DENSITY AND SHAPE FACTOR
OF SODIUM AEROSOL

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ABSTRACT

Measurements were made of effective density, size distribution and dynamic shape factor for sodium fire aerosol particles using centrifugal separation and scanning electron microscopy. The aerosols were formed by burning one pound of sodium in a 90 m³ air filled chamber at initial relative humidities from 16% to 53%. The aerosol particles were primarily sodium carbonate with water of hydration or adsorbed water. Twenty-nine samples of aerosols aged from 34-376 minutes gave an average value of effective density of 0.61 gm/cm³ with relative standard deviation of 22%. This corresponds to a Stokes' correction factor, α , as used in the HAA-3 Code of 0.27. The size distribution was log normal with an average mass median aerodynamic diameter of 1.85 μ m with an average geometric standard deviation of 1.65. The average dynamic shape factor was 1.37 with a relative standard deviation of 44%. For the conditions of this study no clear trends were observed for effective density with relative humidity, age, or aerodynamic diameter.

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LIST OF SYMBOLS

C_a	slip correction factor for D_a
C_e	slip correction factor for D_e
D_a	aerodynamic diameter, equation (5)
D_e	equivalent volume diameter, equation (1) and (4)
g	acceleration of gravity
$\bar{M}$	average particle mass on foil segment
N	number of particles on foil segment
V_{TS}	terminal settling velocity
α	Stokes' correction factor (density modification factor)
η	gas viscosity
ρ_e	effective particle density, equation (1)
ρ_p	particle density, equation (3)
ρ_m	material density, handbook density
σ	standard deviation
χ	dynamic shape factor, equation (1) and (4)

INTRODUCTION

Following certain sodium fire accidents, sodium fume would fill the LMFBR containment vessel and leak to the external environment at a predicted leakage rate (for some designs) of 0.1% of the containment volume per 24 hours. Although the volumetric rate is assumed to be constant, leakage of sodium fume following a single spill will decrease with time, principally because natural sedimentation will reduce airborne sodium concentration within the containment. For a continuous source of burning sodium an equilibrium concentration will be reached where removal by sedimentation will equal production by combustion. To predict the natural sedimentation effect with reasonable confidence, it is necessary to estimate the terminal settling velocity of the sodium aerosol particles accurately. This is done by modifying Stokes' law, which applies only to uniform density spheres, with appropriate correction factors to account for 1) the nonspherical particle shape of agglomerated sodium fume particles and 2) the true density of these particles which is lower than handbook values for the pure material because agglomerated particles are porous.

The objectives of the present research were 1) to measure the effective density of aerosols produced by sodium pool fires in a 90 m³ chamber using a combination of aerodynamic sizing and scanning electron microscopy, 2) to determine the actual particle density and 3) to determine the importance of particle shape on the value of effective density.

Stokes' law can be expressed in terms of an effective particle density, ρ_e , which combines the correction factors for particle shape and density described above,

$$V_{TS} = \frac{\rho_e D_e^2 C_e g}{18\eta} \quad (1)$$

where D_e , equivalent volume diameter, is the diameter of a sphere having a volume equal to that defined by the envelope of an irregularly shaped particle; C_e is the slip correction factor for the equivalent volume diameter; g , the acceleration of gravity; and η , gas viscosity. Unfortunately, there is no theoretical basis for determining an appropriate value for effective particle density.

The computer code HAA-3 described by Greenfield, et al.(1), replaced effective density with the product of the handbook density for sodium oxide, ρ_m , and a "Stokes' corection factor", α , where,

$$\rho_e = \alpha \rho_m \quad (2)$$

A value of 0.25 was used for α based on work done by Lane and Stone(2) on agglomerated particles with geometric diameters at least five times greater than the primary particles. A material density, ρ_m , equal to the handbook value for sodium oxide, 2.27 gm/cm³, is used. The Nuclear Regulatory Commission(3), which refers to the α factor as a "density modification factor", has used a more conservative value of 0.1 for the FFTF project.

The importance of this correction factor and the uncertainty that exists concerning its value is illustrated by a quote from the regulatory analysis(3), "[One] of the most important parameters in aerosol behavior calculations is... α , the correction factor applied in the Stokes' settling equation to account for departure in shape and density of non-spherical aerosols from aerosols which are ideal with respect to sphericity and density. [This parameter is not]...well defined by existing theory for aerosols such as sodium oxide."

Furthermore, a sensitivity analysis(7) revealed that values of α , ranging from 0.05 to 1.0 for the specific conditions and site considered, would produce a 3-fold range in 2-hour site boundary dose and a seven-fold range in 30-day low population zone dose. This report also stated, "In practice, because of insufficient theoretical and experimental support, values of α ...are chosen primarily to assure conservatism rather than realism".

