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## Physicochemical Fundamentals of Obtaining High Purity Manganese (II) Acetate Tetrahydrate

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### Abstract

Influencing the parameters of the crystallization process and the preparation of raw materials upon the quality of manganese acetate tetrahydrate was investigated. Optimum parameters were determined for the process of crystallization. Results are presented concerning studies on the influence of leaching the manganese carbonate upon the process purifying from calcium and chlorine impurities. A low-waste technological scheme is proposed for the production of high purity manganese acetate tetrahydrate.

**Key words:** manganese acetate tetrahydrate, crystallization, leaching, impurities

### INTRODUCTION

Currently manganese acetate is being prepared mainly via the reaction between manganese metal or its compounds and dilute acetic acid. As the result, a solution of manganese acetate is formed, which solution is further subjected to evaporation and crystallization procedures [1–3].

In modern industry, manganese acetate tetrahydrate is used for the production of high purity manganese dioxide, manganese oxide hydrate, oxide-based catalysts, and catalysts for oxidation [4].

The analysis of the current state-of-the-art of the production and quality of manganese acetate in Russia demonstrated that the product released does not exhibit the purity required to produce manganese dioxide used for the production of high-quality capacitors. The technological solutions available do not provide obtaining high-quality manganese acetate; they

are multistage, power-consuming, thus they require for further improving.

The crystallization of salts from contaminated solutions represents a reliable and efficient way to purify crystalline products [5–7]. Under crystallization, the most of impurities are displaced from the solid phase into solution. However, this process is often accompanied by co-crystallization of isomorphic impurities, adsorption of solutes on the faces of the crystals and occlusive capturing the trace impurities by the main substance under crystallization. The distribution character of trace impurities in the course of crystallization from solution is influenced by the following factors: the nature of micro and macro components, the composition of the solvent, the final crystallization temperature, pH value, the presence of a complexing agent, *etc.* [8–10].

In this regard and in connection with the absence a theory concerning the laws of occurring some of the processes, in order to de-

velop and improve the technology of obtaining high purity manganese acetate tetrahydrate we carried out experimental studies concerning the technology of main processes such as leaching the impurities from the initial raw material, purifying the manganese acetate solution from impurities, manganese acetate tetrahydrate crystallization, crystallizate purification.

## EXPERIMENTAL

The chemical composition of the initial raw material (manganese carbonate), both of the solutions and the final product, was analyzed using a PerkinElmer Optima-3000 atomic emission spectrometer with ionization coupled plasma (the USA) as well as chemical analysis according to Russian State Standard GOST 8269.1-97. The investigation of raw material leaching and solution purification from impurities was performed using a reactor with a programmable mixing mode and with measuring pH. In order to investigate the manganese acetate crystallization process we used a set-up consisting of a programmable cooling cryostat LT-30 LIOP, a crystallizer equipped with a cooling jacket, a digitally controlled WiseStir HT50DX vertical rotary agitator and a thermometer. Filming the crystal growth was performed using a thin layer optical cell using an MBS-9 optical microscope and a MYscope 560MCCD digital camera. The statistical analysis of experimental data and the processing of photographic images was performed with the use of Table Curve and MYscope Photo software packages. The level of evaporation for the solutions and the yield of the target product were determined *via* direct measuring the mass of precipitate with solving the material balance equations.

## RESULTS AND DISCUSSION

It is known that the conditions for the creation of supersaturation exert a significant effect on the size, shape and purity of the crystals obtained [11-13]. In this regard, we investigated the stability of solutions under supercooling conditions.

As the object of investigation we chose a solution prepared from purified chemical purity grade manganese acetate tetrahydrate and a technical grade solution of manganese acetate, prepared *via* the reaction between technical grade manganese carbonate and a 20 % solution of chemical purity grade glacial acetic acid at a ratio between the liquid and the solid phases equal to 1.5 : 1. The concentration of the technical solution of manganese acetate obtained this way was equal to 11.8 %. Further, the solution was evaporated to obtain a preset concentration. According to spectrometric data, the technical grade manganese acetate solution contained the following impurities (%): Cl 0.01, Fe 0.0008, Ca 0.02, Cu 0.00066, Pb 0.0027.

