IMPACT OF KRYPTON-85 Beta RADIATION ON AEROSOL PARTICLE FORMATION AND TRANSFORMATION

V. Ulevičius\textsuperscript{a}, D. Butkus\textsuperscript{b}, K. Plauškaitė\textsuperscript{a}, A. Girgzdys\textsuperscript{b}, S. Byčenkiene\textsuperscript{a}, and N. Špirkauskaite\textsuperscript{a}

\textsuperscript{a} Institute of Physics, Savanorių 231, LT-02300 Vilnius, Lithuania
\textsuperscript{b} Vilnius Gediminas Technical University, Saulėtekio 11, LT-10223 Vilnius, Lithuania

E-mail: ulevicv@ktl.mii.lt

Received 6 October 2009; revised 19 November 2009; accepted 18 December 2009

In this study the effect of the air ionization by $^{85}$Kr beta radiation on the new particle formation and evolution of aerosol particle size distribution in the experimental chamber was investigated. During the experiments the interaction between air ionization and gas-to-particle conversion processes was distinctly observed. Results showed that the amplitude of the ionic current was dependent both on the chemical impurity concentration and the ionization source activity. Calculated values of parameters (growth and formation rates) of the particle nucleation process were larger when in the experimental chamber concentrations of SO$_2$ and $^{85}$Kr were higher. The growth rate values (42.1 and 45.3 nm/h) were by one order of magnitude higher than the environmental ones (1.2–9.9 nm/h at the Preila station, Lithuania). Experimental data showed that after injection of high SO$_2$ and $^{85}$Kr concentrations in the chamber during the 20 min interval nanometre-size particles created by nucleation were produced in large amounts. Thus, a larger amount of SO$_2$ significantly influenced the formation of new particles. During the first 5 min the concentration of 10 nm particles increased by 3 orders of magnitude with the formation rate of 7.47 cm$^{-3}$s$^{-1}$. The formation rate of 0.06 cm$^{-3}$s$^{-1}$ in the experiment with the average ambient SO$_2$ concentration (2–3 $\mu$g/m$^3$) was analogous to the environmental one (0.14 cm$^{-3}$s$^{-1}$). The coagulation sink ($\text{CoagS}_{1,2,3}$) was higher in the experiment with the ambient SO$_2$ concentration and resulted in the lower concentration of particles. The smaller values of the coagulation sink at the higher concentration of SO$_2$ gas have shown that these nano-particles in the air could persist for a longer time, probably in a stable size due to the ion charge.

Keywords: aerosol particles, experimental chamber, air ionization, nucleation characteristics, $^{85}$Kr, SO$_2$

PACS: 92.20.Bk, 92.60.Mt, 68.55.AA

1. Introduction

During recent years the concerns about climate of the Earth change effects due to atmospheric aerosol particles have increased considerably. Nucleation mode of particles ($D < 20$ nm) is highly effective in some geophysical processes [1, 2]. The production of nanometre-size particles by nucleation and their growth to detectable sizes have been investigated under various environmental conditions on regional and global scales: at remote [3, 4] and urban [5, 6] sites, in the boreal forests [7, 8], in the coastal zone [9, 10], in the marine environment [11, 12], etc. The specific conditions for the new particle formation might be formed at the location of nuclear facilities (nuclear power plant (NPP), nuclear fuel factory) as well. In these areas due to emission of radionuclides, mainly $^{85}$Kr gas, into the ground level air, the enlarged ionization field is formed in which the deformation of the profiles of ion components in the air and structure of aerosol size distribution are observed [13, 14]. The nuclear power plant of 1 MW releases into the atmosphere about 2.5\texttimes10^{21} atoms of $^{85}$Kr per year, producing radioactivity of 5.1\times10^{12} Bq [15].

