Interactions Between Trace Metals, Sodium and Sorbents in Combustion.

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INTRODUCTION

The proposed research is directed at an *understanding* of how to exploit interactions between sodium, toxic metals and sorbents, in order to optimize sorbents injection procedures, which can be used to capture and transform these metals into environmentally benign forms. The research will use a 17kW downflow, laboratory combustor, to yield data that can be interpreted in terms of fundamental kinetic mechanisms. Metals to be considered are lead, cadmium, and arsenic. Sorbents will be kaolinite, bauxite, and limestone. The role of sulfur will also be determined. The research is divided into five tasks.

Task 1: Combustor Modifications.

The existing laboratory combustor will be modified to allow injection of toxic metal surrogates, and withdrawal of particulate samples for subsequent analysis, without allowing leaks to impact the laboratory room environment.

Task 2: Screening Experiments.

Surrogate trace metals (3, listed above) will be injected through an otherwise "clean" gas flame stabilized in the combustor. Sorbents (3, listed above) will be injected through a port downstream. For each metal/sorbent pair, a statistically correct set of parametric experiments will be performed, quantitatively to determine the effects of a) sodium level, b) sulfur level, c) sorbent injection temperature, d) sorbent residence time, on trace metal capture. Measurements consist of the size segregated composition of the exhaust particulate matter. The objective function is the fraction of metal reactively captured by the sorbent. Solid and surface analyses will provide insight into mechanisms.

Task 3: Mechanisms.

Selected runs (6) from Task 2 will be repeated to obtain time resolved data on metal partitioning, with and without sodium and sulfur. The purpose will be to glean rates and mechanisms from size segregated particulate samples withdrawn. Advanced surface and solid analyses of sampled particulate will aid in mechanism building.

Task 4: Applications.

Three different, well characterized, pulverized coals will be burned, and the partitioning of the three toxic metals, in the presence of sorbents, examined, in the light of the mechanisms uncovered in Tasks 2 and 3. These mechanisms will also be used to determine the optimum application of sorbent injection in the presence of sodium and sulfur.

Task 5: Mathematical Modeling.

Tasks 2 through 4 will be accompanied by mathematical modeling. Empirical model building will be used in Task 2 to correlate, and interpolate the data. Deterministic and mechanistic modeling will be used to correlate and extrapolate the data of Tasks 3 and 4. This modeling will involve models of a) gas/solid reactions, and the appropriate particle size dependencies, b) gas phase reactions, either through partial/global equilibrium arguments (using CET89 software), or through CHEMKIN based detailed reactions, c) aerosol dynamics (using MAEROS), as required and appropriate.

PROGRESS FOR THIS QUARTER

Task 2: To understand the nature of the multiple metal interactions several projects have been underway. The first is the development of a variable leachability protocol to separate the reacted versus unreacted metal in a sample. The second was a fundamental study of multiple metal interactions, sodium, cadmium and lead, in the downflow reactor. This time resolved experiment was conducted to determine the mechanism of particle formation and metal interaction. Finally, screening test are being conducted with multiple metals and sorbents.

Multiple Metal / Sorbent Interactions

The multiple metal/sorbent screening tests are underway and the results are not available at the time of this report. However, these tests are being constructed to test the effect of sodium and either lead or cadmium over sorbents. Previous work, by Mwabe et al, has shown that there is an upper limit to the utilization if sorbent by metal reaction. The maximum utilization of the sorbent according to their work is 50%. Since one of the central hypothesis of this work is that sodium will enhance the capture of other metals, these screening tests were contrived to test the limiting equivalence ratio. These tests are underway with results due by mid-November.

Variable Leachability

As previously reported a methodology is required to discriminate the condensed toxic metal specie, lead and cadmium, from that which is reacted with the sorbent. To this end a variable leachability protocol (VLP) has been under development.

Outlined in figure 1, the VLP is a cold acetic acid leaching protocol that is designed to be used on a single plate of an impactor. The first step is to acquire a sample from the impactor. The substrate is split into two equal sections, separated, and processed. One half is processed in the standard sorbent digestion procedure. The remaining half sample undergoes the variable leachability test. The sample is placed into an acetic acid solution having a pH of 2.3 for 24 hours. A fraction of the leachate is removed and analyzed. A solution of 3 HF: 1 HCl: 1 HNO_3 is added in an amount equal to the fluid volume to the remaining material. This acid addition brings the solution to the composition of the standard sorbent digestion.