THEORETICAL DESCRIPTION

Stokes' law applies to the case of spherical particles undergoing constant velocity settling at low Reynolds numbers where aerodynamic drag force equals gravitational force. Generally, a correction factor must be applied to both these forces to relate them to some measured or known dimensions of an irregular particle. A dynamic shape factor, χ , relates drag force on an irregular particle to that on a sphere of equal volume(5) and a volume shape factor relates the actual volume of an irregular particle to some characteristic dimension cubed(6). This characteristic dimension is usually one that can be measured easily such as the projected area diameter determined microscopically.

The dynamic shape factor, χ , has usually been determined by similarity experiments that measure the settling velocity of particles of known geometry and density in liquids. For these experiments there is no need for a volume shape factor, because the true volume is known a priori. In aerosol studies with irregular particles, the volume is not known and cannot be measured directly. Consequently, it is customary to calculate particle volume by using a volume shape factor and a dimension that can be measured, such as the projected area diameter. Usually volume shape factors have been measured empirically for a specific process producing crushed materials having a known density (such as crushed quartz) and as such have limited general application. It is commonly assumed that the empirically derived volume shape factors are not a function of particle size for these crushed materials. However, the volume shape factor may not be constant with particle size for agglomerated materials such as sodium fume.

The approach that has been used up to now for computer modeling of sodium fires (1,3) is to calculate the terminal settling velocity using an equivalent volume diameter, based on the source term and coagulation theory, and an assumed density modification factor, α . There is little experimental or theoretical basis for assuming a particular value for α . The values that have been used were chosen to assure conservatism or to make computer simulations agree with experimental observations of settling velocity.

The factors that will influence the value of ρ_e in practise are: 1) chemical composition--there will be an unknown mixture of oxide, peroxide, hydroxide, and carbonate, depending on CO_2 and H_2O concentrations in the combustion region and during aging of the cloud; 2) the degree of hydration of the sodium carbonate that is formed; 3) amount of interstices between agglomerated sub-units depending on how loose or compact the primary particles are clustered(2).

For agglomerated particles, Mercer(8) related material density, ρ_m , to particle density, ρ_p , by

$$\rho_p = \rho_m (1-P) \quad (3)$$

where P is the volume fraction of voids in the particle envelope volume. Particle envelope is defined here as the surface of the particle as viewed in the scanning electron microscope. Effective density, ρ_e , can be expressed in terms of particle density, ρ_p , and dynamic shape factor, χ , by,

$$\rho_e = \frac{\rho_p}{\chi} \quad (4)$$

Stokes' law can also be expressed in terms of the aerodynamic diameter, D_a , i.e., the diameter of a unit density sphere that has the same settling velocity as the particle,

$$V_{TS} = \frac{D_a^2 C_a g}{18\eta} \quad (5)$$

From equations (1) and (5), the effective density, ρ_e , can be expressed as,

$$\rho_e = \frac{D_a^2 C_a}{D_e^2 C_e} \quad (6)$$

indicating that ρ_e will be defined when we know both D_e , equivalent volume diameter, and D_a , aerodynamic diameter, for any aerosol particle. Equation (6) is the basic equation used for calculating effective density.

In the experiments to be described, the aerosol was fractionated according to D_a on to a foil strip in an aerosol centrifuge and D_e was estimated directly from SEM (scanning electron microscopy) photographs of the fractionated particles on a narrow segment of the foil strip. As the SEM produces an image of a three dimensional particle with the appearance of depth, analysis is not restricted to using a projected area diameter as would be the case for the silhouette image of transmission electron microscopy. The equivalent volume diameter, D_e , was estimated directly from the appearance of the particle envelope by comparison with SEM photographs of spheres of known volume. These calibration spheres were photographed under conditions identical to those used for the sodium

aerosol samples. As shown in Figure 1 the size of each sphere photo in the series was adjusted to have twice the volume of the preceding sphere. Sizing of sodium particles was done by grouping particles according to calibration sphere sizes. This approach avoids having to determine another unknown, the volume shape factor which relates projected area diameter to particle volume.

Whereas individual determinations of D_e have large errors, only a mean value of D_e is required for each foil segment because it contains only a very narrow range of aerodynamic diameters. The error of this value of D_e is reduced by a factor of $(n)^{-1/2}$, where n is the number of measurements(10). The direct estimation of D_e is more accurate than the alternative of measuring projected area diameter (diameter of circle with same projected area as particle silhouette) and assuming it to be equal to D_e . Direct measurement of D_e is assumed to have systematic errors less than the percent difference between projected area diameter and D_e . In these experiments most particles had an axial ratio of less than 2 but a few were as large as 5, corresponding to maximum systematic errors of 11.4% and 29.8%.

