The Influence of Physically Doping NaCl with Other Salts on Aerosol and Solion Generation

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ABSTRACT

The paper presents the influence of physically doping NaCl grains with 0.5% KCl, KI, $MgCl_2$ and $CaCl_2$ on the release of negative aerosols/solions in dynamic halochambers. The salts used for doping were chosen according to the current procedures to obtain therapeutic and ambient mediums in aerosols with a negative charge based on NaCl. The aerosols were released by pumping an airflow of 1.8 L/min through a cartridge containing 60g of porous granules, with diameters between 4.0 and 6.6 mm, which were obtained by extruding dispersions of aqueous pasty-damp, saline solutions. We used an optical particle counter and a micro-chamber, divided into 10 equal rooms and with a zigzagged airflow delimited into three areas in each room. The upper side was fitted with several injectors to be coupled to the particle counter. Using this device we studied the aerosol emission dynamics over time, by keeping the temperature and humidity in normal conditions, as in the atmospheric air. Based on the evolution of the saline particles, which were divided into two stable groups in the air, namely gaseous microdispersions and gigantic dispersions, we evaluated their concentrations over time, by keeping the airflow that was pumped into the capsule constant. We thus determined the emission ratio over time and the lifespan of the solions in the three areas, over the halochamber functioning period and after the emission ceased. Aerosol/solion generation involves different sets of laws, based on the nature of the doping salt and the conditions in the environment. Therefore, one may select the doping conditions for the aerosol/solion generation granules and the optimal dynamic halochamber functioning time, for use with preventive, therapeutic, or physical performance enhancing applications.

Keywords: Salt aerosols; Solion; Physical doping; Particle size; Halochamber.

INTRODUCTION

The aerosols based on NaCl, as such, or mixed with other types of salts (KCl, KI, $MgCl_2$ and $CaCl_2$), are poly-disperse systems whose particles comprise a wide range of sizes, having special microphysical and nano-structural properties, with multiple practical implications (they are used in the profilaxy nad therapy of certain respiratory affections, in the improvement of the cardio-respiratory and psycho-neuromotory system parameters, for the purification and improvement of air quality etc.) (Pascu and Vasile, 2003; Pascu, 2003; 2008; Sandu *et al.*, 2010a, b, c).

In general, *solions* are hydrated nanostructures formed from dry salt aerosols with diameters ranging from 50 nm to 100 nm, which are larger than the Aitken particles, in presence of water pentahydrol. We know that they may come from both natural sources (marine atmosphere and salt mines) and from artificial sources (artificial halochambers and saline inhalers, or devices) in environments with an air humidity ranging from 75 to 90% (UR) (Sandu *et al.*, 2010a, b). Moreover, in aqueous saline solutions, right below the hypersaturation limit, under the microscope one may note the presence of spherical solions, as glomerules, resulted by structural reformation from nanocrystalites subjected to the balances of dissolution-recrystalisation processes, which, due to the negative charge, form an electrostatic halo around them (Sandu *et al.*, 2011),. The polygonal aerosol nanocrystalites

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absorbed into the tissue (teguments, or pulmonary pleura) may cause damage dehydrating the contact area, while solions, due to processes of deliquescence and solvolysis, enhance the bioactive processes within the contact areas. (Sandu *et al.*, 2011; Canache *et al.*, 2012)

The dynamics of those processes is determined by the intensity of the exogenous factors. In aqueous liquid mediums, the size of the particles varies from the average diameter of the "aquated ion" ($Na^+_{(aq)}$ and $Cl^-_{(aq)}$, respectively) up to some tens of microns of the nanostructured ionic cluster, with the chemical formula $[x(NaCl)_{2n} \cdot y(H_2O)_5]_{(H2O)}{}^{q-}$, called "**solion**". In gaseous mediums there are only "solions" with variable diameters (ranges from tenths of a micron to tens of microns) and structural form which tends to spherical (Sandu *et al.*, 2010a, b; 2011; Canache *et al.*, 2012). The various structures of the "solion" particles in gaseous mediums depends on the degree of hydration with water dipoles and on their way of over-structuring, by taking multiple shapes, with spatial structures similar to snow flakes, only at the nanostructural level. The multiple structural arrangement is considered to be the result of the compatibility between the cubic crystalline lattices of the sodium chloride and of the pentahydrol water $(H_2O)_5$ (Sandu *et al.*, 2002; 2011).

The lifespan of solions varies, according to the degree of negative charging on the surface and the structural complexity of those nanoclusters, from several minutes to several days (Sandu *et al.*, 2003; 2004a, b; 2010a, b). Beside the two endogenous factors (the electrostatic factor and the stereospecific factor), their stability depends to a great extent on a series of exogenous, external or environmental factors (humidity, temperature, pressure, light, the presence of other dispersions with positive charge and especially on the organic ones) There are other types of factors, included by some authors in the group of the endogenous ones, such as: form, dimension, granule nature, obtaining method or source type, speed of production, the capacity or the debit of the source, the rate of coagulation and of sedimentation etc. (Ştefan, 1998; Sandu *et al.*, 2003; 2009; 2010a, b, c; 2011).