The VLP procedure was developed in 3 steps. First, by using pure reagent grade metal oxides and chlorides the pH of the leaching solution was determined to be 2.3. At this pH, all metal oxides dissolve in the 24-hour period of the test. The metal chlorides are soluble in water. The second development step exposed the raw sorbent materials to the leaching solution. Results of these tests were mixed, kaolinite shown no tendency to dissolve in the leaching solution. However as much as twenty-five percent of the lime was shown to dissolve in the leaching. The final phase of the test is a reacted sorbent test. Samples of sorbent reacted with toxic metals reacted with lead and cadmium will be analyzed in this method. As of the writing of this report the results of these tests are not available.

Multiple Metal Interactions

A series of tests were conducted to investigate the interaction of the multiple metals in the reactor. The primary goal was to identify the mechanism by which metal vapors nucleate, condense and/or coagulate in the hope that this information would provide further nsight into the sorbent-metal interactions. In these tests combinations of sodium, lead, and cadmium were injected into the downflow combustor. Time resolved samples were withdrawn by the isokinetic sampling system and analyzed by flame ionization atomic absorption. This work was presented at the Western States Section of the Combustion Institute Fall Meeting. Appendix 1 contains a full copy of the paper.

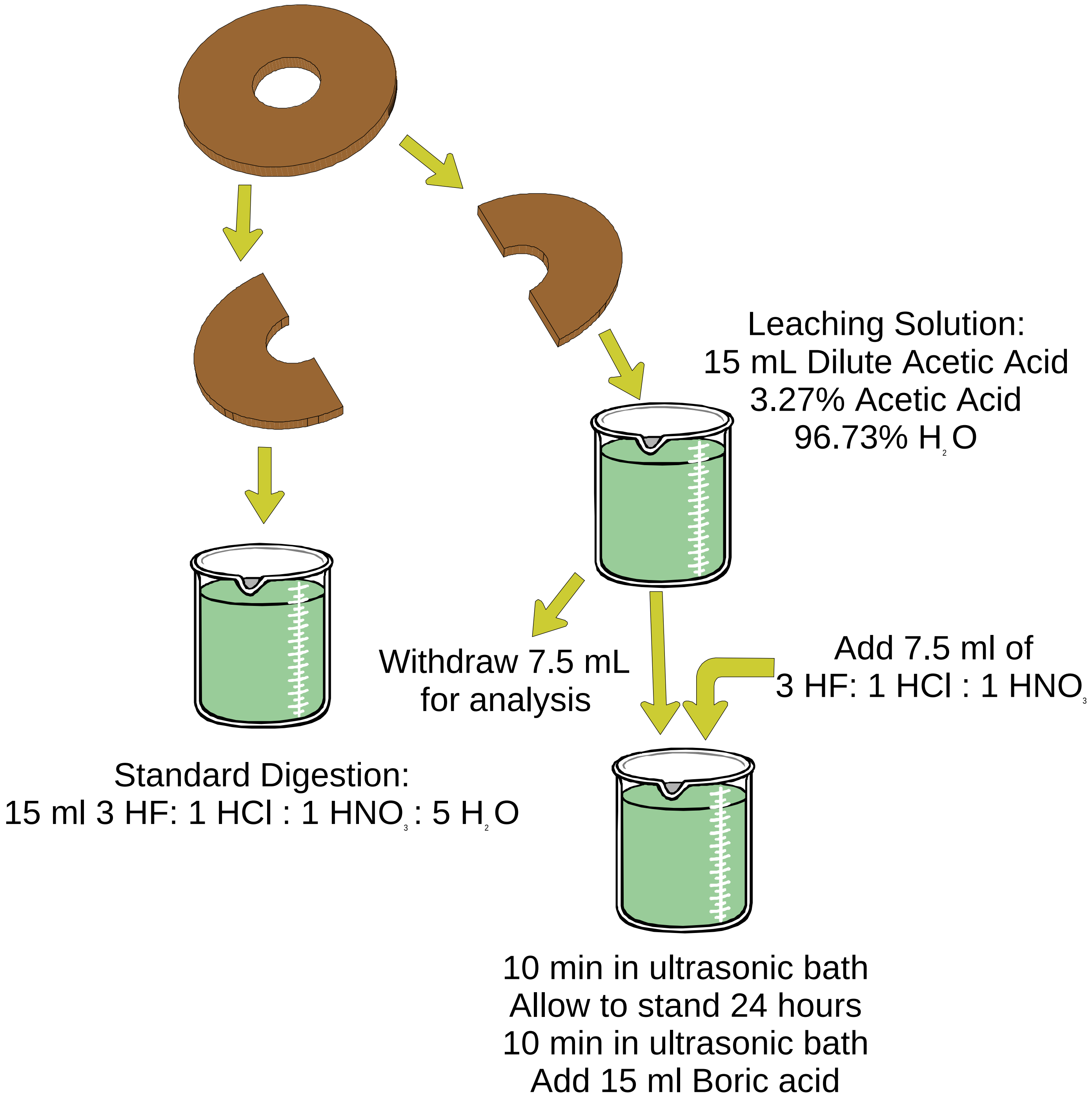

Figure 1: Variable Leachability Protocol

Appendix 1:

