FRACTAL INTERPRETATION OF ULTRASONIC CRYSTALLIZATION OF SOLUTIONS

KATZ Valery, MAZOR Gedalya

SCE - Shamoon College of Engineering, Beer-Sheva, Israel, valery@sce.ac.il

Abstract

Experiments were performed on the crystallization of a $CuSO_4$ solution upon the action of the temperature gradient with the forming of mono crystals three wedges crystal system (prisms). We found that the fractal dimension of crystals equals 2.45, which is consistent with the literature data. Crystal growth is represented as the N -rd translation of each side of the crystal lattice with its own speed and with relation to the formation of similar structures - fractals. A mathematical model of ultrasonic crystallization of a $CuSO_4$ solution was proposed. The model is based on the combined use of differential transport equations of momentum, mass, energy and sound waves and a method of similarity and dimensional analysis. The calculated formulas for the concentration of - C_{cr}, the equivalent diameter of the formed crystals - d_{cr} and the intensity of internal energy source - Φ_* ,associated with the interaction of crystals with the hydro mechanical, heat and sound fields were obtained. Fractal interpretation of ultrasonic crystallization of the $CuSO_4$ solution was made. It was found that on the growth of crystal size - d_{cr} directly affects translation - N, i.e., an increase in the number of sets of crystals of infinitely small size ε, corresponds to the size of the crystal lattice. In turn translation of crystals depends on the geometry of the crystallizer and the physical parameters of external force fields, acting on the $CuSO_4$ solution. A connection of results of the mathematical modeling with the results of fractal analysis of the ultrasonic crystallization of solutions was established.

Keywords: Ultrasonic crystallization of solutions, physical and mathematical simulation, fractal interpretation

1. INTRODUCTION

This paper is a continuation of research problems of ultrasonic crystallization of solutions that were discussed in [1, 2]. In these papers is proposed the ultrasonic crystallizer of the $CuSO_4$ solution, based on the creation of the crystallization front with a gradient of temperature and the exposure of ultrasonic waves using magnetostrictive transducers (**Fig. 1**).

It is noted that in the super cooled or saturated solution a new phase is nucleated: crystallization centers (nuclei) are formed, which are converted into crystals and grow, as a rule, with changing the form, content of impurities and defects. The number of nucleation depends on the cooling rate of the solution: the higher the cooling rate, the more crystal nuclei are formed in the solution while the size of the newly formed crystals will be smaller. The intensity of the nucleation is studied on the basis of the molecular-kinetic theory and is described in general terms in [3]. In recent work on modeling [4] crystallization centers are seen as clusters - conglomerates of molecules. Crystal growth does not occur gradually as a result of deposits on the faces of individual molecules, but rather abruptly, due to the accession of the individual blocks of approximately (10^{-9} ÷ 10^{-5}) m. This causes a change of crystallographic axes in the individual micro blocks on a few minutes and even degrees of arc. Polyhedral crystals, which are irregularly shaped crystals (called crystallites), are formed with rounded crystals-granules (grains) and crystals branching structure (dendrites). The crystallization process of solutions is modeled as a diffusion of accidentally stray particles to the surface of the clusters and this process generates the fractal structures. In this case the clusters are regarded as fractals, that is the complete set of particles (molecules) and these clusters have the property of similarity (any part of a fractal is similar to the whole set).The three-dimensional diffusion is concluded to have the fractal dimension, that is equal to $D \approx 2.5$. In this case the fractal dimension D is defined by formula [5]:

$D = \lg(N)/\lg(\varepsilon^{-1})$, where N - is an increase in the number of sets of objects of infinitely small linear size ε, similar to the nuclei. All objects that have fractional fractal dimension are called fractals.

Examination of the formation of crystalline fractal structures under the influence of various external force fields has been the subject of a number of recent studies [6-11].