According to the type of the source, the activity of the particles, their lifespan and the environmental conditions, the aerosols that generate the solions from the atmosphere feature a somewhat regular concentration and dimensional distribution, as a result of the difference between the speed of production and the speed of extinction or loss, due to processes of condensation, coagulation, peptisation, electroneutralization, sedimentation (destabilization) etc. (Ştefan, 1998; Sandu *et al.*, 2003; 2004a, b; 2009; 2011).

A special feature of those particles is their chemical composition, which varies in time, resulted from their interaction with water dipoles and with other particles, or aquated ions in the environment, which correlate with the charge, the shape and the size of solions (Sandu *et al.*, 2003; 2009; 2010a, b, c). Thus, for therapeutic environments they use submicronic, gaseous microdispersions, both as solions (hygro-, or aquo-aerosols) and as partially dry aerosols. For ambiental environments, to generate the "clean air effect", they primarily use partially dry aerosols with a negative superficial charge. They destabilize, by electro-neutralization,

the positive charged aerosols, such as those resulted from burning/pyrolysis (for example cigarette smoke), as well as the nanodispersions resulted from the metabolism of certain fungi, or moulds (Sandu *et al.*, 2010a, b, c).

Depending on the characteristics of the source and the environmental conditions in which they are produced, solions may come in various shapes, grain sizes, electrical charges and concentrations. The sources, especially the artificial ones, have three characteristic generation zones: the active layer, or the generation-nucleation zone, the diffuse layer, or the reformation-condensation-accumulation zone, which differ in the activity of the aerosols, according to the concentration ans size of the particles (Sandu *et al.*, 2004a, b; 2011).

Saline aerosols resulted from natural or artificial sources, depending on their practical application, should have well monitored specific lifespan and activity, that is, a minimum concentration value, a grain size variation range and a specific negative surface charge (Sandu *et al.*, 2003; 2009a).

Currently, there is an increasing number of studies on the applications of aerosols (Laskin *et al.*, 2003; Schalek *et al.*, 2004). We know that many of the solid microparticles, such as the aerosols dispersed into the atmosphere, contain a large variety of chemical compounds classes, with very different chemical and physical-structural behaviors, hence the dimensions of those aerosols are distributed trimodally, according to *the mode of nucleation* (a diameter below 10 nm), *the accumulation mode* (app. 100–500 nm) and a *rough sedimentation mode* (supermicronical) (Seinfeld and Pandis, 1998). The wide range of atmospheric temperatures (180K to 305K, that is, between −93 and 32°C) and humidity (from 10 to 150% UR), provides an optimal environment for variable grain sizes, with many important disperse phases and chemical transformations. Particle growth, occurring due to processes of deliquescence following water absorption, or by electroneutralization with positive air ions, affects their chemical, physical-structural and optical properties (Martin, 2000, Hu *et al.*, 2010). For instance, the atmospheric microparticle hygroscopicity effect of saline aerosols significantly reduces sight range and affects the optical properties of the atmosphere. Moreover, the nature of aerosol phases effects their chemical reactivation and the speed of those reactions, as atmospheric saline aerosols systems are very dynamic, hard to control and estimate in real time (Sandu *et al.*, 2004a, b; 2010a, b, c).

Depending on their activity and their lifespan, the aerosol particles have a somewhat steady dimensional distribution, a balance between production and loss speed achieved by different processes. From this view point, they can be divided into five groups, or dimensional levels, according to various measuring methods and techniques: *small simple ions* with diameters under 0.5 nm, which can be determined only in solution or smelt by *electrochemical methods* (Gulea *et al.*, 1994); *Aitken particles* with diameters between 0.5 and 50 nm, detected with the *Aitken Particle Counter* (Junge, 1963) or by *mass spectroscopy* (Mitchell and Nagel, 2000); *average-size particles*, with diameters between 50 and 100 nm, detected with the *Laser (phase) Doppler System* (Mitchell and Nagel, 2000), *Angular*

Intensity Light Scattering (Mulholland *et al.*, 1985) and *Quasi-elastic Light Scattering* (Mitchell and Nagel, 2000) methods; **big particles**, with diameters between 100 and 500 nm, detected with the *Laser Diffractometer* (LD) (Mitchell and Nagel, 2000), by *Electronic Microscopy Transmission* (MET) (Lettieri and Hembre, 1989) and by an *Electrical Sensing Zone* (ESZ) (Mitchell and Nagel, 2000) method; **huge particles**, with diameters between 500 and 1,000 nm (up to some tens of microns), detected with the *Electrical Mobility Analyser* (Kinney *et al.*, 1991) and by *Optical Microscopy/image Analyser* (Thom *et al.*, 1985; Hartman *et al.*, 1991; Lettieri *et al.*, 1991; Hartman and Doiron, 1992).

Solion dimensions range between those of the Aitken particles and huge particles the latter tending to cause destabilization through their sedimentation.

Among those five groups of dispersible particles in gaseous environments, only the Aitken particles and those between 50 and 100 nm can generate solions. Solion has in its cluster structure NaCl nano polyhedrons and water oligomers, as pentahydrol, which are in-situ structuraly reformed. The NaCl polyhedron structures larger than 100 nm do not allow diffusion of water in the block structure, but only on the surface as mono or polymolecular layers.

