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TECHNOLOGY OF ORGANIC
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Technology of Magnesium Hexafluorosilicate Production

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Abstract—Systematic study of parameters of the techological process for producing crystalline magnesium hexafluorosilicate from hexafluorosilic acid and caustic magnesite: reagents concentrations and ratio, temperature of the synthesis and evaporation, order of pouring the reagents (caustic magnesite suspension and hexafluorosilic acid), intensity of the solution stiring at its crystallization. Optimal values providing maximal yield of the targeted product are elucidated.

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Currently in the Republic Belarus' increased demand on the magnesium hexafluorosilicate, the main component for producing the impregnating compositions for the increase endurance limit of concrete and ferroconcrete constructions. However, in the countries of former Soviet Union including Republic Belarus' this product did not produce on the industrial scale. The current demand is covered by import from USA, Germany, Italy and other countries.

Reviewing published sources and patent data showed that in distinct to other fluorine-containing salts the bivalent metal hexafluorosilicates, those of magnesium, calcium and zinc in particular, are the poorly studied compounds. Publications [1–8] are not complete and often contradict one another, up to now there is no general opinion concerning optimal technological parameters for producing the bivalent metal hexafluorosilicates. Therefore the aim of this research is development of technological process for producing magnesium hexafluorosilicate from crude raw material.

In this study we used hexafluorosilic acid of the company "Gomel' Chemical Plant", the side product of the production of extractive phosphoric acid. The authors [1–5] have used for the synthesis of magnesium hexafluorosilicate the hexafluorosilic acid of 8–15 wt % concentration; the solution obtained then should be evaporated for isolation of $MgSiF_6 \cdot 6H_2O$. In this sense, it would be preferable to use concentrated acid (up to 33 wt % H_2SiF_6) [6], to obtain in the process of the synthesis a suspension of magnesium hexafluorosilicate in its saturated solution. However, in the "Gomel' Chemical Plant" at the producing extractive phosphoric acid, in the process of absorption of fluorine gases with water is formed hexafluorosilic acid with concentration 12–14 wt%. It is technologically difficult to increase its concentration, because it would lead to sharp increase in aggressive action on the material of evaporating unit. Therefore in the study we used hexafluorosilic acid of 14% concentartion. As a neutralizing agent was used caustic magnesit PMK-75 (State standard GOST 1216-87) with the composition, wt%: MgO 75–80, CaO 2.5–3.0, SiO_2 2.0–2.5.

For the development of the magnesium hexafluorosilicate regime of synthesis the following technological parameters were varied: concentration of each reagent and their ratio, temperature of the synthesis and evaporation of solution, order of pouring the reagent, caustic magnesite and solution of hexafluorosilic acid, intensity of stirring the solution in the process of crystallization.

For the synthesis of magnesium hexafluorosilicate we used a three-neck flask placed into a thermostate unit, to provide stability of chosen temperature. The following order of operations was applied: To the reaction vessel was loaded given precalculated amount of hexafluorosilc acid taken with excess against stoichometry. At the permanent stirring to the acid was poured caustic magnesit in one portion. The suspension obtained was filtered and the filtrate was evaporated on a water bath. The crystalline product obtained was dried in a drier to constant weight.

For identification of the targeted product were applied chemical method (complexometry) and X-ray phase analysis (difractometer DRON-3 with CuK illumination) and IR spectroscopy (SPECORD-751R).

In the first step we studied effect of the order of pouring the initial reagent on the yield of magnesium hexafruorosilicate. The synthesis temperature was maintained at 50°C, hexafluorosilic acid concentration 14 wt%, its excess 2 wt% over stoiciometry. The magnesit suspension concentration was varied. This reagent was loaded to the reactor in one portion. The results obtained are shown in Table 1. As seen, at the same other parameters of the synthesis the order of pouring when hexafluorosilic acid is added to the suspension of caustic magnesit in the most cases leads to decrease in the yield of $MgSiF_6 \cdot 6H_2O$. This obviously is connected with two-step formation of magnesium hexafluorosilicate: In the initial step the solution is oversaturated with Mg^{2+} ions relatively to SiF_6^{2-} resulted in formation of magnesium fluoride [9]. In the further process the solution is oversaturated with SiF_6^{2-} ions leading to dissolution of magnesium fluoride and formation of magnesium hexafluorosilicate. However, up to 4% of magnesium fluoride remains in the precipitate, which leads to decrease in the yield of crystalline magnesium hexafluorosilicate and its contamination with the products of the synthesis. At the alternative order of pouring, the magnesium hexafluorosilicate is formed in one step alongside the reaction:

$$MgO + H_2SiF_6 = MgSiF_6 + H_2O \qquad (1)$$

Reverse order of pouring reagents, namely, adding of caustic magnesit suspension to the solution of the acid restrict its homogenous dozing. Therefore further research on the regime of synthesis of magnesium hexafluorosilicate was carried out at mixing initial components by adding caustic magnesit as a powder to the solution of hexafluorosilic acid, to provide maximum yield of the targeted product and simplify the technological process by excluding the step of preparation of water suspension of caustic magnesit.

The next step of research was denoted to the problem of effect of the reagents ratio on the yield of the final product. For this purpose was varied the hexafluorosilic acid excess relatively to stochiometric amount from 0 to 14 wt%.

The dependence of magnesium hexafluorosilicate yield on the excess of hexafluorosilic acid over stoichiometry is shown in Table 2

It is seen that increase in the acid excess to 7–10 wt% leads to increase in the yield. This can be explained by decrease of magnesium hexafluorosilicate solubility in the $MgSiF_6 \cdot H_2SiF_6 \cdot H_2O$ system at the increase of free hexafluorosilic acid content in the mother liqueur [6] affecting positively the yield of $MgSiF_6 \cdot 6H_2O$.

Excess of hexafluorosilic acid over 10 wt% does not affect significantly the magnesium hexafluorosilicate yield. On the basis of the data obtained on the influence of reaction product yield on the ratio of the components we conclude that hexafluorosilic acid excess should be applied, because this leads, all other conditions are the same, to more complete proceeding of the reaction and practical absence of amorphous silicon oxide in the crystalline reaction product.

Table 1. Effect of the order of pouring reagents on the yield of magnesium hexafluorosilicate

Magnesite suspension concentration, wt%	Magnesium hehafluorosilicate yeld depending on the pouring order, wt%	
	direct hexafluorosilic acid to caustic magnesite suspension	reverse suspension of caustic magnesite to hehafluorosilic acid
5	93.6	97.0
10	95.5	97.4
20	96.9	98.1

Table 2. Effect of technological parameters on the yield of magnesium hexafluorosilicate

Excess of hexafluorosilic acid over stoichiometry, wt%	Magnesium hexafluorosilicate yield(%) at the temperature of synthesis,°C			
	20	40	60	70
0	92.1	93.8	88.7	87.0
2	92.9	95.5	89.5	87.2
5	92.8	97.2	90.0	87.3
7	93.2	97.9	90.0	87.5
10	93.1	98.1	90.4	87.0
14	93.7	98.0	90.4	88.1

X-ray diffraction analysis of a sample obtained with optimal regime showed that the main phase consists of magnesium hexafluorosilicate, which contains as admixed phase calcium hexafluorosilicate. IR spectrum contans the bands characteristic of both $MgSiF_6 \cdot 6H_2O$ and $CaSiF_6 \cdot 2H_2O$. These obtained experimental data well conform to the published ones [10]. According to chemical analysis the product obtained has a composition, wt%: $MgSiF_6 \cdot 6H_2O$ 96–98, $CaSiF_6 \cdot 2H_2O$ 2.0–2.5, other is admixture of amorphous silica. The content of main product obtained experimentally well conform to the calculated value.

At the study of the effect of temperature on the yield of magnesium hexafluorosilicate crystals we varied the temperature in the range from 20 to 70°C. At the temperature above 70°C the synthesis was not performed due to beginning of hydrolysis of magnesium hexafluorosilicate leading to formation of magnesium fluoride and silic acid [1, 2].

As seen from thr data in Table 2, increase in temperature of reaction mixture to 30-40°C while all other parameters remain unchanged leads to increase in nagnesium hexafluorosilicate yield, while at further increase in temperature occurs the yield falls down. The temperature factor in the range is known important at the synthesis of well soluble substances because rate of formation is proportional to $e^{-1/T}$, while the rate of formation of poorly soluble substances is proportional to e^{-T} [11]. From the x-ray diffraction data of the sample obtained at 30°C is seen that the main phase is magnesium hexafluorosilicate, and the admixed phase is calcium hexafluorosilicate.