In order to determine the stability of manganese acetate solutions, in our experiments we measured the values of the maximum supersaturation and supercooling those correspond to beginning the mass crystallization starts. The investigations performed resulted in obtaining data concerning the influence of different factors upon the stability of the solutions under study. The effect of stirring intensity ( $Re$ ) on the stability of supersaturated solutions ( $\Delta T$ ) exhibits an exponential form:

$$\Delta T = a + b \exp(-Re/c) \quad (1)$$

where  $a$ ,  $b$ ,  $c$  are kinetic constants.

It was revealed that the purity of the solutions exerts a significant effect on the stability (Fig. 1). So, the supersaturation limit value for pure manganese acetate solution exceeds the

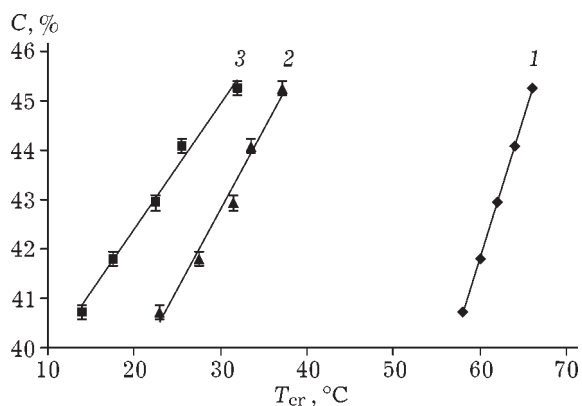


Fig. 1. Effect of  $Mn(CH_3COO)_2$  solution purity on the supersaturation limit: 1 – solubility curve; 2, 3 – supersaturation limit values for technical grade and pure solutions, respectively;  $C$  is the concentration of the solution, mass %;  $T_{cr}$  is the crystallization temperature, °C.

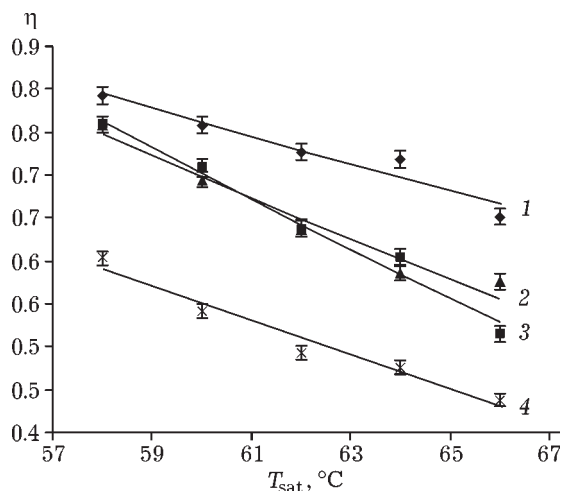


Fig. 2. Relative supercooling limit ( $\eta$ ) for the solutions of  $\text{Mn}(\text{CH}_3\text{COO})_2$  depending on the saturation temperature ( $T_{\text{sat}}$ ): 1, 2 – pure and technical grade solutions without stirring, respectively; 3, 4 – pure and technical grade solutions with stirring, respectively.

supersaturation limit value inherent in the technical grade solution. It is most likely that the impurities those are present in the technical grade solution of manganese acetate, undergo hydration, thereby the hydration level of the main substance is caused to decrease, and hence the stability of supersaturated solution exhibit a decrease, too. Furthermore, the presence of alien impurities in the electrolyte solution results in some changes the ionic strength value, which also exerts an effect on the solution stability.

For the mathematical description of the supersaturation, we used an equation proposed by the authors of [14]. With the help of this equation we calculated the supersaturation limit of the solution under different conditions of the crystallization process:

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

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

The influence of temperature and stirring the solution upon the relative supercooling limit ( $\eta$ ) 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  $K_0$  and  $K$  are empirical coefficients those depend on the physicochemical properties of the solution.