The Partitioning of Multiple Semi-Volatile Metals in a Downflow Combustor

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Abstract

This paper focuses on mechanisms governing the partitioning of multiple semi-volatile metals, which are simultaneously injected into a furnace. Three metals considered here are sodium, cadmium and lead, all of which are known to vaporize at combustion temperatures and condense downstream to form tiny particles. These metals were injected first, individually, then in pairs, and finally all three together, as salts in aqueous solution, into a natural gas flame, supported in a 6m long 0.15cm ID downflow laboratory combustor. The evolution of the ensuing metal aerosols was determined through time resolved sampling of particles in the exhaust. The latter was achieved through a specially designed isokinetic dilution probe, followed by a Berner low pressure impactor, capable of segregating particles in the sub-micron size range. Samples were analyzed by atomic absorption/emission.

For cadmium and sodium injected individually, nuclei of less than 0.07 micron coagulated to form particles of 0.4 micron in the exhaust, which is the particle size range that is least benign to human health. Lead particles had larger aerodynamic diameters, as would be expected from its greater density. However, when all three metals were injected together, they all followed the lead particle

size distribution (PSD), suggesting condensation as well as nucleation phenomena. These results are currently being investigated further through additional experimentation and aerosol dynamics modeling.

Introduction

The emission of toxic metals, such as lead and cadmium from incinerators and coal-fired boilers is a major concern. These metals have been associated with negative health effects, many of which are exacerbated by the nature in which these metals are emitted. These metals are found enriched in submicron particles, which at this size are very difficult to collect in air pollution control devices. Once emitted the relatively slow settling velocities allow them to persist over long distances. Upon inhalation, these particles are capable of penetrating deep into the lung and collecting. In the body, lead has been found to impact the central and peripheral nervous system (Landrigan, 1989). Reductions in IQ of children have been correlated to the presence of low and high levels of lead (Sarofim and Suk, 1992). Cadmium has been included in a group of potential human carcinogens (Vouk and Piver, 1983). Sodium is often present in systems containing the other two.

As can be seen in Figure 1, sources of toxic metals in combustion systems can be varied and plentiful. Introduced into the system as liquid or solid, these metals may follow many pathways to partition into submicron or supermicron particles. One hopeful control technique has been to introduce sorbent material into the post-flame combustion stream to capture the metal, thus shifting the partitioning of the metal toward the larger collectable supermicron particles. While past research has focused on single metal species in the presence of sorbents (Mwabe and Wendt, 1996, Scotto et al, 1992, Linak et al, 1994), most practical systems involve multiple metals, rather than only one single individual metal. Different metals will condense at different temperatures, and so one might expect multiple metals to interact with each other in complex ways. However, there are to date very few systematic studies concerned with the partitioning of multiple metals. Although much data describing the partitioning of multiple metals in the ash aerosol from coal combustion are available, these processes are controlled primarily by the initial form of the metals and mineral matter in the coal, and less by the processes of nucleation and condensation in the far post flame (Gallagher, Peterson and Wendt, 1996, Seames et al, 1998). In this work we wish to understand how multiple metals interact with one another during the condensation processes that occur after they have been vaporized.

In this work, mixtures of lead and cadmium were studied in the presence of sodium. Lead and cadmium are both semi-volatile toxic metals. Sodium is ubiquitous in most fossil fuels and is captured by the same sorbent materials as lead and cadmium; therefore, its role is important in understanding the dynamics of the metal interactions (Mwabe et al, 1996).

This research differs from that of Biswas and co-workers (1997), where the interactions between lead and silica were studied when each were introduced as vapor into laminar bench scale flames. The lead-silica system was designed to study a reactive transformation similar to that found in the sorbent studies. This study hopes to elucidate the physical transformations of the metals without the presence of the sorbent material.

Theory

One approach to conduct a systematic study of multiple metal interactions is to introduce controlled quantities of lead, cadmium and sodium into the system in the form of similar aqueous salt solutions. As illustrated in Figure 1, droplets of dissolved metal are introduced. These droplets are vaporized and form a submicron aerosol. It is possible to envision two extreme scenarios by which these aerosols develop. In one scenario, the majority of the metal nucleates and coagulates to form submicron particles with little film condensation occurring to the surface of the nuclei. In the other, a few nuclei form with the majority of the metal then condensing to the surface to form these submicron particles. Thus the question, does one of these two extreme scenarios dominate?