The ground level air undergoes constant ionization (0.8\times10^6 ions/(m$^3$s)) due to ionizing radiation produced during the decay of natural radionuclides on the Earth’s crust and by the penetrating component of cosmic rays. The calculated ion generation rate in the NPP jet was 1.0\times10^6 ions/(m$^3$s), but in some cases under suitable meteorological conditions a ionization increase up to 1000 times in the vicinity of NPP can be expected [13, 16]. Therefore, in the environment of

\textsuperscript{*} This scientific publication of colleagues is dedicated to Dr. Arvydas Juozaitis (1959–1999), the initiator of research in this field at the Institute of Physics, Lithuania

© Lithuanian Physical Society, 2009
© Lithuanian Academy of Sciences, 2009

ISSN 1648-8504
operating nuclear objects potentially favourable conditions for aerosol particle formation events might be formed only over short time periods (from hours to a few days) or locally during the emergency situation of radionuclide emission.

However, in cases such as the Chernobyl accident when large soil areas (>10^4 km^2) with the high concentration of various life-time and type radiation radionuclides were polluted and more than 20 years passed, the increased ionization level in the air and aerosol size distribution deformation in these territories at present are observed [17, 18]. The aerosol particle concentration and the size distribution were mainly dependent on a few factors such as activity of the ionization source and duration, amount of water vapour, gas impurities in the air, etc. [14, 19].

Laboratory experiments demonstrated that alpha decay of short-lived actinon (²¹⁹Rn, half-life of 3.9 s) had a well pronounced influence on the aerosol particle nucleation and its evolution in time [20]. Repeated injection of ²¹⁹Rn resulted in formation of the bimodal aerosol particle size distribution. Madelaine et al. [20] considered coagulation of newly nucleated aerosol particles as a main process governing the aerosol particle growth toward larger diameters. Winklmyar et al. [21] studied radiolytically induced aerosol nucleation processes in a N₂–SO₂–H₂O mixture using ²⁴¹Am as an ionization source. Aerosol particles with the modal diameter of about 2 nm were registered within 1 s after nucleation under dry air conditions. At higher water vapour and SO₂ concentrations the aerosol particle concentration increased significantly and observed particles grew to a larger diameter.

The growth rate of aerosol particles is dependent on the type of chemical reactions involved in aerosol formation [22–24]. Chemical reactions can occur in the gas phase forming low vapour pressure products which condense on already existing aerosol particles or form new ones. Trace gases can also be adsorbed on the aerosol particle surface or absorbed within the airborne droplet. Theoretical expressions which give the dependence of the aerosol particle diameter growth rate, ΔD_p/Δt, on the particle diameter, D_p, are different for each type of chemical reactions and are called growth laws.

McMurry and Wilson [22], Ulevičius et al. [23], Verheggen and Mozurkewich [24] have shown that, if gas phase chemical reactions lead to the particle growth by a low pressure vapour condensation, ΔD_p/Δt is proportional to D_p⁰ in free molecule regime (D_p ≫ mean free path, λ), to D_p⁻¹ in continuum regime (D_p >> λ) and to D_p · f(Kn) in transition regime, where Knudsen number Kn = 2λ/D_p. If chemical reactions leading to the aerosol particle growth take place on its surface, then ΔD_p/Δt is proportional to D_p² over the entire size range. This means that rates of chemical reactions on the particle surface are slower than collision rates between aerosol precursor gases and aerosol particles. When aerosol precursor gases dissolve in the droplet and react at a uniform rate throughout the droplet volume, ΔD_p/Δt is proportional to D_p⁻¹.

Although the influence of the radioactive substances on the electrical properties of the atmosphere and transformation processes of aerosol particles is an indisputable fact, the majority of studies did not give information on the characteristics of the particle formation stages and evolution over time.

The aim of this study was to experimentally investigate the effect of the ionization by the ⁸⁵Kr beta radiation on the new particle formation in the air subject to chemical pollutant (SO₂) and the evolution processes of the aerosol particle size distribution.

2. Methods

2.1. Experimental set-up

The system of instruments for the experiment is schematically shown in Fig. 1. A plexiglass chamber (0.6 m³) was constructed at the Institute of Physics, Lithuania. It was equipped with a number of sensors for measurements of air temperature, relative humidity, pressure, and ⁸⁵Kr activity. The temperature was kept constant (20±0.2 °C) during each experiment using a mixture of water and alcohol, which was circulated through metallic radiators and stabilized by a thermostat. A temperature-controlled humidifier was used to establish a required level of relative humidity (80±2%).