In general both aerosols and any kind of solions, especially those as formed as liquid microparticles, but also the solid ones, raise a number of problems in regard to their study. Specialised publications mention a number of methods by employing instrumental techniques, whose results frequently involved the corroboration and coassistentance with other physico-chemical interdisciplinary methods.(Sandu *et al.*, 2003; 2004a, b). *The conductometric differencial method* developed by our team is a method that allows a real time assessment of the behavior and mutual influence of the various aerosol species and of solions. Moreover, *chromatography by ionic exchange* is also a frequently used method (Patnaik, 1997; Standard D4327-97, 1999) Both methods are also successfully used to monitor their behavior, irrespective of generating source and the environmental conditions at their moment of generation (Sandu *et al.*, 2004a, b; 2010a, b, c; Alexianu *et al.*, 2012; Sandu *et al.*, 2012).

Our paper studies the effect of physically doping NaCl granules with other salts based on K, Ca, Mg, as well as KI chlorides, on the solion generation capacity and lifespan, as well as the solions that reform in the air. The results of our research are intended to elaborate procedures of obtaining porous granules, with surface bloomings of solion generating salt mixes, with multiple practical applications. Moreover, this initial note is part of a larger series involving modern complementary analytical techniques, which will allow us to emphasize the various *in situ* solion generation modes, from saline aerosol microparticles originating in halite, or in various salt mixes.

EXPERIMENTAL PART

The Salt Granules Used for Generating Solions

In our experiments we used salt granules obtained by a procedure of recrystallization from hypersaturated aqueous solutions, (water evaporation in time, in normal conditions of temperature) followed by extrusion into particles with a diametre ranging from 4.0 to 6.3 mm. To obtain the granules we used the following compositions: NaCl 100% (Sample P0), NaCl 95% + KCl 5% (Sample P1), NaCl 95% + KI 5% (Sample P2), NaCl 95% + $MgCl_2$ 5% (Sample P3) and NaCl 95% + $CaCl_2$ 5% (Sample P4). We chose those ratios as being the limits to the impurification with other salts of (natural) halite, which is used since ancient times to generate aerosols and bioactive solions (Sandu *et al.*, 2010a, b). Initially, the salt mix obtained by recrystalization, weakly humidified after decanting, was well homogenized by pestle milling until obtaining a hypersaturated paste. That paste was dried in an oven at 80°C for 2–3 hours, obtaining a mass of fine crystallites, which were extruded, with a stainless steel screw conveyer, as granules with a diameter ranging from 4.0 to 6.3 mm, on exit being cut with a knife. After extrusion, the granules were heated for 4 hours in ovens with hydric and heat regulators, at 85–90°C and U.R. 65–70%, until the granules formed superficial bloomings. They were stored in airtight polyetylene bags kept in dry environments or in exicators with a maximum RH of 45–60%.

Determining the Characteristics of the Emitted Particles

To determine the characteristics of the particles emitted by the airflow running through the cartridge with activated granules, so as to evaluate the influence of the doping with other salts, we used an experimental micro-halochamber, consisting of a glass container, with ten internal routing walls (Fig. 1). The container measured 800 × 500 × 400 mm, which meant that the active volume was 160 L. The 10 routing walls divide it into 11 microchambers, first of 20L and the rest, each with a capacity of 14 L. As aerosol source for generating solions that would disperse in the air, we used cylindrical capsules made of plastic (Fig. 2), with a diameter of 43 mm and a length of 62 mm, similar to the filtering cartridges, fitted with flexible tubes to connect them to the pump and to the micro-halochamber. Inside them, the granules are set between two unwoven polymeric nets. When full, the capsules contain 60g of granules (Samples P0-P5).

The air was driven through the capsule into the micro-halochambers by a Resun AC9601 pump, with a debit of 1.8 L/min. Right after the granule capsule, the air flows to the first micro-halochamber through a Bechhold micro-ultrafilter, with a millipore membrane fitted on a stainless steel sieve. The millipore filter is fitted into a raylon gasket, which ensures an easy detachment thereof from the micro-ultrafilter, for periodic weighing of the sedimentable, *rough particles*. For our measurements we used a high precision (0.0001mg), PARNER AS220/S/2 digital analytic weighing scale.

The position of the routing walls in the micro-halochamber and the small size of the slits left at their ends, allowed us to create three different generation zones: an *active,* or *nucleation zone,* where the formation of the solion is started, a *diffuse,* or *solion condensation-accumulation zone*
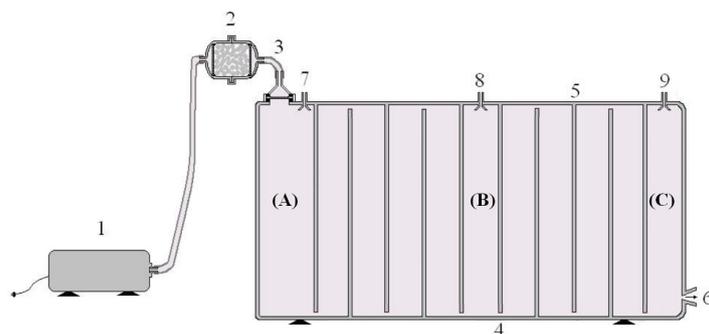
Fig. 1. Experimental halochamber with routing walls, used to determine the lifespan of the solions: 1 - air pump, 2 - capsule with saline granules, 3 - Bechhold micro-ultrafilter; 4 - glass container (halochamber), 5 - routing walls, 6 - exhaust outlet with pressure regulator, 7, 8, 9 - aerosol sampling points for the three zones: A - active zone, B - central, or diffuse zone and C - passive, or residual zone.