An interesting complication arises from the choice of these three metals. Equilibrium predicts that for these metals, the dewpoints are very similar. Using NASA's Chemical Equilibrium Applications (CEA), a new version of the CET89 program, the effect of temperature on the equilibrium predicted fraction of the solid metal. Shown in Figure 2, the dewpoints are predicted to be within twenty-five degrees Celsius of each other. At the composition of the experiments, the sodium and cadmium solid fraction appears to have nearly the same temperature dependence. Within the database that was utilized, there are no interactions between the metal species of interest. The dominant predicted condensed species are lead (II) oxide, cadmium oxide and sodium carbonate. Also, it is reasonable to expect that the metal species are attempting to nucleate and/or condense at approximately the location in the combustor.

Experimental

Experiments were conducted on a 6 meter tall, 0.15m ID, 12kW downflow combustor. The facility, illustrated in Figure 3, was designed to have a time and temperature history similar to a full-scale system; yet, it is well defined and can be considered to be one-dimensional. Primary air and natural gas are introduced through a burner assembly that consists of a variable swirl burner with a centerline plain-jet, air-blast atomizer. Aqueous metal solutions are introduced through the atomizer at a rate of 10 ml/min. Metal acetates are dissolved in distilled water in a quantity such that the concentrations of each metal on an elemental basis are 100ppmV in the flame.

Particulate samples are withdrawn by the isokinetic sampling and size segregation system shown in Figure 4. The samples are drawn into a sampling probe, immediately mixed with a controlled amount of nitrogen. The nitrogen immediately quenches the stream and stops all subsequent reactions. The diluted sample is directed immediately to a Berner low pressure cascade impactor which performs the size segregation on the particles.

The Berner low pressure impactor (BLPI) is the experimental centerpiece of this research. Conventional cascade impactors operate at atmospheric pressure under which separations are performed purely by varying the gas velocity. This methodology has its limitations as it approaches the particles of 0.1µm in diameter. The BLPI by operating at low pressures is able to take advantage of the compressible flow properties and attain much smaller particle cut-off diameters than atmospheric impactors. The BLPI is pictured in Figure 5 along with the plate cut-off diameters.

The BLPI is composed of eleven stages having aerodynamic cut-off diameters ranging from 15.7µm to 0.0324µm. Each stage is composed of an orifice plate above a substrate and a substrate holder. The substrate is held in place by a ring that also acts as a spacer between the orifice plate and the substrate. The flowrate through the BLPI is regulated by the last orifice plate, which acts as a sonic orifice. The absolute pressure after this final orifice plate is approximately 8 kPa. A full description of this apparatus and its performance can be found in Hillamo and Kauppinen (1991).

Samples were captured on substrates of greased polycarbonate nucleopore filters or ungreased aluminum foil. The grease was applied by airbrush in the form of a 10:1 (by volume) solution of PEG-600 grease and chloroform. The substrates were then vacuum desiccated for a minimum of 12 hours to remove the solvent. The aluminum substrates were prepared ungreased to facilitate scanning electron microscopy (SEM).

Samples are withdrawn at three different ports as shown in Figure 3. The first sample is drawn at a temperature of 1420K and a superficial residence time of 0.37 s. This point is above the metal dewpoint and in the post flame region. The second sample, withdrawn at 1.9 s and 973K, was taken at a point below the dewpoint of the metals. The third sample is withdrawn approximately 1 second later allowing sufficient time for coagulation to occur. The samples were analyzed by either flame ionization atomic absorption or by field emission SEM. Samples for chemical analysis were withdrawn for 30 minutes. The substrates for the SEM compatible sample were exposed for on average 3 minutes.

Two difficulties were encountered. The first difficulty is larger material recoveries in samples composed of larger particles. Particles with smaller diameters have lower overall transmission efficiencies in the sampling system due to increase diffusion to the walls of the system. The second difficulty was poor recovery of the sodium in the system as compared to the other metals.

Results

For the sake of brevity, four test cases are reported in this paper. In the first three, sodium, cadmium or lead was injected separately. Then the combination of the three metals was injected simultaneously with each metal having a concentration 100ppmV in the furnace.

