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TITLE

HIGH TIME RESOLUTION MEASUREMENTS OF DROPLET EVAPORATION KINETICS AND PARTICLE CRYSTALLISATION IMAGING

High-time resolution measurements of droplet evaporation kinetics and particle crystallisation imaging

RESUME

Dans le présent article, nous étudions l'influence de la cinétique de séchage d'une gouttelette sur les caractéristiques morphologiques des particules produites, dans le but de modéliser les propriétés aérodynamiques des aérosols ainsi formés.

Nous présentons le développement d'un nouveau dispositif permettant d'analyser en détail l'évaporation de gouttelettes, depuis leur production jusqu'a la formation d'une particule sèche, en passant par la nucléation des premiers cristaux. Cette expérience permet d'étudier l'évaporation des gouttes avec une résolution temporelle inférieure à la microseconde, et ainsi de détecter très présisément, par analyse d'images, le début de la cristalisation. Nous présentons une première étude réalisée sur un sel inorganique et qui montre, suivant les conditions de séchage, une grande variété de morphologies de particules.

ABSTRACT

This article deals with the study of the relationship between factors governing droplet drying and resultant particle morphologies, with a specific interest in the aerodynamic properties of dried particles.

This work describes a new Falling Droplet Column (FDC), which offers the capability to analyse in detail the entire evaporative lifetime of individual droplets, from generation to dry particle formation, with capability for sub-microsecond temporal resolution and subsequent offline analysis of dried particles by SEM. A comparison of evaporative profiles and resulting morphologies produced in a range of conditions for different inorganic salts is presented. We will explore the specific crystallisation events through detailed imaging of aerosol droplets.

KEYWORDS: spray drying, droplet crystallisation, evaporation kinetics, particle morphology

1. CONTEXT

Powder production by spray drying is used in a variety of industries including the food industry and the pharmaceutical industry. It is advantageous over other methods of powder production in that it is a controllable continuous process, produces consistent particle quality and is applicable to both heat-sensitive and heat resistant systems [1]. In the nuclear industry, large amounts of radioactive materials are handled in the liquid phase. In an accident scenario, this material can be aerosolised, producing droplets which dry rapidly forming solid particulates. Spray drying typically involves the heated production of aerosol droplets which then dry quickly. A jet formed from a clean break in a heated container may be considered similarly. Thus, the phenomena observed in spray drying and the underlying principles may be applied directly to particle formation from ruptured pressuried systems.

2. INTRODUCTION

The parameters governing the droplet-drying process impact the final dry particle morphology. This, in turn, determines the aerodynamic and transport properties of the dry particles. One way to understand the effect of evaporation rate on final morphology is to with the Péclet number [2]. The Péclet number compares the evaporation rate of a droplet, κ, to the rate of diffusion of a solute, D, and is shown in $P\acute{e} = \frac{\kappa}{8D}$ Equation 1. For values greater than one, the evaporation rate is dominant and surface enrichment is likely. In this case, droplets have a propensity to form a skin or crust. For a Péclet number less than one, the rate of diffusion is dominant and surface enrichment does not occur.

$$P\acute{e} = \frac{\kappa}{8D} \qquad \text{Equation 1}$$

There are a limited number of techniques to make measurements on single droplets during evaporation. Observation of droplets from droplet generation to dry particle formation is rarely achieved and instruments

DOI : 10.25576/ASFERA-CFA2021-24842

are often limited by temporal resolution or ability to collect dried particles for further analysis. Evaporative processes and morphological changes can occur in a matter of milliseconds under industrially relevant conditions. To probe the phenomena that occur in these systems, a sub-millisecond temporal resolution is required.