Fig. 2. Filtering cartridge with saline granules.

and a *residual,* or *solion coagulation-termination zone,* where microcrystalites are also sedimented. By compartmentalizing the space with the 10 routing walls we induced a zigzagged aerosol transporting stream, which, at a moderate air debit, optimal for the formation and maturation of the solions and compatible with the device which determines the characteristics of the particles emitted by the cartdridge and of the solions formed *in situ*, allowed a differentiated analysis thereof within the three zones of the halochamber. We should note that the volume of the halochamber and the compartmentalization design, which was intended to create the three solion activity zones and the solions formed *in situ*, were perfected during certain previous studies, whose results were presented in a series of published articles (Sandu *et al.*, 2010a, b; 2011; Canache *et al.*, 2012).

In the present experimental system, the pump drives the air at a constant flow of 1.8 L/min, which collects frail salt microparticles from the cartridge and disperses them into the atmosphere of the halochamber through the milipore filter, which captures the huge or rough (sedimentable) particles. The other particles (submicronic and micronic), formed as aerosols and as solions reformed *in situ*, are dispersed differently into the three zones of the halochamber, where precise sampling points were set, to determine the grain size and the concentration of aerosols/solions. Those sampling points, consisting of outlets with a valve to be

coupled to the optical particle counter, were placed right after the microfilter, at the inlet into the first zone, which was considered as the *active, or nucleation zone*, on the upper side (A) of the container, in the center of the container, also on the upper side (B), for the second zone (the *diffuse, or solion maturation zone)* and for the third zone (the *residual, or solion termination zone* and of unstabilized microcrystalite sedimentation), at the end of the last compartment (C), on the outlet of the container, where a pressure regulator, set on its lower side, evacuates the flux of solions and of active, residual microcrystallites.

Within the three zones, we determined the number and the granulometric distribution of aerosols, by using a SIBATA GT 321 optical particle counter, which employs a measuring technology based on laser. The device allowed us to evaluate the average concentration of solions, the number and distribution of particles according to their size and the number of particles with a diameter above d_i/m^3.

The particle counter recorded the following evaluation graphs: between 0 and 10^8 particles/m^3; five dimensional domains: 0.3; 0.5; 1.0; 2.0; 5.0 μm (for the diameter of the particles); the working temperature ranges in a gaseous environment: 0–50°C; the processed gas debit containing aerosols: 1.8 L/min.

Therefore, according to the afferent methodology (Sandu *et al.*, 2010a, b; 2011; Canache *et al.*, 2012), first we determined the number of particles, based on dimension groups and the total volume thereof and then we calculated the solion concentration, in mg/m^3, by approximation, based on the specific weight of halite, which is $2,165 \times 10^6$ g/m^3 and on the debit of the pumped air, which was 1, 8 L/min, during our experiment. For every experiment 5 measurment sets were made and the average value was presented. The measurment error was 0.5%.

For the doped granules, we used a specific average weight, calculated according to the ratios in which each saline component participated to the mass of the mixture, namely: for sample P1(95% NaCl + 5% KCl), the specific average weight was 2.156×10^6 g/m^3 (2.05675 + 0.0992), for sample P2 (95% NaCl + 5% KI), 2.213×10^6 g/m^3 (2.05675 + 0.1565), for sample P3 (95% NaCl + 5% MgCl$_2$), 2.1726×10^6 g/m^3 (2.05675 + 0.1158), for sample P4 (95% NaCl +

5% $CaCl_2$), 2.1824×10^6 g/m^3 (2.05675 + 0.1256). The total volume of the particles was evaluated considering them of spherical shape (the most plausible shape for the solion particles).

The microhalochamber was coassisted during our experiments by devices used to determine the environmental parameters in real time (temperature, pressure, illumination and atmospheric humidity).

The experimental device we used allowed us to maintain a concentration within a margin of tenths of mg/m^3, the minimum level necessary for various practical applications (homeopathic treatment or the prevention of airspreading viral contamination, for improving physical performance and to obtain an environment with a clean atmosphere).

Because the microparticles are collected from the salt grains by air erosion, they come in a wide range of sizes. Therefore, in order to characterize the dynamics of bioactive aerosols and solion emissions, we took into account only the *submicronic* particles (with a diamenter below 0.1 μm) and the *micronic* ones (with diameters between 0.1 and 10 μm). Our study of the influence that doping the granules has on their capacity to generate aerosols/solions also took into account the dynamics of the *huge, or rough particles* (with diameters above 10 μm), even if their behavior differs from the other aerosols (the small simple ions, the big ions and small ionic aggregates, or Aitken particles and solions particles). We know that certain aquated aerosols and solions have a limited stability time, their lifespan ranging from tens of minutes, to tens of hours, according to certain endogenous and exogenous factors in the three zones of the generation flux, whereas the huge particles have a lifespan practically equal to "zero", because they are gravitationally unstable in the air, due to sedimentation. The huge particle layer accumulated in the filter and in the compartments of the halochamber, may become a weak solion source, under certain cryptoclimate conditions. That explains the fact that after cutting the airflow through the cartridge and the resulting decrease to a minimum in aerosol and solion activity, the three zones maintain a residual level of activity.

