Asian Journal of Atmospheric Environment
Vol. 7-3, pp.161-168, September 2013
doi: http://dx.doi.org/10.5572/ajae.2013.7.3.161

Laboratory-scale Experiment and Model Calculation on the Washout Mechanism of Asian Dust Particles

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ABSTRACT

In this study, an investigation was conducted to assess the washout mechanism of Asian dust particles through both laboratory-scale experiment and model calculation. To artificially simulate Asian dust particle, $CaCO_3$ particles were generated inside an experimental chamber. They were then scavenged by the artificial rain drops. The abundant $CaCO_3$ particles scavenged on a rain drop were successively identified by SEM observation. The concentrations of Ca in residual $CaCO_3$ particles on individual droplet were quantified by PIXE analysis. There was a tendency toward a high accumulation of Ca on a relatively small drop (e.g., <1.0 mm diameter). It is thus suggested that smaller rain drops can effectively scavenge a significant amount of Asian dust particles in ambient atmosphere. The numerical estimation can account for 92.1% and 83.2% of Ca that were measured in small (<1.0 mm diameter) and large (>2.0 mm diameter) size drops, respectively.

Key words: Asian dust, Washout, Raindrop, Wet deposition, Scavenging, PIXE

1. INTRODUCTION

Asian dust storm is a serious and growing environmental problem in East Asia as well as the Pacific Basin. Although particles are removed from the atmosphere by wet and/or dry depositions, the former proceeds more efficiently in the form of precipitation such as rain, fog, snow, etc. Aerosols including Asian dust particle penetrate cloud droplets or ice crystals through the nucleation process, acting as cloud condensation or ice nuclei, and through the process of impaction with cloud droplets or ice crystals (Pruppacher and Klett, 1997). A fraction of these droplets will then precipitate and fall from the atmosphere (Croft *et al.*, 2010). In spring time, the Yellow rainfall episode has been measured in Korean Peninsula, Japanese Island, and Pacific Ocean (Kawamura and Hara, 2006; Ma, 2006). This yellow coloration of rain can be attributed to the soil particles originating from the desert and loess areas in China.

In order to understand the influence of Asian dust on precipitation chemistry, Kawamura and Hara (2006) analyzed the precipitation datasets of a nationwide monitoring network in Japan. These authors observed the enhancement of pH and non-sea salt calcium concentration levels during Asian dust event relative to non-Asian dust period. They suggested that this phenomenon should occur by the dissolution of the calcium carbonate (in Asian dust particles) into precipitation.

In order to better understand the wet scavenging properties of Asian dust particles and their fraction removed by wet deposition, the chemical characteristics of the rain sample collected during the Asian dust storm event need to be elucidated. However, there have been only a few studies which focused on the environmental significance of the wet scavenging as the controlling mechanism of Asian dust storm particles. Moreover, researches on the wet scavenging of Asian dust particle have scarcely been made to date by the laboratorial scale model experiment. The washout of Asian dust particle cannot be explained simply by mineral composition of rainwaters because their chemical content is variable in relation to the size of rain drop (Ma *et al.*, 2001; Tenberken and Bächmann, 1996). The modeling study of wet scavenging accompanied by experimental verification is thus expected to provide a better knowledge concerning the removal characteristics of Asian dust particles.

This study has been carried out to help improve our understanding of the scavenging of Asian dust particle by rainfall. To provide detailed insights into such removal mechanism, a laboratory-scale experiment was conducted. In addition, the amount of Asian dust particles scavenged by size-fractionated raindrops was estimated on theoretical basis.

2. EXPERIMENTAL METHODS

2.1 Description of the Experimental Setup

For the experimental measurement of washout of Asian dust particle, a laboratory-scale experimental setup was designed. It consists of a chamber (D 0.2 m, H 9.5 m), an artificial Asian dust particle distributer, a drop generator, a drop collector, and an optical particle counter. For the rainfall generation in the laboratorial experiment, the height of experimental chamber has to be the height required to leach to terminal velocity of drop.

