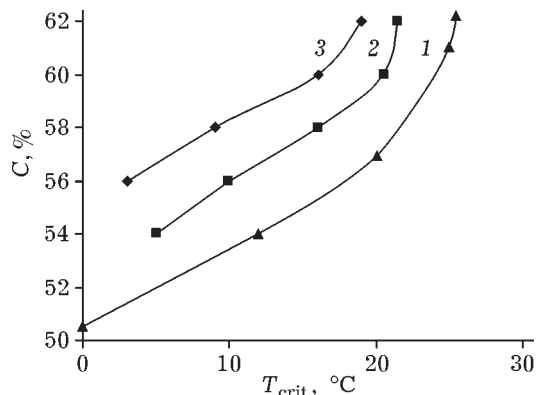


Fig. 1. Effect of $\text{Mn}(\text{NO}_3)_2$ solution purity on the ceiling of supersaturation: 1 - solubility curve; 2, 3 - the ceiling of supersaturation for pure and technical solutions, respectively.

ring intensity (Re) on the stability of supersaturated solutions (ΔT) has an exponential form:
$$\Delta T = a + b \exp(-\text{Re}/c) \quad (1)$$
 where a , b , c are kinetic constants.

It was found that the purity of solutions has a significant impact on their stability (Fig. 1). Thus, the ceiling value of the maximum supersaturation for crude manganese nitrate solution exceeds the maximum supersaturation for pure solution. This could be explained from the standpoint of adsorbing the impurities on the clusters forming nuclei. At the boundaries of the crystal nucleus, as it grows, the impurity molecules form a layer with a higher concentration, making difficult supplying the main substance of the liquid phase to the nucleus.

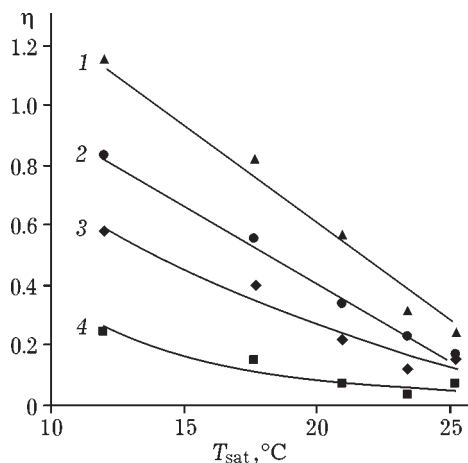


Fig. 2. Relative maximum supercooling level (η) for $\text{Mn}(\text{NO}_3)_2$ solutions depending on the saturation level temperature (T_{sat}): 1, 2 - technical solution without stirring and with stirring, respectively; 3, 4 - clear solution without stirring and with stirring, respectively.

For the mathematical description of the supersaturation we used an equation proposed by E. I. Akhumov [11], whereby we calculated the maximum supersaturation level for the solutions under different conditions of the crystallization process:

$$\log C = b \log C_0 + a \quad (2)$$

where a , b are constants; C_0 is the salt solubility, %; C is the maximum concentration of the supersaturated solution, %.

The nature of the influence of temperature and stirring the solution upon the value of relative maximum supercooling level (η) is demonstrated in Fig. 2.

The relative supercooling level depending on temperature is satisfactorily described by equation

$$\eta = 1 + K_0 \exp(K/T) \quad (3)$$

where K_0 , K are empirical coefficients depending on the physical and chemical properties of the solution.

An effect of inorganic and organic substances on the stability of the solutions was established. For the solutions of manganese nitrate it was found that the impurities of iron, copper, calcium nitrate increase the maximal supersaturation level of the solution. Increasing the concentration of dissolved impurity molecules at the boundaries of a nucleus those are not participating in the construction of the crystal lattice, to either extent hinders supplying the main substance from the liquid phase to the nucleus, which results in increasing the activation energy. As the activation energy decreases the rate of crystal nucleation and the supersaturation level demonstrate an increase.

Measuring the growth rate of manganese nitrate hexahydrate single crystals was performed at constant supercooling level values. An effect of supercooling and crystallization temperature on the rate of growth was established (Fig. 3).