By erosion, the airflow collects the salt nanoparticles from the frail crystallites in the surface bloomings and disperses them into the atmosphere of the halochamber, where, under the influence of air humidity, due to the difference in hygroscopicity, they reform structurally as pentahydric olygomers and those nanocrystalites, differentiated according to salt types, when they form the spherical glomerules, coated by a layer of surface, negatively charged, water dipoles, are known as solions. Their formula is $[x(MeHal_v)_{2n} \times y(H_2O)_5]^{\delta-}_{(aq)}$, where Me is Na^+, K^+, Ca^{2+} and Mg^{2+}, Hal^- –

Cl^-, Br^- or I^-, v is the charge type of the metallic ion, n is the packing degree of the elementary cell of the nanocrystalite (n > 3), x and y are the combination ratio in the glomerule and δ is the superficial charge of the solion. Solions contain a single type of salt and are formed in descending order of salt hygroscopicity and they coexist within the halochamber, in a certain balance, with aerosol particles. The balance varies according to the exogenous factors in the halochamber and also according to the presence of other aerosols with which they can interact (Sandu *et al.*, 2010a, b).

The temperature and relative humidity (UR) were measured with a digital electronic hygrothermometer, the pressure with a barometer and the illumination with an electronic light meter.

RESULTS AND DISCUSSION

Since the dynamics of the aerosol emissions and that of the solions reformed *in situ* by the granules in the capsule that we used for our experiment are influenced by environmental conditions, our measurements were performed while keeping the parameters of the pumped air at a constant level and by closely monitoring the cryptoclimate that formed in the microhalochamber.

Those parameters are presented in Table 1. We must note that during our experiment, we based the environmental conditions on those from the laboratory.

In our presentation of the experimental data, we took into consideration the fact that the weight of a full cartridge is 60 g, and that the size of granules varies between 4.0 and 6.3 mm. Moreover, the values for the quantity of sedimental, or rough microparticles (considered outside the range of solions) emitted by the cartridge, are to be correlated with those of the particles able to turn into solions in the presence of hygroscopic water, through structural reformation processes, by nucleation and condensation.

Fig. 3 presents the variation in the quantity of huge microparticles (> 1000 nm) emitted after the activation of the capsules by means of the Resun AC9601 pump, by using the gravimetric method with gradual determination in time, done by weighing the milipore filter that retained the rough particles.

According to the data in Fig. 3, the rate of rough, huge particle (gravitationally sedimentable) emissions from the 60 g of granules in sample p0 (100% nacl) during the first 200 minutes, decreases on average from 8.00 mg/h to 2.67 mg/h and afterward there is an abrupt change in slope during the following 200 minutes, when the rate suddenly drops to 0.30 mg/h and then continues to drop for 5 hours,

Table 1. The parameters of the pumped air and of the cryptoclimate formed in the microhalochamber.

Parameter / Location	Temperature (°C)	Relative humidity (%)	Atmospheric pressure (mmHg)	Light (lx)
Laboratory microclimate of pumped air	23 ± 5	60 ± 2	760 ± 5	120 ± 3
The cryptoclimate formed in the aerosol container	20 ± 3	58 ± 2	760 ± 5	120 ± 3
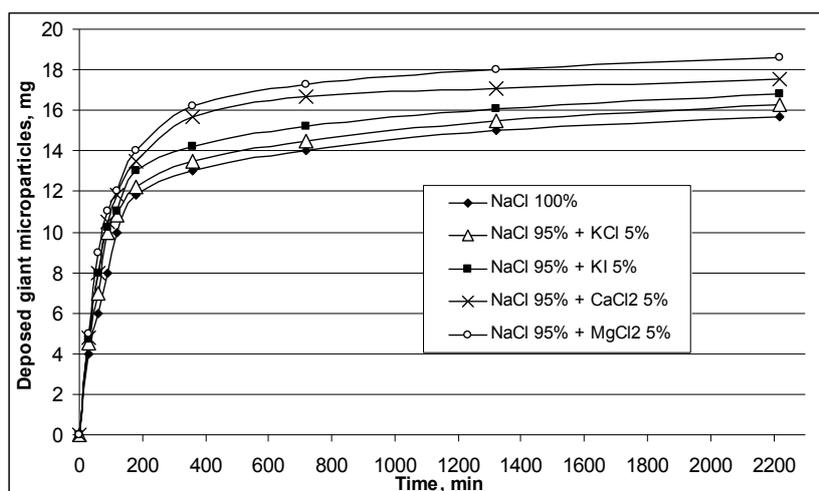
Fig. 3. The variation in the quantity of huge microparticles emitted right after the cartridge.

until reaching 0.20 mg/h and then the generation practically remains constant for 25 hours, at a rate of 0.06 mg/h.