Individual Metal Injection Experiments

Figure 5 and 6 show the sampled size distribution for the individual metal injection cases as measured by FIAA. The abscissa, shown on a log scale, is the aerodynamic diameter for spherical particles of unit density. The 50% aerodynamic cut-off diameter is represented by the value of the left side of each bar. The ordinate is the fraction of the total metal species found on a specific plate. In each case, the similar behavior is observed for the particle size distributions. At 0.37 seconds and a temperature of 1420K, the metals are found to be on the lowest plates corresponding to the smallest particle sizes. Since this sampling point is significantly above the dewpoint of the all metals in the system, these fumes are generated in the probe and might represent nuclei of the metals. The slight difference between the lead, cadmium and sodium cases are due to density differences between the particles since the reported aerodynamic diameters have not been corrected for density. The following panels clearly show the evolution of the aerosol from nuclei to larger particles. In Figure 6 panel (b), it appears that an accumulation mode is forming. At 1.9 seconds, the cadmium mode has shifted into larger size range; coagulating from the small nuclei that are formed at the dewpoint. Then at 3.0 seconds the size range has not shifted but the central peak appears to have grown. This resultant mode is in a size range is most harmful.

Simultaneous Metal Injection Experiments

In Figure 8, the PSD for the simultaneous injection of lead, cadmium and sodium is pictured for the three separate sampling locations. In these plots, the total amount of elemental metal in micromoles is plotted on the ordinate while the aerodynamic diameter is again shown on the abscissa. Each bar is composed of the contributions of the individual metals.

An interesting result appears in the 0.37 second distribution. When compared to the individual metals cases, two differences are apparent. First, if the assumption that the aerosol in this panel enters the probe as a vapor and subsequently forms nuclei is true, then it is reasonable to expect that the distribution should from the superposition of the PSD's of the three single metal cases. This does not appear to happen for the ternary mixture; the sodium and cadmium more appear to track lead in the PSD. The second difference is that the median aerodynamic diameter of the ternary mixture is larger than any resulting from the individual metals. A possible explanation may that sodium and cadmium is condensing onto lead particles. This would seem unlikely since the lead dewpoint is slightly lower than sodium or cadmium. Another postulated explanation is that multi-component nucleation is occurring. Further research is required to discern the transformation mechanism. Currently, the aerosol dynamic modeling and experiments with a system of a semi-volatile metal and a refractory metal like nickel are planned.

Conclusions

The aerosols generated grow from a size that is easily removed by the body to a size that is most likely to penetrate deep into the lungs and cause damage. The PSD for the ternary metal system differed from the superposition of the single metal system PSD's. This suggests film condensation as well as coagulation. Modeling and experiments are required to further elucidate the pertinent transformation mechanisms.

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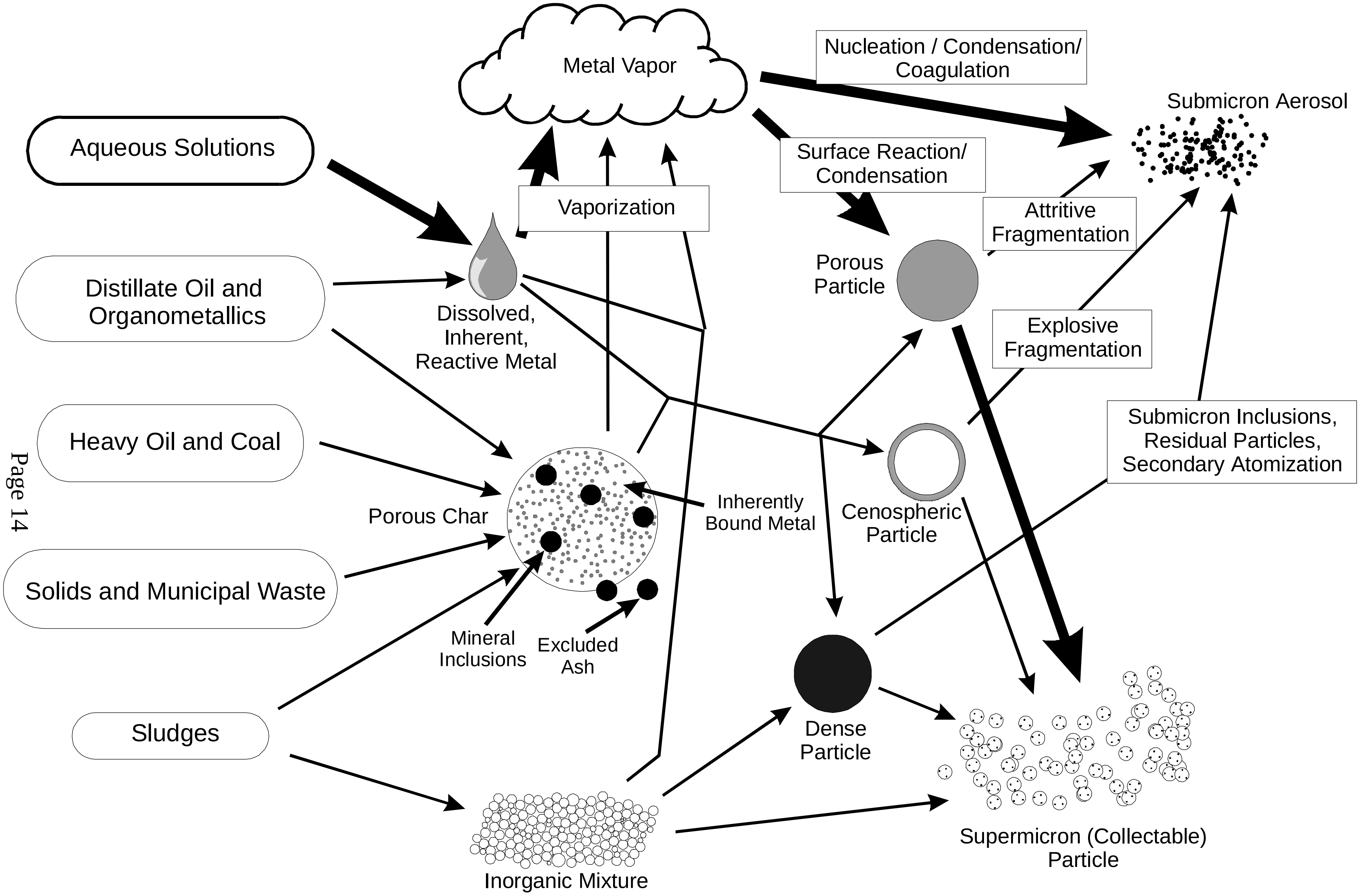