A quantitative theoretical and experimental investigation of Wang and Pruppacher (1977) showed that at 1000 mb and 20°C, the drops of equivalent radius with 100, 200, 300, 400, 500, 600, 700, 800, 900, 1000 and 2000 μm require 0.15, 0.71, 1.6, 2.8, 3.9, 5.2, 6.3, 7.3, 8.4, 9.5 and 14.0 m to accelerate up to 99% of their terminal velocity, respectively. Accordingly, 9.5 m of height is not sufficient for the experimental chamber to thoroughly assess wet scavenging of Asian dust particle compared to ones with at least several tens of meters for a quasi-real scale model.

As mentioned earlier, because the analysis of rain as bulk phase will not necessarily provide detailed information of droplet scavenging, the size-classified droplets were collected and analyzed individually in this study. Our raindrop collector illustrated at the bottom leftside of Fig. 1 consists of a Dewar vacuum flask (Jencons Co.) filled with liquid nitrogen and a stainless steel sieve (Nonaka Rikaki Co.) with 0.2 mm mesh size. Raindrops fallen into the liquid nitrogen were frozen and handled for subsequent elemental analysis.

2.2 Procedures of a Laboratorial Model Experiment

The procedures adopted in this study for the laboratory-scale experiment were as follows:

(1) As the artificial Asian dust particle, $CaCO_3$ particles (98.8% of assay, Linzunyaku co.) fractioned into 2 size classes (2-5 μm and >5 μm) were diluted by 99% ethyl alcohol.

(2) The particle number concentration in a chamber was continuously measured by the end of each experimental period.

(3) The diluted $CaCO_3$ particles were brought into a

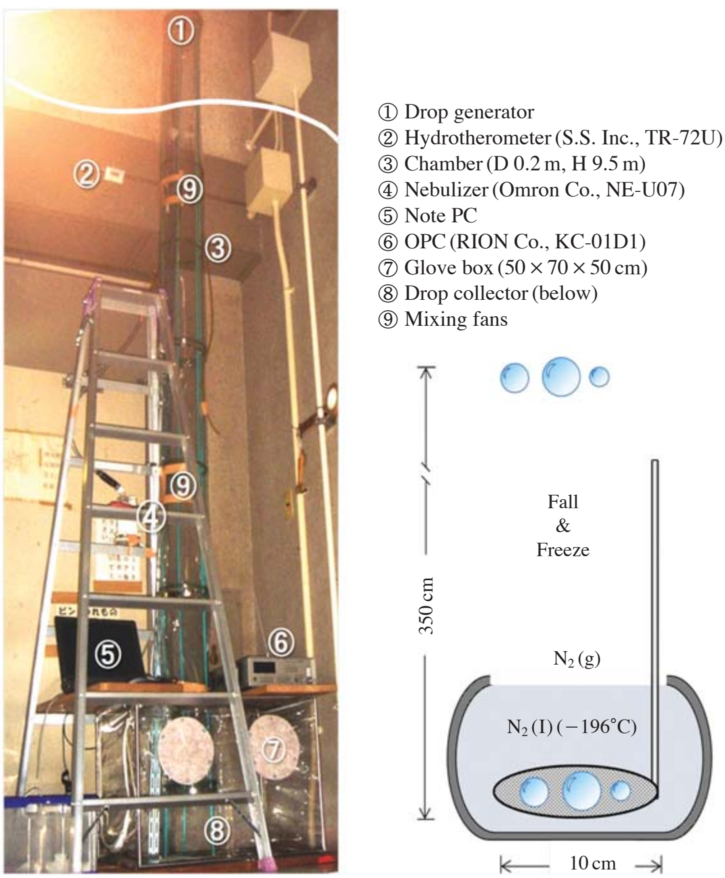

Fig. 1. Experimental set up to study the scavenging of dust particles by rainfall.