An effect of inorganic and organic impurities exerted on the stability of the solutions was established. For the solutions of manganese acetate we have found that in the presence of impurities such as hydrochloric acid, ethylene glycol, butylene glycol, toluene the stability of the solutions exhibit an increase. Increasing the concentration of the molecules of dissolved impurities those are not involved in the construction of the crystal lattice at the boundaries of the nucleus, to either extent makes it difficult to supply the main substance molecules from the liquid phase to the nucleus, which promotes increasing the activation energy. However, increasing the activation energy results in decreasing the rate of crystal nucleation and thus the supersaturation level exhibits an increase. Adding sulphuric acid, calcium acetate, glycerol, or acetone causes the solution resistivity against supercooling to be reduced.

We performed the investigations of growth rate for the single crystals of manganese acetate tetrahydrate at a constant supersaturation level. An influence of supercooling and crystallization temperature upon the rate of growth was revealed (Fig. 3).

The resulting kinetic data were processed with the help of different mathematical models of crystal growth. From the analysis of the models we established that an adequate description of the process results from the Botsaris equation corresponding to a complicated nuclear dislocation mechanism of the crystal growth of the substances under analyzing:

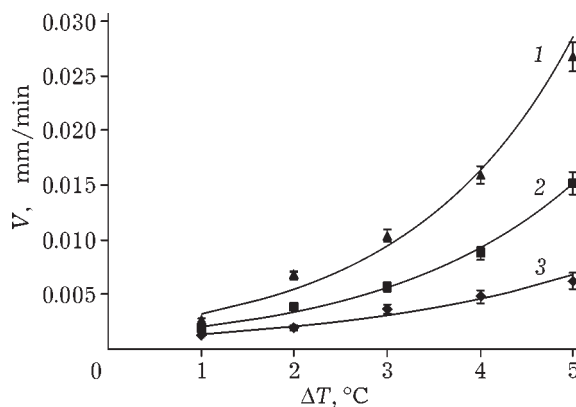


Fig. 3. Growth rate ( $V$ ) at the front face of the  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  crystal depending on the solution supercooling level ( $\Delta T$ ) at different saturation temperatures ( $^\circ\text{C}$ ): 50 (1), 40 (2), 27 (3).

TABLE 1

Values of  $k_1$ ,  $k_2$ ,  $k_3$  coefficients in the Botsaris equation

$T_{\text{sat}}, ^\circ\text{C}$	$k_1 \cdot 10^6$	$k_2 \cdot 10^4$	$k_3$
27	2.1	0.29	0.11
40	4.5	2.2	0.23
50	6.8	2.9	0.24

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

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

From the analysis of data in presented in Table 1 one can see that the increase in the saturation temperature and the supersaturation level of the solution causes increasing the rate of crystal growth, which, in turn, facilitates the capture of impurities from the mother liquor.

We have investigated the influence of the solution stirring intensity upon the rate of crystal growth. It is demonstrated that for the crystals of manganese acetate tetrahydrate the maximum growth rate of the faces is achieved at the stirring intensity corresponding to the Reynolds criterion value  $Re = 200$ . At low stirring rate values the crystal growth rate increases owing to an increase in the rate of the substance convective diffusion toward the surface of the crystal. However, with increasing the frequency of the stirrer rotation beyond the critical value the removal of the substance micro blocks embedding into the crystal begins to exceed the rate of supply the material to the faces of the crystal. The micro blocks are washed out of the crystal surface under the action of hydraulic and centrifugal forces, whereby the rate of crystal growth exhibits a decrease. It should be also expected that in the course of such a hydrodynamic regime the crystal surface would be cleaned purified from adsorbed impurities.

In the course of studying the process of the mass crystallization of manganese acetate it was found that increasing the mass of the solid phase is described by S-shaped curves those exhibit different slope values depending on the cooling rate. For the mathematical description of these curves we proposed to use Erofeev equation:  $a = 1 - \exp(-k\tau^n)$  (5)

where  $a$  is the level of crystallization;  $\tau$  is time;  $k$ ,  $n$  are rate constants for crystal formation.

The coefficients  $k$  and  $n$  were determined depending on the solution cooling rate. For the crystallization of manganese acetate tetrahydrate such dependences are presented by equations  $k = -2.053 \cdot 10^{-6} + 1.643 \cdot 10^{-6} \exp(W_{\text{cool}})$  (6)

$$n = 3.805 + 0.304 W_{\text{cool}}^2 \quad (7)$$

where  $W_{\text{cool}}$ , is the solution cooling rate,  $^\circ\text{C}/\text{min}$ .