The quantity ρ_e is the ratio of particle density, ρ_p , to dynamic shape factor, χ , Equation (4). To determine the latter two quantities requires additional information such as average particle mass, $\bar{M}$. Particle density for agglomerated particles was calculated by,

$$\rho_p = \frac{6 \bar{M}}{\pi \bar{D}_e^3} \quad (7)$$

where $\bar{D}_e$ is the mean equivalent volume diameter calculated by,

$$\bar{D}_e = \left(\frac{\sum n_i (D_e)_i^3}{\sum n_i} \right)^{1/3} \quad (8)$$

The average particle mass is determined by,

$$\bar{M} = \frac{R M_{Na}}{N} \quad (9)$$

where M_{Na} is the sodium mass for an ensemble of N particles and R is the ratio of total mass to sodium mass.

Having calculated ρ_e and ρ_p , Equation (6) and (7), the dynamic shape factor, χ , was calculated by,

$$\chi = \frac{\rho_p}{\rho_e} \quad (10)$$

EXPERIMENTAL PROCEDURE

Sodium fume was generated by heating to combustion a one pound charge of metallic sodium and allowing it to burn in a 90m³ air-

filled chamber. The aerosol was sampled with an aerosol centrifuge(4) for 10 to 75 minutes depending on chamber concentration at the time of the sample. The sample inlet was located 2 meters above the chamber floor. The centrifuge, shown in Figure 2 is a spectrometer that continuously fractionates the aerosol (i.e., produces a continuous size spectrum) according to aerodynamic diameter along a removable 40 cm metal foil. Every point along the foil can be characterized by a known aerodynamic diameter. At a centrifuge speed of 1,100 rpm, six lpm of the chamber atmosphere enters the centrifuge and 75 ml/min of this volume is drawn into the deposition channel as a thin film along the inside wall (radius = 6.0 cm) of the channel at the same speed as the carrier air. The design of the centrifuge minimized inlet losses and plugging by highly agglomerated aerosols. The foil was prescored with a stylus so that narrow segments of foil could be separated and examined in a scanning electron microscope to determine the average equivalent volume diameter. These data were used to calculate ρ_e as a function of particle size. To determine ρ_p and χ , SEM photographs were used to calculate the total number of particles on each foil segment and then aerosol mass was determined on each segment by atomic absorption spectrophotometry for sodium. A gravimetrically determined calibration between elemental sodium and total aerosol mass was obtained by weighing filter samples and then analyzing the deposit for elemental sodium.

CALIBRATION PROCEDURE

The aerodynamic size calibration of the centrifuge was made with monodisperse polystyrene latex and polyvinyl toluene spheres of known size and density. Aqueous suspensions of these spheres were aerosolized using a DeVilbiss D-40 nebulizer operated at 3.5 lpm of compressed air and dried by mixing with 1:1 vol/vol of dry air. The concentration of spheres in aqueous suspension was adjusted to produce large numbers of singlet, doublet, and triplet particles whose aerodynamic diameters have been determined previously(8). The instrument was calibrated by sampling these particles for one to two hours to produce visible bands on the deposition foil that corresponded to singlet, doublet, etc. particles. The position of these bands, measured from the deposition channel inlet, gave the calibration data shown in Figure 3.

An absolute calibration of the SEM magnification and photographic system was made by direct measurement of photographic enlargements of replicas of diffraction gratings having 54,864 lines per inch.

DATA BASE

A total of nine individual centrifuge runs associated with five separate 1 lb. sodium fires in an air-filled 90 m³ chamber, 4 meters in height, were analyzed. The test conditions for each run are summarized in Table 1. The range of initial relative humidity for the tests was from 16% to 53%. The range of average aero-

sol mass concentrations during the centrifuge measurements was from 0.28 gm/m³ to 3.54 gm/m³. Samples were begun from 34 minutes to 376 minutes after initiation of a fire. Fire initiation was judged to occur at the first appearance of a visible aerosol. Sample duration ranged from 3 to 75 minutes, with longer durations associated with lower mass concentrations. The total aerosol mass concentration decay profile for each of the fires is shown in Figure 4.

The results for 29 measurements of selected 3mm wide foil segments from which complete data were obtained are shown in Table 2. Particle number, N , and elemental sodium mass, M_{Na} , are the total number of particles and sodium mass present on the foil segments used for SEM analysis. The sodium mass values were calculated using smoothed curves of areal sodium density versus foil position. With these data, determination of the ratio of total mass to sodium mass, discussed below, defines the total mass of the foil deposits. The number of particles on each segment was calculated from low-magnification (500-1000x) SEM photographs. SEM photographs at 2000 to 5000x, as shown in Figures 5-9, were used to determine an average D_e for each foil segment. In most cases more than 100 particles were sized to determine the average value of D_e . This was accomplished by randomly selecting equal numbers of SEM fields from each of the small 1mm x 3mm rectangles prescored on the foil segment as shown in Figure 10.