Crystallizers with the ultrasonic exposure on the substance are used for producing homogeneous crystalline products [12]. The use of ultrasound as a means of exposure on the solution is due to the phenomenon of cavitation, i.e. the formation of bubbles in the liquid under the influence of sound waves. Hydraulic shocks caused by bursting of bubbles are successfully applied to dispersing many substances, particularly true during crystallization [1, 2]. Typical areas of ultrasound application are intensification of hydro mechanical and heat-mass transfer processes in an ultrasonic field, e.g. by emulsification, dispersing, homogenization and crystallization of complex poly disperse systems (dispersions), which are accompanied by fluctuations of basic physical parameters. Therefore, the calculation of technological parameters of such processes must be based on a reasonable combination of physical and mathematical models.

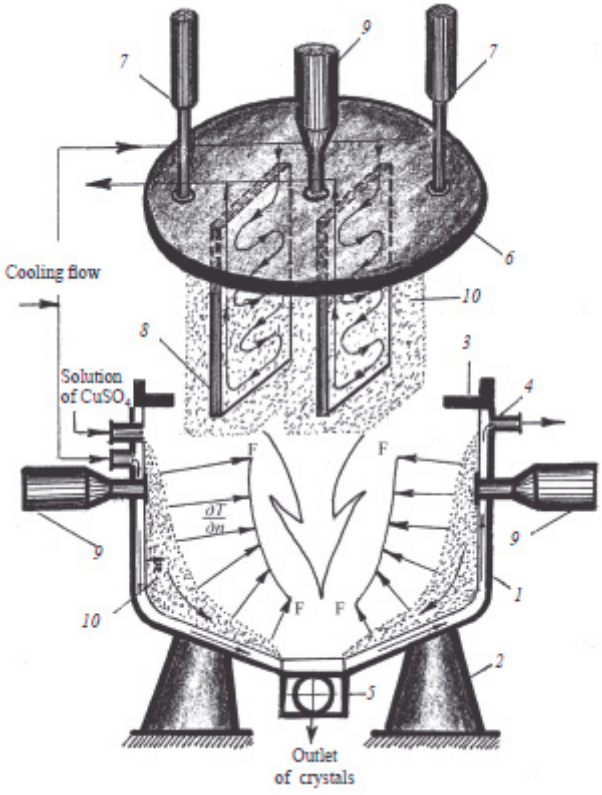

Fig. 1 Crystallizer body with support 2, elastic supports for the installation cover 3 and pipes 4 for inlet and outlet of cooling flow. 5 - outlet valve, 6 - installation cover with hydraulic lift 7, crystallization panels 8 with cooling liquid flow, 9 - magnetostrictive transducers (MST) with ultrasonic waves concentrators. 10 - crystals, F - crystallization front.

Research objectives:

- Physical modeling of crystallization solutions under the influence of the temperature gradient at the crystallization example of $CuSO_4$ solution formed in the separation of copper from tungsten in accordance with the following chemical reaction: $W + Cu + H_2SO_4 + H_2O_2 = CuSO_4 + 2H_2O + W$.
- Fractal interpretation of crystallization of $CuSO_4$ solution under the influence of the temperature gradient.

- Development of a mathematical model of crystallization of solutions under the influence of various external force fields using differential transport equations of substances and the method of similarity and dimensional analysis.
- Fractal interpretation of the results of a mathematical model: linking of equivalent (conditional) theoretical crystal sizes with their real geometrical shapes and sizes through the use of the theory of fractals.

2. PHYSICAL MODELING OF THE CRYSTALLIZATION SOLUTION OF COOPER SULFATE $CuSO_4$ UNDER THE INFLUENCE OF THE TEMPERATURE GRADIENT

2.1. Experimental studies and results

Experimental studies were carried out at "Metal-Tech Ltd.", a chemical plant (Israel). We used a crystallizer with a 1 m^3 volume. The temperature of the solution of $CuSO_4$ was 70 °C and the temperature of the cooling stream (water) was 20 °C (**Fig. 1**). The front of crystallization F has been created due to the temperature gradient between the cold inner surfaces of the crystallizer and the hot solution of $CuSO_4$. The crystallization process lasted 8 hours. The result of experiments conducted inside the crystallizer was the formation of a druze of crystals - a group stuck together mono crystals, directed along the normal to the inner surface of the crystallizer (in the direction of the crystallization front). During splitting the druze is broken into many mono crystals triclinic systems (prisms) bright blue in color with sizes of R = (0.5 ÷ 3) cm in the cross section and (3 ÷ 10) cm in a length.

