The effect of coagulation on the processes of growth and changes in the numerical concentration of carbon dioxide crystals

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Abstract. The process of phase transition to the solid state of carbon dioxide vapors contained in an expanding gas mixture stream consists of the formation of crystallization centers and subsequent growth of the crystals formed, due to an increase in the degree of supercooling of the stream. Crystals nucleate in certain sections of the flow part of the expanders and grow as they move in the flow. Therefore, crystals of carbon dioxide of various sizes can be found in each of certain sections. As a result of their interaction, coagulation, expressed as the adhesion of smaller crystals to larger ones, can occur. The influence of the coagulation process on the change in the number of smaller crystals and on the growth of larger ones is considered. Equations are given on the basis of which the calculations of the studied processes are made.

1. Introduction
A mathematical model of the process of formation of carbon dioxide crystals in the volume of an expanding gas stream [1] allows determining, among other things, the numerical concentration of the formed carbon dioxide nucleus crystals and their size, as well as the size of crystals growing as the flow moves along the flow part of the expansion device [2]. Although this model is designed to evaluate the quantitative and dispersed composition of crystalline carbon dioxide, it does not take into account coagulation, i.e. adhesion of one crystal to another as a result of their collision with each other [3]. In the above-mentioned research works, it was shown that in the presence of particles of various sizes in the stream, collisions and coalescence of these particles occur due to differences in their velocities. Two methods for calculating coagulation are presented: the Euler method (coagulation of predetermined fractions) and the Lagrange method (coagulation of individual particles).

For the stated problem, we apply the Euler method. Carbon dioxide crystals formed and growing in an expanding flow have a size of less than 1 μm [4], therefore, they can be attributed to the class of highly dispersed aerosols [5]. Such aerosols display coagulation due to the Brownian motion of particles, i.e. thermal coagulation. The calculation of coagulation by the Euler method involves
the one-dimensional motion of all particles, which, when they collide, necessarily stick together [6]. Based on this method, one should solve the problem of creating a mathematical apparatus for describing the process of coagulation of carbon dioxide crystals and verify the practical effect of coagulation on the numerical concentration of crystals and their size growth.

2. Results and discussion

**Coagulation of carbon dioxide crystals.** In each of the subsequent sections of the flowing part of the expansion device (expander), there may be several groups of carbon dioxide crystals having different sizes. These are both embryonic crystals formed in this section and crystals formed in the previous section and grown in this section, as well as crystals formed and grown in previous sections. Since the equilibrium shape of the carbon dioxide crystal is a cube, it is assumed that the crystals growing both by increasing the degree of supercooling of the flow and by coagulation will have a cubic shape.

If we consider a crystal that moves relative to other motionless crystals of the same size, then its contact with the motionless crystals will occur when the distance between the centers of these crystals is equal to \(a\) (\(a\) is the size of the face of the cubic crystal). The center of the moving crystal, each side face of which (relative to the direction of movement) touched the motionless crystals, will be in the center of the parallelepiped with a base area of \(4a^2\) (square area with side \(2a\)). The volume of such a parallelepiped per time unit can be expressed as

\[ V = 4a^2 \cdot c_c, \]

where \(c_c = \sqrt{3kT/m_c} - \) average value of the relative velocity of Brownian motion of crystals in a moving stream [7];

- \(k\) – Boltzmann constant;
- \(T\) – flow temperature;
- \(m_c\) – crystal mass.

Number of contacts

\[ Z = V \cdot N, \]

where \(N\) is a number of crystals per volume unit.

Considering that all crystals in the flow move with an average speed \(\bar{v}_c\), the average speed of motion relative to other crystals should be used

\[ \bar{v}_{reg} = \bar{v}_c \cdot \sqrt{Z}. \]

In order to reduce the recording of patterns of the coagulation process, we introduce the coagulation constant

\[ K = 4a^2 \cdot \bar{v}_c \cdot \sqrt{Z}. \]

In each contact, two crystals participate. In order not to take into account one contact twice, the actual coagulation constant must be reduced by half

\[ K_r = \frac{K}{2} = 2a^2 \cdot \bar{v}_c \cdot \sqrt{Z}. \]

Then, the number of contacts per time unit

\[ Z_r = 2a^2 \cdot \bar{v}_c \cdot \sqrt{Z} \cdot N = K_r \cdot N. \]

If we multiply the number of crystals per volume unit by the number of contacts per time unit, we obtain the number of crystals, which decreased as a result of the coagulation process in a volume unit per unit time

\[ \frac{dN}{dt} = -N \cdot Z_r = -K_r \cdot N^2. \]
Let us turn to the real picture of the formation of carbon dioxide in the flow part of the expander, when in the same section there are several groups of crystals of different sizes (with different facet sizes \(a\)). In this case, the growth of larger crystals can occur due to coagulation with smaller crystals, the number of which will decrease (up to the disappearance of whole groups of crystals).