The kinetic data obtained were processed using different mathematical models of crystal growth. It was established that Botsaris equation is the most appropriate one corresponding to a complex nuclear dislocation mechanism of crystal growth for the substances under analysis:

$$V = k_1 + k_2 e^{(-k_3/\ln s)} \quad (4)$$

where k_1 , k_2 , k_3 are coefficients depending on the temperature of crystallization; s is the coefficient of supersaturation.

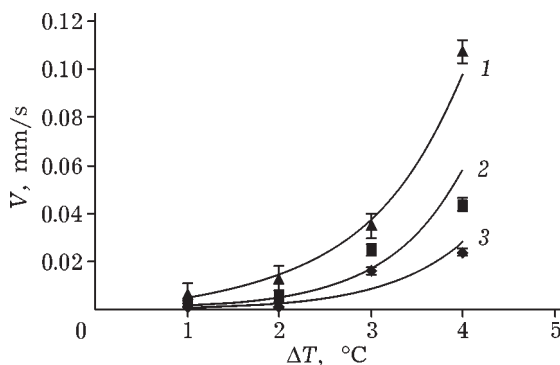


Fig. 3. Growth rate of the front face of the crystal (V) $\text{Mn}(\text{NO}_3)_2$ depending on the solution supercooling level at different saturation temperature values, °C: 25 (1), 21 (2), 17 (3).

The analysis of data from Table 1 demonstrates that the increase in the saturation temperature and the supersaturation of the solution results in increasing the rate of crystal growth, and this, in turn, results in the capture of impurities from the mother liquor.

An effect of the intensity of stirring the solution on the crystal growth rate was investigated. It was demonstrated that for the crystals of manganese nitrate hexahydrate the maximum growth rate is attained with the intensity of stirring that corresponds to the value of Reynolds criterion $\text{Re} = 100$. At low values of the stirring rate, the crystal growth rate increases due to increasing the convective diffusion of substances to the surface of the crystal. However, with increasing the rotation frequency of the stirrer beyond the critical value, the removal of substance microblocks under embedding into crystal substance starts to exceed the rate of supplying the material to the faces of the crystal. The microblocks are washed from the surface of the crystal due to hydraulic and centrifugal forces, which results in the fact that the growth rate decreases. It should also be expected that such a hydrodynamic regime would provide purifying the surface of the crystals from adsorbed impurities.

TABLE 1

Coefficients k_1 , k_2 , k_3 in the Botsaris equation

| T_{sat} , °C | k_1 | k_2 | k_3 |
|-----------------------|---------------------|---------------------|-------|
| 17 | $5.0 \cdot 10^{-5}$ | $2.0 \cdot 10^{-2}$ | 0.12 |
| 21 | $7.0 \cdot 10^{-4}$ | $2.1 \cdot 10^{-2}$ | 0.13 |
| 26 | $1.0 \cdot 10^{-3}$ | $8.3 \cdot 10^{-2}$ | 0.24 |

In the course of studying the process of manganese nitrate bulk crystallization we found that the increasing the mass of the solid phase is described by S-shaped curves having different slopes depending on the cooling rate. For the mathematical description of these curves we suggested using the Erofeev equation:

$$a = 1 - \exp(-k\tau^n) \quad (5)$$

where a is the level of crystallization; τ is time; k , n are the rate constants of crystal formation.

The coefficients k and n were determined depending on the solution cooling rate. For the crystallization of manganese nitrate hexahydrate, these dependence were presented according to the following equations:

$$k = \exp(-25.537 + 1.571W_{\text{cool}}) \quad (6)$$

$$n = 4.769 - (0.198/W_{\text{cool}}) \quad (7)$$

Here W_{cool} is the cooling rate of the solution, °C/min.

The equations are valid for the studied conditions of crystallization and allow establishing the impact of these conditions on the level of crystallization substances obtained. The revealed laws of the formation of $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solid phase were then be used in order to choose an optimal mode of the crystallization process.