2.2. Fractal interpretation of the crystallization solution of $CuSO_4$

According to the literature [13], the density of the $CuSO_4$ crystals and the sizes of the crystal lattice correspond to the following values:

$$\rho_{CuSO_4} = 2290\, kg \cdot m^{-3}; \quad \bar{r} = \bar{a} + \bar{b} + \bar{c}; \quad a = 7.15 \cdot 10^{-10} m; \quad b = 10.7 \cdot 10^{-10} m;$$
$$c = 5.97 \cdot 10^{-10} m; \quad \alpha = (\bar{c}, \bar{b}) = 97.7°; \quad \beta = (\bar{a}, \bar{c}) = 125.3°; \quad \gamma = (\bar{a}, \bar{b}) = 94.3°.$$

In [14] the crystal lattice is considered as an elementary prism with angles α, β, γ and sides a, b, c, which are called as translations. Crystal growth is represented as the N-rd translation of each side with its own speed, with the formation of similar structures - fractals. All crystals are objects that have fractal properties. It is noted that there are many fractal generators (programs) that are used to generate fractal images [15].

If we identify the sizes ε of the seed crystals (nuclei) with the sizes r of the crystal lattice ($\varepsilon \approx r$), the number of translations of seed crystals (crystals growth) N and their fractal dimension D will be determined as follows:

$$N = \frac{M_{cr}}{m_{cn}} \approx \left(\frac{\rho_{cr}}{\rho_{cn}}\right) \cdot \left(\frac{R}{\varepsilon}\right)^3, \quad D = \frac{1}{2}\sum_{i=1}^{2} \frac{\lg N_i}{\lg(\varepsilon_i^{-1})}, \tag{1}$$

where M_{cr}, ρ_{cr}, m_{cn}, ρ_{cn} are the mass and density of mono crystals and crystal nuclei respectively; (i = 1) corresponds to a minimum size R for mono crystals and to a maximum size ε for crystal nuclei, (i = 2) corresponds on the contrary: to a maximum size for R and to a minimum size for ε. Assuming that ($\rho_{cr} = \rho_{cn}$), then for the number of translations - N (growth in the number of sets of objects - crystals of infinitely small size ε) we obtain values: $N_1 = 1.02 \cdot 10^{20}$, $N_2 = 4.73 \cdot 10^{24}$, which corresponds to the fractal dimensions D_1 = 2.23, D_2 = 2.675 and the average value D = 2.45. Thus, we can say that the fractal dimension of $CuSO_4$ crystals equals D = 2.45, which is consistent with the conclusion made above that at the three-dimensional diffusion in solutions the fractal dimension is of the order of 2.5 [5]. Numerical analysis of the data showed that in the axial direction (b) (at the front of crystallization), the number of translations (growth of microcrystals) is approximately 2000 times greater than in the axial direction of crystallization (a) and only 6 times greater as compared with

the direction of the axis (*c*). This means that under the influence of the temperature gradient in the absence of other external force fields increases in crystallization (growth of crystals) occurs mainly in the direction normal to the inner surface of the crystallizer. The effect of additional external force fields will lead to a change in shape and properties of the produced crystals.