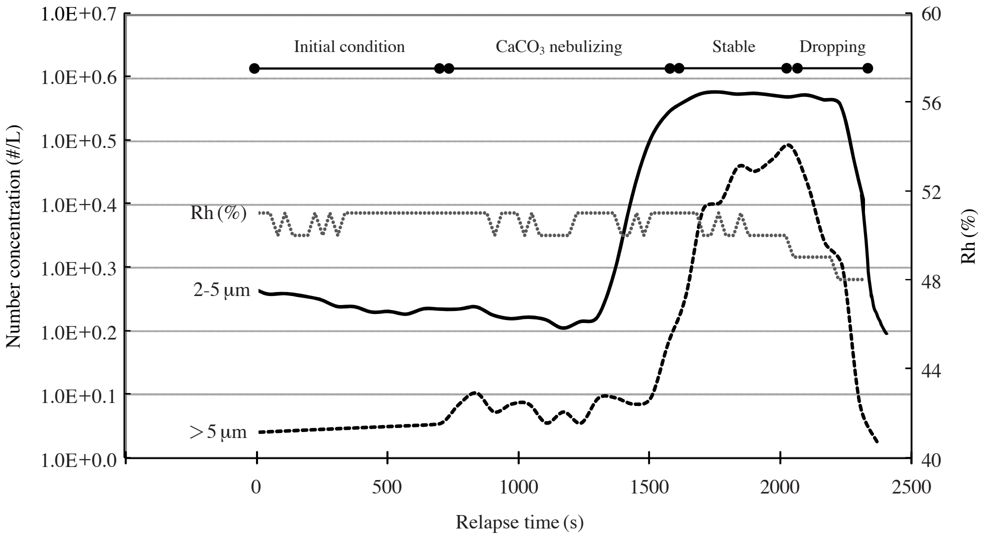

Fig. 2. Variation of particle number concentration and relative humidity during model experiment.

chamber through a nebulizer.

(4) The number concentration of $CaCO_3$ particles was maintained constantly in a chamber prior to dropping of artificial raindrops.

(5) Raindrops were generated at the upper side of a chamber and then fell through a chamber.

2.3 Handling, Pretreatment, and Analysis of Individual Drop

Artificial raindrops were collected during about three minutes. After collection, a sieve was pulled out from the dewar vacuum flask, and the raindrops frozen on the sieve were placed on Nuclepore filter (10 μm thickness) by using a vacuum pipette. The frozen raindrops were melted and dried under an infrared lamp for five minutes. Every handling process was performed in a clean air system filled with the cool nitrogen gas. Then the residual solid particles on Nuclepore filter were subsequently analyzed.

The elemental concentration of Ca on the residues of individual drop was determined by the particle induced X-ray emission (PIXE) installed at the Cyclotron Research Center of Iwate Medical University. As widely known, this PIXE system has the great advantages such as an excellent sensitivity, a nondestructive technique for multielement with a wide range of elements ($Z > 10$). The sensitivity, if defined by the ratio between PIXE yield per unit dose and mass thickness, can be determined for all objective elements both experimentally and theoretically. For instance, the sensitivity of calcium was calculated to be 1700 (counts · cm^2/μC · μg) with a detection limit of 9.4×10^{-3} (μg/cm^2). The more detailed analytical procedures and experimental setup for PIXE analysis were described elsewhere (Sera *et al.*, 1999).

3. RESULTS AND DISCUSSION

3.1 Variation of Particle Number Concentration during a Period of Model Experiment

In this work, the number concentrations of two-size particle fractions (i.e., 2.0-5.0 μm and >5 μm) were adjusted to include those of real ambient Asian dust particles measured in Kyoto Japan (Ma and Choi, 2007; Ma *et al.*, 2005). On the average of five-time model experiments in which $CaCO_3$ particles were nebulized into a chamber, the number concentrations of $CaCO_3$ particles with 2.0-5.0 and >5 μm diameter ranges were between 3.7×10^2 and 6.1×10^5 and between 10 and 5.5×10^4 particles L^{-1}, respectively.

