



Size Evolution of Sodium Combustion Aerosol with Various RH%

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ABSTRACT

Studies on sodium aerosol characteristics are very important for fast reactor safety. Physical and chemical changes that occur at various times at various atmospheric conditions to sodium aerosols would result particles in various diameters. In this context, a study has been conducted in Aerosol Test Facility, Radiological Safety Division, in which sodium combustion aerosols were generated in a controlled manner and made to hover in a confined volume. The particle diameter (Mass Median Diameter - MMD) is measured on-line with progress of time by using Mastersizer. The experiments are conducted by generating aerosols in two different mass concentrations viz. 3.0 g m^{-3} and 0.5 g m^{-3} and in three different relative humidity conditions viz. 20%, 50% and 90% to show the influence of relative humidity on the particle diameter. A theoretical simulation of particle growth due to coagulation is drawn and compared with the experimental value. It is observed that sodium combustion aerosols size grow due to absorption of moisture (hygroscopic growth) in the initial period of times say in first 20 minutes followed by Brownian coagulation. An empirical relation is determined based on the difference between coagulation growth and experimental observation and applied to match experimental observation of particle diameter. A detailed experimental procedure, theoretical simulation and comparison of results of particle growth between experimental observation and theoretical simulation are presented in this paper.

Keywords: Sodium combustion; Aerosol size; Growth; Relative humidity.

INTRODUCTION

In sodium cooled fast reactors (SFR), the leakages in the secondary sodium pipes lead to sodium fires, which are classified as Pool fire, Spray fires and Column fire. The hot sodium burns in air and gives rise to aerosols. The aerosols are mainly sodium oxide (Na_2O) or higher oxides of sodium (Na_2O_2 and NaO_2) depending upon the ratio of sodium to oxygen available during the onset of fire. Since these oxides are highly reactive, they are further converted to sodium hydroxide, sodium carbonate and sodium bicarbonate upon reaction with water vapour and carbon dioxide present in the environment (Clough and Garland, 1971). These sodium aerosols pose serious problems such as chemical toxicity, corrosion of building materials and equipments. Sodium peroxide and harmful corrosive nature of soda (NaOH) are responsible for chemical attack. The Threshold Limiting Value (TLV) by American Conference of Governmental industrial Hygienists (ACGIH), for the atmospheric concentration of soda is 2 mg m^{-3} for humans

(<http://www.osha.gov/>). Hence several studies have been initiated in Aerosol Test Facility (ATF), Radiological Safety Division (RSD), Indira Gandhi Centre for Atomic Research (IGCAR) related to physical and chemical characterization of sodium aerosols which help in hazard evaluation of Sodium cooled Fast Reactors with respect to sodium fire and dispersion of sodium aerosols.

The vapour phase combustion of the sodium, results in the generation of sodium oxide aerosols in the flame zone (Newman, 1974). The physical and chemical changes of sodium oxide aerosols after leaving the flame zone are very important to understand the sodium oxide aerosol process. Hence, the particle size after leaving the flame zone is an important factor for the aerosol process. In our earlier studies, the initial size distribution of aerosols was studied by varying ignition temperature for a confined pool and by varying relative humidity of the surroundings. It is reported that, higher the humidity the bigger will be the initial size of the aerosols (Subramanian and Baskaran, 2007) and the species would be fully sodium hydroxide. Cooper, 1980, studied the initial radius of the aerosol formed under relative humidity condition varying from 35–90% and derived an empirical relation as

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$$r \text{ (initial radius)} = (r_0 \text{ (dry particle radius)} \times 0.87)/(1 - RH)^{1/3} \quad (1)$$

and showed that by considering r_0 equal to 0.5 μm , the initial particle size increases with increase of relative humidity. The bigger sized particle is formed, at higher humidity conditions, until the partial pressures of the water vapour inside the particle become equal to saturated water vapour of the surroundings (Newman, 1983; Cooper, 1989; Malet, 1996). At this juncture, the carbon dioxide prevailed in the atmosphere diffuses into the particle and converting the species as carbonate. When the initial particle diameter is large, i.e., at high humidity conditions (at 90% RH), the particles have larger surface area, the particle is nothing but the solution of hydroxide, which enhance the diffusion of CO_2 into the particle, resulting carbonate conversion (total conversion) in lesser time (Ramsdale et al., 1989). An experimental investigation was carried out to determine the chemical speciation of aerosols with progress of time and reported that carbonation is faster in higher humidity condition (Subramanian et al., 2009; Ananthanarayanan et al., 2015). The carbonation of sodium aerosols is studied and a phenomenological modeling is carried out based on shrinking core model by considering of diffusion of CO_2 into a particle of hydroxide formed at various RH conditions i.e., shrinking of hydroxide core with progress of time as carbonation progress from the surface (Gilardi et al., 2013). In addition to all these studies, the particle size is important to be considered for the settling phenomena, as the aerosols are formed inside a confined environment undergo coagulation followed by gravitational settling (Misra et al., 2010; Subramanian et al., 2011).