3. ULTRASONIC CRYSTALLIZATION OF $CuSO_4$ SOLUTION: MATHEMATICAL SIMULATION

In [1, 2] is proposed to work on the hot solution of $CuSO_4$ with the ultrasonic waves that are generated by means of magnetostrictive transducers (MST) (**Fig. 1**). Recommended the following technological characteristics of MST: power of concentrators of ultrasonic waves - (0.3 ÷ 2) kW, oscillation frequency of the ultrasonic waves - (16 ÷ 30) kHz and intensity of sound waves - $(0.1 \div 10)\cdot 10^{-4}$ W·m^{-2}. Calculation of the most important parameters of the process of crystallization solution $CuSO_4$ in this crystallizer is made using a combination of differential equations for momentum, mass, energy, sound waves and a method of similarity and dimensional analysis. Calculation formulas are obtained for the concentration C_{cr}, the equivalent diameter d_{cr} of the resulting crystals of $CuSO_4$ and the intensity of the source of internal specific energy Φ_*, which depends on the interaction of the crystals with hydro-mechanical, thermal and acoustic fields:

$$C_{cr} = C_{cn}\cdot f\left(\frac{\beta\cdot H_a}{\nu},\frac{p+p_s}{\rho\cdot V^2}\right),\quad d_{cr} = \left[\frac{3D_a^2\cdot H_a}{2n\rho_{cr}}\cdot C_{cn}\cdot f_1\left(\frac{\beta\cdot H_a}{\nu},\frac{p+p_s}{\rho\cdot V^2}\right)\right]^{1/3} = \frac{I_s}{\Phi_*\cdot f_2\left(Nu_t,\mathrm{Pr}_t,Eu\right)},$$

$$\Phi_* = \frac{I_s}{\left[\frac{3D_a^2\cdot H_a}{2n\rho_{cr}}\cdot C_{cn}\cdot f_1\left(Nu_D,\mathrm{Pr}_D,Eu\right)\right]^{1/3}\cdot f_2\left(Nu_t,\mathrm{Pr}_t,Eu\right)},\quad I_s = \frac{p_s^2}{2\rho\cdot U}, \tag{2}$$

$$f_1 = \eta_1\left(\frac{\beta\cdot H_a}{\nu}\right)^{b_1}\cdot\left(\frac{p+p_s}{\rho\cdot V^2}\right)^{c_1},\quad f_2 = \eta_2\cdot\frac{\nu}{a_t}\left(\frac{\alpha\cdot H_a}{\lambda}\right)^{b_2}\cdot\left(\frac{p+p_s}{\rho\cdot V^2}\right)^{c_2}$$

Here η_1, η_2, b_1, b_2, c_1, c_2, are the dimensionless coefficients of proportionality and constants which to be determined experimentally. As can be seen from the above formulas the value of the equivalent diameter d_{cr} of the formed crystals of $CuSO_4$ is directly proportional to the intensity of sound waves I_s; it depends on the diffusion, thermal and hydro-mechanical criteria and on the geometrical simplexes involved in the calculations. If in the heat transfer equation (Equation Fourier Kirchhoff) [1] we add additional specific energy sources, which depend, for example, upon radiation, chemical reaction, electromagnetic fields, etc., then in to functional dependence for Φ_* need to add additional criteria that contain appropriate physical parameters.

3.1. Fractal interpretation of ultrasonic crystallization solution of $CuSO_4$

Using the above formula (1) and the expression for d_{cr} (2), gives the fractal relationship between the diameter of formed crystals - d_{cr} and the geometric parameters of the crystallizer and the physical parameters of external force fields acting on the solution of $CuSO_4$:

$$d_{cr}\approx 2R = 2\varepsilon\left[N\left(\frac{\rho_{cn}}{\rho_{cr}}\right)\right]^{1/3} = \frac{I_s}{\Phi_*\cdot f_2(Nu_t,\mathrm{Pr}_t,Eu)} = \left[\frac{3D_a^2\cdot H_a}{2n\rho_{cr}}\cdot C_{cn}\cdot\eta_1\left(\frac{\beta\cdot H_a}{\nu}\right)^{b_1}\cdot\left(\frac{p+p_s}{\rho\cdot V^2}\right)^{c_1}\right]^{1/3} \tag{3}$$