The variation of particle number concentrations at two-size fractions with relative humidity during a period of model experiment is displayed in Fig. 2. This time serial particle number concentration severely fluctuated throughout the whole experimental period (initial condition - $CaCO_3$ nebulizing - stable (uniform $CaCO_3$ particle number concentration) - raindrop falling (drop falling with 12 mm hr^{-1} rainfall intensity)) of five-time model experiments. The experiments were carried out at relative humidity varying from 48 to 51%. The particles showing a slight varying of number concentration at initial condition in Fig. 2 mean the initial background particles in the chamber of model experiment. The number concentrations of both sizes

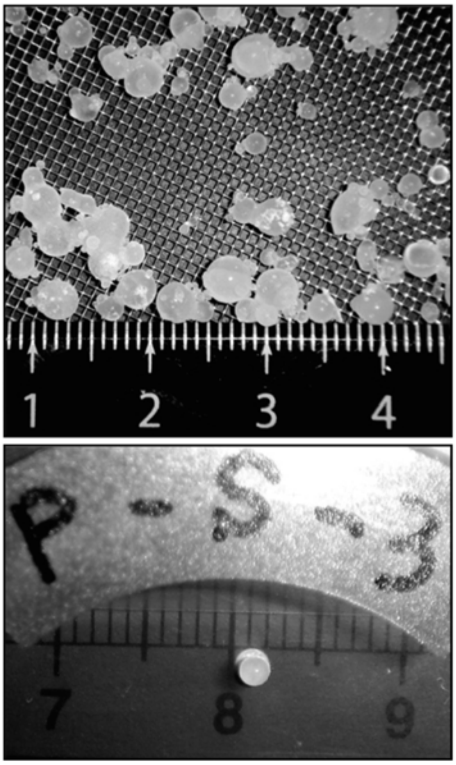

Fig. 3. Spherical frozen raindrops artificially dropped at the top of experimental chamber.

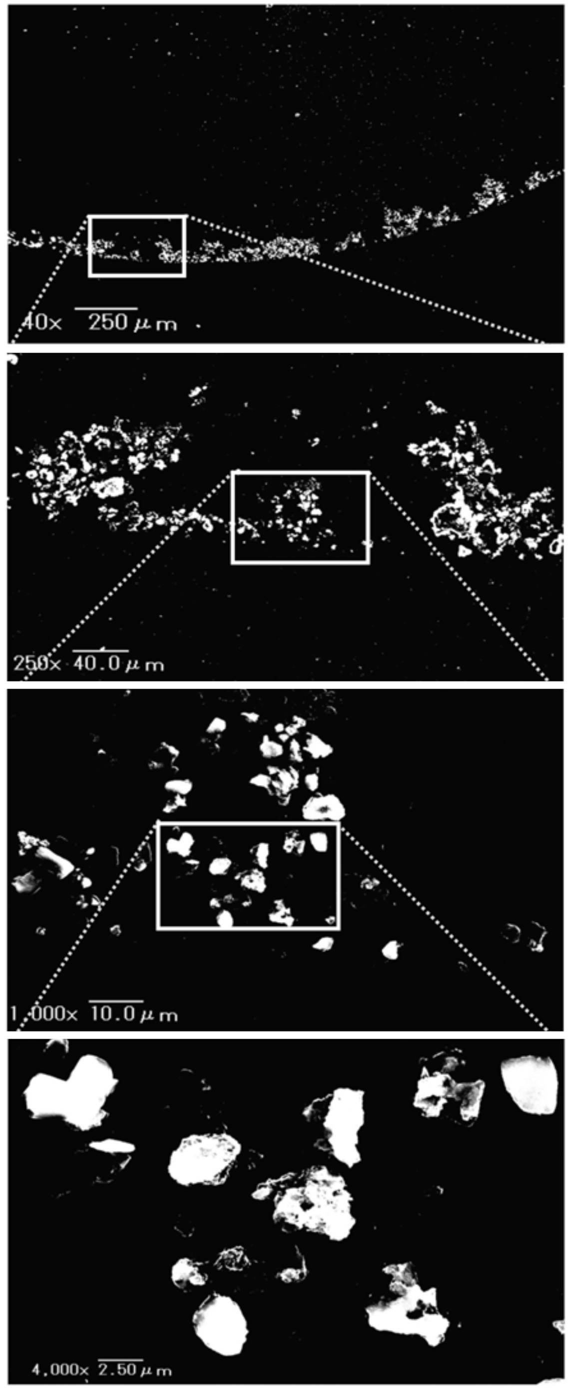

Fig. 4. Residual $CaCO_3$ particles distributed at a portion of the rim of a dried drop.