Hence, the size of the sodium aerosols, formed at given humidity condition and suspended in a confined environment, changes by (i) accumulation of water vapour over particle followed by chemical conversion (Sitarski, 2012) and (ii) coagulation by physical process. Hence an experimental investigation was conducted by generating aerosols in a closed chamber and on-line measurement of particle size (Mass Median Diameter - MMD) with progress of time is carried out. The enlargement of particle size observed in the experimental study is compared with enlargement of particle size simulated due to Brownian coagulation and the comparison would yield the extent of hygroscopic growth. Since the initial particle size is different for different RH conditions, experiments are conducted by keeping the atmosphere in 20%, 50% and 90% RH conditions. Further, the initial particle size and hygroscopic growth is independent of initial concentration, while the coagulation is dependent on concentration, hence, experiments conducted in two different initial mass concentrations in order to differentiate the particle enlargement measured by experimental study and by theoretical simulation. In addition to the above, an empirical relation is derived and applied in the model in order to match the hygroscopic growth condition. In this paper, the generations of sodium combustion aerosol, aerosol sampling system, measurement of aerosol size with evolution of time, theoretical simulation of change in particle size with time and comparison of results are presented.

THEORETICAL SIMULATION

Sodium aerosols are formed by combustion process by exposing the hot sodium into the ambient atmosphere. As the combustion is progressing, the sodium aerosols are in the form of sodium oxide in flame zone and they are converted into sodium hydroxide immediately after leaving the flame zone. When these aerosols are suspended in a confined volume, these aerosols are removed from the suspended space continuously by several mechanisms i.e. concentration is reduced by gravitational settling, wall plating, and ventilation if there. Since, all the removal mechanisms are dependent on particle size, a theoretical model is developed using standard mass and number concentration decay equation by including initial mass concentration and various removal mechanisms. A first order differential equation is formulated to predict the decay of mass and number concentration of sodium aerosols in closed chamber with progress of time. Taking initial size of the aerosols as an input from the experimental results obtained from ATF, the equilibrium aerosol size is evolved by solving rate equation of mass concentration and number concentration numerically by finite difference method. In this model, the inputs parameters are (i) initial sodium aerosol mass concentration, (ii) geometry of the vessel (diameter and height of the vessel) and (iii) initial radius of sodium aerosol. The rate equations for mass concentration, number concentration and inter-relating equation of mass and number concentration of the aerosols are given below:

$$\frac{dc}{dt} = -\lambda c \quad (2)$$

$$\frac{dN}{dt} = -\lambda N - KN^2 \quad (3)$$

$$c = \frac{4}{3} \pi r^3 \rho N \quad (4)$$

where N – Number concentration (cm^{-3})
 c – Mass concentration (g cm^{-3})
 λ – Decay rate (gravitational, wall plating and ventilation) (s^{-1})
 K – Coagulation rate (s^{-1})
 ρ – Particle density (g cm^{-3})
 r – Radius of particle (cm)

The initial conditions are taken as: the initial mass concentration $c = c_0$ obtained from the experimental value (for two different concentrations) and initial particle size is taken from the empirical relation derived from the previous experimental results conducted in ATF, (Subramanian and Baskaran, 2007) in which Cooper's relation (Cooper, 1980) is modified by taking an empirical constant as 0.97 and dry particle radius (r_0) = 0.45 measured in ATF at RH% of 20. The initial radius at various RH% is modified as

$$r (\text{initial radius}) = r_0 \times 0.97 / (1 - RH)^{1/3} \quad (5)$$

By taking initial sodium aerosol radius from the modified Cooper relation, the parameters λ , and K are calculated.

Using these values, equations are solved for next time step and the process continued till the convergence of size is reached.