3. EXPERIMENTAL

This work describes a new Falling Droplet Column (FDC), which offers the capability to analyse in detail the entire evaporative lifetime of individual droplets, from generation to dry particle formation, with a sub-microsecond temporal resolution. A diagrammatic representation of the FDC is shown in Figure 1. The instrument operates by establishing a chain of uniform falling droplets within a temperature and humidity-controlled environment. This is achieved using a piezoceramic droplet on demand dispenser, actuated using a square-wave voltage waveform, typically with a frequency of 10 Hz. Stroboscopic brightfield imaging, using the same frequency, of droplets within the chain enables direct measurement of droplet diameter from the image and calculation of aerodynamic diameter by evaluating a droplet settling velocity. Increased time-resolution is achieved by shifting the phase difference between the droplet generation frequency and imaging frequency. This means variable time resolution is possible with a minimum temporal separation in droplet lifetime of < 1 µs between measurements. Scattered laser light may be collected to analyse droplet structure during the drying process. Dry particles are deposited at the bottom of the FDC and imaged using SEM. This allows evaporative dynamics to be studied in conjunction with final morphologies produced for a range of conditions.

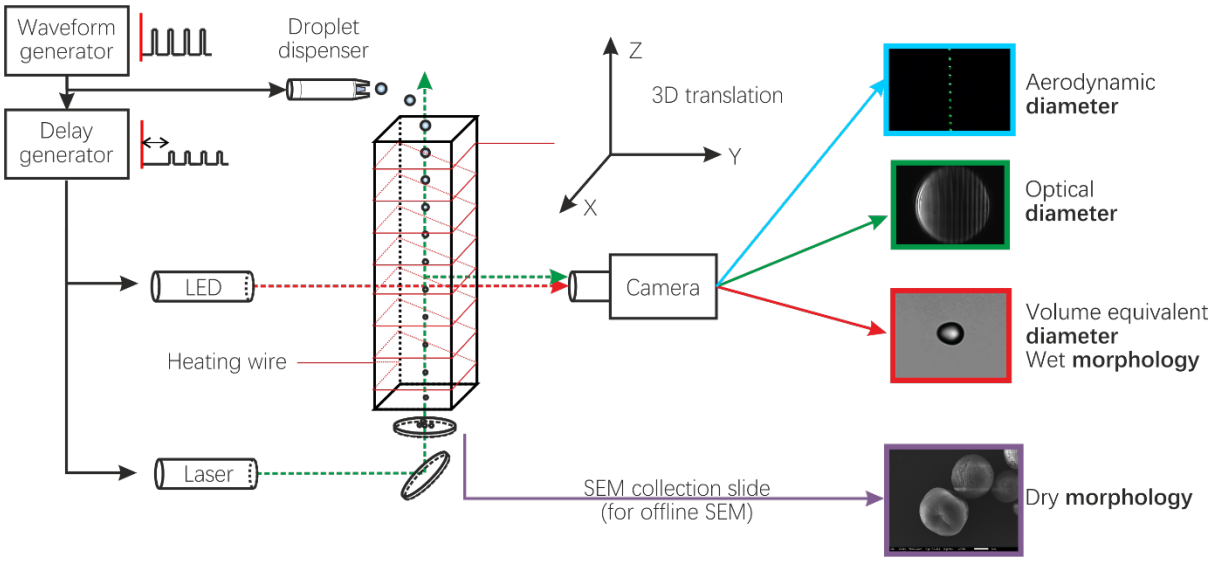

Figure 1 Schematic of the FDC instrument, including the main components of the control and measurement systems with example images.

4. RESULTS

Comparative evaporation profiles of sodium chloride droplets evaporating in different conditions are shown in Figure 2 and accompanying images showing crystallisation processes in Figure 3.