At further increase in temperature to 50°C and over despite the decrease in viscosity and diminished deceleration at the penetration of acid into the magnesit particles the yield of magnesium hexafluorosilicate falls. It is explainable by hydrolytic decomposition of magnesium hexafluorosilicate at the temperature above 50°C with formation of amorphous silicon oxide and magnesium fluoride, the latter is registered by x-ray diffraction. Besides, the SiF_6^{2-} ions existing in the solution are also unstable and inclined to hydrolysis alongside the reaction equation: $SiF_6^{2-} + 2H_2O \rightarrow SiO_2 + 4H^+ + 6F^-$. Our experimental data correlate with data in [10].

Thus, the optimal temperature for the synthesis of magnesium mhexafluorosilicate falls to the range 30–40°C, which provides maximum yield of the product (up to 98 wt%), all other conditions are the same.

In respect of isolation crystalline magnesium hehafluorosilicate from its solution, we studied effect of the crystallization temperature on the yield. The magnesium hexafluorosilicate solubility changes by ~10% only when the slution temperature is varied in the range from 0°C to 60°C, therefore crystallization under cooling in this case is not effective. Therefore over-saturation in the system was created by partial removing the solvent by evaporqation.

As noted above, at the temperature over 50°C magnesium hexafluorosilicate exerts hydrolytic decomposition, therefore for its isolation in crystalline form the process of evaporation was carried out at the lower temperature. While studying the effect of evaporation temperature on the yield of magnesium hexafluorosoilicate crystals the temperature was varied in the range from 20°C to 50°C (see Fig. 1).

As seen, increase in the temperature affords crystalline magnesium hexafluorosilicate in higher yield. It can be assumed that at higher temperature the rate of formation of the crystal nuclei grows not only due to diminishing of their critical size but also because the ions are less hydrated and their joining into the nucleus is easier. Besides, at the elevated temperature falls the surface tension on the board between the solution and forming

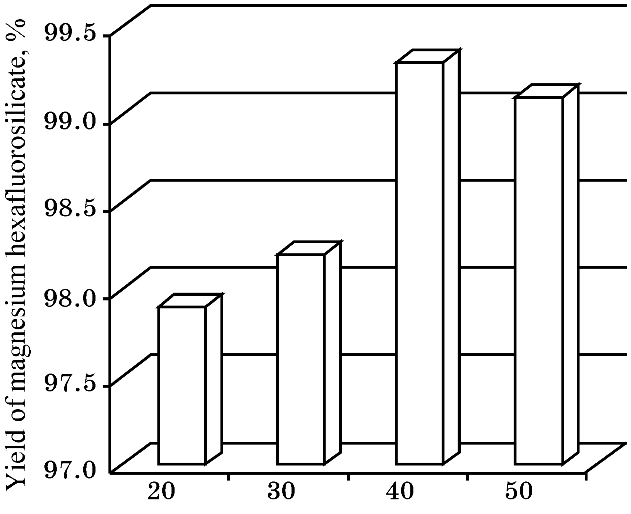

Fig. 1. Dependence of the yield of crystalline magnesium hexafluorosilicate on the temperature of evaporation of its solution.

Table 3. Dependence of magnesium hexafluorosilicate crystals size on the excess over stoichiomettry of water and evaporation temperature

Excess of hexafluorosilicate acid over stoichiomettry, wt%	Size of the crystals $MgSiF_6 \cdot 6H_2O$ at evaporation temperature, °C			
	20	30	40	50
5	2.4	2.4	2.3	1.9
7	2.5	2.6	2.5	1.9
10	3.8	3.8	3.6	2.1
14	3.7	3.8	3.7	2.2

nucleus and hence degreases the work function of their formation 11].

In the process of the experiment was found that not only the yield, but also the size of the $MgSiF_6 \cdot 6H_2O$ crystals grows with increase in the temperature (Table 3).

Obviously crystallization in the region of higher temperatures promotes increase in the size of crystals of the targeted product. This fact can probably be explained by decrease in the hydration of ions thus making much easier their transfer from the structurized in a certain degree laminar layer of the solution on the crystal surface to the crystal lattice, thus promoting faster grow of the crystals. A certain role probably plays also decrease in the solution viscosity, thus diffusion of the substance to the growing crystal edges accelerates.