We denote the size of small and large crystals as \(a_s\) and \(a_l\), respectively. A small moving crystal comes into contact with large motionless (as an assumption) crystals within a parallelepiped with a volume per time unit

\[ V = (a_s + a_l)^2 \cdot \bar{c}_{s}. \]

Given the speed of large crystals, it is possible to calculate the average Brownian motion velocity of crystals of various sizes

\[ \bar{c}_{avg} = (\bar{c}_s + \bar{c}_l)/2 \]

The actual coagulation constant can be represented as

\[ K_r = (a_s + a_l)^2 \cdot \frac{\bar{c}_{avg}}{2} \]

The number of contacts of small crystals with large crystals (the number of small crystals whose centers lie inside the box) per time unit

\[ Z_r = K_r \cdot N_s. \]

Multiplying the number of large crystals per volume unit by the number of collisions of small crystals with them per time unit, we obtain the number of small crystals that disappear during coagulation with large crystals in volume unit per time unit

\[ \frac{dN_s}{dt} = -N_l \cdot Z_r = -K_r \cdot N_s \cdot N_l. \] (1)

**Conditions for the implementation of the process of coagulation of carbon dioxide crystals.** Two consequences can be considered the result of coagulation: a reduction in the number of small crystals (or their complete disappearance) and growth of large crystals due to this. If we talk about small crystals, then coagulation can be considered significant when the number of vanishing small crystals \(dN_s\) is comparable with their number \(N_s\). When the number of \(dN_s\) is several orders less than the number of \(N_s\), then this group of small crystals will not significantly decrease.

It should be noted that in the flow part of the expander, nucleating crystals are formed with a cube facet size \(a\) equal to 3 \(a_m\) and 2 \(a_m\) (\(a_m\) is the parameter of a molecular crystal of carbon dioxide) [4]. The number of crystals per volume unit formed in different sections of the flowing part varies from \(1 \cdot 10^4\) (crystals with the parameter \(a = 3 \ a_m\)) to \(1 \cdot 10^{18}\) (crystals with the parameter \(a = 2a_m\)). This group of formed crystals will always be smaller in size than the groups of already grown crystals that appeared earlier; therefore, the number of such crystals per unit volume can be denoted as \(N_c\).

Now let us trace the growth of larger crystals due to the addition of small crystals to them. We will consider the growth of a cubic crystal with parameter \(a\). It is assumed that the crystal grown as a result of coagulation will also have a cubic shape (equilibrium with the gas phase). Then a crystal with parameter 2\(a\) will consist of 8 crystals with parameter \(a\) (other 7 of the same crystals should join the crystal with parameter \(a\)), a crystal with parameter 3\(a\) will consist of 27 crystals, etc. If we denote the parameter of the grown crystal \(na\), where \(n\) is a positive integer larger than 1, then the number of crystals with the parameter \(a\), which should join it, can be expressed as \(n^3 - 1\) (coagulation of crystals of the same size).

In fact, the size of the attached crystals will be smaller than \(a\). If the parameter of small crystals is \(f\) times smaller than \(a\), i.e. \(a/f\), then to increase the crystal with parameter \(a\) to size \(na\), it will be necessary to attach small crystals to it in the amount of \((n^3 - 1) \cdot f^3\).
For example, the number of crystals with parameter \(a/2\), which must be attached to the crystal with parameter \(a\) in order to increase it to parameter \(2a\), will be \((2^3 - 1) \cdot 2^3 = 56\).

Given the number of large \(N_l\) crystals, we can calculate the number of small crystals necessary for their growth

\[
dN_s = (n^3 - 1) \cdot f^3 \cdot N_l. \tag{2}
\]

If the value of \(dN_s\) determined by equation (2) is larger than the value of \(dN_s\) expressed from equation (1), then the growth of large crystals as a result of coagulation will not occur.