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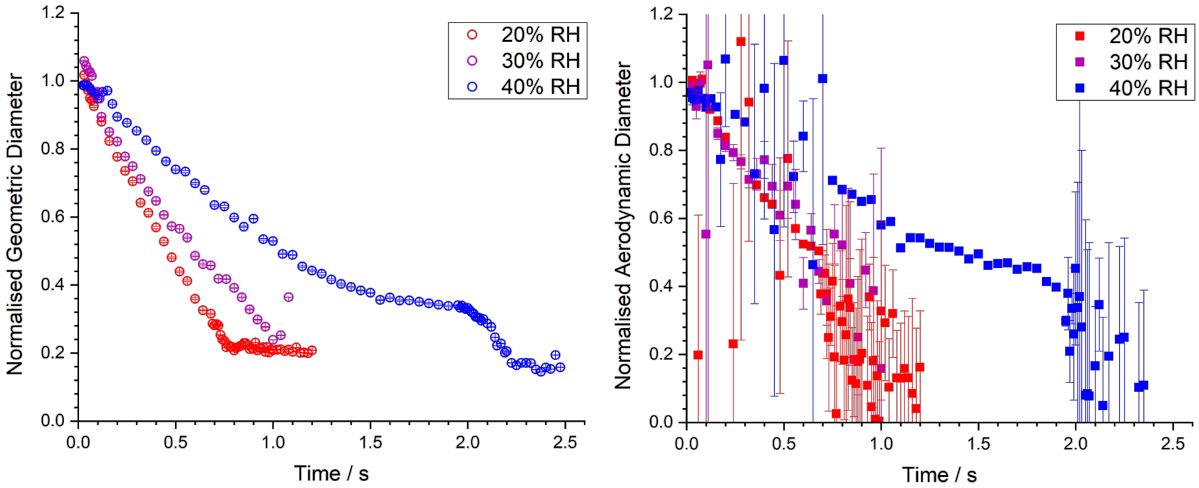

Figure 2 Geometric and aerodynamic diameter measurements of sodium chloride droplets evaporating in different relative humidity values. Measurements are normalised to droplets' initial diameter (approx. 30 µm) for direct comparison.

In Figure 2, the geometric diameter measurements enable precise extraction of evaporative kinetics and a clear point of crystallisation is observed when evaporation ceases. Aerodynamic diameter measurements, although of lower precision, are able to resolve a final aerodynamic diameter of the particles formed. This may be considered in conjunction with the images in Figure 3 to relate the morphology of particles to their aerodynamic diameter.

Homogeneous droplets are easily identified by a single bright spot in the centre of the image and a circular outline. Crystallisation can be observed as optical inhomogeneities appearing within the droplet. These become more significant and the droplet no longer presents a circular image as the remaining solvent evaporates and solid features begin to define the particle shape. After the solvent is fully evaporated, a final morphology may be observed 'in-flight'.

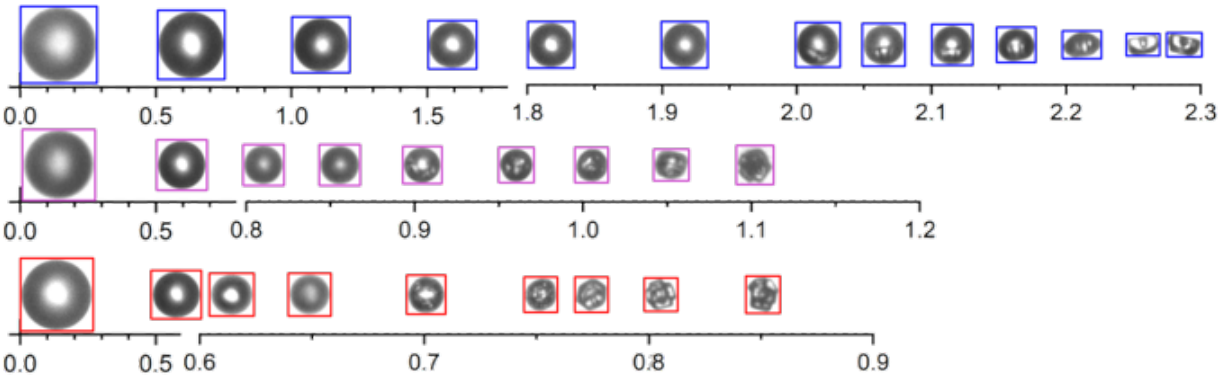

Figure 3 Images of sodium chloride solution droplets with bounding boxes colourmapped to the respective data shown in Figure 2, blue: 40% RH, purple: 30% RH and red 20% RH. Time scales have been optimised to display morphological changes during solidification.

