Measurement of Model Aerosols Containing Two Metal Components Formed via Cooling and Dilution Routes
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Received 30 May 2011
Accepted 23 August 2011

Abstract The emission of alkali and heavy metals in combustion processes is an important contributor to environmental load. However, little is known of the mechanism by which gas-to-particle conversion occurs during cooling and dilution with the atmosphere at the exit of stacks. In the present work, particles generated from model exhaust gases derived from NaCl and CdCl₂ were investigated experimentally in the laboratory. An on-line, gas-phase measurement system showed that the mean diameters of aerosol particles in single-metal evaporation of NaCl and CdCl₂ were 35 and 30 nm, respectively, when the dilution ratio of the model gas was 1:20. However, the value was 50 nm in two-metal co-evaporation of NaCl with CdCl₂ at the same dilution ratio. FE-SEM images of aerosol particles collected with a quartz fiber filter in the two-metal system showed a morphology similar to that of NaCl. It is thus concluded that Cd-containing vapors nucleate at and grow on the surface of NaCl particles. These results may be informative for predicting phenomena related to gas-to-particle conversion at the exit of stationary emission sources, from which such condensed particles are suspected to be released into the atmosphere.

Keywords : Stationary Sources, Condensation, Coagulation, Combustion, Size Distribution, Particles.

1. Introduction
The emission of particles from stationary sources such as coal-fired power plants, waste incinerators, blast furnaces, and cement plants is a known cause of air pollution. It is estimated that emissions from stationary sources will become more serious in the future (Ibusuki, 2000). Although it is possible to use a dust collector such as a bag-type filter or an electrostatic precipitator located downstream from the source to collect the particles and prevent their emission, some components of the emissions, such as heavy metals, could potentially pass through such collectors at temperatures of 100–300°C and then subsequently condense and form particles in the atmosphere (below 100°C) (Lin and Biswas, 1994; Linak et al., 1994; Tsukada et al., 2008). To understand this mechanism, it is necessary to measure these emissions at the exit point of the gas (in most of cases, a chimney stack). However, because these emission sources are located at a significant height, they are difficult to measure on-site. The traditional procedure of sampling condensed particles is by using a series of traps in an ice bath downstream of an in-stack filter (such as EPA method 202). However, this is not a realistic method for measuring the condensed particles since the particles are collected in the liquid. Filadelfia et al. (1996) pointed out the substantial artifacts that occur in atmospheric processes. It is necessary to develop a more realistic representation of the condensed particles in the atmosphere produced during dilution, cooling, and aging at the hot exhaust prior to sampling. Therefore, systems using diluters that simulate the release of exhaust gases have been developed (Chang et al., 2004; England et al., 2000; Hildemann et al., 1989; Lipsky et al., 2004; Lipsky...
and Robinson, 2005). In Japan, a direct air-cooling-type system was evaluated, in addition to both an indirect water-cooling type (Kogure et al., 1997) and a direct water-cooling type (EPA method 202), by the Japan Quality Assurance Organization (JQA) commissioned by the Ministry of the Environment, Japan (Japan Quality Assurance Organization, 1997). Direct air-cooling type sampling more realistically reproduces the formation of condensed particles but there has been little study to clarify the mechanism behind the formation of condensed particles. The objective of the current study is to observe the gas-to-particle conversion processes in combustion flue gasses that are cooled and diluted with a laboratory-based model exhaust gas. Since Tsukada et al. (2008) have discussed the emission potential of single heavy metals, this study also explored mixtures of metallic components. Tsukada et al. (2007) found high rates of cadmium (Cd) and lead (Pb) emission from the combustion of a refuse derived fuel (RDF) in a small fluidized bed combustor, thus strongly implicating waste incineration plants in the emission of condensed aerosols. These heavy metals are estimated to be the main components of condensed particles. Thus, we chose cadmium chloride (CdCl2), which has a low melting point, as one of the components of a model gas to simulate the exhaust gas from a waste incineration plant. In addition to this, sodium chloride (NaCl), an alkali metal with a higher melting point, was selected as another component of the model gas. The reason for choosing NaCl in addition to CdCl2 was that it can also be a source of chlorine, which can be expected to be easily released from the incineration of plastics and cooking salt.