The results of the calculation of the coagulation process for crystals of carbon dioxide. As an example, carbon dioxide crystals were formed and grown during the expansion of a gas mixture containing 10% CO2 in a centripetal turboexpander from a pressure of 200 kPa to a pressure of 110 kPa [4]. The values of the main parameters of the crystal formation process necessary for calculating coagulation are shown in table 1. Several explanations should be given to this table:

- in section 6 of the flow part of the turboexpander, for the first time a significant number of embryonic crystals appear;
- after section 11, the process of crystal formation and growth is completed;
- the subscript "s" refers to embryonic crystals formed in the considered sections;
- the subscript "\(l1\)" refers to crystals formed in previous sections and grown in the sections under consideration;
- the subscript "\(l2\)" refers to crystals formed two sections before the considered one;
- subscripts "\(l3\)", "\(l4\)", "\(l5\)" refer to crystals formed three, four and five sections before the considered, respectively.

Table 1. Design parameters of carbon dioxide crystals in various sections of the flow part.

| No | Parameters, sizes | Sections |                |                |                |                |                |
|----|-------------------|----------|----------------|----------------|----------------|----------------|----------------|
| 1  | \(a_s\) \(\cdot 10^9, m\) | 1.701    | 1.700          | 1.132          | 1.131          | 1.131          | 1.131          |
| 2  | \(a_{l1}\) \(\cdot 10^9, m\) | –                    | 6.848          | 7.262          | 5.821          | 6.084          | 6.210          |
| 3  | \(a_{l2}\) \(\cdot 10^9, m\) | –                    | –              | 18.620         | 20.360         | 18.282         | 19.233         |
| 4  | \(a_{l3}\) \(\cdot 10^9, m\) | –                    | –              | –              | 38.971         | 43.230         | 40.894         |
| 5  | \(a_{l4}\) \(\cdot 10^9, m\) | –                    | –              | –              | –              | 68.702         | 75.411         |
| 6  | \(a_{l5}\) \(\cdot 10^9, m\) | –                    | –              | –              | –              | –              | 106.404        |
| 7  | \(N_s\) \(1/m^3\) | 2.33 \(\cdot 10^5\) | 0.44 \(\cdot 10^5\) | 4.55 \(\cdot 10^{17}\) | 1.99 \(\cdot 10^{17}\) | 0.79 \(\cdot 10^{17}\) | 0.73 \(\cdot 10^{17}\) |
| 8  | \(N_{l1}\) \(1/m^3\) | –                    | 2.33 \(\cdot 10^5\) | 0.44 \(\cdot 10^5\) | 4.55 \(\cdot 10^{17}\) | 1.99 \(\cdot 10^{17}\) | 0.79 \(\cdot 10^{17}\) |
| 9  | \(N_{l2}\) \(1/m^3\) | –                    | –              | 2.33 \(\cdot 10^5\) | 0.44 \(\cdot 10^5\) | 4.55 \(\cdot 10^{17}\) | 1.99 \(\cdot 10^{17}\) |
| 10 | \(N_{l3}\) \(1/m^3\) | –                    | –              | –              | 2.33 \(\cdot 10^5\) | 0.44 \(\cdot 10^5\) | 4.55 \(\cdot 10^{17}\) |
| 11 | \(N_{l4}\) \(1/m^3\) | –                    | –              | –              | –              | 2.33 \(\cdot 10^5\) | 0.44 \(\cdot 10^5\) |
| 12 | \(N_{l5}\) \(1/m^3\) | –                    | –              | –              | –              | –              | 2.33 \(\cdot 10^5\) |
| 13 | \(m_s\) \(\cdot 10^{24}, kg\) | 7.891      | 7.887          | 2.278          | 2.334          | 2.332          | 2.332          |
| 14 | \(m_{l1}\) \(\cdot 10^{22}, kg\) | –                    | 5.160          | 6.164          | 3.179          | 3.627          | 3.866          |
| 15 | \(m_{l2}\) \(\cdot 10^{20}, kg\) | –                    | –              | 1.038          | 1.360          | 0.986          | 1.148          |
Table 2 shows the calculated indicators of the number of smaller crystals that should disappear as a result of coagulation with larger crystals, the crystals designated as “l1” will be smaller relative to the crystals “l2”, the crystals “l2” will be smaller relative to the crystals “l3”, etc. These indicators should be compared with the number of smaller crystals themselves, presented in table 1.