As seen from Table 3, the crystal size depends substantially on the presence in the solution of hexafluorosilic acid excess. Studying the effect of silic acid excess in the system on the size of depositing crystals of magnesium hexafluorosilicate we found that decrease in the hexafluorosilic acid concentration leads to decrease in the average size of the crystals $MgSiF_6 \cdot 6H_2O$. This can be explained as follows. On one side, the magnesium hexafluorosilicate hexahydrate solubility falls with increase in hexafluorosilic acid content in the solution, that is, the solution becomes oversaturated by SiF_6^{2-} ions relatively to the ions of Mg^{2+}. Thus, when oversaturation of the solution increases, also increases concentration of submicro nuclei and becomes easier their joining together. On the other hand, the rate of appearance of the nuclei also grows, but not all them form further a crystal. Some of them join together or combine with a macrocrystal accelerating grow of the latter. By this

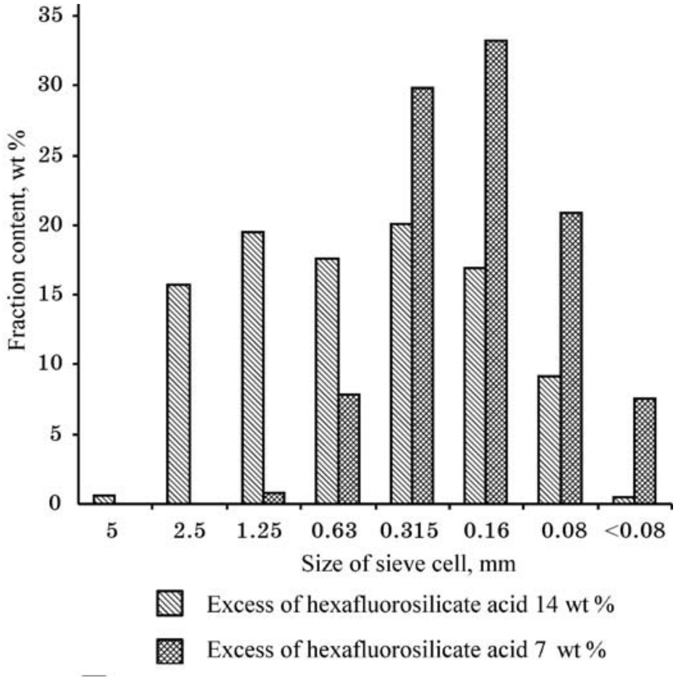

Fig. 2. Size distribution of magnesium hexafluorosilicate particles.

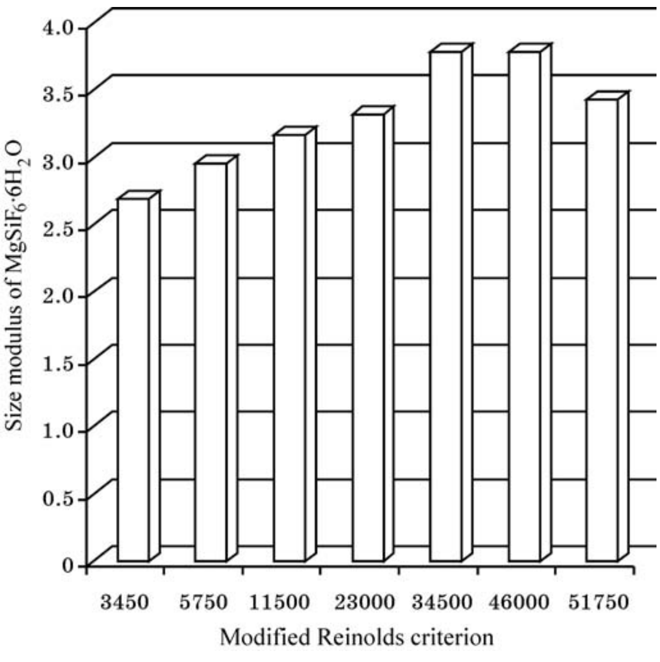

Fig. 3. Influence of hydrodynamic situation in the reaction vessel on the size modulus of $MgSiF_6 \cdot 6H_2O$ crystals.

reason, the higher oversaturating due to higher evaporation temperature and presence of hexafluorosilic acid excess, the less a number of appearing nuclei that then form separate crystals. The increase in crystal size with increase in oversaturation in a system at the sedimentation of soluble salt has been noted in literature [11, 12].