As droplets loose their spherical nature and become unique crystalline particles, their aerodynamic behaviour begins to diverge and the associated uncertainty in measurements increases. Particles that approximate a sphere, such as those produced in 20% in Figure 3, exhibit a more consistent aerodynamic diameter. At present, it is not possible to report clear aerodynamic diameter measurements for irregularly shaped particles with certainty but, by measuring larger numbers of particles over longer periods of time, it will be possible to reduce the uncertainty. The aerodynamic diameter of particles is dependent upon both their shape and density. This means while evaporating particles remain spherical, their density may be extracted by comparison of the geometric and aerodynamic diameter. Thus the evolution of density may be observed and crystallisation may be clearly resolved as the moment when droplet shape deviates and the aerodynamic diameter reduces dramatically.

SEM analysis of particles provides detailed insight into morphological features. Solute diffusion and nucleation rates and droplet evaporation rate are amongst determining factors for particle morphology. In this work, we have found that higher Péclet numbers for sodium chloride droplets produce cage-like particles comprised of

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multiple crystals as seen in Figure 3 for 20% and 30% relative humidity. For low Péclet numbers (slower evaporation processes), sodium chloride has been observed to form single crystal particles that appear to have their morphology constrained by the droplet geometry. This can be seen in Figure 3 for 40% RH and SEM analysis of particles produced under replicated condition are shown in Figure 4.

This study will progress to investigate the relationship between the initial concentration of a droplet and its final size and aerodynamic diameter. Sodium nitrate will also be studied to make comparison between different salts and resolve the importance of a solute behaviour in determining final particle morphology. This work aims to provide insight into the aerodynamic properties and morphology of particles produced by droplet drying through considering the influence of drying kinetics, solute properties and solution concentration, and by resolving the effects of these factors individually.

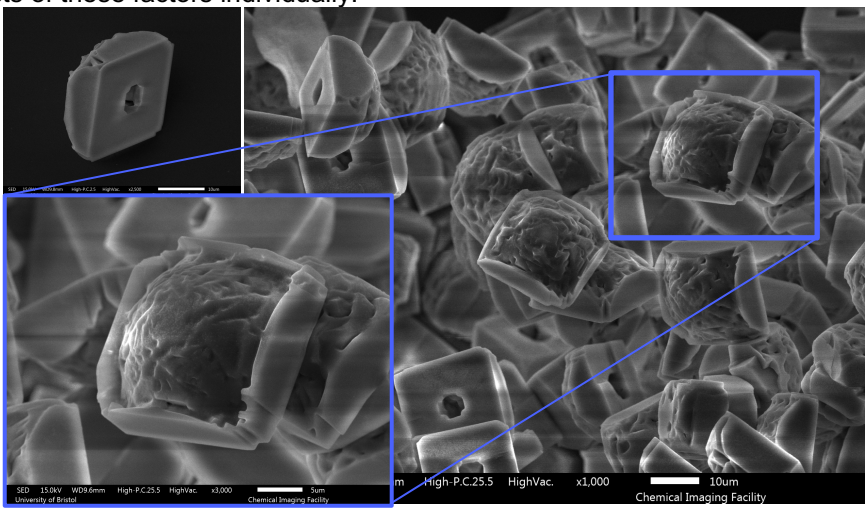

Figure 4 SEM images of single crystal particles formed from 0.15 MFS NaCl solution at approximately 295 K and 40% RH.

In this talk, we will compare evaporative profiles and resulting morphologies produced in a range of conditions for different inorganic salts. We will explore the specific crystallisation events through detailed imaging of aerosol droplets. We will provide insight into the competition of factors determining final morpholgy or particles and SEM images of particles to validate this understanding.

This work is supported by the IRSN (grant S100100-101) and the EPSRC (grant EP/N025245/1).

[1] A. Ziaee, A. B. Albadarin, L. Padrela, T. Femmer, E. O'Reilly and G. Walker, Eur. J. Pharm. Sci., 2019, 127, 300–318.
[2] R. Vehring, W. R. Foss and D. Lechuga-Ballesteros, J. Aerosol Sci., 2007, 38, 728–7

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