Figure 1: Metal partitioning in a combustion system

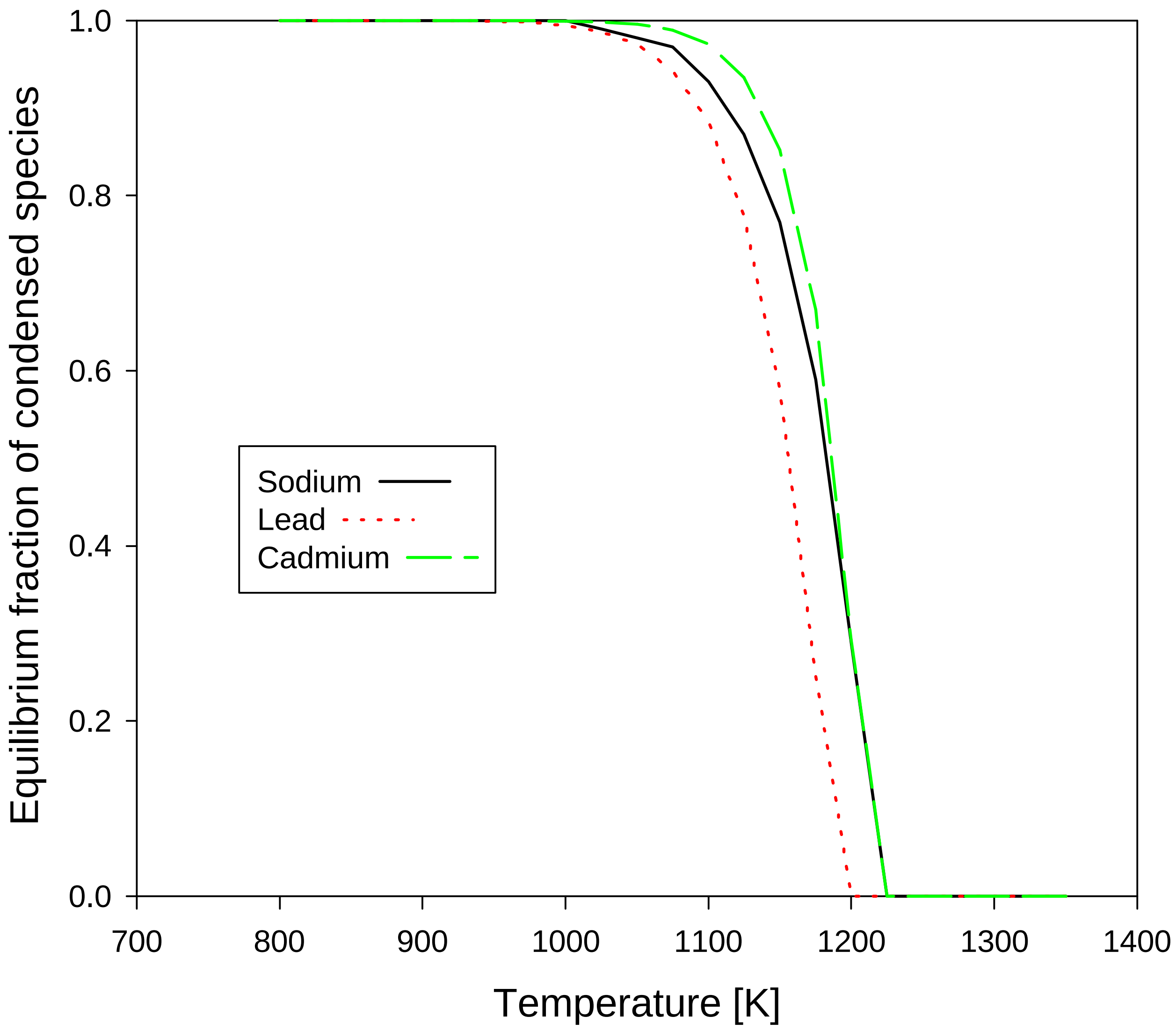

Figure 2: Equilibrium predicted condensation of lead, cadmium and sodium. Mixture Composition: CH_4= 1.23 mol, O_2= 2.75 mol, N_2= 10.34 mol Pb= 0.00143 mol, Cd=0.00143 mol, and Na=0.00143 mol