of $CaCO_3$ particles fell right down to the level of initial condition during the 5 minutes. Therefore, although $CaCO_3$ particles are not very soluble and do not easily react in water, nearly all of them including a portion of background particles in the experimental chamber were scavenged. Gravitational settling of large particles (>5 μm) can be negligible due to the facts: (1) the $CaCO_3$ particles simulated for the Asian dust particle are smaller than 7 μm, and (2) two small scale fans were operated to distribute $CaCO_3$ particles uniformly in our experimental chamber.

The real size of $CaCO_3$ particles retained in a drop could be identified by the photograph of a scanning electron microscope (SEM, KYENCE, VE-7800) (Fig. 4).

3.2 Identification of $CaCO_3$ Particles Embedded in Drop

Fig. 3 shows the individual frozen drops collected on a stainless steel sieve (top) and a drop placed on a filter media (bottom). The raindrops maintained their spherical shape during the freezing process. Consequently, it was possible to separate the frozen raindrops according to their size for the further analysis. The size fractions of individual drops classified as <1.0 mm, 1.0-2.0 mm, and >2.0 mm were 67.5%, 20.5%, and 12%, respectively.

In order to certify the existing of $CaCO_3$ particles in the melted and dried drop, a microscopical observation was carried out by means of a SEM. As shown in Fig.

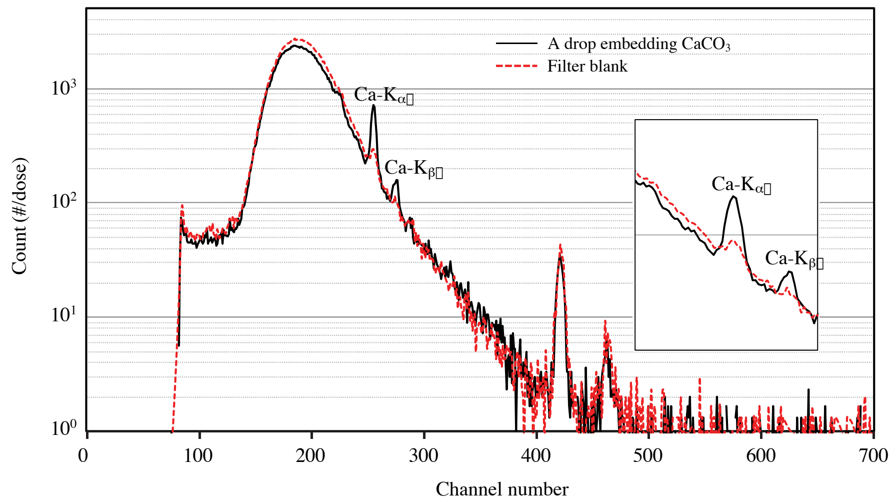

Fig. 5. PIXE spectrum of $CaCO_3$ particles embedded in a drop.

4, the detailed morphology of the residual $CaCO_3$ particles indicates a large number of $CaCO_3$ residual particles retained in a drop, while most of them were distributed at the rim of a dried drop. It thus suggests undoubtedly that raindrop should be capable of scavenging significant quantities of Asian dust particles in the ambient atmosphere too.

3. 3 Quantification of Chemical Components in a Single and Size-fractionated Drop

In order to quantitatively describe the raindrop scavenging of $CaCO_3$ particle, an analysis was made to determine chemical components in a single and size-fractionated drop by use of a PIXE. Fig. 5 shows the PIXE spectra of the residual particles embedded in a drop as well as filter blank. It was possible to resolve the Ca peaks corresponding to channel number of PIXE spectra, whereas no meaningful peaks of other elements were detected. Although the lighter elements ($Z < 10$) cloud not be measured by a PIXE, the analysis of PIXE spectra for residual particles indicates that the peak of Ca-K_α coexisting with Ca-K_β, drawn between 200 to 300 channel numbers, was derived from $CaCO_3$ particles nebulized into a chamber instead of chamber background particles.