Since only the mass of elemental sodium and not total deposited mass on the foil segments was measured, an auxiliary measurement of, R , the ratio of total mass to elemental sodium mass was needed. This was obtained from filter samples of the aerosol that were immediately weighed to get total deposited mass. Then the filters were washed in deionized water and the solutions analyzed for elemental sodium. The results are plotted in Figure 11 as a function of aerosol age and they show that there is no significant trend in the value of R with aerosol age although there is considerable dispersions around the average. The average value of R from 24 measurements is 3.0 with a standard deviation of 0.6.

A check on our instrumental technique was made by determining R by wet chemical analysis for Na_2CO_3 . This procedure gave values of R from 2.84 to 2.93 for aerosol ages ranging from 28 to 268 minutes. In the subsequent analysis it is assumed that R is 3.0 for all particles collected on the centrifuge foil.

Burning of one pound of sodium in the 90 m³ chamber gave peak aerosol mass concentrations from 1.6 to 3.6 gm/m³. Quantitative chemical analysis of the aerosol for initial relative humidity of 40% indicates that the sodium oxide particles are rapidly converted to hydroxide and then to some form of carbonate with less than 1% of the hydroxide remaining (see Note 1). The final aerosol, at the time of sampling is sodium carbonate with significant amounts of water of hydration or adsorbed water or both. The latter is presumably retained by the particles after being adsorbed by the sodium hydroxide prior to conversion to carbonate. These results are consistent with the rates of reaction from oxide to hydroxide to carbonate that were described by Clough and Garland(11) and with the stoichiometric quantity of

carbon in the chamber atmosphere. Other tests conducted over a greater range of mass concentrations have shown that significant concentrations of sodium hydroxide are only found for peak aerosol mass concentration higher than observed in this study(10).

RESULTS

Figure 12 shows the most significant polynomial regression line for equivalent volume diameter, D_e , versus aerodynamic diameter, D_a . The equation of this regression line is,

$$D_a \sqrt{C_a} = -0.754 + 1.56 D_e \sqrt{C_e} - 0.139 (D_e \sqrt{C_e})^2 \quad (11)$$

Effective density as a function of particle size, shown in Table 5, was calculated from Equations (11) and (6). Over the equivalent volume diameter range of 1 to 5 μm the effective density varied from 0.39 to 0.77 gm/cm^3 with an average value of 0.61 gm/cm^3 .

If measured values of M_{Na} in Table 2 are multiplied by $R=3.0$ and then divided by the corresponding measured number of particles, N , the average particle mass on a 3 mm foil segment, $\bar{M}$, is obtained which has a functional relation to the average equivalent diameter computed from SEM data. Figure 13 is a log-log plot of average particle mass, $\bar{M}$, as defined above, versus equivalent particle diameter, D_e , at specific known aerodynamic diameter locations on the centrifuge foil. The resulting equation for the least square regression on logarithmic axes is,

$$\bar{M} = 0.410 D_e^{2.90} \quad (14)$$

The fitted exponent is close to three, the theoretical value for constant density for all particle sizes from the modeling equation,

$$M = \rho_p \frac{\pi}{6} D_e^3 \quad (15)$$

If one assumes a constant particle density, the coefficient, 0.410 from Equation (15) yields a particle density, ρ_p , equal to 0.78 gm/cm^3 according to the model of Equation (15).

The values of p_e from Table 5 and the particle density determined in the above analysis, can be combined using Equation (10) to give the values for dynamic shape factor, χ , shown in Table 5. The average value of χ is 1.37 over an equivalent diameter range of 1 to 5 μm .

Our data were obtained from centrifuge runs made over a range of initial relative humidities from 16 to 53% and times after the initiation of the sodium fire from 34 to 376 minutes. Over this range of conditions we were unable to perceive consistent trends in the effective particle density, ρ_e . Table 3 shows average values of ρ_e arranged in order of increasing initial relative humidity and Table 4 shows average values of ρ_e in order of increased aerosol age. The values of ρ_e were computed from measured data according to Equation (6). In neither table does there appear to be a rational trend. The dip in ρ_e between 16 and 35% relative humidity shown in Table 3 is probably not a systematic real effect but rather a consequence of the spread in our data and the limited number of humidity conditions tested. The variability in ρ_e which is apparent in the tables is simply a manifestation of the spread of the data in Figure 13 around the regression line.