For the other four samples (P1, P2, P3 and P4), with the same cartridge load of 60 g of granules with a specific composition, the rate of emissions decreases similarly, with the difference that the salts involved in doping increase the quantity of huge particles (sedimentable), which can be explained by their high affinity for the hygroscopic water, in the series: $KCl < KI < MgCl_2 < CaCl_2$, and the saline bloomings are also formed differently.

The highest rate of sedimentation was recorded for those crystallites generated/emitted by mixes based on NaCl (95%) + $CaCl_2$ (5%) from sample P4 and on NaCl (95%) + $MgCl_2$ (5%) in sample P3, which drop from 10.00 mg/h during the first 30 minutes, to 0.08 mg/h during the next 25 hours. The other samples (P1 and P2), fall within the two groups of sedimentation rate values registered for samples P0 and P4, which ranged between 8 and 10 mg/h in the first 30 minutes, then decreasing logarithmically in the next 15 hours, between 0.06 and 0.08 mg/h. Their variation curves comply with the above mentioned pattern.

Based on the data in Fig. 3, we evaluated the debit of huge particles, knowing that the volume of air driven by the pump was 1.8 L/min. Thus, in Table 2, we present the variation in the debit of sedimentable (rough) particles during the emission.

We should note that during the first hour the huge (sedimentable) particles emission rate for all of the five samples was greater than 50 mg/m³ and that it drops to half

of that after three hours and then it continues to drop logarithmically to app. seven times less after 12 hours, 14 times less, after 24 hours and 20 times less, after 36 hours, without completely ceasing the generation thereof. That happened due to the reactivation of crystallites on the surface of granules, under the influence of hydric processes caused by the hygroscopicity of salts, triggered by the atmospheric humidity.

With the optical particle counter we determined the grain size of the aerosol and solion particles that formed *in situ* (particles with sizes between the Aitken, with a diameter of 50 nm, and the medium particles, with diameters of up to 500 nm). Based on the number of particles emitted during a set period of time, at a debit of 1.8 L/min, we evaluated their total volume and then the concentration of aerosols and solions emitted by the five samples. P0, P1, P2, P3 and P4 (Table 3).

According to the data in Table 3, we noted that the difference in hygroscopicity for the salts we used for doping, in balance with that of NaCl, lead to a decrease in the number of small solion forming particles (< 1.0 μm) and to an increase in the number of large particles (between 2.0 and 5.0 μm), sedimentable by processes of coagulation and recrystallization.

Fig. 4 presents the variation in time of the total concentration of particles with a diameter d_i ranging from 0.3 to 5.0 μm, emitted in the active area of the halochamber, at an air debit of 1.8 L/min, by the samples P0, P1, P2, P3 and P4.

Table 2. The variation in time of the emission debits (mg/m³) of huge particles (> 1000 nm) by the granules in samples P0, P1, P2, P3 and P4.

Samples	Flow (mg/m³)						
	0.5h	1.0h	3.0h	6.0h	12.0h	24.0h	36.0h
P0	70.37	57.41	30.86	20.06	10.80	5.86	4.09
P1	75.93	64.81	32.41	20.83	11.19	6.06	4.19
P2	85.19	74.07	33.95	21.99	11.57	6.21	4.37
P3	88.89	75.93	35.49	23.92	12.73	6.56	4.58
P4	96.30	81.48	37.04	25.08	13.35	6.94	4.81

Table 3. The variation in time of the number of particles with a diameter d_i, in dimensional groups, in the active zone.

Samples	Particle diameter, d_i (μm)	The number of particles with the diameter d_i, n_i (10^6 x/m³)							
		10 min	30 min	60 min	120 min	300 min	600 min	1440 min	2880 min
P0	0.3	172.30	478.08	950.10	1883.40	3766.20	7256.50	10884.70	11973.20
	0.5	9.80	29.89	59.70	127.30	242.90	485.20	727.80	800.50
	1.0	0.60	2.02	3.90	8.00	16.30	31.80	47.80	52.50
	2.0	0.30	1.08	2.10	4.20	8.60	16.70	25.10	27.60
	5.0	0.10	0.26	0.50	1.10	2.20	4.20	6.40	7.00
	Total	183.10	511.33	1016.30	2024.00	4036.20	7794.40	11691.80	12860.80
P1	0.3	92.24	255.94	508.63	1008.27	2016.22	3884.73	5827.07	6409.80
	0.5	8.81	26.87	53.67	114.44	218.36	436.18	654.28	719.63
	1.0	0.62	2.09	4.03	8.27	16.83	32.86	49.39	54.25
	2.0	0.33	1.19	2.31	4.62	9.46	18.37	27.61	30.36
	5.0	0.15	0.39	0.75	1.65	3.30	6.30	9.60	10.50
	Total	102.15	286.48	569.39	1137.21	2264.17	4378.44	6567.95	7224.54
P2	0.3	89.04	247.07	413.13	973.29	1946.27	3749.96	5624.92	6187.43
	0.5	8.61	26.27	52.45	111.84	213.41	426.28	639.42	703.30
	1.0	0.65	2.17	4.22	8.67	17.66	34.45	51.78	56.88
	2.0	0.37	1.36	2.59	5.18	10.61	20.60	30.96	34.04
	5.0	0.18	0.54	0.90	1.98	3.96	7.56	11.52	12.60
	Total	98.85	277.40	473.29	1100.96	2191.91	4238.85	6358.60	6994.25
P3	0.3	74.92	207.89	413.13	818.95	1637.63	3155.29	4732.92	5206.22
	0.5	7.80	23.80	47.52	101.32	193.33	386.18	579.27	637.13
	1.0	0.63	2.10	4.10	8.40	17.12	33.39	50.19	55.13
	2.0	0.42	1.54	2.94	5.35	12.04	23.38	35.14	38.64
	5.0	0.21	0.63	1.05	2.31	4.62	8.82	13.44	14.70
	Total	83.98	235.96	468.74	936.33	1864.74	3607.06	5410.96	5951.82
P4	0.3	72.83	202.09	401.60	796.10	1591.95	3067.27	4600.89	5060.99
	0.5	7.60	15.82	46.30	98.72	118.37	376.28	564.42	620.80
	1.0	0.62	2.07	3.90	8.27	16.84	32.86	49.39	54.25
	2.0	0.48	1.76	3.36	6.11	13.76	26.72	40.02	44.16
	5.0	0.26	0.78	1.30	2.86	5.72	10.92	16.64	18.20
	Total	81.79	222.52	456.46	912.06	1646.64	3514.05	5271.36	5798.40