Fig. 6 shows the variation of Ca concentration as a function of rain drop diameter. Ca concentration of individual drop shows a continuous decrease with increasing drop size.

Based on the representative diameter of $CaCO_3$ particle (3.5×10^{-4} cm), the density of $CaCO_3$ (2.93 g cm^{-3}), and the ratio of $CaCO_3$ molecular weight of to Ca atomic weight, the number concentration of $CaCO_3$ particle (# L^{-1}) at each drop size was also calculated (see Fig. 6). It is expected that several mechanisms should be responsible for the Ca enrichment in the smaller drop (< 1.0 mm). In the ambient atmosphere, it is acknowledged that smaller raindrops should have higher elemental concentration because of their low settling velocities and associated longer lifetimes. Such pattern may also be accounted for by the effect of evaporation. As small raindrop shows a much higher degree of evaporation than larger ones, the former is likely to exhibit an increase of the elemental concentration. However, in this study, both longer lifetime and active evaporation of small size drop cannot justify enhanced Ca concentrations. This is because the height of experimental chamber is not more than 9.5 m in consideration of the terminal velocity of a drop. The humidity in

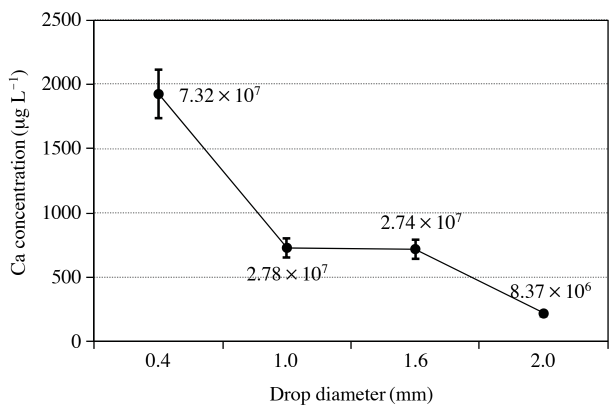

Fig. 6. Drop size dependence of Ca concentration estimated by PIXE analysis. The numbers inside the figure indicate the number concentration of $CaCO_3$ particle (# L^{-1}) at each drop size.

the chamber was also not so low (around 50% through a whole experimental period). Therefore, the drop size dependence of Ca concentration might be accounted for by the combined effects of such factors as: the processes of Brownian diffusion, interception, and impaction between $CaCO_3$ particles and falling drops. Meanwhile, Brownian diffusion might not play a critical role in $CaCO_3$ scavenging because, as mentioned above, the size of $CaCO_3$ particles nebulized into the experimental chamber were larger than 2 μm.

Kim *et al.* (2007) carried out the study on the number size distribution of atmospheric aerosols during both the Asian dust and precipitation events. These authors reported that during precipitation particles in the coarse mode were scavenged by impaction mechanism and the degree of scavenged particle varied depending on the rainfall rate, raindrop size distribution and aerosol size distribution.

3.4 Theoretical Model Calculation of $CaCO_3$ Particles Scavenged by Falling Drops

In order to make a quantitative estimation of the washout properties of $CaCO_3$ particles as a function of raindrop size, a theoretical model calculation was carried out. The schematic of model concept and three scavenging processes are illustrated in Fig. 7. This model is a Lagrange type model that can set the special coordinates as the one-dimensional vertical direction from the top to bottom of the experimental chamber (H_T). For a model calculation, we assumed several parameters as follows: the uniform distribution of $CaCO_3$ particles existing in a volume ($V=h_t \times \pi d_r^2/4$ in Fig. 7) swept by falling drop, no diffusion by the operating of fans, and no evaporation and coalescence of drops.