A by-product of the investigation was the determination of an average mass-median aerodynamic diameter (MMAD) for the aerosol. In addition to preparation for SEM microscopy, the foil centrifuge deposition strips were segmented into 10 to 14 intervals and these analyzed for elemental sodium along with a downstream filter that collected all particles having an aerodynamic equivalent diameter less than collectable in the centrifuge. Distributions of sodium mass vs. aerodynamic diameter, such as the one plotted on log-probability axes in Figure 14 were obtained. Uniformity of the ratio of elemental sodium mass to total aerosol mass over the sampled size range was assumed and the data were fitted to log-normal distributions. A value of $1.85 \mu\text{m} \pm 0.26$ was obtained for average MMAD from 12 centrifuge runs. The average geometric standard deviation (GSD) of the 12 distributions, determined by slope of the fitted distribution lines, was 1.65 ± 0.22 .

ERROR ANALYSIS

To characterize the variability in these results, an error analysis was performed according to methods outlined in Wilson(12). Errors were assigned as shown in Table 5 for the experimental parameters which influence the quantities, ρ_e , ρ_p , and, χ , which are defined by Equations (16), (17), and (18), respectively.

$$\rho_e = \left(\frac{D_a}{D_e} \right)^2 \frac{C_a}{C_e} \quad (16)$$

$$\rho_p = \frac{6 \bar{M}}{\pi D_e^3} \quad (17)$$

$$\chi = \rho_p \left(\frac{D_e}{D_a} \right)^2 \frac{C_e}{C_a} = \frac{\rho_p}{\rho_e} \quad (18)$$

The general theory of error analysis shows that the functional relationship, $y = F(X_1, X_2, X_3, \dots, X_n)$ has a general expression for the combined effect of random errors in the variables,

$$\sigma_y^2 = \sum \left(\frac{\partial F}{\partial X_i} \right)^2 \sigma_i^2 \quad (19)$$

where σ_i^2 is the variance of the i th component. This can be expressed in terms of fractional errors as,

$$\frac{\sigma_y}{y} = \pm \sqrt{\sum \left(n \frac{\sigma_{X_i}}{X_i} \right)^2} \quad (20)$$

where n is the exponent of X_i .

For example, the measured number of particles on a foil strip, N , is given by

$$N = \frac{S \eta_A}{A} \quad (21)$$

where A = area of foil examined by SEM

S = area of foil segment

η_A = number of particles counted in the fields examined by SEM

Therefore, for the particle count error,

$$\frac{\sigma_N}{N} = \pm \sqrt{\left(\frac{\sigma_S}{S} \right)^2 + \left(\frac{\sigma_{\eta_A}}{\eta_A} \right)^2 + \left(\frac{\sigma_A}{A} \right)^2} \quad (22)$$

Aerodynamic diameter assignment to various locations along the foil strip was made after careful calibration using polystyrene latex spheres, but errors caused by uncontrolled changes in gas flow and rotational frequency, and uncertainties in position measurements can contribute to errors in D_a . There is also an error associated with D_a that is caused by the finite width of the entrance slit and the resulting resolution blurring, $\frac{\sigma_d}{d}$. Quantitatively,

$$D_a^2 = \frac{\text{const. } Q}{\ell_D C_a v^2}, \quad (23)$$

where Q = winnowing air flow rate

ℓ_D = position along the foil

v = angular frequency of the centrifuge.

The error in the mean value of D_e for each foil segment ranged from 0.01 to 0.1. This error depends on the error in individual determination of D_e , which were estimated to be plus or minus one calibration sphere size range, and the number of particles sized on each segment. To err on the conservative side and to include the effect of the systematic errors described previously, we chose a fractional error of D_e equal to 0.1.

Substituting the error estimates into equations with the form of Equation (20) provides relative standard deviations, shown in brackets, for our previously derived results for ρ_e , ρ_p , χ , and α

$$\begin{aligned}\rho_e &= 0.61 \text{ gm/cm}^3 & (22\%) \\ \rho_p &= 0.78 \text{ gm/cm}^3 & (38\%) \\ \chi &= 1.37 & (44\%) \\ \alpha &= 0.24 & (22\%) \text{ for } \rho_m = 2.53 \text{ gm/cm}^3 \text{ (Na}_2\text{CO}_3\text{)} \\ \alpha &= 0.27 & (22\%) \text{ for } \rho_m = 2.27 \text{ gm/cm}^3 \text{ (Na}_2\text{O)}\end{aligned}$$

DISCUSSION

The aggregate result for ρ_e combined with the known material density of Na_2CO_3 ($\rho_m = 2.53 \text{ gm/cm}^3$) yields an α value of 0.22 with a relative standard deviation of 22%. This is in agreement with the α values of 0.1 to 0.25 which have been used for aerosol modeling(1) and nuclear regulatory purposes(3). For the conditions of this study no clear trends were observed for effective density or Stokes' correction factor as a function of initial relative humidity, aerosol age, or aerodynamic diameter.