MATERIALS AND METHODS

Aerosol Chamber

The experiments reported in this work were conducted in ATF (Baskaran *et al.*, 2004). The schematic of the experimental set up is presented in Fig. 1. The major components of ATF are (i) combustion cell made of SS-304 L, in which, sodium will be heated using electrical bunsen burner under Argon environment, (ii) aerosol chamber (having volume 1 m³ with height = 60 cm and diameter = 150 cm), (iii) auxiliary systems such as pneumatic control system, data acquisition system for temperature, pressure and RH during experiments, (iv) filter paper samplers to collect samples for the measurement of mass concentration, and (v) Mastersizer for the measurement of real time particle size distribution and MMD. The aerosol chamber is maintained with ambient temperature (25–30°C) and required RH% and CO₂ content, before injection of aerosols.

AEROSOL DIAGNOSTIC EQUIPMENT

Mastersizer

In our studies, for the real-time measurement of sodium aerosol volume –size distribution, a laser based aerosol measurement instrument called Mastersizer (M/s Malvern, UK) is used. The instrument is working on ensemble diffraction technique. The Mastersizer integrated with the aerosol chamber with a help of an aerosol flow cell. Aerosol flow cell is a hollow stainless steel pipe with rectangular cross section of 14.3 mm width (standard length for optical path specified by Mastersizer) and 103 mm breadth and it has a length of 730 mm. suitable opening are made in side plates of the flow cell and laser window are connected. The aerosols are drawn through the aerosol flow cell whose optical window is aligned with the laser path of Mastersizer (within ± 0.1 deg.). A constant air flow (~0.5 L min⁻¹) from the aerosol chamber is maintained by a pump to avoid turbulence and giving laminar flow of the aerosol in flow cell. Performance test of the aerosol flow cell was carried out with polystyrene latex particles of diameter 2.799 μm and methylene blue aerosols (Baskaran *et al.*, 2006).