At the applied oversaturations while other synthesis parameters remains the same (synthesis temperature 30–40°C, hexafluorosilic acid concentration 14 %, excess of hexafluorosilic acid over stoichiometry 10 %, evaporation temperature 40°C) the magnesium hexafluorosilicate crystals precipitate with the size modulus in the range 3.6 to 3.8.

The precipitates obtained are polydisperse ones, due to non-simultaneous formation of critical nuclei and difference in the rate of grow of small and large particles [13]. Fig. 2 shows a histogram of distribution of magnesium hexafluorosilicate particles by the size.

As seen from the histogram, crystalline magnesium hexafluorosilicate consists of the particles with the size within a certain range of dispersion. Decrease in the excess of hexafluorosilic acid in the system leads to narrowing of this range and shifting it to the side of formation of the finely divided crystalline product.

Among the many factors affecting the rate of crystals growing in the mother liqueur, a significant one is intensity of supplying of the "building material" to the growing crystal edges. The growing of crystals is known depending in a great extent on the concentration fluctuations appearing in the process of stirring or sometimes due to changes in density in the reaction process or due to changes in temperature due to the exothermic reaction. Direction and intensity of the concentration fluctuations affect the rate of the crystal growing. Therefore it is significant to study effect of the intensity of stirring at the evaporation the magnesium hexafluorosilicate on its crystallochemical parameters..

For the description of the stirring process we used the modified Reynolds criterion (Re_M) [14, 15]. In the investigation we varied rotation frequency of the propeller-type agitator in the range from 30 rpm (Re_M = 3450) to 450 rpm (Re_M = 51750). Diminishing in the rotation frequency below 30 rpm ($Re_M < 3450$) leads to restrictions in stirring the crystalline magnesium hexafluorosilicate suspension in its saturated solution and the process is not homogenous.

Influence of hydrodynamic situation in the reaction vessel on the size of the formed crystals of magnesium hexafluorosilicate is shown in Fig. 3. It is seen that increase in modified Reynolds criterion from 3450 (rotation frequency 30 rpm) to 34500 (rotation frequency 300 rpm), all other conditions of the synthesis and evaporation are the same, leads to increase in average size of $MgSiF_6 \cdot 6H_2O$ crystals. But further increase in the rotation rate either leads to some decrease in the average size, or does not affect the crystals size.

Thus, from the data obtained we can conclude that increase in the intensity of stirring of the solution at its evaporation to a certain value (Re_M = 34500) makes easier access of "building material" to the face of growing crystal and the rate of the crystal growing increases resulting in the increase of its average sizes. However, at the increase in the modified Reynolds criterion above this value the rate of dissolving of surface layers of the growing crystal becomes higher than the positive effect of acceleration of diffuse supply of the substance and the rate of crystal growing falls [11]. Besides, there is an opinion [12] that under such conditions of crystallization can occur acceleration in the growing of big crystals and deceleration in the growing of the crystals of small size. This all leads to decrease in the average size of the magnesium hexafluorosilicate crystals at the increase in modified Reynolds criterion over 34500. Therefore we accept this intensity of stirring the solution at its evaporation as the optimal.

On the basis of this research we optimized regime of the sybthesis of magnesium hexafluorosilicate from caustic magnesit and hexafluorosilic acid. We established that the optimal parameters are: hexafluorosilic acid concentration 14 wt%, excess of hexafluorosilic acid over stoichoiometric amount is 7–10 wt%; temperature of the synthesis 35–45°C; temperature of evaporation 40–50°C [16].

These optimized conditions of the synthesis are taken as a basis for the technology of industrial scale producing magnesium hexafluorosilicate hexahydrate (Fig. 4).

The developed technological regime of the synthesis of magnesium hecxafluorosilicate allowed to produce this material with the quality some as imported analogs. Experimental bathes produced in the plant "Gomel' Chemical Plant" showed a possibility of organization of industrial producing of magnesium hexafluorosilicate.