2. Experimental methods

In this study, the dilution ratio or residence time and temperature of the dilution gas were altered as the model parameters. As mentioned before, NaCl and CdCl2 were generated as the components comprising the model exhaust gas. The generation of these components should be “stable” and have high repeatability for modeling exhaust gas. For this purpose, sample pellets with smooth surfaces were prepared as follows: 1) Aqueous solutions of the metal salts were nebulized and the solvent was evaporated (the spray-drying method). 2) The dried powders were collected in a cyclone-type collector. 3) The collected powders were compressed at a constant pressure (50 MPa for 1 min) to prepare the sample pellets. The smooth surface of the pellets allowed the generation of a steady stream of particles by thermal evaporation because the surface area of evaporation was constant, which is in contrast to the concave-convex surface of normal pellets. High repeatability of particle generation was observed and confirmed beforehand through experimentation.

To decide the heating temperature of the two components, thermogravimetry–differential thermal analysis (TG-DTA; Thermo plus EVO TG 8120, Rigaku, Japan) was used to investigate the changes in sample weight versus differential thermal parameters. NaCl decreased in weight soon after passing its melting point (801°C). The differential thermal analysis results showed that NaCl started to vaporize when heated to temperatures greater than 600°C. Thus, the operation temperature for NaCl was set at 740°C. CdCl2 began to lose weight soon after reaching its melting point as well (568°C). Its operation heating temperature was set at 400°C.

Fig. 1a shows a schematic diagram of the experimental setup. Pellets (1 g) of each sample (CdCl2, NaCl, or both CdCl2 and NaCl) were placed into a tubular electric furnace set to the appropriate temperature. The individual metals or the combination of the two were evaporated and carried away by a 0.2-L/min flow of nitrogen (N2) gas. The N2 gas was transported through a HEPA filter and then through two valves, which allowed switching the transport line to either pass through a bubbler (to add 10% volume H2O vapor) or not before reaching the electric furnace (each line was heated to 70°C). The addition of moisture mimicked the conditions at a stationary source (e.g., a coal-fired power plant), where the atmosphere is not dry. After passing the electrical furnace, the evaporated CdCl2 and NaCl aerosols were filtered using a bag-type filter (pre-filter), which was heated to 150°C. Then, the model gas went into the diluter, where the dilution ratio, cooling conditions, and residence time were controlled by changing the flow of dilution gas (N2) at room temperature. Table 1 shows each condition with the different dilution ratios. The Reynolds number (Re) of the main stream of the diluter was also calculated and is shown in the table. All of the flow conditions were laminar. The

<table>
<thead>
<tr>
<th>Dilution ratio</th>
<th>Flow rate of N2 gas (L/min)</th>
<th>Residence time (sec)</th>
<th>Reynolds number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:10</td>
<td>2.0</td>
<td>2.1</td>
<td>335</td>
</tr>
<tr>
<td>1:20</td>
<td>4.0</td>
<td>1.1</td>
<td>640</td>
</tr>
<tr>
<td>1:30</td>
<td>6.0</td>
<td>0.7</td>
<td>945</td>
</tr>
<tr>
<td>1:40</td>
<td>8.0</td>
<td>0.5</td>
<td>1250</td>
</tr>
</tbody>
</table>

Table 1 Parameters at different dilution ratios
vapor-phase metals may condense into particles during this dilution process. Downstream of the diluter, particle size was measured in real-time by a Scanning Mobility Particle Sizer (SMPS; model 3034, TSI, USA). The particles were collected onto the quartz fiber filter to observe particle morphology and size by field emission–scanning electron microscope (FE-SEM; JSM-6335F, JEOL, Japan).