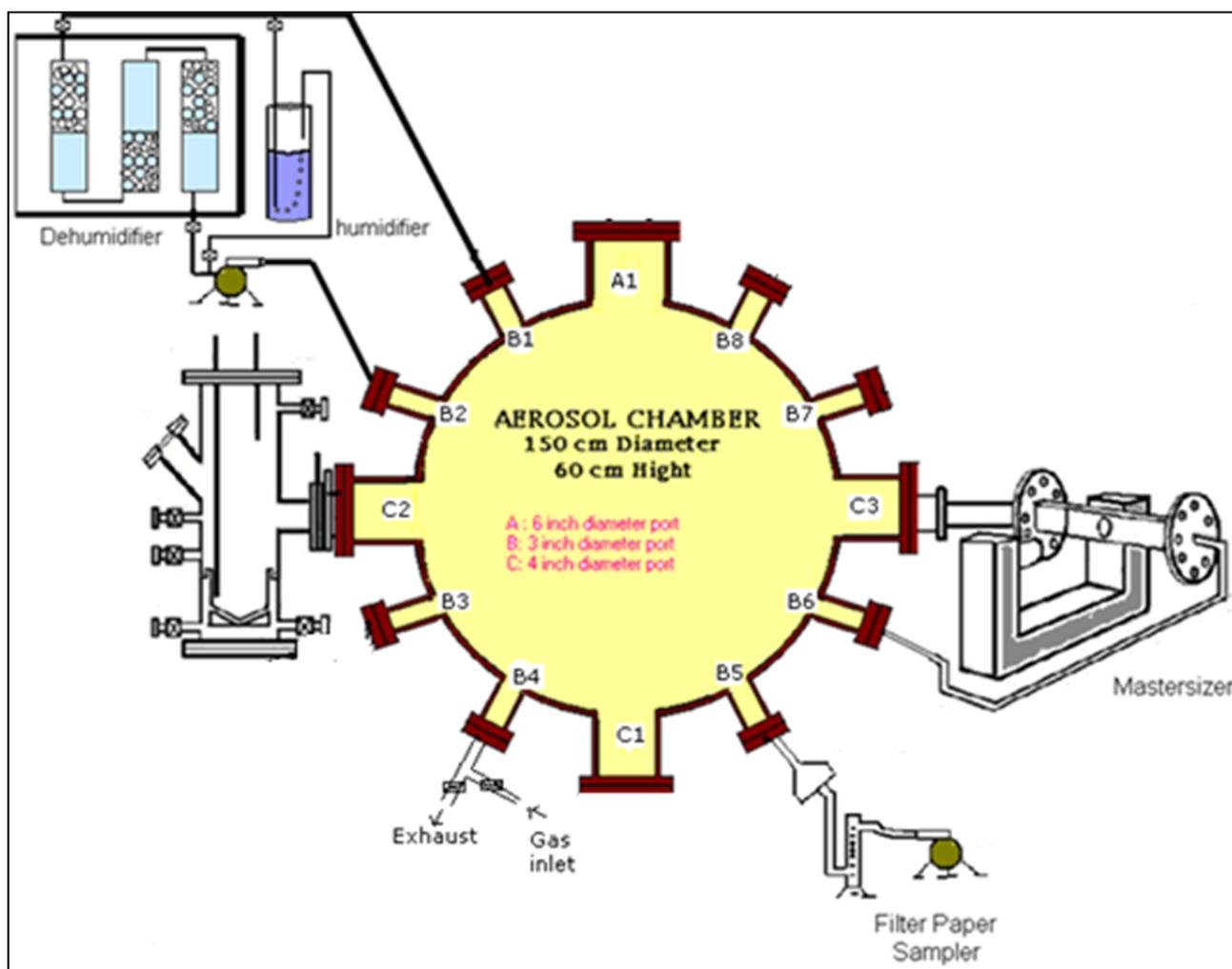


Fig. 1. An integrated view of the aerosol chamber, the sodium combustion cell, Filter paper sampler and Mastersizer.

Filter Paper Sampler

This technique is used to determine the aerosol mass concentration by gravimetric analysis. A closed face type filter paper sampler (47 mm) and a non-lubricant rotary vane pump with a capacity of 20 L min^{-1} coupled with rotameter were used for the measurement of mass concentration. An analytical balance with an accuracy of 0.1 mg (Model No. GR 200, M/s AND Corporation, Japan) was used for the gravimetric analysis. Aerosol sampling was carried out for 1 minute at a flow rate of 10 L min^{-1} . The cumulative experimental errors associated with measurement in time, flow rate and mass is nearly $\pm 10\%$. Glass fiber filters (M/s Whatman) are used for the present experimental study.

SAMPLING

About 10 g of sodium was heated upto 550°C (the temperature of the sodium in primary loop of fast reactor) in the sodium combustion cell under argon environment. The hot sodium was ignited by exposing it to compressed air, after letting out the argon gas. By combustion, the sodium oxide aerosols were formed in the combustion cell. Immediately, the valve separating the aerosol chamber and combustion cell was opened and the aerosols get filled into the chamber. Since the initial pressure at the combustion cell was at 50–70 kPa excess over atmospheric pressure, it helps to fill the aerosol into the chamber and its diagnostic port immediately. The combustion last for about two minutes and the cell is isolated by closing the gate valve. Immediately, the real time measurement of particle size measurement is carried out by using Mastersizer. The sodium aerosol size is measured continuously for about 1 hour. The experiments on sodium aerosol size evolution were conducted at three relative humidity conditions viz. 20%, 50% and 90%. The required relative humidity of aerosol chamber is maintained with the use of humidity controller. At the same time, the suspended aerosol mass concentration inside the chamber is measured by using filter paper sampling in the first minute and it is taken as initial mass concentration of aerosols. The desired initial mass concentration is obtained by optimizing the parameters viz. quantity of sodium, combustion time,

rate of injection of air etc.