For example, in section 7, when coagulating with crystals “l1” in a volume unit, 5.12 · 10−10 crystals “s” should disappear, while in this section in a volume unit there are 0.44 · 105 such crystals, t. e. 14 orders more. Therefore, in this section, a significant reduction of smaller crystals as a result of coagulation will not occur. In the same section 7, the number of crystals “s”, which must join the crystals “l1” to increase their parameter a by a factor of two, is determined by equation (2) and amounts to 1.066 · 108 per volume unit, which is more than the number of these crystals themselves (more than three orders), and even more so than the number of small crystals that can be reduced as a result of coagulation (more than 17 orders).

| No | Crystal Groups | Parameters, Sizes | Sections |
|----|----------------|-------------------|----------|
| 1  | s – l1         | $\Delta N_s / \Delta \tau \cdot \frac{1}{m^3 \cdot s}$ | 7 | 8 | 9 | 10 | 11 |
|    |                | 6.20 · 10−06 | 2.01 · 10−7 | 6.28 · 10−09 | 1.16 · 10−19 | 4.40 · 10−18 |
|    |                | $\Delta N_v / m^3$ | 5.12 · 10−10 | 1.76 · 10−4 | 5.92 · 10−15 | 1.18 · 10−15 | 5.05 · 10−14 |
| 2  | s – l2         | $\Delta N_s / \Delta \tau \cdot \frac{1}{m^3 \cdot s}$ |  – | 5.58 · 10−8 | 5.46 · 10−7 | 1.81 · 10−20 | 3.18 · 10−19 |
|    |                | $\Delta N_v / m^3$ |  – | 4.91 · 10−4 | 5.15 · 10−3 | 1.85 · 10−16 | 3.66 · 10−15 |
| 3  | s – l3         | $\Delta N_s / \Delta \tau \cdot \frac{1}{m^3 \cdot s}$ |  – |  – | 9.90 · 10−6 | 9.10 · 10−7 | 7.73 · 10−20 |
|    |                | $\Delta N_v / m^3$ |  – |  – | 9.34 · 10−4 | 9.28 · 10−3 | 8.88 · 10−16 |
|   |   |   | $\Delta N_s / \Delta \tau$, $1 \text{m}^3 \cdot s$ | $\Delta N_{\omega}$, $1 \text{m}^3$ |
|---|---|---|---|---|
| 4 | $s - l4$ |   |   |   |
|   |   |   |   |   |
| 5 | $s - l5$ |   |   |   |
|   |   |   |   |   |
| 6 | $l1 - l2$ |   |   |   |
|   |   |   |   |   |
| 7 | $l1 - l3$ |   |   |   |
|   |   |   |   |   |
| 8 | $l1 - l4$ |   |   |   |
|   |   |   |   |   |
| 9 | $l1 - l5$ |   |   |   |
|   |   |   |   |   |
| 10 | $l2 - l3$ |   |   |   |
|   |   |   |   |   |
| 11 | $l2 - l4$ |   |   |   |
|   |   |   |   |   |
| 12 | $l2 - l5$ |   |   |   |
|   |   |   |   |   |
| 13 | $l3 - l4$ |   |   |   |
|   |   |   |   |   |
| 14 | $l3 - l5$ |   |   |   |
|   |   |   |   |   |
3. Conclusion

Based on the calculation results of the coagulation process of carbon dioxide crystals formed during the expansion of the gas mixture with the initial parameters: pressure 200 kPa and a concentration of carbon dioxide of 10%, the following conclusions can be drawn.

The most significant possible reduction of smaller crystals will occur in section 10 during the interaction of the “s – l2” crystal groups, where $1.85 \cdot 10^{16}$ can disappear from the total number (per volume unit) of “s” crystals equal to $7.9 \cdot 10^{16}$, that is 23%.

But to increase at least 2 times the size a of crystals “l2”, the number of crystals “s” (per unit volume) equal to $1.35 \cdot 10^{22}$, which is almost 6 orders larger than their number in this section, will be required. Therefore, even this interaction of groups of crystals will not lead to the growth of larger crystals. It can be assumed that the number of crystals “s” that is capable of coagulation with crystals “l2”, but which is not enough to increase the size of crystals “l2”, will participate in the formation of crystals “l1” in the following section (along with other crystals “s” in the considered section).

In all the indicated sections of the flow part, the interaction of all groups of crystals will not lead to the growth of larger crystals due to the addition of smaller crystals to them, and the number of small crystals capable of coagulation is insignificant.

Further studies will be devoted to calculations of the process of coagulation of carbon dioxide crystals formed during the expansion of gas mixtures with different initial parameters and in other expansion machines, which will allow evaluating the effect of coagulation under conditions of different rates of crystal formation and growth.

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