Let us define the mass concentration of $CaCO_3$ particles with diameter d_{CaCO_3} in the experimental chamber as $C_{CaCO_3 0}(d_{CaCO_3})$ and the collection efficiency of drop with d_r for $CaCO_3$ particles with diameter d_{CaCO_3} as $E_0(d_r, d_{CaCO_3})$. Then, the mass (m_{CaCO_3}) of $CaCO_3$ particles (d_{CaCO_3}) in drop (d_r), which falls through V for one second, can be written as following.

$$m_{CaCO_3}=\frac{\pi d_r^2}{4}\upsilon_t \cdot C_{CaCO_3 0}(d_{CaCO_3}) \cdot E_0(d_r, d_{CaCO_3}) \tag{1}$$

Therefore, the total mass (M_{CaCO_3}) of $CaCO_3$ particles (d_{CaCO_3}) in drop (d_r), which falls in the chamber from top to bottom, can be rearranged into the following equation.

$$M_{CaCO_3}=\int_0^t \frac{\pi d_r^2}{4}\upsilon_t(h_t, d_r) \cdot C_{CaCO_3}(h_t, d_{CaCO_3}) \cdot E(h_t, d_r, d_{CaCO_3})dt \tag{2}$$

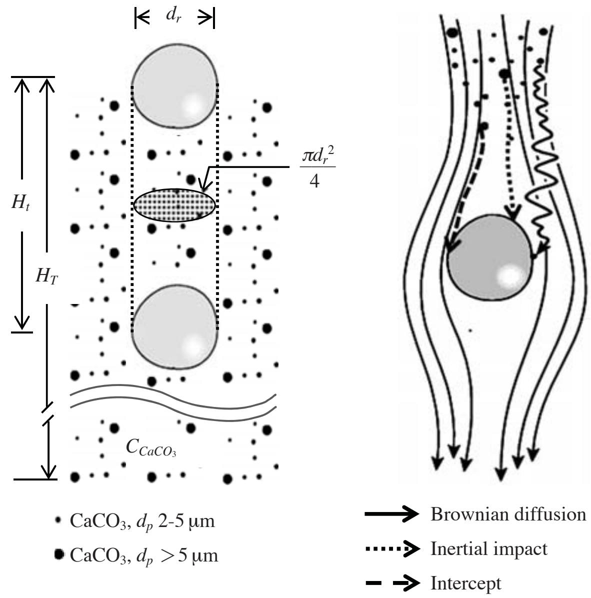

Fig. 7. The conceptional illustrations of the model calculation of dust particles by rainfall scavenging (left) and three scavenging processes (right).

where $\upsilon_t(h_t, d_r)$ is the terminal velocity of drop (d_r) at height (h_t), $C_{CaCO_3}(h_t, d_{CaCO_3})$ is the mass concentration of particles existing at height (h_t), and $E(h_t, d_r, d_{CaCO_3})$ is the collection efficiency of raindrop (d_r) for $CaCO_3$ particle (d_{CaCO_3}) at height (h_t).

Slinn and Hales (1971) proposed three particle collection efficiencies (E), i.e., Brownian diffusion (E_{dif}), E by interception (E_{int}), and E by inertial impaction processes (E_{imp}). Furthermore, Strauss (1975) suggested the following combined particle collection efficiency (E_{com}) equation:

$$E_{com}=1-(1-E_{dif}) \cdot (1-E_{int}) \cdot (1-E_{imp}) \tag{3}$$

Meanwhile, to calculate the $CaCO_3$ particle collection efficiency ($E(d_r, d_{CaCO_3})$), Strauss's E_{com} (Strauss, 1975) was modified further because Brownian diffusion is not meaningful for the $CaCO_3$ particles in this study with large diameter (>2 μm).

$$E_{com}=1-(1-E_{int}) \cdot (1-E_{imp}) \tag{4}$$

The following are E_{int} and E_{imp} applied in this work.

$$E_{int}=4\frac{r_{CaCO_3}}{r_r}\left(\frac{\mu_a}{\mu_r}+(1+2Re^{1/2})\frac{r_{CaCO_3}}{r_r}\right) \tag{5}$$

$$E_{imp}=\left(\frac{St-S^*}{St-S^*+2/3}\right)^{3/2} \tag{6}$$

where r_{CaCO_3} is $CaCO_3$ particle radius (μm), r_r is drop radius (μm), μ_a is dynamic viscosity of air (Pa · s), μ_r is dynamic viscosity of water (Pa · s), Re is the Rey-