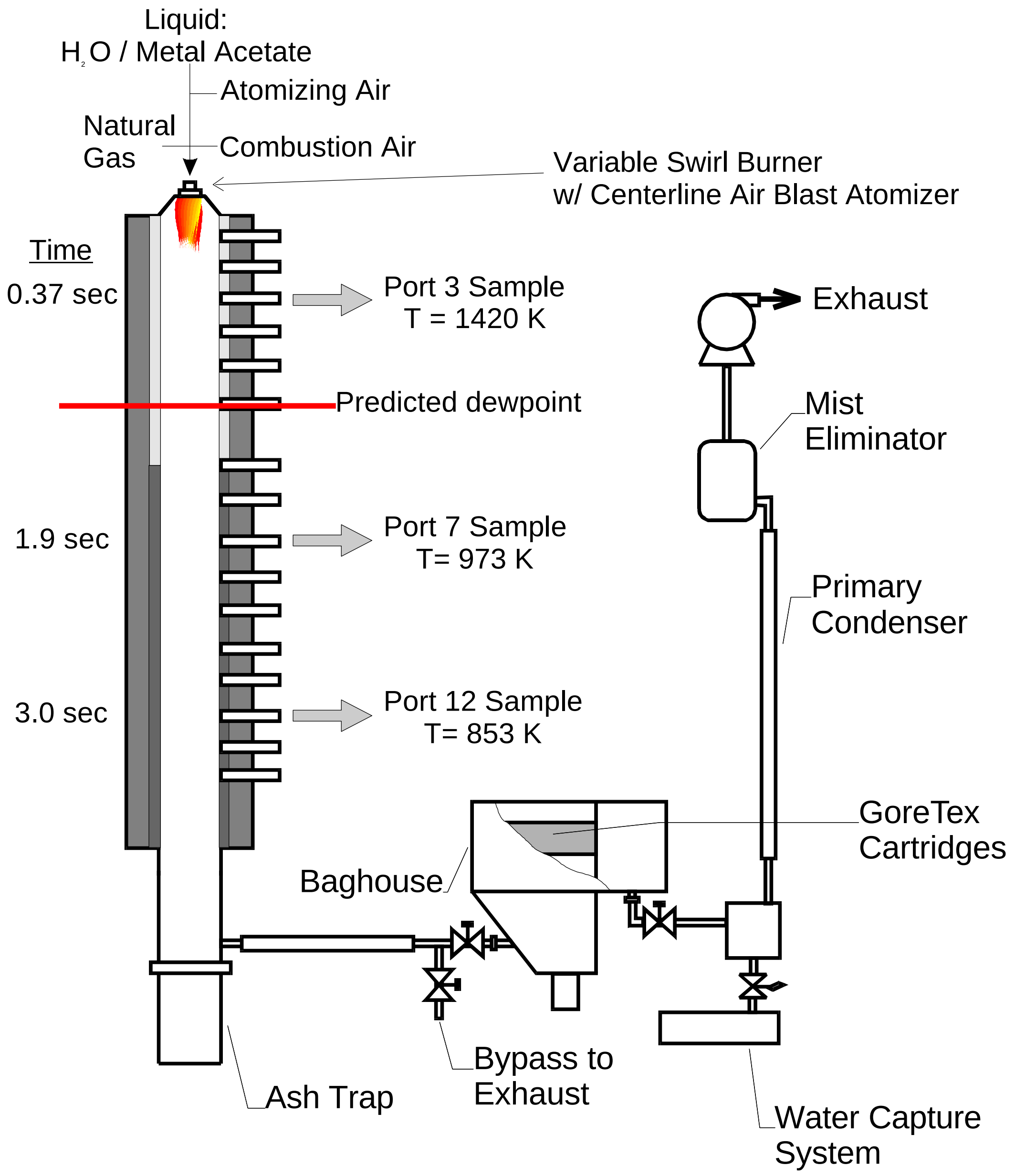

Figure 3: Laboratory downflow combustor and support apparatus