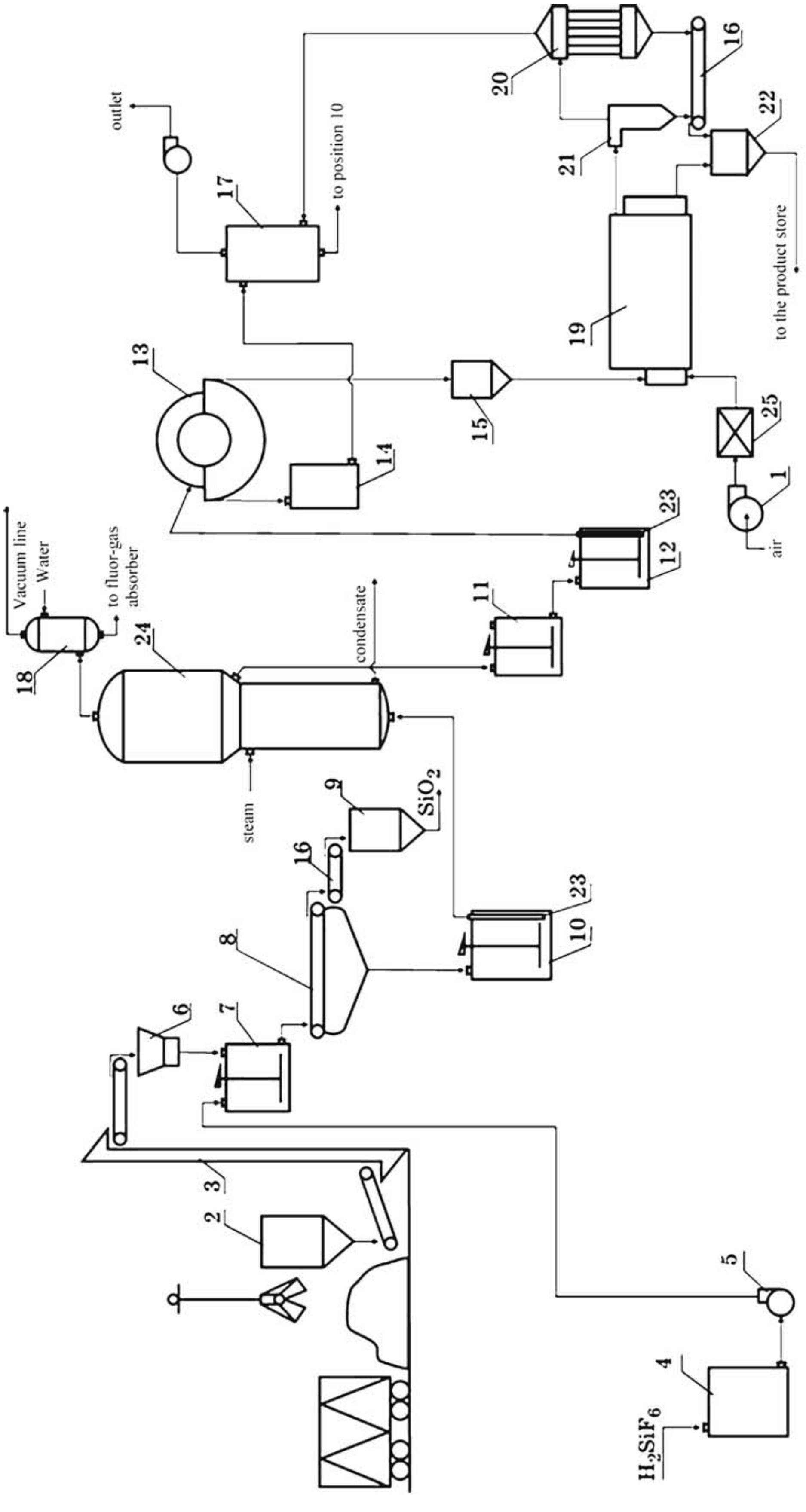

Fig. 4. Influence of hydrodynamic situation in the reaction vessel on the size modulus of $MgSiF_6 \cdot 6H_2O$ crystals. (1) blower, (2) receiver for caustic magnesite, (3) elevator, (4) receiver for hehafluorosilic acid, (5) pump, (6) weight dosing unit, (7) reactor, (8) tape vacuum filter, (9) receiver for silicate gel, (10, 12) intermediate receivers, (11) crystallizer, (13) drum vacuum filter (14) collector for mover liquor, (15) receiver, (16) conveyer, (17) absorber, (18) barometric condenser, (19) drier, (20) electric filter, (21) cyclone, (22) buncer for final product, (23) immersion pump, (24) evaporator, (25) heater. .

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