The analysis and comparison of the composition of metal manganese and manganese nitrate hexahydrate feedstock resulted in establishing that the main impurities whose contamination level exceeds permitted values for the feedstock used for obtaining finished product are presented by chlorine ions, calcium, iron, lead and copper. Therefore, the main objective of experiments on improving the technology of obtaining pure manganese nitrate hexahydrate was to develop methods for removing these impurities from the raw material and crystalline product precipitates.

The process of obtaining the crystalline precipitates was carried out in three stages: 1) obtaining the solution of manganese nitrate from metal manganese *via* its interaction with nitric acid, 2) evaporating the solution obtained up to a certain concentration in order to reach a saturation level at the initial crystallization temperature T_0 ; 3) crystallizing the evaporated solution *via* cooling.

Hot solution was supplied to a crystallizer where we maintained constant temperature

close to the temperature of crystallization using a cryostat. After reaching the solution saturation temperature in the apparatus, we carried out a gradual temperature decrease to a final value of T_f using a thermostat, which provided the precipitation of crystals from the analyte. At the end of each experiment, the resulting crystallizate was filtered through a vacuum filter, washed and analyzed for traces of chloride, calcium, iron, lead, and copper ions.

Among the factors those affect the quality of the product, we investigated the temperature difference between the beginning and the end of the crystallization process ($\Delta T = T_0 - T_f$), the initiation of nucleation, precipitate ripening (crystallizate mixing at the final temperature T_f) and washing the crystallizate by special solutions, changing the pH of the medium.

From analyzing the results obtained in the course of the investigation, it follows that lowering the content of iron, calcium and lead ions exerts a positive effect on maturing the precipitate at the final temperature (this process results in the destruction of crystal agglomerates and the reduction of mother liquor capture) and subsequent washing of the precipitate. It should also be noted that the shift of the temperature range of crystallization within in the region 23–13 °C results in decreasing the content of iron, calcium, lead, and copper ions. Within this temperature range, the nucleation rate is lower than the rate of growth, which results in the formation of coarse product with a lower surface area than that exhibited by fine crystals. As a consequence, capturing the impurities by the crystal surface of the phase forming substance.

Washing the pure saturated solution of manganese nitrate allowed three times reducing the content of chloride ions in the sample.

A noticeable effect on the reduction of iron, lead and calcium impurities is exerted by alkalinizing the solution with ammonia water up to pH 6.5–7. In this case, there is a process of co-precipitation of impurities in the manganese hydroxide precipitate under formation.

It is noted that when the initiation of manganese nitrate hexahydrate crystallization is performed in a gradual manner, that is, immediately after the solution was cooled, the

TABLE 2

Content of impurities in the crystalline product after purifying

| Impurities | Content of impurities according to Merck standard (Germany), % | Actual content of impurities in the crystalline product, % |
|------------|--|--|
| Total iron | <0.0005 | 0.000041 |
| Copper | <0.0005 | 0.000010 |
| Lead | <0.0005 | 0.00016 |

resulting crystals have a coarser shape, which also provides obtaining a more pure product.

The experiments on the crystallization of manganese nitrate hexahydrate resulted in the fact that it was found that under certain conditions of the process, one could achieve a substantial purifying the $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ crystal from iron, lead, and copper ions (Table 2). These conditions are they: the alkalization of manganese nitrate solution with ammonia water, certain temperature range for the crystallization of the solution, intense stirring the suspension over the entire volume, a certain time of precipitate maturation and the use of washing the precipitate by pure saturated solution.

Reducing the content of calcium and chlorine impurities in the final product below recommended standards no possible neither *via* washing nor *via* crystallization.

In connection with this, we conducted the investigations concerning the feedstock purification from metal manganese used for obtaining the solution of manganese nitrate. According to chemical analysis, the metal manganese contains the following impurities, %: Cd 0.0008, Fe 0.0361, Cu 0.0102, Pb 0.0122, Zn 0.0077, Co 0.0011, Ca 0.0593, Cl 0.01, and Ni 0.0015.