**Furnace**

The length of the quartz tube located in the furnace reactor was 404 mm. The temperature inside the quartz tube was previously measured to determine the positions of the metal components for a set temperature of 700°C. During the measurement of temperature, 0.2 L/min of carrier air was introduced and the outlet of the quartz tube was heated to maintain a temperature of 150°C by a ribbon heater. A thermo-couple was used to measure the actual temperature inside the quartz tube, and temperature was measured at 50-mm increments from the inlet. **Fig. 2** shows the results of the temperature distribution inside the quartz tube for the set temperature of 700°C. It shows the actual temperature reached above the set temperature at distances ranging from 100 mm to 300 mm from the inlet of the quartz tube. The maximum temperature was 740°C and therefore it was decided to place the pellet of NaCl at 200 mm from the inlet. Regarding the results of the TG-DTA, the heating temperature of the CdCl₂ was decided to be 400°C, thus pellet of CdCl₂ was placed at 20 mm from the inlet.

**Diluter**

**Fig. 1** shows the schematic diagram of a direct air-cooling-tube diluter. This diluter was similar type of the diluter as Kogure et al. (1997) used. It was made of glass and was composed of an inner and outer tube. The inner diameter of the inner tube was 10 mm and the outer tube had an inner diameter of 35 mm. Dilution air came from the outer tube into the inner tube and mixed with the exhaust gas to be diluted and cooled inside the inner tube. Twelve holes were located upstream of the inner tube to help the dilution air pass into the inner tube. These holes had diameters of 4 mm. Thermocouples were placed at positions upstream and downstream of the diluter to monitor the changes of temperature in real-time. The measured temperatures were around 150°C and 20°C, respectively.
3. Numerical simulation

To investigate the differences in changes of dilution ratio inside the diluter, a numerical simulation was achieved (COMSOL Multi-Physics ver. 3.5a, COMSOL AB., Stockholm). Fig. 3 shows the boundary condition of the inner tube of the diluter. The difference in settings was only the flow velocity of the dilution air, which enters through 12 holes of diameter 4 mm. In this 2D-based simulation, only six holes were considered in order to simplify the simulation model, and the wall was set as an insulating material. Meshes were automatically fabricated by the software. The meshes used were in order of 20 k cells. Two governing equations were used for numerical simulation:

\[-\eta \nabla^2 u + \rho (u \cdot \nabla) u + \nabla p = 0,\]  \hspace{1cm} (1)
\[\nabla \cdot u = 0,\]  \hspace{1cm} (2)

where \(\eta\) donates the dynamic viscosity, \(\rho\) the density, \(u\) the velocity field, and \(p\) the pressure.

The first equation is the momentum transport equation; incompressible Navier-Stokes equations (steady state) and the second is the equation of continuity for incompressible fluids.

In addition to Equations (1) and (2), the mathematical model for heat transfer by conduction and convection is followed with the heat balance equation:

\[\rho C_p u \nabla T = \nabla \cdot (k \nabla T),\]  \hspace{1cm} (3)

where \(\rho\) is the density, \(C_p\) is the specific heat capacity, \(u\) is the velocity field, \(T\) is the temperature, and \(k\) is the thermal conductivity. The thermal conductivity \(k\) describes the relationship between the heat flux vector \(q\) and the temperature gradient \(\nabla T\) as in \(q = -k \nabla T\) (Fourier’s law of heat conduction).

4. Results and discussion

4.1 Single metals

NaCl and CdCl₂ pellets were heated individually at 740°C and 400°C, respectively, and the size distribution of the formed particles was measured. Fig. 4 shows each size distribution with different dilution ratios. The mean diameter of the NaCl (Fig. 4a) did not change (35 nm) even when it was diluted and cooled from dilution ratio of 1:10 to 1:25. It is suspected that the NaCl particles had formed soon after evaporation in the furnace and the diluter parameters did not affect anything (the dilution only took place at the diluter). Figs. 5a and 5b show the particles which were collected at a pre-filter (Fig. 5a) and a filter which was located downstream of the diluter (Fig. 5b) with dilution ratio of 1:20. NaCl particles were cube-shaped. Particles which were collected at downstream of the diluter were only one particle in an area of SEM image (i.e. 1.5 \(\mu\)m²). Additionally, a particle had size of less than 200 nm was observed at the filter downstream of the diluter. Again, this also suggests that particle formation was completed before the particles arrived at the pre-filter and most of the particles were collected at the pre-filter. Only a few of the penetrated particles that were less than 200 nm got caught in the filter downstream of the diluter.