The data in Fig. 3 and Fig. 4 and in Tables 2 and 3, clearly emphasizes the influence of doping NaCl granules with other solion generating salt types. We should mention that the data only refer to the active area and that the salts and the concentrations used for doping were those involved my various practical applications of solions (Sandu *et al.*, 2012).

The evolution of the characteristics of particles emitted within that zone indicated a series of facts in regard to the dynamics in the production of solions and of other particles. Compared to the huge particles, that destabilize easily right from the first minute after emission start, solions are more stable and, irrespective of their size, they follow the same laws of evolution, as regards the dynamics of their emission. The fluctuation of the curves in first period are due to the fact that small particles are coagulated under the influence of air humidity. P3 and P4 curves are close due to similar hygroscopicity, being different from the other salts.

If we look at the variation in the concentration in time, for submicronic (0.3 and 0.5 μm) and micronic (1.0, 2.0 and 5.0 μm) particles together (Fig. 4), we notice that by doping with KCl and KI, we caused a slight increase of the

rate, compared to P0, but that the evolution curves are completely different, atypical, compared to P0, which had a gauss with a maximum concentration of app. 130×10^{-5} g/m³ between 60 and 120 minutes of emission. Thus, the curves for the samples doped with KCl and KI registered a minimum during the first 30 minutes and then a gaussian maximum at app. 120 minutes, followed by a gradual decrease similar to the curve of P0, a period when the dynamics of emission follow the same laws as in the case of undoped granules (100% NaCl). The granules doped with MgCl₂ and CaCl₂, which have a higher hygroscopicity, have a completely different behavior, reaching a gaussian maximum after the first 30 minutes. After 240 minutes of emission, the variation of the concentration gradually decreases for all the five samples, according to the same laws of concentration decrease, without total depletion thereof.

Fig. 5 presents the variation of the concentration of submicronic and micronic particles emitted by sample P0 in time, for the three sampling points of the halochamber (container), determined with the optical counter.

Fig. 5 emphasizes that, during the first 3 hours of emission, the P0 sample emitted half of the maximum obtained
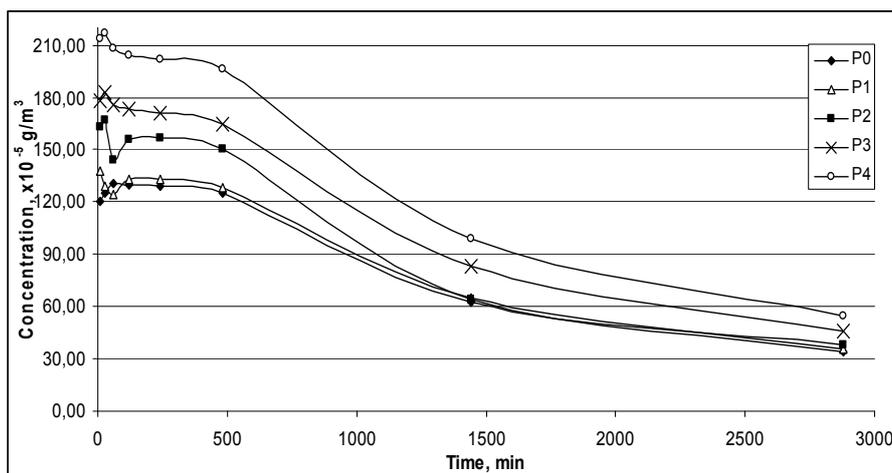
Fig. 4. The variation in time of the total concentration of particles with a diameter d_i ranging from 0.3 to 5.0 μm, in the active area of the halochamber, at an air debit of 1.8 L/min.
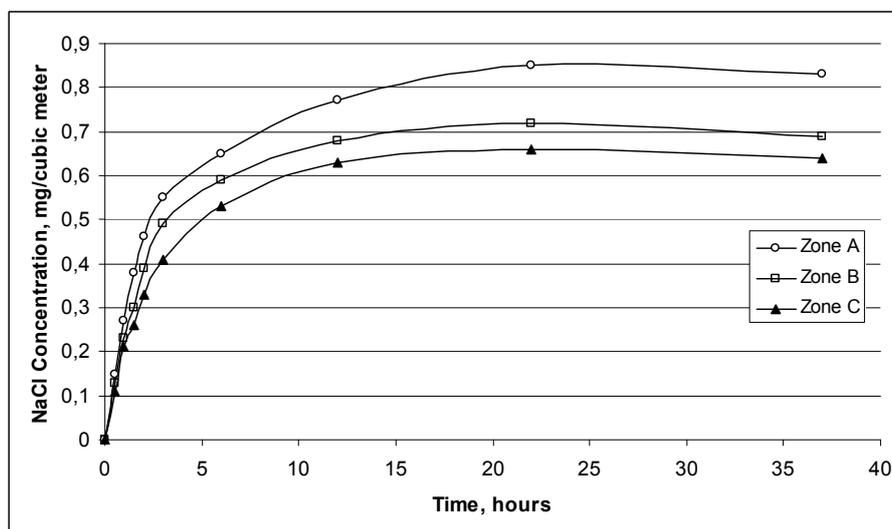