A flexible bag (0.04 m³) with ⁸⁵Kr concentration equivalent to 10¹⁰ Bq/m³ radioactivity was used as a source of ⁸⁵Kr gas. The desirable concentration of ⁸⁵Kr in the experimental chamber was achieved by the dosage of ⁸⁵Kr gas entering the chamber from this bag through a particulate filter.

Prior to the experiment the plexiglass chamber was carefully brushed to avoid radioactive contamination. Once chamber was mechanically cleaned, the particle free air was flushed through this chamber at a flow rate of 60 l/min. Experiments were started when the aerosol particle number concentration dropped below the desired “background” level (0.01 particles/cm³).
The ionization current in the experimental chamber was measured with an apparatus consisting of the capacitor and the picovoltmeter. The electrodes of the capacitor were cylindrical, their size and distance between them as well as the air flow rate were selected to have a laminar air flow through the capacitor.

The capacitor was installed outside the experimental chamber. To measure the concentrations of aero ions within the mobility band of $4 \cdot 10^{-6} - 4 \cdot 10^{-3}$ cm$^2$/(V s) the difference of potentials between the electrodes of the capacitor was changed from 5 to 500 V. The current between the electrodes of the capacitor created by aero ions was equal to the current through the resistance.

Two experiments of the aerosol particle formation in ionization air by different activities of the $^{85}$Kr ($1 \text{ Bq/m}^3$, $4.6 \cdot 10^6 \text{ Bq/m}^3$) and SO$_2$ concentrations ($2$–$3 \text{ g/m}^3$, $23 \text{ g/m}^3$) were performed.

### 2.2. Aerosol size distribution and deposition in the chamber

The aerosol particle number concentration and size distribution in the diameter range from 0.01 to 0.3 μm were measured with an aerosol size spectrometer developed at the Institute of Physics, Lithuania [25, 26]. This spectrometer consists of a differential mobility analyzer (DMA) and a condensation particle counter (CPC).

The aerosol flow entered DMA through a bipolar charger $^{239}$Pu which was used to establish the bipolar charge distribution on polydisperse aerosol particles. The inlet and outlet flow rates of DMA were the same and were equal to 2 l/min. The particle free air flow in the differential mobility analyzer was equal to 201/min and was cycled through a high efficiency particulate (HEPA) filter by means of the two-way pump. The outlet flow of DMA carried charged monodisperse aerosol particles with the geometrical diameter $D_{pm}$ which was dependent on the voltage $U_i$ applied to the centre rod of DMA, the particle free air flow rate $Q_0$ through DMA, the number $\gamma$ of elementary charges $e$ on the particle, and the geometry of the analyzer:

$$D_{pi} = \frac{2\gamma e U_i l C_c}{3\eta Q_0 \ln(r_2/r_1)}.$$  

$C_c$ is the Cunningham slip correction factor which is a function of the particle diameter, $\eta$ is the dynamic viscosity of the suspending air, $l$ is the distance along the DMA centre rod from aerosol entry to extraction, and $r_1$ and $r_2$ are the radii of the DMA centre rod and the housing, respectively.

The number of aerosol particles at the exit of DMA was registered with a mixing type condensation particle counter. Three quarters of the aerosol flow entered CPC through a saturation chamber thermostated at 20 °C. The remaining aerosol flow passed through a HEPA filter into a saturation chamber thermostated at 80 °C. The two airflows saturated in the butanol vapour were mixed in a supersaturation chamber. The degree of supersaturating was sufficient to grow all aerosol particles larger than 0.01 μm to sizes compatible with the optical single particle counting. Grown aerosol particles were registered with an optical particle counter.

For the submicrometre particle size range measured, the effluent aerosol from DMA primarily consisted of charged particles with the geometric diameter $D_{pm}$ carrying one elementary negative charge. At the same time, there were particles carrying two or more negative elementary charges. These had different geometric diameters, as seen from Eq. (1). Therefore, the ambient aerosol particle concentration and size distribution were calculated from the measurement data applying the data inversion routine previously developed by Whitby [27] and Hoppel [28].