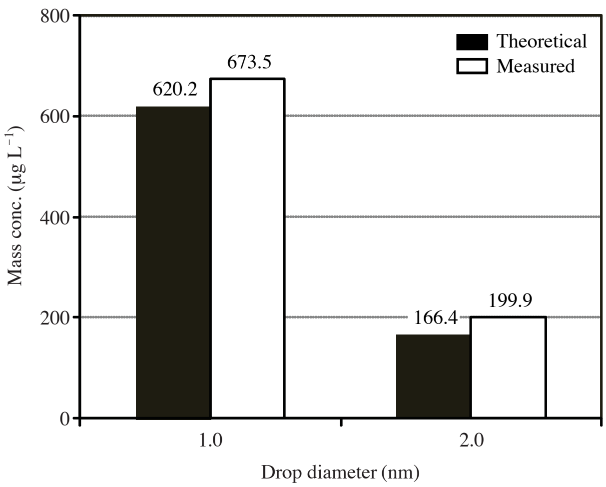

Fig. 8. A comparison between experimentally and theoretically estimated Ca concentrations.

nolds number of drop based on its radius (($r_r \cdot \upsilon_t \cdot \rho_a$ (air density kg m^{-3}))/μ_a), St is the Stokes number of collected $CaCO_3$ particle ((2C (Cunningham slip factor) $\cdot$ ρ_{CaCO_3} ($CaCO_3$ particle density kg m^{-3}) $\cdot$ r_{CaCO_3} $\cdot$ υ_t)/(9$\mu_a \cdot r_r$)), and S^* is the critical Stokes number ((1.2+(1/12)ln(1+Re))/(1+ln(1+Re))).

The result of model calculation of Ca concentration in the fractionated drop size (i.e., 1.0 mm and 2.0 mm drop diameter) is plotted along with the actual PIXE results in Fig. 8. Here, the theoretically estimated Ca concentration was determined by $CaCO_3$ mass concentration. The result of this intercomparision exhibits the severe drop size fluctuation, although both theoretical and measured Ca concentrations were enriched consistently in small drop size (1.0 mm drop diameter). The theoretical Ca concentrations accounted for 92.1% and 83.2% of those measured from small and large size drops, respectively. This result suggests that the processes of interception and inertial impaction should be the essential components of scavenging mechanisms of $CaCO_3$ particles. One of the reasons for these discrepancies between measured and calculated Ca concentrations might be the limitation on our experimental chamber (i.e., partially inhomogeneous particle distribution from top to bottom, insufficient H_T, etc.). The Ca amount, underestimated by model calculation, can nonetheless be compensated by other mechanisms like electrostatic force and thermophoresis between $CaCO_3$ particles and drops.

4. CONCLUSIONS

Asian dust particles are ultimately removed from the atmosphere by the natural processes generally referred to as wet precipitation and dry deposition. The former also called as washout and wet scavenging is the most important natural removal mechanisms of ambient air pollutants including Asian dust particles. The episodically yellowish rain falling during Asian dust storm is a good proof of this wet precipitation.

In this study, in order to describe the wet removal characteristics of Asian dust particles, both a laboratory-scale experiment and a model calculation were carried out at the same time. While there were several limitations in the experimental set up, by a combination of these two approaches, the concentrations of $CaCO_3$ particles used for the simulation of artificial Asian dust particles were successfully quantified as a function of raindrop size. At laboratory scale, the processes of interception and inertial impaction were responsible for the high Ca concentration in the rain drop smaller than 1.0 mm. Although the in-cloud scavenging (i.e., rainout mechanism) of Asian dust particles was not considered in this study, the results of this study strongly support the idea that wet precipitation is one of the effective dissipation mechanisms of Asian dust storm particles.

ACKNOWLEDGEMENT

The second author acknowledges partial support made by a National Research Foundation of Korea (NRF) grant funded by the Ministry of Education, Science and Technology (MEST) (No. 2010-0007876).

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(Received 27 July 2013, revised 28 August 2013, accepted 29 August 2013)