*1 In current study, results will be discussed when N₂ gas pass through a bubbler.
On the other hand, CdCl$_2$ (Fig. 4b) exhibited varying size distribution with various dilution ratios. As it was diluted more, the mean diameters grew smaller. This result may have been the result of particle formation taking place inside the diluter where the colder dilution air mixed together and condensation and nucleation processes occurred. These phenomena were not observed in the use of NaCl particles. The average diameter of CdCl$_2$ aerosol particles was 30 nm. 

Figs. 6a and 6b show the CdCl$_2$ particles, which were collected at the pre-filter (Fig. 6a) and the filter that was located downstream of the diluter (Fig. 6b) at a dilution ratio of 1:20. The sizes of particles, which were collected at both the pre-filter and the filter downstream of the diluter, were similar. Additionally, it was visually observed that the number of particles at the filter downstream of the diluter was higher than that observed at the pre-filter. This result is different comparison with the observations with the NaCl particles. This may be because, unlike previously stated, the particle formation started from the pre-filter and accelerated the condensation and nucleation processes inside the diluter.

Table 2 shows the corrected total number concentration for each dilution condition. Total number concentration is calculated from result of particle size distribution of SMPS.

![Fig. 4](image1.png)  
**Fig. 4** Size distribution of a) NaCl and b) CdCl$_2$ with different dilution ratios.

![Fig. 5](image2.png)  
**Fig. 5** Images of NaCl derived particles at a) pre-filter and b) back-filter.

![Table 2](image3.png)  
**Table 2** Corrected total number concentration of each dilution condition for individual NaCl or CdCl$_2$

<table>
<thead>
<tr>
<th>Dilution ratio</th>
<th>Total number concentration [$\text{#/m}^3$]</th>
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<tbody>
<tr>
<td></td>
<td>NaCl</td>
</tr>
<tr>
<td>1:10</td>
<td>$2.45 \times 10^{13}$</td>
</tr>
<tr>
<td>1:15</td>
<td>$3.45 \times 10^{13}$</td>
</tr>
<tr>
<td>1:20</td>
<td>$3.60 \times 10^{13}$</td>
</tr>
<tr>
<td>1:25</td>
<td>$3.75 \times 10^{13}$</td>
</tr>
<tr>
<td>1:30</td>
<td>–</td>
</tr>
<tr>
<td>1:40</td>
<td>–</td>
</tr>
</tbody>
</table>
The values of CdCl₂ at each dilution condition were not equal or similar. This may be because the diffusion loss inside the diluter caused a decrease in the number of particles. To obtain the evidence for this, the equation of Gormley and Kennedy (1949), which was cited in Brockmann (2001), was used. The transport efficiency \( \eta_{\text{diff}} \) in laminar tube flow as a function of the dimensionless deposition parameter \( \xi \) is written as

\[
\eta_{\text{diff}} = 1 - 2.56\xi^{0.66} + 1.2\xi + 0.177\xi^{1.33} \quad \text{for } \xi < 0.02
\]

(4)

and

\[
\eta_{\text{diff}} = 0.819e^{-3.657\xi} + 0.097e^{-2.32\xi} + 0.032e^{-5.78\xi} \quad \text{for } \xi > 0.02
\]

(5)

where,

\[
\xi = \frac{\pi DL}{Q}
\]

(6)

and \( D \) is the diffusion coefficient, \( L \) is the tube length, and \( Q \) is the aerosol volume flow rate. The transport efficiency of particle size ranges in this study was between 98 and 99%. Most of particles could be transported through the diluter. Therefore, the diffusion loss was unconfirmed as the main loss of the particle number.