These equations are valid for the crystallization conditions under investigation and they one allow to establish the influence of these conditions upon the crystallization level the substances obtained. The patterns revealed for the formation of the solid phase of  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  were further used in order to choose an optimal crystallization process.

The analysis and comparison of the composition of the initial feedstock (manganese carbonate) and manganese acetate tetrahydrate demonstrated that the main impurities, whose pollution level exceeds the acceptable values in the initial feedstock used to obtain the final product, are presented by chloride, calcium, iron, lead and copper ions. In this regard, the main task of experiments concerning the improving of the technology for obtaining pure manganese acetate tetrahydrate consisted in the development of methods for removing these impurities from the feedstock and the precipitation of crystalline product.

The process for preparing crystalline precipitates was carried out in three stages: 1) obtaining the solution of manganese acetate from manganese carbonate via the reaction with acetic acid, 2) the evaporation of the resulting solution to obtain a preset concentration in order to reach saturation at the initial crystallization temperature  $T_0$ , and 3) the crystallization of the evaporated liquor *via* cooling.

A hot solution was supplied to a crystallizer, where a constant temperature was maintained close to the temperature of crystallization by means of a cryostat. Upon reaching the saturation temperature in the apparatus, the solution temperature was gradually lowered using the thermostat to the final value of  $T_{\text{cr}}$ , which resulted in the precipitation of the crystals of the substance under analyzing. At the end of each experiment, the resulting crystal-

TABLE 2

Content of impurities in the crystalline product after purification

Impurities	Impurity content according to Merck standards (Germany), %	Real impurity content in the crystalline product, %
Total iron	<0.0005	0.00032
Copper	<0.0005	0.00001
Lead	<0.0005	0.00038

lizate was filtered using a vacuum filter, washed and analyzed for the content of trace chlorine, calcium, iron, lead, and copper ions.

As the factors those affect the quality of the product, we investigated a temperature difference between the beginning and the end of the crystallization process ( $\Delta T = T_0 - T_{cr}$ ), the initiation of nucleation, maturing the precipitate (stirring the crystallizate at  $T_{cr}$ ) and washing the crystallizate with special solutions.

We have found that decreasing the content of iron, calcium and lead ions is positively affected by the procedure of precipitate maturation at  $T_{cr}$ , which procedure promotes the destruction of crystal agglomerates and decreasing the capture of mother liquor, as well as further rinsing the precipitate. Noteworthy is the fact that shifting the crystallization temperature range to the region of 40–20 °C results in a decrease in iron, calcium, lead, and copper content. Within this temperature range the rate of nucleation is lower than the growth rate thereof, which causes to form a coarse-grained product with a lower specific surface as to compare with small crystals. This, in turn, promotes reducing the capture of impurities by the crystal surface of the phase-forming substance.

Rinsing the precipitate with pure saturated manganese acetate allowed three times reducing the content of chloride ions in the sample.

A noticeable effect on decreasing the content of iron, calcium and lead impurities is exerted by alkalizing the solution with aqueous ammonia to obtain pH 7.5–8, whereat a coprecipitation of the impurities occurs on the precipitate of manganese hydroxide under formation. The subsequent stage of filtering the suspension allows one to separate the precipitate obtained from the solution. The loss of manganese with the slurry does not exceed 1.5–2 %.

We have found that in the case when the initiation of manganese acetate tetrahydrate crystallization is performed in a gradual manner (immediately after beginning the solution cooling), the crystals obtained are larger, which also promotes obtaining a more pure product.

As the result of the experiments concerning the crystallization of manganese acetate crystalline hydrates we have found that a substantial purification of  $Mn(CH_3COO)_2 \cdot 4H_2O$  crystals from iron, lead and copper ions is provided at the following process conditions: alkalinizing the solution of manganese acetate with aqueous ammonia to obtain pH 7.5–8, the temperature of the solution crystallization ranging within 40–20 °C, intense stirring the suspension throughout entire volume ( $Re = 200$ ), the precipitate maturing time being of 20–30 min, washing the precipitate with pure saturated solution at the ratio between the liquid and the solid phases not less than 3 : 1 (Table 2).