RESULT AND DISCUSSION

The initial volume - size distribution of sodium combustion aerosol for various RH% is shown in Fig. 2. It is observed from Fig. 2, that the initial size distribution is mono model with MMD 0.98, 1.1 and $1.8 \mu\text{m}$ for 20%, 50% and 90% RH respectively, for the initial mass concentration of 3 g m^{-3} . The particle size distribution and corresponding MMD is measured continuously with progress of time (every minute). The experimentally measured particle size (MMD) with progress of time for 50% RH is shown in Fig. 3(a) (for 3 g m^{-3}). It is observed from Fig. 3(a), the measured initial particle size is $1.1 \mu\text{m}$ and size enlarges upto $1.56 \mu\text{m}$ in 20 minutes and thereafter, the size enlarges to reach a saturated value around $1.7 \mu\text{m}$ in about 60 minutes. The theoretically simulated particle size with progress of time due to coagulation is included in Fig. 3(a). In the case of theoretical simulation, the particle size enlarges progressively from $1.1 \mu\text{m}$ and in 20 minutes it increases around $1.4 \mu\text{m}$ then slowly increases to the saturation value of $1.7 \mu\text{m}$ at about 80 minutes. It is evidenced in the Fig. 3(a), the difference in the particle size at 20 minutes is about 12% and it would be due to hygroscopic growth. The rate of growth in both theoretical simulation and experimental observation is nearly same after 40 minutes. But within 30 minutes, the particle size enlarges upon absorption of moisture. In order to distinguish the hygroscopic growth in sodium aerosols, the experiment is conducted with initial mass concentration of 0.5 g m^{-3} by burning 2 g of sodium. Fig. 3(b) shows that particle size growth with progress of time observed in the experimental measurement and theoretical simulation for the case of initial mass concentration of 0.5 g m^{-3} and RH at 50%. It is observed from the experimental measurement, the initial particle size is $1.1 \mu\text{m}$ and it enlarges to $1.55 \mu\text{m}$ in 20 minutes and increases to $1.6 \mu\text{m}$ in 80 minutes. But in the case of simulated particle size due to coagulation, the initial particle size is also $1.1 \mu\text{m}$ and it increases marginally in 80 minutes reaching $1.15 \mu\text{m}$ only. It is noted from Figs. 3(a) and 3(b), the measured initial particle size is same

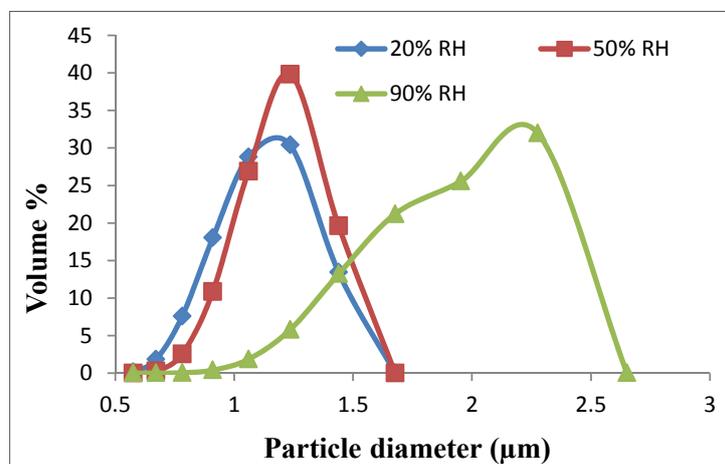


Fig. 2. Initial volume – size distribution of sodium combustion aerosol for various RH%.