From (3) follows an analytical formula for the number of translations of produced crystals - *N*, i.e., an increase in the number of sets of infinitely small size ε crystals which form a real fractal shape of crystals:

$$N = \eta_N\cdot\left(\frac{C_{cn}\cdot D_a^2\cdot H_a}{\rho_{cn}\cdot n\cdot\varepsilon^3}\right)\cdot\left(\frac{\beta\cdot H_a}{\nu}\right)^{b_1}\cdot\left(\frac{p+p_s}{\rho\cdot V^2}\right)^{c_1},\quad \eta_N = \eta_1\frac{3}{16} \tag{4}$$

4. CONCLUSION

The experiments were performed on a crystallization solution of $CuSO_4$, which was obtained by the separation of copper from tungsten. During crystallization under the influence of a temperature gradient a druze of crystals was formed. During splitting the druze was broken into many mono crystals triclinic systems (prisms) bright blue in color with sizes of R = (0.5 ÷ 3) cm in the cross section and (3 ÷ 10) cm in length.

It was established that the fractal dimension of mono crystals of $CuSO_4$ equals D = 2.45, which is consistent with the literature data. It was also shown, that with three-dimensional diffusion the fractal dimension of the resulting structures was of the order of 2.5. Experimental values of the number of translations N - growth in the number of sets of objects crystals of infinitely small size ε, corresponding to the size of the crystal lattice (the nuclei) were $N \approx (10^{20} \div 10^{24})$. Crystal growth is represented as the N-rd translation of each side of the crystal lattice with its own speed, relative to the formation of similar structures - fractals.

A mathematical model of ultrasonic crystallization of a $CuSO_4$ solution was proposed. The model is based on the combined use of differential transport equations of momentum, mass, energy, sound waves and a method of similarity and dimensional analysis. Calculated formulas for the concentration C_{cr} with an equivalent diameter of the formed crystals d_{cr} and intensity of internal energy source Φ_* associated with the interaction of crystals with the hydro mechanical, heat and sound fields were obtained. As can be seen from the above formulas (2) the value of the equivalent diameter d_{cr} of the formed crystals of $CuSO_4$ is directly proportional to the intensity of sound waves I_s and depends on the diffusion, thermal and hydro-mechanical criteria and the geometrical simplexes involved in the calculations.

The fractal interpretation of ultrasonic crystallization of a $CuSO_4$ solution was made**.** It was found that the growth of crystal size - d_{cr} directly affects translation N that is an increase in the number of sets of crystals of infinitely small size ε, corresponding to the size of the crystal lattice (the size of the crystal nuclei). In turn translation of crystals N depends on the geometry of the crystallizer and the physical parameters of external force fields, acting on the solution of $CuSO_4$ (formulas 3, 4). Thus, a connection of results of mathematical modeling with the results of fractal analysis of ultrasonic crystallization of solutions was established.

There currently remains without a final solution a number of problems, including: problem intensification of ultrasonic fields, using MST; further experimental studies and calculation of hydro-mechanical - V, p, v, heat-mass transfer - C_{cn}, C_{cr}, α, β, a_t, λ, D_{cr}, ρ, ρ_{cr}, ρ_{cn}, ultrasonic - p_s, I_s, U parameters to determine the unknown coefficients in the above equations and for the implementation of the process of ultrasonic crystallization of solutions.

ACKNOWLEDGEMENTS

The authors are grateful to Mr. B.M. Tarakanov, Chief Scientist Enterprise "Metal-Tech Ltd" (Israel) for his help in carrying out experimental studies.

DESIGNATIONS

a_t is thermal diffusivity, ($m^2 \cdot s^{-1}$); C_{cr} is a concentration of the formed crystals, ($kg \cdot m^{-3}$); C_{cn} is a concentration of the formed crystal nuclei, ($kg \cdot m^{-3}$); D_{cr} is the effective diffusivity of crystals, ($m^2 \cdot s^{-1}$); D_a is crystallizer diameter, (m); d_{cr} is the equivalent diameter of the formed crystals, (m); H_a is the height of crystallizer, (m); I_s is the intensity of the sound wave, ($W \cdot m^{-2}$); n is an amount of crystals of the diameter d_{cr} in the crystallizer volume; p is the pressure into liquid, ($N \cdot m^{-2}$); p_s is the pressure of sound wave, ($N \cdot m^{-2}$); U is the speed of sound, ($m \cdot s^{-1}$); V is the speed of liquid flow, ($m \cdot s^{-1}$).

