Finely dispersed salt particles morphometric properties obtained by carnallite solutions spray drying

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Abstract. Currently, there is no consensus on the salt caves aero ionic environment effects mechanism on the human body, however, there is physiotherapy a separate type, based on such exposure health-improving effect, known as speleotherapy. To recreate the salt cave environment aero ionic composition, a halo chamber is used. To reduce their cost, recreating the air environment methods by contacting flowing air means with carnallite rock finely dispersed powder and dry and wet aerosols generators have been developed. When implementing these methods, both the powder obtained directly by crushing the rock and the powder obtained by salt solutions evaporation drying can be used. The study aim is to reveal finely dispersed salt particles morphometric properties obtained by carnallite solutions spray drying based on different dispersion raw materials. It has been established fine salt particles those morphometric properties obtained by spray drying of carnallite solutions based on different dispersion raw materials differ in average size, sphericity factor, topography character and chemical composition. Particles formed by solution evaporation on the macro disperse raw materials (3-5 mm) basis have larger size, smaller fractional range, more compact shape and relief characterized by multifractality. At the same time, solution-based particles from macro disperse raw materials contain more impurities. Particles a distinguishing characteristic from solution-based lumpy raw materials is the potassium cluster distribution on the surface.

1. Introduction
Carnallite rock (KCl-MgCl₂-6H₂O + NaCl) is a valuable raw material for producing products a wide range, from agricultural fertilizers to auxiliary materials for metallurgy; however, it is also known for providing salt caves a specific aero ion environment [1-3], which has positive effects on human health [4-6]. The salt cave environment beneficial effects have been confirmed by various studies [7-10], however, no consensus on this effect mechanism has been formulated to date. Despite the existing discussion, the aero ion environment positive effect is actively used in practice [11-15], there is physiotherapy a separate type based on the salt caves aero ion environment healthful effect, known as speleotherapy. Since natural and man-made salt caves are not an optimal and accessible resource, various methods have been developed to artificially recreate the salt caves aero ion environment; in particular, a halo chamber is used for this purpose [16].

A halo chamber is an enclosed space, where the air similar to aero ionic composition to that of salt caves is reproduced and controlled; these space parameters are such that it can accommodate one or
more patients for the time a long period (from several hours to a day). To recreate the salt cave environment aero ionic composition in the halo chamber, most often rock plates are used, which may be sawn from a solid layer or made by finely dispersed rock pressing. To reduce the manufacturing halo chambers cost, a salt cave recreating the air environment methods by contacting flowing air means with finely dispersed carnallite rock powder and dry and wet aerosols generators have been developed. During these methods implementation both the powder obtained directly by crushing the rock and the powder obtained by salt solutions, evaporation drying can be used.

Salt solutions for evaporation are obtained from rock debris of 3-10 mm dispersion or by large pieces ‘soaking’. As a result, the same concentration solutions can be obtained, however, the question remains as to whether the dispersed particles’ properties that form the sediment during their evaporation are different.

In [17] it is noted that the sedimentary structures morphology during droplet drying correlates with the solution composition and physical characteristics, which allows suggesting that the particles’ study formed during salt solutions evaporation on various disperse bases is relevant. Previously, researchers have identified distinctive characteristics in assessing particle morphometric parameters [18]; the authors note [19] that among all particle morphometric parameters, surface topography is the most informative in comparative assessment.

The study aim is to reveal fine salt particle morphometric properties obtained by carnallite solutions spray drying based on different dispersion raw materials.

2. The solutions characteristics are used in the work
The paper considers particles forming sediment during two types’ solutions evaporation: a solution based on crushed rock and a solution based on the lumpy rock. In the first case, dissolved rock dispersion was 3-5 mm, in the second case, 100x50x15 mm rock chunks were used. Solution two types were obtained, each in a volume of 1 l with a total concentration of NaCl and KCl of 8%, the concentration was monitored with an AS-SO-1 areometer.

3. The fine particle generation method
In the spray drying process, solutions evaporation was carried out from the jet in hot gas a stream. The scheme of the above method is shown in figure 1. The jet was formed by forced feeding through a high-pressure nozzle, the droplets’ diameter forming the jet was 80-120 microns, atmospheric air heated to 220°C was used as hot gas.