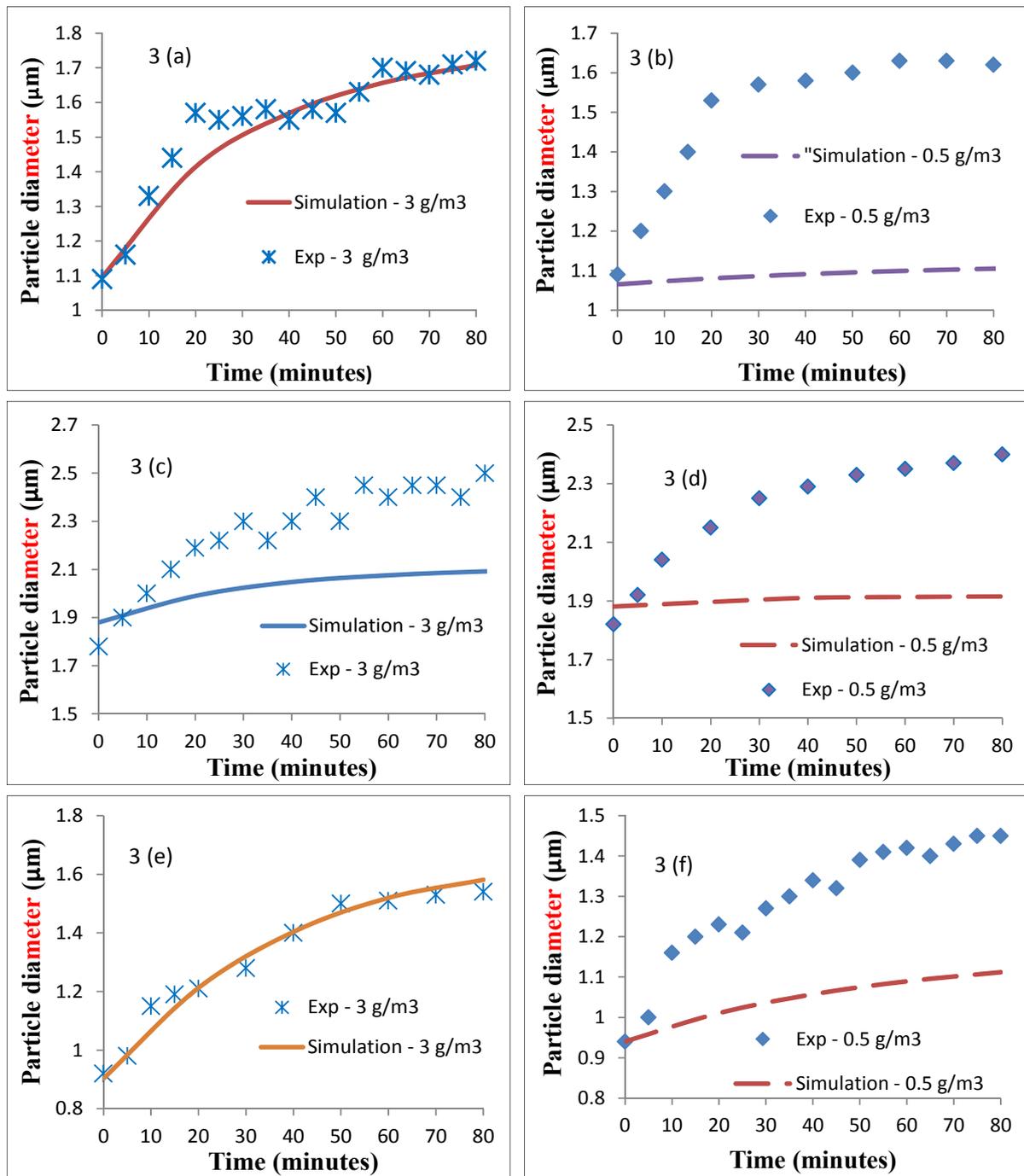


Fig. 3. Growth of particle size with time (experimental observation and simulation due to coagulation) for various conditions (a) 50%, - 3.0 g m^{-3} (b) 50%, - 0.5 g m^{-3} (c) 90%, - 3.0 g m^{-3} (d) 90%, - 0.5 g m^{-3} (e) 20%, - 3.0 g m^{-3} and (f) 20%, - 0.5 g m^{-3} .

($\sim 1.1 \mu\text{m}$) for the both mass concentrations, which shows that initial particle size is independent of mass concentration. In the case of 0.5 g m^{-3} , the hygroscopic growth of sodium aerosols is clearly evidenced from the difference in particle size between measurement and theoretical simulation. It is to be noted here that, the experimental observation includes hygroscopic, chemical and coagulation changes. The difference in particle size in the first 20 minutes between measurement and theoretical simulation is attributed to hygroscopic growth and chemical conversion.

Fig. 3(c) shows the particle size with progress of time for both experimental observation and theoretical simulation for 90% RH condition with initial concentration of 3 g m^{-3} . The measured initial particle size is 1.8 μm and enlarges to reach about 2.4 μm (saturated value), whereas the simulated particle size is found always well below the experimental value (in the range of 2.0 μm) (saturated value) and found to have 20% deviation. The growth rate after 40 minutes is found to be similar for both experimental and theoretical values (slope) but with different starting size. The same

experiment is repeated with initial mass concentration 0.5 g m^{-3} . Fig. 3(d) shows the particle enlargement in both theoretical and experimental observations. The measured initial particle size for 0.5 g m^{-3} condition is again $1.8 \text{ }\mu\text{m}$, which is found to be independent of initial mass concentration and reaches about $2.35 \text{ }\mu\text{m}$. The simulated curve for 0.5 g m^{-3} is also found to have values below the experimental observations (in the range of $1.9 \text{ }\mu\text{m}$). The difference between experimental values and the simulated values (for both mass concentrations) is attributed to hygroscopic growth due to presence of more moisture content in the chamber than 50% RH case (all values found above the theoretical prediction).