Fig. 5. The variation of micronic and submicronic particle concentration in the three sampling points of the halochamber: 1 - active zone; 2 - diffuse zone; 3 - residual zone.

concentrations in the three sampling points. The maximum concentration of was reached after app. 25 hours registering 0.85×10^{-2} mg/m^3 in the active zone, 0.73×10^{-2} mg/m^3 in the central-diffuse zone and 0.66×10^{-2} mg/m^3 in the residual zone, at the outlet of the halochamber. Afterward there is a slight decrease in concentration, presumably caused by the processes of condensation/peptization/coagulation, marking the aging and fading of solions. That effect becomes obvious after stopping the emission (Fig. 6), when solion concentration decreases in time due to the processes of hydric condensation and coagulation, followed by recrystallization in anhydric state and gradual sedimentation. During the first 24 hours there is a slight decrease in concentration, regulated by the processes of nucleation and condensation; then there is an abrupt drop during the next 48 hours, when the processes of peptization/coagulation compete with those of recrystallization and afterward the concentration decrease rate gradually drops in three stages: between 72 and 240

hours, then between 240 and 480 and finally between 480 and 720 hours; the last stage is dominated by the process of aging of fading, when fine, of accumulation, sedimentable, recrystallized particles form.

CONCLUSIONS

We studied the evolution in time of the aerosol and solion emissions, as well as that of huge, sedimentable particles, by using porous granules of NaCl, as such and also doped with 0.5% KCl, KI, MgCl$_2$ and CaCl$_2$, and we reached the following conclusions: aerosol emissions rate decreases with rising of affinity for salts hygroscopicity: NaCl < KCl < KI < MgCl$_2$ < CaCl$_2$; using dopants with high hygroscopicity (MgCl$_2$, CaCl$_2$) leads to reduction of small particle generation, which are able to form solions, and increase the sedimentable particles generation. In the first 2 areas (active and diffuse areas) a part of the aerosols
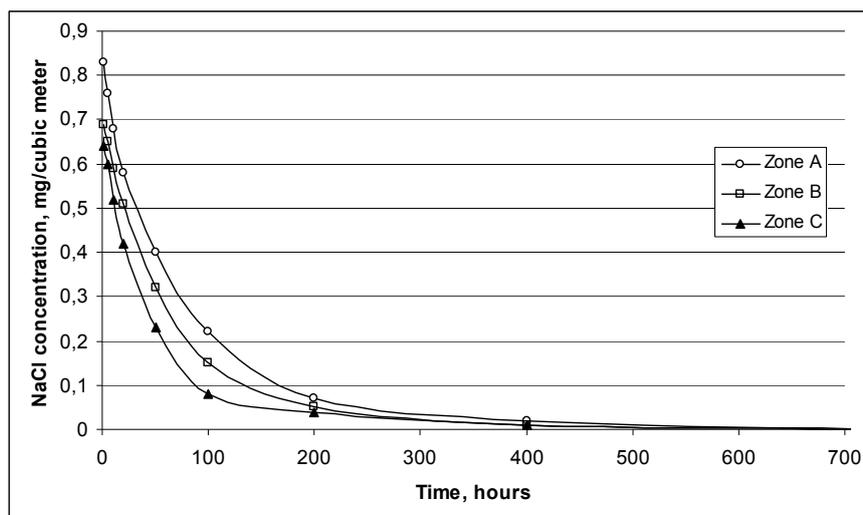
Fig. 6. The variation of aerosol concentration in the halochamber, after stopping the emission.

nanoparticles are structurally reformed into solions in the presence of water pentahydrol. The solions generation is higher in the first zone. Since most particles generated are below 300 nm, results a higher quantity of solions generated in situ, which are benefic for the human body, due to the dimensional compatibility with the pores of the live tissue with which come in contact.

DISCLAIMER

Reference to any companies or specific commercial products does not constitute an advertise.

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