4. Research methods
Particles morphometric parameters (reduced diameter Feret, sphericity coefficient, surface relief) formed as spray drying a result were determined by scanning electron microscopy (SEM) from SEM images using software product ImageJ-Fiji (open source software, developer Wayne Rasband, National Institutes of Health, USA, module Analyze particles). The chemical elements distribution in the particle’s composition was established during microprobe X-ray spectral analysis using an analyzer complete with an electron microscope, the Cluster Indicator module (ImageJ-Fiji) was used to analyze the distribution.

Differences in significance between the particles’ characteristics obtained by solutions evaporation on different bases were established by Fishe’s F-criterion method at a given significance level of 0.05. Curves characterizing the particles surface relief were investigated for multifractality and mono fractality signs. The multifractality sign is the curve breaks presence with different fractal dimensions, multifractality is characterized by multifractal spectrum parameters [20]. For its construction we take the curve characterizing the relief as a series \( R(i) \) for \( i = 1, \cdots, N \), where \( N \) indicates the series length. We calculate the “profile” \( Y(i) \):

\[
Y(i) = \sum_{i=1}^{i} (R(i) - R_{cp})
\]
The profile $Y(i)$ is then divided into length non-overlapping segments $s N_s \equiv (N/s)$ and their trend for each of the $2N_s$ segments is determined using the series a least squares approximation. Then the variance is calculated using the following equation:

$$F^2(s, v) = \frac{1}{s} \sum_{i=1}^{s} \{Y[(v-1)s + i] - y_v(i)\}$$

for each segment $v$, $v = 1, \cdots, N_s$, and

$$F^2(s, v) = \frac{1}{s} \sum_{i=1}^{s} \{y[(v-N_s)s + i] - y_v(i)\}$$

for $v = N_s + 1, \cdots, 2N_s$, where $y_v(i)$ is a polynomial approximation on the interval $v$.

After that, averaging over all segments is carried out to obtain the function $q$-th order fluctuations:

$$F_q(s) = \left\{ \frac{1}{2N_s} \sum_{v} 2^{N_s} \left[F^2(s, v)\right]^{q/2} \right\}^{1/q} ; q \neq 0$$

$$F_q(s) = \left\{ \frac{1}{N_s} \sum_{v} \ln \left[F^2(s, v)\right] \right\} ; q = 0$$

Finally, we determine the fluctuation function scaling factor for any fixed $q$ and obtain the relation between $F_q(s)$ and $s$. If $F_q(s)$ is a power law, the series is on a logarithmic scale for that particular $q$:

$$F_q(s) \propto s^{h_q}$$

where $h_q$ is the generalized Hurst exponent.

The curve characterizing the relief is multifractal, if the index $h_q$ varies with $q$, $h_q$ can be expressed as the Renyi index a function, $\tau(q)$:

$$\tau(q) = q h_q - 1$$

The following expression is used to construct the multifractal spectrum:
\[ f(\alpha) = q\alpha - \tau(q) \]  \tag{8}

\[ \alpha = h_q + q \frac{dh_q}{dq} - \tau(q) \]  \tag{9}

where \( \alpha \) is the Gölder exponent (the function smoothness characteristic).

5. Results and discussion

Figure 2 shows particles images obtained by solutions evaporative drying obtained on bases with different dispersities. The particles main morphometric parameters are given in table 1, figure 3 shows data on particles fractional composition. Curves characterizing the particle surface relief are presented in figure 4. Chemical elements distribution in particles composition is given in figure 5, particles average chemical composition in table 3.

![Particles images](image1)

(a) (b)

![Particles images](image2)

(c) (d)

(a), (b) - on the 3-5 mm fraction feedstock basis;
(c), (d) - on the 100x50x15 mm fraction feedstock basis

**Figure 2.** Particles obtained by carnallite rock salt solutions evaporation drying with 8% concentration.
Table 1. Particles morphometric parameters obtained during carnallite rock salt solutions evaporation drying with 8% concentration.

| Parameter                  | Particles from raw material-based mortar of 3-5 mm fraction | Raw material-based mortar particles of 100x50x15 mm fraction |
|----------------------------|--------------------------------------------------------------|-------------------------------------------------------------|
| Average Feret diameter, mm | 0.06±0.008* (F = 4.9; F_cr = 1.16; p = 0.0095)              | 0.04±0.03                                                   |
| Average sphericity coefficient | 0.6±0.05* (F = 1.52; F_cr = 1.24; p = 0.0050)               | 0.3±0.09                                                   |

*reasonable distinction

Figure 3. Particles fractional composition obtained by carnallite rock salt solutions evaporation drying with 8% concentration on a different fractional basis.

