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Investigation of the dynamics and kinetics involved in saline aerosol generation under air erosion of pure and contaminated halide salts

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ABSTRACT

This study presents results from an investigation of the dynamics and kinetics involved in saline aerosol generation under air erosion of pure and contaminated halide salts. Investigations have been performed in a microhalochamber filled with active efflorescent pure or doped NaCl salt granules. The performed work allows the suggestion that pure NaCl salt presents the highest potential to generate saline aerosols. The generation capacity of saline aerosols decreased in doped NaCl, and the efficiency of the doping salts to inhibit aerosol generation was in the order $(KI+KCl) > KI \approx KBr > KCl > CaCl_2$. Emission/erosion rate constants (min^{-1}) were estimated by applying a simple kinetic treatment to the experimental data set (i.e. trends of $\ln([S_0]/[S])$ vs. time, where S represents the salt). The pseudo-first order erosion rate constant value (k_e), characteristic of the emission/erosion of aerosol from salt granules, decreased in the order $NaCl_{\text{pure crystallite}} > NaCl_{\text{doped with CaCl2 or KCl salts}} > NaCl_{\text{doped with KBr or KI salts}}$. For the doping salt the emission/erosion rate constants varied in the order: $k_{e(KI)} < k_{e(KBr)} < k_{e(KCl)} < k_{e(CaCl2)}$. The emission/erosion process is most probably controlled by the morphology of the used salt granules. The latter would be related to the solubility of the doping salt, the radii of the involved ions and the properties of the saline aqueous solutions that are used to obtain active efflorescent salt granules. Such properties could affect the surface enrichment of NaCl and of the doping salt, because surface composition is expected to play an important role at least in the first stage of the erosion process. The obtained results may have relevant implications in both atmospheric and medical fields.

1. Introduction

Sodium chloride (NaCl) aerosols, on their own or in mixture with other halides, are usually polydisperse systems with individual components in the size range from Aitken nuclei (particle radii smaller than 0.1 μm) to large (particle radii

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between 0.1 and 1 μm) and giant (particle radii larger than 1 μm) particles. However, in the aerosol size range spectrum, Junge and Jaenicke (1971) report about a concentration maximum of particles around 0.001 μm radius, supporting the idea of a dynamic equilibrium in the size distribution of the aerosol. The observation of Junge and Jaenicke (1971) was later confirmed by the data of Haaf and Jaenicke (1980), who observed a bimodal distribution in the Aitken range of atmospheric aerosols. According to Whitby (1978) and depending on the aerosol production mechanisms, aerosols are classified into nucleation (particle diameter < 0.1 μm), accumulation (particle diameter in the 0.1–2 μm size range) and coarse (particle diameter larger than 2 μm) mode particles. Hygroscopicity is an important aerosol property, especially in aerosols that contain water-soluble substances. Many inorganic salt aerosols are hygroscopic by nature and exhibit the property of deliquescence in humid air (Tang, 1996). Tang (1996) also underlined that when the relative humidity in the surrounding air reaches the deliquescence point, a particle rapidly takes up water and becomes a saturated droplet. The droplet thus formed usually does not recrystallize when the relative humidity falls below the deliquescence point. However, it is generally admitted that the hygroscopicity of inorganic aerosols is directly interrelated to the initial particle size and relative humidity (Hu et al., 2010). Furthermore, evaporation and growth of multicomponent aerosols can be directly linked to the use of a laminar flow humidifying system, by controlling the vapor partial pressure along the humidifying tube in a known manner (Kreidenweis et al., 1987). Moreover, thermodynamic analysis has shown that phase partitioning of multicomponent aerosol particles occurs during crystallization, and particles dried from multicomponent aqueous aerosols do not have a homogeneous chemical morphology except at the eutonic point (the point on a phase diagram where the mixture of chemical compounds has a single chemical composition that solidifies at a lower temperature than any other composition) (Ge et al., 1996).

Specific physico-chemical properties of selected saline aerosols represent key points for some of their multiple practical applications (e.g. prophylaxis and treatment of respiratory diseases, improvement of the cardio-respiratory parameters, purification and air quality improvement) (Chervinskaya and Zilber, 1995; Hedman et al., 2006; Sandu et al., 2010a; Cho et al., 2011). In particular, natural or generated saline sodium chloride (NaCl) aerosols have considerable importance in creating therapeutic environments (Smaldone et al., 1989; Beck-Broichsitter et al., 2009; Horowitz, 2010). It is believed that an important characteristic of saline aerosols is represented by the critical limit of the relative humidity that controls the formation of condensation nuclei through the deliquescence process (McGraw and Lewis, 2009). Up to now much work was devoted to the hygroscopicity and the dynamic shape of NaCl aerosols (Wise et al., 2007). Organic compounds may affect the hygroscopic properties of NaCl aerosol particles at relative humidity in the range of 30–90% (Hansson et al., 1998). For NaCl nanoparticles, there is suggestion that the dynamic shape is strictly related to the drying rate (Wang et al., 2010). Moreover, there are also reports about theoretical calculations on the total and regional depositions of dry NaCl aerosols in the human respiratory tract for initial particle diameters ranging from 0.01 to 10 μm (Xu and You, 1985). A theoretical model has been used to predict the efflorescence relative humidity (ERH) of NaCl particles in sizes ranging from 6 nm to 20 μm (Gao et al., 2007). Gao et al. (2007) found that when the NaCl particles are larger than 70 nm, the ERH decreases with decreasing dry particle size and reaches a minimum around 44–45% RH. In contrast, for particles smaller than 70 nm, the ERH increases with decreasing dry particle size because of the Kelvin effect. Usually, time variability in the chemical composition of NaCl aerosols seems to be induced by the interaction with water dipoles and other ions or particles during their structural reorganization. However, there is suggestion that the composition correlates with the aerosols shape and size (Sandu et al., 2003, 2010b, 2010c).

Submicron dispersions of dried saline aerosols are mainly used for therapeutic purposes (Mendes et al., 2009), while for ambient environments dried aerosols are of high interest (Stanier et al., 2004). The last situation is often associated to conditions equivalent to the “clean air effect”. In practical applications, the efficiency of aerosols and nanoparticles in prevention, care and cardio-respiratory function improvement is believed to depend on aerosols life time, abundance and shape, which should be very strictly controlled (Tang et al., 2006; King and Zayas, 2007; Beck-Broichsitter et al., 2009). There are reports on the effect of salt chamber treatment on bronchial hyperresponsiveness in asthmatics (Hedman et al., 2006) and on the use of specially designed halochambers, constructed to simulate the microclimate of salt mines (Chervinskaya and Zilber, 1995). Javaheri et al. (2013) suggested that when hygroscopic aerosols are inhaled, the size and temperature of the dispersed droplets (as well as the temperature and moisture content of the carrier gas) may change due to heat and mass transfer between the dispersed phase and the carrier gas, and also between the gas and the walls of the respiratory tract. The lowest deposition fraction in the extra-thoracic region and the highest deposition fraction in the alveolar region corresponded to droplets with low mass fraction, inhaled with an helium–oxygen mixture.

The present paper reports about the experimental evidence of the influence of doping Na, K and Ca halides on the generation mechanism of saline aerosols. The obtained results may have implications in the optimization processes of particles generation by dynamic halochambers used in medical applications.

2. Experimental

2.1. Salts used in saline aerosol generation

Reagent-grade salts from Sigma-Aldrich were used in the present investigation. Pure and doped NaCl salts were obtained by recrystallization from supersaturated aqueous solutions of binary salts mixed in different ratios. The contamination limit with other salts was established according to information related to the chemical composition of natural mine salt often