Our results can be compared to previously published experimental results on the properties of agglomerated particles. Although detailed studies have been conducted to determine shape factors of aerosol particles formed from fractured quartz, coal dust, UO_2 , (13)(14), the results may not be compared with those from the present study because these particles are not agglomerated and particle density was known to be the same as the handbook value. Although, studies have been conducted to determine a dynamic shape factor for agglomerated polystyrene latex particles, (9)(15), experiments were restricted to simple geometries containing only a few equal-sized spheres of known density. No previous studies have been performed to determine experimentally the agglomerated properties of sodium combustion aerosols.

The quantitative data on the density of agglomerated smokes has been summarized by three authors (15)(16)(17). Beekmans presented data from Whytlaw-Gray and Patterson(18) and Johnstone(19) on the ratio of effective density to true material density, $\rho_e/\rho_m = \alpha$, for aerosols of MgO , HgCl_2 , Au, and W. Collectively, these results give α values from 0.01 to 0.34. Reference 17 presented average values from Whytlaw-Gray and Patterson(18) for true and floc density for Ag, Hg, CdO , MgO , HgCl_2 aerosol agglomerates. The α values calculated from their results range from 0.08 to 0.45. Fuchs(5) also evaluated data from Whytlaw-Gray and Patterson(18) and concluded that α values for cluster shaped aggregates ranged from 0.1 to 0.7. These prior studies are not in disagreement with our results that show α to be 0.24 ± 0.05 for sodium aerosol particles generated in a sealed volume of normal air that contains more than the stoichiometric quantity of sodium reactants (i.e., CO_2 , O_2 , and water vapor).

This study by its nature was limited in the range of conditions evaluated, however, based on the experimental results pre-

sented here, inferences can be made about the properties of sodium fire aerosols at other conditions. For mass concentration greater than used in this study the atmospheric CO_2 will be exhausted and given adequate atmospheric moisture there will be significant amounts of NaOH in the aerosol particles. Such particles will remain as wet slurries or droplets for relative humidities greater than 35% with effective density approaching 1 gm/cm^3 and dynamic shape factors approaching 1.0 as initial humidity approaches saturation. For lower peak mass concentrations and lower relative humidities particles will form chain like agglomerates or loose clusters with attendant reduction in effective density and increase in dynamic shape factor. The situation is less clear at low peak concentrations and moderate initial humidities but particles may form chains or loose agglomerates if the carbonate formation is faster than the adsorption of water by sodium hydroxide. It is also difficult to speculate as to the aerosol properties for low oxygen sodium fires. All of these conditions are fruitful areas for future studies.

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REFERENCES

1. Greenfield, M., Koontz, R., Johnson, R., and Morewitz, H., Proceedings of the 11th Air Cleaning Conference, Richland, Washington (31 August - 3 September 1970) p. 26.
2. Lane, W. R., and Stone, B. R. D., International Conference on Mechanisms of Corrosion by Fuel Impurities, Butterworths (1963).
3. Supplement No. 1 to the Safety Evaluation of the Fast Flux Test Facility, Project No. 448, U.S.A.E.C., Directorate of Licensing, Washington, D.C., Dec. 13, 1974, p. 48.
4. Tillery, M.I., "A Concentric Aerosol Spectrometer," Am. Ind. Hyg. Assn. J., 34:62, 1974.
5. Fuchs, N. A., The Mechanics of Aerosols, MacMillan, New York, 1964.
6. Herden, G., Small Particle Statistics, 2nd ed., Butterworths, London, 1960.
7. Radiological Assessment Models, Seventh Quarterly Report March-May 1976, GEAP-14034-7 (June 1976).
8. Mercer, T. T., "Aerosol Technology in Hazard Evaluation", Academic Press, NY (1973).
9. Stober, W. and Flachsbart, H., "Size Separating Precipitation of Aerosols in a Spinning Spiral Duct", Env. Sci. Tech., 3:1280, 1969.
10. Mallove, E. F. and First, M. W., "Direct In-Vessel Application Experiments at Harvard Air Cleaning Laboratory", Progress Report for January 1, 1976-March 31, 1976, COO-2801-2 (1976).
11. Clough, W. S. and Garland, J. A., "The Behavior in the Atmosphere of the Aerosol From a Sodium Fire", United Kingdom Atomic Energy Authority Report, AERE-R 6460, 1970.
12. Wilson, E. B., Jr., An Introduction to Scientific Research, McGraw-Hill Book Company, Inc., New York, 1952, 262-275.
13. Kotrappa, P., "Shape Factor for Quartz Aerosol in Respirable Size Range", J. Aerosol Science, 2:353-359 (1971).
14. Kotrappa, P., Shape Factors for Aerosols of Coal, UO₂ and ThO₂ in Respirable Size Range, in Mercer, Morrow and Stober (eds.) Assessment of Airborne Particle, Thomas, Springfield, Ill., 3310356 (1972).
15. Stober, W., Dynamic Shape Factors of Nonspherical Aerosol Particles in Mercer, Morrow, and Stober (eds.) Assessment of Airborne Particles, Thomas, Springfield, Ill. 249-288 (1972).