Figure 4. Particles surface relief obtained by carnallite rock salt solutions evaporation drying with 8% concentration.

1 - based on 100x50x15 mm fraction raw materials; 2 - based on raw materials with 3-5 mm a fraction.
Table 2. Particles chemical composition obtained at carnallite rock salt solutions evaporative drying with 8% concentration.

| The element | Particles from the raw material-based mortar of 3-5 mm fraction | Raw material-based mortar particles of 100x50x15 mm fraction |
|-------------|---------------------------------------------------------------|-------------------------------------------------------------|
| Cl          | 31.62                                                         | 43.56                                                       |
| K           | 9.84                                                          | 11.27                                                       |
| Mg          | 1.42                                                          | 0.95                                                        |
| S           | 1.56                                                          | 0.89                                                        |
| Ca          | 2.50                                                          | 2.74                                                        |
| Na          | 28.70                                                         | 32.57                                                       |
| Al          | 0.74                                                          | 0.00                                                        |
| O           | 24.41                                                         | 8.02                                                        |

(a) - on the 3-5 mm feedstock fraction basis;
(b) - on the 100x50x15 mm feedstock fraction basis

Figure 5. Chemical elements distribution in particles obtained by carnallite rock salt solutions evaporation drying with 8% concentration.

Particles obtained by solutions evaporation on a macro disperse basis are characterized by large size, this index is 1.5 times higher than for particles from solution on a lumpy basis. However, among the latter, there are particles about 2 mm in size which look like branched dendrites (figure 2 (b)). The fractional composition confirms such large particles presence only during the lump based solution evaporation. Taken together, we can say that the particles fractional composition obtained by solution evaporation on a macro disperse basis is more uniform.

The sphericity coefficient, which allows us to judge the particles' shape, indicates that the particles from the solution on a macro disperse basis have a predominantly compact cubic shape, while the
particles from the solution on a lumpy basis exhibit shape a greater dispersion and in general have an elongated oblong shape, far from compact.

The relief average height for particles from the solution on the macro disperses basis is 192.9 microns, which is almost 2 times higher than the same indicator for the solution on the lumpy basis. The curve fragmentation describing the particles relief from solution on lumpy base is higher in this case. Curves fractal characteristics describing the relief are shown in figure 6. Renyi index dependence (figure 6 (c)) for particles from solution on lumpy base is linear which indicates mono fractality curve, spectrum (figure 6 (d)) also has multifractality no signs. In contrast, the particles curve describing relief from solution on macro disperse basis demonstrates Rainier index dependence exponential character (figure 6 (a)) and shows multifractality spectrum (figure 6 (b)). The surface topography fractal properties suggest the particles' reactivity, and studies a number suggest that the more complex the surface, the more active it is, other conditions being equal [21]. According to the particles obtained fractal characteristics from solution based on macro disperse raw materials, they have greater activity.

Figure 6. Curves multifractal analysis results characterizing the particles relief from raster.
The particles chemical composition has no noticeable differences, while the particles from the solution on a lumpy basis have impurities a lower content, at the 3% level, which is on average 2 times lower than when assessing the particles' composition from the solution on a macro disperse basis. Oxygen trapping by impurities in the latter is also higher. In the aggregate, due to higher purity, the particles from the solution on the lumpy base have chlorides a higher content. The chemical elements distribution in the particles' composition indicates that potassium is distributed in particles from lump-based solutions in the individual clusters form, whereas potassium no clustering on the surface was detected in particles from solutions on the macro disperse basis (figure 7).

(a) 
(b) 

(a) (b) 

Figure 7. The chemical elements distribution cluster analysis results in particles obtained by carnallite rock salt solutions with 8% concentration evaporation drying.

6. Conclusion
It has been revealed that finely dispersed salt particles morphometric properties obtained by carnallite solutions spray drying based on different dispersion raw materials differ in average size, sphericity factor, relief character and chemical composition. Particles formed by solution evaporation based on macro disperse raw materials (3-5 mm) have larger size, smaller fractional range, more compact shape and relief characterized by multifractality, which together indicates particles greater reactivity from solutions based on macro disperse raw materials than similar particles based on solution from lumpy raw materials (over 100 mm). At the same time, solution-based particles from macro disperse raw materials contain more impurities. A particle distinguishing characteristic from lumpy raw material solution is the potassium cluster distribution on the surface.

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