At the dilution ratio of 1:40, the mean diameter was 18.4 nm, and at the dilution ratio of 1:10, the diameter was 58.3 nm. Residence time in the diluter for each dilution ratio was 0.5 seconds and 2.1 seconds, respectively (i.e., the particle grew from approximately 18.4 nm to 58.3 nm in 1.6 seconds). This result may indicate that coagulation of the particle is the main reason for the particle loss. The coagulation process can be estimated by means of the following equation:

\[
N(t) = \frac{N_0}{1 + N_0 K_0 t}
\]

(7)

where, \( t \) is the residence time, \( N(t) \) is the number concentration at residence time \( t \), \( N_0 \) is the initial number concentration, and \( K \) is the average coagulation coefficient \([\text{cm}^3 \text{ s}^{-1}]\). The average coagulation coefficient \( K \) of polydisperse aerosol can be expressed as

\[
K = \frac{2kT}{3\eta} \left[ 1 + \exp \left( \frac{\ln^2 \sigma_g}{\text{CMD}} \right) \right]
\]

(8)

where, \( k \) is Boltzmann's constant, \( T \) is temperature in Kelvin, \( \eta \) is dynamic viscosity, \( \lambda \) is the mean free path, CMD is Count Median Diameter, and \( \sigma_g \) is geometric standard deviation, (Hinds, 1999). At a dilution ratio of 1:40, the total concentration was \( 1.28 \times 10^{14} \text{ m}^{-3} \). When this value is substituted into Equation (7) and calculated with Equation (8), the total number concentration after the coagulation process can be calculated. In this study, after 1.6 seconds, which was the same as the residence time from a dilution ratio of 1:40 to 1:10, was substituted as well. When CMD was 18.4 nm and geometric standard deviation was 1.22, the total number concentration after 1.6 seconds became \( 7.80 \times 10^{12} \text{ m}^{-3} \). This is approximately the same amount of total concentration at a dilution ratio of 1:10. This result indicates that the main cause of CdCl₂ particle loss in the diluter was a coagulation process.

Numerical simulation data of gas flows also showed evidence of a coagulation process. Fig. 7 shows the simulation results of gradient of temperature at the inner tube of the diluter. When Fig. 7a (at a dilution ratio of 1:40) and Fig. 7b (at a dilution ratio of 1:10) are compared, the area of higher gradient of temperature is larger at the dilution ratio of 1:40. Thermophoresis might have taken place and this allowed more particle coagulation at the dilution ratio of 1:40. Similar results were observed with the results of flow dynamics. More turbulence flow was observed at the dilution ratio of 1:40. This condition may lead to an increase in the coagulation process as well.

4.2 Mixture of Na-Cd components

Two metal components were heated and generated by thermal evaporation method at same time but the positions of NaCl and CdCl₂ pellets were separated as previously discussed. Thus, CdCl₂ was heated at 400°C and NaCl was heated at 740°C. To estimate the phase of two components at each heating temperature, a thermodynamic equilibrium analysis had been performed by using a commercial package software (FactSage 5.3.1, Germany). Fig. 8 shows the result. At the position of CdCl₂ pellet inside the furnace reactor, it was heated at 400°C. Solid phase of CdCl₂ starts melting and at same time, Cd and Cd (OH)₂ start vaporizing to be gas phase. These gases increase their amount by heating up to 740°C. Meanwhile, few of CdO and Cd (OH)₂ gas appears. At 740°C, where, a pellet of NaCl is positioned, solid phase of NaCl starts melting and at same time gas phase of NaCl is present. This is significant with the model result of Wey et al. (1999). As the NaCl was present, sodium chloride existed as either liquid or gas at higher temperature (700 to 900°C). In this case, metal oxide (for case of Cd, CdO) was the dominant species. This was expected to remain since NaCl was expected to remain since NaCl does not decompose at temperatures of 900°C or less and the heavy metals (Cd) cannot form chlorides as there was little or no vapor-phase
chlorine species (Cl₂ or HCl) to react with under those conditions.