16. Beeckmans, J. M., "The Density of Aggregated Solid Aerosol Particles", Ann. Occup. Hyg., 7, 299-305 (1964).
17. Silverman, L., Billings, C. E., and First, M. W., Particle Size Analysis in Industrial Hygiene. Academic Press, New York (1971).
18. Whytlaw-Gray, R. and Patterson, H. S., Smoke, Arnold, London (1932).
19. Johnstone, H. F., Inhaled Particles and Vapors, C. N. Davies (ed.) Pergamon Press, p. 95 (1961).

NOTES

1. No detectable sodium hydroxide (indicate as less than 1%) was found for one pound sodium fire samples taken from 14 to 268 minutes after fire initiation. Initial relative humidity for these measurements was 40%. The standard method described in "Fundamentals of Analytical Chemistry" (Skoog and West, Holt, Rinehart, and Winston, 1963), was used for both carbonate and hydroxide analysis. Handling of the samples results in a few seconds exposure to ambient air. Samples were stored prior to analysis in a desiccator containing crystalline NaOH to remove water vapor and CO₂. As described in reference 10, the same technique was used for larger sodium fires where significant amounts (up to 50%) of NaOH were found.

TABLE 1.

Test Conditions for Centrifuge Runs

Centrifuge Test #	Time of Sampling Start (Minutes After Start of Fire)*	Duration of Sampling (Minutes)	Initial Cham- ber Relative Humidity %	Aerosol Mass Concentration Time of Sample** (GM/M ³)
13-1	54	10	19	1.54
17-1	34	6	20	1.71
17-2	328	50	20	0.28
21-1	25	3	35	3.54
23-1	89	3	53	1.96
23-2	376	50	53	0.37
30-1	102	6	16	1.37
30-2	187	60	16	0.86
30-3	338	75	16	0.31

* Average duration of fire after initiation of aerosol production was 25 minutes.

** Gravimetric determination of aerosol in chamber without reference to compounds present.

TABLE 2.

Basic Data and Derived Parameters from Centrifuge Tests

Centrifuge Test #	D _a for Segment (μ m)	N _c , # Particles Counted in Field	N, Scaled # of Particles Whole Segment	D _e (μ m)	M _{Na} (μ gm)
13-1	3.4	133	0.88×10^5	4.53	0.65
"	1.7	220	9.85×10^5	2.22	0.927
"	0.91	82	3.9×10^5	1.26	0.054
17-1	3.34	114	0.56×10^5	5.13	0.342
"	1.72	48	2.72×10^5	2.26	0.945
"	.80	161	7.09×10^5	1.23	0.063
17-2	3.34	60	0.32×10^5	6.71	0.468
"	1.72	104	4.12×10^5	2.14	0.400
"	.80	35	1.5×10^5	1.31	0.027
21-1	3.34	122	0.661×10^5	4.53	0.396
"	1.72	269	12.3×10^5	1.73	1.16
"	.80	149	6.57×10^5	1.15	0.072
23-1	2.65	1962	3.64×10^5	2.50	0.833
"	1.80	1645	3.51×10^5	1.69	0.284
"	1.18	1464	2.50×10^5	1.45	0.076
"	.80	176	0.417×10^5	1.38	0.01
23-2	3.99	3082	0.429×10^5	4.56	0.369
"	2.65	2161	1.75×10^5	2.72	0.756
"	1.80	2555	4.78×10^5	1.77	0.396
"	1.18	2266	2.33×10^5	1.49	0.157
"	.80	124	0.280×10^5	1.03	0.002
30-1	1.80	1390	5.67×10^5	2.02	1.29
"	1.18	1425	7.56×10^5	1.19	0.342
"	.80	164	1.39×10^5	0.98	0.01

TABLE 2. (cont.)