In order to purify the raw material from associated impurities of calcium and chlorine the metal

manganese was ground to a particle size of 1 mm. Then manganese was treated with a 5 % solution of pure nitric acid (pure grade) with continuous stirring for 30 min, and the ratio between the liquid and solid phases ranging within (5–10) : 1 and the temperature values of 25–50 °C. Further precipitate of metal manganese was filtered using a vacuum filter, washed with distilled water and dried in a drying oven. In the resulting manganese and filtrate we determined the content of calcium and chloride ions (Table 3).

The results of our investigations demonstrated that the use of 5 % nitric acid solution for previous purifying metal manganese at 25–50 °C and phase ratio L/S = (5–10) : 1 is highly efficient: the level of manganese purification ranges within 97.64–98.88 %, whereas the loss of manganese does not exceed 2.92 %. Raising the temperature of leaching from 25 to 50 °C significantly affects the efficiency of leaching; therefore it is worthwhile to carry out the process at a room temperature. Increasing the ratio of phases L/S in leaching from 5 : 1 to 10 : 1 exerts a little effect on the efficiency, so the recommended L/S ratio is less than 5 : 1.

Data on changing the mass of the initial and refined manganese indicate that alongside with calcium, other impurities (iron, heavy metals) are also removed from manganese.

TABLE 3

Experimental results on the treatment of metal manganese *via* leaching by the solution of nitric acid

| Parameters | Number of experiments | | | | |
|---|-----------------------|---------------------|----------------------|----------------------|-----------------------|
| | 1 | 2 | 3 | 4 | 5 |
| Leaching temperature, °C | 25 | 25 | 50 | 50 | 25 |
| L/S ratio at leaching | 5/1 | 10/1 | 5/1 | 10/1 | 10/1 |
| Ca ²⁺ content in purified manganese, % | $6.62 \cdot 10^{-4}$ | $1.4 \cdot 10^{-3}$ | $7.25 \cdot 10^{-4}$ | $7.17 \cdot 10^{-4}$ | $1.132 \cdot 10^{-3}$ |
| Level of manganese purification from Ca ²⁺ , % | 98.88 | 97.64 | 98.77 | 98.79 | 98.09 |
| Cl ⁻ content in purified manganese, % | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| Level of manganese purification from Cl ⁻ , % | 90 | 90 | 90 | 90 | 90 |

TABLE 4

Content of impurities in manganese nitrate hexahydrate obtained by the technology developed

| Components (impurities) | Content of impurities according to Merck standard (Germany), % | Actual content of impurities in the crystalline product, % |
|-------------------------|--|--|
| Main substance | >99.0 | 99.9 |
| Chloride ions | <0.001 | 0.000321 |
| Sulphate ions | – | 0.00075 |
| Total iron | <0.0005 | 0.000211 |
| Calcium | <0.001 | 0.0004913 |
| Copper | <0.0005 | <0.000005 |
| Cadmium | <0.0005 | 0.00006 |
| Cobalt | <0.0005 | 0.00014 |
| Lead | <0.0005 | 0.00018 |
| Nickel | <0.0005 | 0.00047 |
| Zinc | <0.0005 | 0.00001 |
| Fluoride ions | – | 0.000061 |

CONCLUSION

The investigation performed resulted in the development of low-waste technology for obtaining crystalline high purity manganese nitrate, which technology includes the following stages: preparing the raw material (grinding), leaching the raw with HNO₃ solution; dissolving the purified material in nitric acid, the precipitation of heavy metal impurities from the solution followed by filtration, the evaporation of the purified solution to obtain a desired concentration, controlled Mn(NO₃)₂ · 6H₂O crystallization, maturing the precipitate with the desorption of contaminants from crystallizate, the filtration of the crystalline product.

From the analysis of the complete composition of high purity manganese nitrate hexahydrate (Table 4) obtained by the technology presented, it follows that the product meets the requirements of the standards of the German company Merck.

The developed modification of the low-waste technology can be recommended for the imple-

mentation to replace expensive imported raw materials by a cheaper raw material with a poor quality at the lowest cost of purification, as well as for producing a high quality final product that meets international standards.

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