Fig. 9 shows the size distribution of mixed Na-Cd components at various dilution ratios. When the dilution ratio decreased, the mean diameter decreased. This phenomenon is similar to that of the single CdCl₂. The average diameter of the mixed aerosol particles was 50 nm. This is larger than the average diameter of individual CdCl₂ and NaCl particles. FE-SEM pictures of particles at the pre-filter and the filter located downstream of the diluter show more detail (Figs. 10a and 10b). At a pre-filter, two different morphologies of particles are existed. One is that of rounded particles and
other is that of square-shaped particles. Due to small particle size, it was difficult to detect the chemical compositions by using an EDS system in FE-SEM. Rounded particles may be as predicted the Cd derived particles and square-shaped particles as the NaCl particles when it is compared with Fig. 5a and Fig. 6a. The sizes of particles inside the pre-filters are roughly from 20 nm to a few hundred nm. The number of particles which are less than 50 nm in size decreased at the downstream filter, which may be the result of the following mechanism: NaCl, which has a higher melting point, nucleates and becomes a solid particle first and then Cd derived components were condensed from the gas phase and coagulated with the NaCl particles inside the diluter. The NaCl particles are as assumed to be the core particles and condensed Cd derived particles adhered to them, forming a shell. Additionally, formed particles which contain the two metals’ morphology are cube-shaped. This may be evidence of the Cd derived particles adhering to the surface of the NaCl particles. The size dependency of each dilution condition may be the result of the coagulation process of CdCl\(_2\) particles.

4.3 Prediction of processes at “real” stationary sources

In this study, the behavior of a laboratory-based model gas which contains two metal components was observed to simulate the behavior of alkali and heavy metals during the gas-to-particle conversion during the process of combustion, cooling, and dilution when it is released into the atmosphere from stationary sources. In this study, the following points were found;

1) Individual NaCl - Alkali metal, which has higher melting point, did not change its size distribution at each dilution condition. This indicates that the particle formation had finished at furnace.

2) Individual CdCl\(_2\) - Heavy metal, which has lower melting point, changed its size distribution with different dilution condition. The particle formation was observed during the transport of the pre-filter and the diluter. The particle formation was accelerated inside the diluter where dilution air mixed. The observation also found the main cause of particle loss was a coagulation process.

3) Mixture of Na-Cd components - NaCl became particles first, and then Cd derived components were condensed from the gas phase and coagulated with the NaCl particles. The NaCl particles are as assumed to be the core particles and condensed Cd derived particles adhered to them.

Alkali metals may form particles at an earlier stage after combustion and most of the particles may be caught by a bag type filter (based on Point 1). On the other hand, combusted...
and evaporated heavy metals may pass through a bag filter in gas phase and when it is released into the atmosphere, particles may form after the condensation and nucleation processes (based on Point 2). Additionally, in more realistic conditions when two or complex components are combusted, evaporated heavy metals and particles, which are formed at an earlier stage (as in Point 1) and not caught by the bag filter, may be released into the atmosphere and these may combine together to form larger particles (based on Point 3). Released condensed particles may influence the atmospheric environment. If this prediction is adequate, it is better to take action.

5. Conclusion

In this study, NaCl and CdCl₂ were generated from a laboratory-based experimental setup to simulate the behavior of particles from a stationary source. There is a possibility that condensed particles can pass through a bag filter when they are in a gas phase. Additionally, some formed particles may not be collected by a bag filter. Regarding the simulation results and predictions, for higher collection efficiency, it is better to take action, for instance by increasing the filter efficiency of bag-type filters and by adding an electrostatic precipitator.

Acknowledgments

This study was partially supported by the Ministry of Education, Culture, Sports, Science and Technology through the Special Coordination Funds for Promoting Science and Technology (administered by Japan Science and Technology Agency) for I.W.L., and the Grant-in-Aid for Scientific Research on Innovative Areas (20120010 (I.W.L.) and 20120004 (H.K.)).

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