Several processes may cause the aerosol particle size distribution change during the experiment. Deposition of particles on surfaces may also be an important factor, especially in a small chamber. Chen et al. [29] have
shown that time change in the aerosol particle number concentration, \( N(t) \), can be expressed as

\[
\frac{dN(t)}{dt} = -\beta N(t),
\]

where \( \beta \) is a constant which can be found experimentally:

\[
\beta = -\frac{\ln \left( \frac{N(t)}{N(0)} \right)}{t},
\]

\( N(0) \) is the initial number concentration of the aerosol particle.

Aerosol particle size distributions were measured immediately after the injection of aerosol into the chamber and after 300 seconds. The constant \( \beta \) calculated from the measurement data was size-dependent (Table 1). It decreased from \( 56 \times 10^{-5} \) to \( 4.0 \times 10^{-5} \) \( \text{s}^{-1} \) when the aerosol particle size increased from 0.01 to 0.1 \( \mu m \).

These values of the constant \( \beta \) were used in our data analysis.

### 3. Theoretical approach

A log-normal fitting of the aerosol particle size distribution was carried out. For both experiments the growth rate was calculated graphically from the contour plots (such as Figs. 3(b) and 4(b)), and, furthermore, the concentration of condensable vapour can be estimated from the growth rate. Since the exact identity of the condensable vapour is unknown, the concentrations were estimated by using transport values of sulphuric acid. Using given Eqs. (4)–(7), the characteristics of the new particle formation and growth during the investigation were calculated. The results of those calculations are presented in Table 2. The observed particle formation and growth, the source rate of condensable material, and the changes of hygroscopic properties were analysed using three equations describing the rate of change of the vapour concentration, the aerosol particle number concentration, and the particle growth using the method by Dal Maso et al. [8]. Considering that condensable vapour molecules are of species \( X \), the time dependence of vapour concentration (\( C \)) can be expressed by [30]

\[
\frac{dC}{dt} = Q - CS \cdot C,
\]

where \( Q \) is the source rate of vapour and \( CS \) is its condensation sink rate on pre-existing aerosol. The time evolution of the aerosol number concentration (\( N \)) in the size class \( i \) can be presented by [31]

\[
\frac{dN_i}{dt} = J_i - \text{CoagS} \cdot N_i,
\]

where \( J_i \) is the formation rate of particles and \( \text{CoagS} \) is the coagulation sink rate for size \( i \) particles. The growth rate can be expressed as [32]

\[
\frac{dr}{dt} = \frac{m_v \beta_m DC}{r \rho}.
\]

Here \( r \) is the particle radius, \( m_v \) is the molecular mass of condensable vapour, \( \beta_m \) is the transitional correction factor for mass flux, \( D \) is the diffusion coefficient, and \( \rho \) is the particle density. Equation (6) can be integrated from \( r_0 \) to \( r \) to obtain

\[
C = \left\{ \rho \left[ \frac{r^2 - r_0^2}{2} + \left( \frac{4}{3 \alpha} - 0.623 \right) \lambda (r - r_0) \right] \right\}(\Delta t D m_v)^{-1}.
\]

Here \( \alpha \) is the mass accommodation coefficient (i.e., sticking probability) and \( \lambda \) is the mean free path. Directly from measurements of the aerosol size distribution changes and hygroscopicity properties, \( dr/dt \), \( CS \), \( \text{CoagS} \), \( dN_{10 \text{nm}}/dt \), \( N_{\text{nucleation mode}} \), and the soluble fraction can be obtained. Detailed analysis of these equations can be found in Dal Maso et al. [8].