Greek symbols: α is the coefficient of heat transfer from the wall into the liquid or in the opposite direction, ($W \cdot m^{-2} \cdot K^{-1}$); β is the mass transfer coefficient, which characterizes the rate of mass transfer from the liquid to

the boundary of the crystals, (m·s^{-1}); λ is thermal conductivity of the fluid, (W·m^{-1}·K^{-1}); v is kinematic viscosity, (m^2·s^{-1}); ρ is liquid density, (kg·m^{-3}); ρ_{cr} is the density of crystals, (kg·m^{-3}); ρ_{cn} is crystal nuclei density, (kg·m^{-3}); Φ_* is the intensity of the specific energy source associated with the forces of the fluid friction and impact on the crystals of thermal and sound fields, (N·m) (m^{-3}· s^{-1}).

Criteria: $\mathrm{Pr}_D = \frac{\nu}{D_{cr}}$, $\mathrm{Pr}_t = \frac{\nu}{a_t}$ - diffusion and temperature Prandtl number

$Nu_D = \frac{\beta \cdot H_a}{D_{cr}}$, $Nu_t = \frac{\alpha \cdot H_a}{\lambda}$ - diffusion and temperature Nusselt number; $Eu = \frac{p + p_s}{\rho V^2}$ - Euler number.

REFERENCES

[1] KATS V.Y., MAZOR G., KATS, S., TARAKANOV B.M. Ultrasonic crystallizer of $CuSO_4$ solution: Engineering simulation. Russian Journal of Applied Chemistry, Vol. 86, No. 7, 2013, pp.1141-1145. DOI: 10.1134/S1070427213070287.

[2] KATS V., MAZOR G., KATS, S. Magnetostrictive transducers - The use and problems in ultrasonic crystallization solutions. Chemical Industry. Processes and equipment of chemical plants, Vol. 91, No. 7, 2014, pp. 333-336.

[3] TODES O.M., SEBALLO V.A., GOLTSIKER, A.D. Mass Crystallization from Solutions. Leningrad, 1984.

[4] OSTASHKOV V.N., SKOROBOGATOVA N.V. Graphic visualization of dendritic structures. Oil and Gas Business. *2006, pp. 7-13*, http://www.ogbus.ru/autors/Ostashkov/Ostashkov_1.pdf

[5] SHABETNIK V.D. Fractal geometry in the annex to the fractal physics. Russian Academy of Cosmonautics, Cheboksary, 2001.

[6] ISAEV I.L. Formation of crystalline and fractal structures in ensembles of nanoparticles and plasma media under the influence of optical radiation. Dissertation of the candidate of physical and mathematical sciences. Krasnoyarsk, 2011. http://kirensky.ru/ru/zdoc/iil.pdf

[7] FEDOSEEV V.B. Using fractal geometry with the thermodynamic description of three-dimensional crystal structure elements. Letters of Materials, Vol. 2, 2012, pp.78-83.

[8] CEDRIC M.S. Physical properties of crystals family tree-glycine depending on growing conditions. Science and Technology, 1986, 216 p. http://www.twirpx.com/file/632759/.

[9] http://earthpapers.net/formirovanie-prostranstvennyh-neodnorodnostey-v-raspredeleni...

[10] http://elar.urfu.ru/bitstream/10995/21447/1/fedorova_1.2.2.3.pdf

[11] http://www.medintegra.lv/images/PDF/TekstsRu.pdf

[12] GOLYAMINA I.P. Ultrasound: Small Encyclopedia. Moscow: Sovetskaya Entsiklopediya, 1979, 400 p.

[13] http://www.cniga.com.na/index.files/medkuporos.htm

[14] KUZMICHEVA G.M. Geometric Micro Crystallography. Part 2, Moscow, 2002, 41 p.

[15] MANDELBROT V. Fractal geometry of nature. Institute of Computer Science, Moscow, 2002.