The experiment is conducted by keeping aerosol chamber at 20% RH condition. Fig. 3(e) shows the experimental and theoretical simulated particle size with progress of time in the case of initial mass concentration of 3.0 g m^{-3} . The initial particle is found at $0.9 \text{ }\mu\text{m}$. The particle size enlarges to reach $1.2 \text{ }\mu\text{m}$ in 15 minutes with deviation of about 5% found between experimental and theoretical prediction (due to less moisture content when compared to 50% case). Thereafter, from 20 minutes, the measured values and simulated values of particle size is found to be almost same. Fig. 3(f) represents the particle size with progress of time in the case 0.5 g m^{-3} condition. The initial particle size is found to be in the range of $0.9 \text{ }\mu\text{m}$. The deviation in the particle size in the 15th minute is about 21%. However, the growth rate after 20 minutes for both experimental and theoretical simulation is almost same from the different starting size at 20 minutes.

It is observed from Figs. 3(b), 3(d) and 3(f), in the case initial mass concentration of 0.5 g m^{-3} , there exists definite demarcation between the experimental observation and theoretical simulation by coagulation growth. In order to match the experimental observation, an empirical equation of 2nd polynomial is derived based on the difference between the two curves (between coagulation growth and experimental observation) for 50%RH condition and it is given as follows:

$$d' = -0.00006 \times t^2 + 0.0079 \times t + 1.0466 \quad (6)$$

where d' – particle diameter (μm) and t – time in minutes.

Upon multiplying the value of “ d' ” obtained by simulation due to coagulation effect with above polynomial equation for d' , the resultant value D (the final particle diameter determined experimentally) for any time would be obtained. The value of D includes particle diameter due to coagulation, chemical conversion and hygroscopic growth. The value of D obtained for various times for the three Relative Humidity conditions along with experimental observation is shown in Fig. 4. It is to be noted here that, the above equation for d' is valid only for the mass concentration of 0.5 g m^{-3} . The variation in d' for all the three RH%, is very less, such that, d' for 50% RH case is taken. The resultant D would found to have deviation of about 10%.

SUMMARY

It is determined clearly that, initial particle size of sodium aerosols (after coming out of flame zone) is independent of mass concentration. It is clearly observed that the size of the sodium aerosols undergo hygroscopic growth due to adhesion of moisture over the solid particle of sodium oxide released out of flame zone. The coagulation growth is dominant for higher mass concentration (3.0 g m^{-3}) condition, whereas, the hygroscopic growth is dominant in the lower mass concentration (0.5 g m^{-3}) condition. Higher the RH%, the particle enlargement is also found higher. If we compare the rate of enlargement in size after the initial period of time say 20 minutes, both theoretical growth and experimental growth are almost same but only with the difference of particle radius at 20 minutes (say starting diameter). Further, the growth of particle size is also included with chemical speciation of particle with time, as conversion of sodium oxide to sodium hydroxide and further to sodium carbonate. The saturated value of the particle measured experimentally

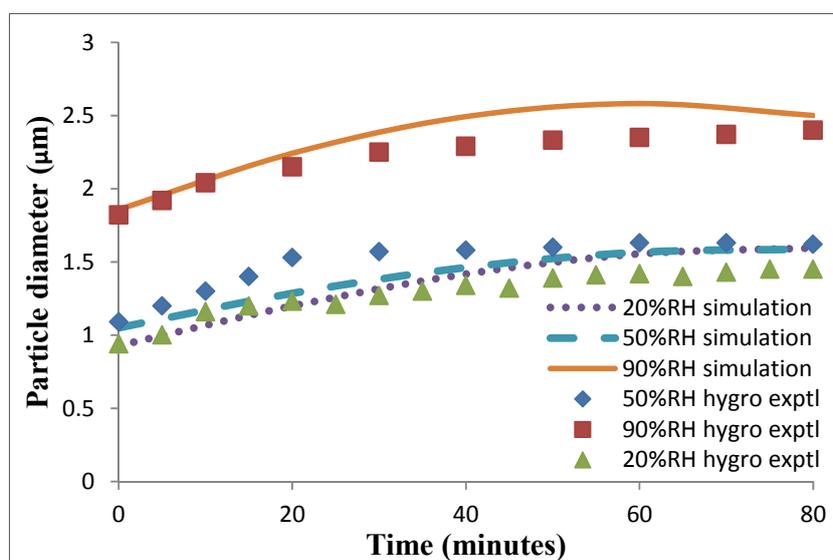


Fig. 4. Growth of particle size with progress of time (experimental observation and theoretical simulation due to coagulation and hygroscopic) for 0.5 g m^{-3} .

in both concentration regions is found to have only less variation, showing seizure of moisture absorption and chemical transformation (The final chemical composition would be NaHCO_3). Further experiments are in progress to correlate the chemical speciation with respect to particle size at various times.

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