We did not succeed in reducing the content of calcium and chlorine impurities in the finished product lower than the recommended norm both *via* washing and *via* crystallization.

In this connection, we performed investigations concerning the purification of the initial feedstock (manganese carbonate) used to prepare the solution of manganese acetate. According to the chemical analysis, manganese carbonate contains the following impurities (%): chloride ions 0.0173, Ca 0.09614, Fe 0.001, Pb 0.005, Cu 0.0018.

In order to purify manganese carbonate we carried out two series of investigations concerning leaching the impurities by acetic acid solutions and nitric acid solutions.

In the first series of the experiments the initial manganese carbonate powder was treated with 5 % acetic acid solution under permanent



TABLE 3

Impurity content in manganese acetate tetrahydrate obtained *via* the technology developed

Impurities	Impurity content according to Merck standards (Germany), %	Real impurity content in the product obtained, %
Main substance	>99.0	99.9
Chloride ions	<0.001	0.0005
Sulphate ions	–	<0.005
Total iron	<0.0005	0.0002
Potassium	<0.001	0.001
Copper	<0.0005	<0.000005
Cadmium	<0.0005	0.000046
Cobalt	<0.0005	0.00003
Lead	<0.0005	0.00038
Nickel	<0.0005	0.0001
Zinc	<0.0005	0.00002
Fluoride ions	–	0.00047

stirring for 30 min, the ratio between the liquid and the solid phases ranging within (5–10)/1 at the temperature of 25–50 °C. Further, the manganese carbonate precipitate was filtered using a vacuum filter, washed with distilled water and dried in a drying oven. Manganese loss in the course of leaching amounted to 4–5 %.

The purification results demonstrated that increasing the heating temperature for the suspension exerts a little effect on the efficiency of calcium leaching, so the process is appropriate to perform at a room temperature. Increasing phase ratio L/S in the course of leaching from 5 : 1 to 10 : 1 causes increasing the manganese loss, but exerts a little effect on the efficiency of the leaching, therefore the recommended ratio between the phases L/S should be less than 5 : 1.

The second series of experiments aimed at purifying the manganese carbonate powder from impurities involved using a 5 % solution of nitric acid. The starting materials were placed into a reactor, where a permanent stirring of the components was carried out for a preset time, the ratio between the liquid and solid phases was equal to 5 : 1, the process temperature amounting to 25 °C. Further, the manganese carbonate precipitate was filtered using a vacuum filter, washed with distilled water and dried in a drying oven. In this case, the manganese loss amounted to 5–6 %.

Thus, preliminary purifying the manganese carbonate with the nitric acid solution at a room temperature and at a ratio between the phases L/S = 5 : 1 seems to be a very efficient way. So, in the case of acetic acid solution, the level of purification from calcium and chlorine ions is equal to 68 and 9 %, respectively, whereas in the case of using nitric acid solution the mentioned value amounts to 73 and 94 %, respectively.

The optimal parameters revealed for the process of initial feedstock leaching allowed increasing the level of purification from the associated calcium and chlorine impurities up to 73–94 %. Rinsing solutions containing manganese nitrate, further should be directed toward the processing in order to obtain crystalline manganese nitrate.

From the analysis of the total composition of the high purity manganese acetate tetrahydrate (see Table 3) obtained by means of the technology presented, one could conclude that the product obtained meets the standards of the Merck Co. (Germany).

## CONCLUSION

As a result of the studies performed a low-waste technology was developed for obtaining high purity manganese acetate hydrate crystals which comprises the following stages: leaching the initial feedstock by the solution of

HNO<sub>3</sub>; dissolving the purified manganese carbonate in acetic acid, the precipitation of heavy metal impurities from the solution, followed by filtration, the evaporation of the purified solution to obtain a preset concentration; controlled crystallization of Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O; the precipitate maturation and the desorption of impurities from the crystallizate; filtering the crystalline product. The yield of manganese into the final product with the use of the technology developed should equal to about 80–85 %.

The developed variant of the low-waste technology could be recommended for industrial application. It allows replacing expensive imported raw materials by cheaper poor quality raw materials at the minimum cost of purification to produce a high-quality end product that meets the requirements of international standards.

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