Basic Data and Derived Parameters from Centrifuge Tests

Centrifuge Test #	D _a for Segment (μ m)	N _c , # Particles Counted in Field	N, Scaled # of Particles Whole Segment	D _e (μ m)	M _{Na} (μ gm)
30-2	.80	295	1.53×10^5	1.10	0.01
30-3	2.65	730	2.39×10^5	2.55	2.88
"	1.80	675	1.90×10^5	2.49	1.66
"	1.18	740	3.21×10^5	1.26	0.288
"	.80	194	5.18×10^5	0.85	0.1

TABLE 3.

Effective Particle Density at Different Initial
Relative Humidities

<u>Fire #</u>	<u>Initial Relative Humidity %</u>	<u>Effective Particle Density, ρ_e (gm/cm³)</u>
R-30	16	0.74
R-13	19	0.56
R-17	20	0.45
R-21	35	0.67
R-23	53	0.81

TABLE 4.

Effective Particle Density at Different
Times After Initiation of the Sodium Fire

Centrifuge Test #	Time After Initiation of Sodium Fire (Minutes)	Effective Particle Density, ρ_e (gm/cm ³)
21-1	25	0.67
17-1	34	0.48
13-1	54	0.56
23-1	89	0.81
30-1	105	0.81
30-2	227	0.73
17-2	328	0.42
30-3	374	0.70
23-2	376	0.81

TABLE 5.

Effective Particle Density at Different
Equivalent Volume Diameters

Equiv. Vol Dia., D_e , μm	1	2	3	4	5
$D_e\sqrt{C_c}$, μm	1.08	2.08	3.08	4.08	5.08
$D_a\sqrt{C_a}$, μm	0.67	1.82	2.69	3.29	3.60
Effective Density ρ_e , gm/cm ³	0.39	0.77	0.76	0.65	0.50
Stokes' Corr. Factor, α ($\rho_m=2.53$)	0.15	0.30	0.30	0.26	0.20
Dynamic shape factor, χ	2.0	1.0	1.0	1.2	1.6

TABLE 6.
Component Errors

$$\left. \begin{aligned} \frac{\sigma_{M_{Na}}}{M_{Na}} &= 0.05 \\ \frac{\sigma_R}{R} &= \frac{0.63}{2.95} = 0.21 \end{aligned} \right\} \frac{\sigma_M}{M} = 0.22$$

$$\left. \begin{aligned} \frac{\sigma_S}{S} &= 0.05 \\ \frac{\sigma_A}{A} &= 0.05 \\ \frac{\sigma_{\eta_A}}{\eta_A} &= 0.01 \end{aligned} \right\} \frac{\sigma_N}{N} = 0.07$$

$$\left. \begin{aligned} \frac{\sigma_Q}{Q} &= 0.04 \\ \frac{\sigma_v}{v} &= 0.04 \\ \frac{\sigma_{\ell_D}}{\ell_D} &= 0.02 \text{ max} \\ \frac{\sigma_{C_a}}{C_a} &= 0.01 \\ \frac{\sigma_r}{r} &= 0.05 \end{aligned} \right\} \frac{\sigma_{D_a}}{D_a} = 0.05$$

$$\frac{\sigma_{\overline{D}_e}}{\overline{D}_e} = 0.1 \text{ (actual values depend on number of particles sized and ranged from 0.01 to 0.1)}$$

FIGURE 1.
CALIBRATION SPHERES FOR SCANNING ELECTRON MICROGRAPHS.

FIGURE 2.

DIAGRAM OF AEROSOL CENTRIFUGE.

FIGURE 3.

AEROSOL CENTRIFUGE CALIBRATION.

FIGURE 4.

TOTAL AEROSOL MASS CONCENTRATION AS A FUNCTION OF TIME

FIGURES 5 AND 6.

SEM PHOTOGRAPH OF SODIUM AEROSOL PARTICLES.

FIGURES 7 AND 8.

SEM PHOTOGRAPH OF SODIUM AEROSOL PARTICLES.

FIGURE 9.

SEM PHOTOGRAPH OF SODIUM AEROSOL PARTICLES.

FIGURE 10.

DIAGRAM OF CENTRIFUGE FOIL SEGMENT FOR SEM.

FIGURE 11.

RATIO OF TOTAL AEROSOL MASS TO SODIUM MASS
AS A FUNCTION OF AEROSOL AGE.

FIGURE 12.

EQUIVALENT VOLUME DIAMETER VERSUS
AERODYNAMIC DIAMETER.

FIGURE 13.

AVERAGE PARTICLE MASS VERSUS
EQUIVALENT VOLUME DIAMETER.

FIGURE 14.

AERODYNAMIC DIAMETER DISTRIBUTION OF SODIUM AEROSOL.