### 4. Results and discussion

Curve 2 in Fig. 2(a) shows that the ionic current increased by a factor of about 1.6 when a high concentration of \( ^{85}\text{Kr} \) (about 1.0 Bq/m\(^3\)) was injected into the chamber containing the ambient activity concentration of \( ^{85}\text{Kr} \). A similar increase in the ionic current due to the injection of \( \text{SO}_2 \) (2–3 \( \mu \text{g/m}^3 \)) was observed in the chamber containing high activity concentration of \( ^{85}\text{Kr} \) (4.6 \( \times \text{10}^6 \) Bq/m\(^3\)), (see \( J \) in Fig. 2(b)). The only difference was that the magnitude of the ionic current in the second case (2 in Fig. 2(b)) was about five times higher in comparison with the ionic current shown by 2 in Fig. 2(a). During the experiment the high concentrations of \( \text{SO}_2 \) (23 g/m\(^3\), to verify \( \text{SO}_2 \) impact

**Table 1. The constant \( \beta \) calculated from the measurement data.**

<table>
<thead>
<tr>
<th>( \beta ), ( 10^{-5} ) ( \text{s}^{-1} )</th>
<th>0.01</th>
<th>0.02</th>
<th>0.03</th>
<th>0.04</th>
<th>0.05</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta ), ( \mu m )</td>
<td>56.0</td>
<td>23.0</td>
<td>17.0</td>
<td>11.0</td>
<td>5.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>
on the new particle formation and growth) and \(^{85}\)Kr activity (4.6±0.5)×10^6 Bq/m^3 in the chamber were injected.

The functional dependence of the ionic current on the voltage applied to the centre rod of the capacitor gives us information about mobility of aero ions generated in the experimental chamber. It is seen that the main increase in the ionic current was achieved when the voltage \(U\) was increased up to 100 V. This shows that light aero ions with the mobility above 2.0×10^−5 cm^2/(V s) have been mostly responsible for the ionic current observed in our experiments. The measured slight increase in the ionic current after raising the voltage from 100 to 500 V demonstrates that aero ions with the mobility between 4.0×10^−6 and 2.0×10^−5 cm^2/(V s) have also been present in the chamber, however, at much lower concentrations.

Air ionization promotes the oxidation of ambient gases as well as affects the surface properties of aerosol particles, therefore, it was expected that comparatively large aerosol particle formation and growth rates should be observed at high \(^{85}\)Kr activity concentration. Data shown in Figs. 3 and 4 confirm this assumption.

In Fig. 3 it is shown that the injection of \(^{85}\)Kr gas into the experimental chamber promotes the hygroscopical growth of aerosol particles and subsequently changes their size distribution. The models describing the hygroscopical growth of aerosol particles usually do not take into account the state of the air ionization. However, the data shown in Fig. 3(a, b) provides clear evidence that the hygroscopical growth factor is dependent on the air ionization.

As can be seen from Fig. 3(a, b), the concentration of aerosol particles of all sizes increases more than 10 times. Figure 4(a, b) shows the effect of the \(^{85}\)Kr beta radiation on the time change in the aerosol particle size distribution when \(^{85}\)Kr and sulphur dioxide are present in the experimental chamber at high concentrations. There was a sudden increase in the aerosol number concentration after injecting \(^{85}\)Kr into the experimental chamber.
Table 2. Calculated characteristics of nucleation events in both experimental cases.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>GR, nm/h</th>
<th>$J_{10}$, cm$^{-3}$s$^{-1}$</th>
<th>Coag$S_1$, s$^{-1}$</th>
<th>Coag$S_2$, s$^{-1}$</th>
<th>Coag$S_3$, s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$ (2–3 µg/m$^3$), $^{85}$Kr (4.6±0.5)·10$^6$ Bq/m$^3$</td>
<td>42.1</td>
<td>0.06</td>
<td>3.20E-03</td>
<td>1.10E-03</td>
<td>6.00E-04</td>
</tr>
<tr>
<td>SO$_2$ (23±2.5) g/m$^3$, $^{85}$Kr (4.6±0.5)·10$^6$ Bq/m$^3$</td>
<td>45.3</td>
<td>7.47</td>
<td>2.70E-03</td>
<td>9.00E-04</td>
<td>5.00E-04</td>
</tr>
</tbody>
</table>

Fig. 4. (a) Size dependent variation of aerosol particle concentration and (b) time evolution of aerosol particle size distribution at 23±2.5 g/m$^3$, $^{85}$Kr (4.6±0.5)·10$^6$ Bq/m$^3$ of $^{85}$Kr.

chamber. During 5 min the concentration of aerosol particles with the diameters of 10 nm increased by three orders of magnitude. The concentration of aerosol particles larger than 30 nm increased more than 10 times. During the next 15 min the concentration of aerosol particles in the size range from 10 to 20 nm still increased due to the nucleation of new aerosol particles, while the number of aerosol particles larger than 30 nm remained stable. This means that the increase in the aerosol particle number concentration due to the gas-to-particle conversion in this size range is of the same magnitude as the chamber wall losses.

All calculated values of parameters of the particle nucleation processes were higher, while the concentrations of SO$_2$ and $^{85}$Kr in the experimental chamber were higher, except the coagulation sink (Coag$S_{1,2,3}$).

5. Conclusions

During the experiments the interaction between air ionization and gas-to-particle conversion processes was distinctly observed. Our results showed that the amplitude of the ionic current was dependent both on the chemical impurity concentration and the ionization source activity in the experimental chamber. Calculated values of parameters (growth and formation rates) of the particle nucleation process were larger when concentrations of SO$_2$ and $^{85}$Kr were higher. Experimental data showed that after injection of high SO$_2$ and $^{85}$Kr concentrations in the chamber during the 20 min interval nanometre-size particles (as most dangerous for human health) created by nucleation were produced in large amounts. The difference of growth
rate values during experiments was not very significant and the notable increase of the concentration of larger particles was not observed. The growth rate values (42.1 and 45.3 nm/h) were by one order of magnitude higher than the environmental ones (1.2–9.9 nm/h at the Preila station). The larger amount of SO$_2$ significantly influenced the formation of new aerosol particles. The largest formation rate ($J_{10}$) of aerosol particles was detected at high ionization, 80% relative humidity, and high SO$_2$ concentration, 80% relative humidity. 

The smaller values of the coagulation sink at the higher concentration of the formed particles was observed. The smaller values of the coagulation sink at the higher concentration of SO$_2$ gas have shown that these nano-particles in the air could persist for a longer time, probably in a stable size due to the ion charge. Although the processes occurring in the experimental chamber may differ significantly from those observed in the natural environment, however, during the nuclear accident after penetration of large amounts of radionuclides involving also Kr isotopes and various gaseous chemical compounds, such processes are possible in the atmosphere as well.

References


[18] V. Smirnov, Electrical characteristics of the air in the zone of the Chernobyl NPP accident, Collections IEM 19(152), 111–122 (1992) [in Russian].


$^{85}$Kr BETA SPINDULIUOTĖS ĮTAKA AEROZOLIO DALELIŲ FORMAVIMUISI IR TRANSFORMACIJOMS

V. Ulevičius $^a$, D. Butkus $^b$, K. Plauškaitė $^a$, A. Girgždys $^b$, S. Byčenkienė $^a$, N. Špirkauskaitė $^a$

$^a$ Fizikos institutas, Vilnius, Lietuva

$^b$ Vilniaus Gedimino technikos universitetas, Vilnius, Lietuva

Santrauka

Eksperimentini įtaka kamerose tirtas $^{85}$Kr beta spinduliuotės jonizacijos, sukeltos ore, poveikis aerozolio daleių susidarymui ir jų dydžių spektrui. Aerozolio daleių formavimuisi poveikį turėjo ir jonizacijos laipsnis, ir cheminės priemašos (SO$_2$) koncentracija. Įvedus į kamерą didesńios SO$_2$ ir $^{85}$Kr koncentracijas, per pirmaisias 20 min. aerozolio daleių koncentracijos padidėjo net kelios procentų. Yučių aerozolio daleių koncentracija padidėjo pavidalo kamerose SO$_2$ koncentracija. Esant didesniams SO$_2$ koncentracijai, greičiausiai formavosi ir aerozolio daletés, o formavimosi grei-