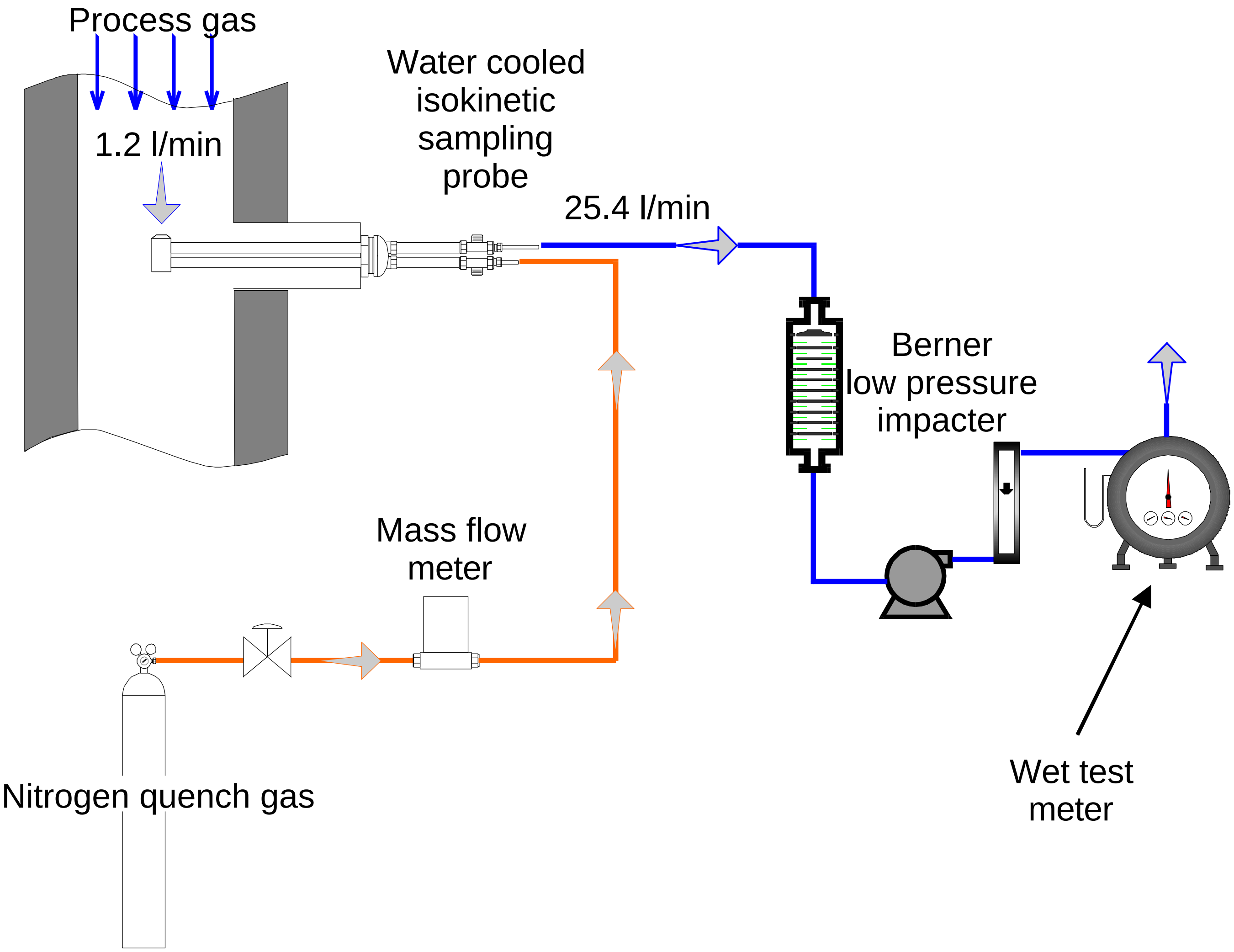

Figure 4: Particulate sampling and size segregation system

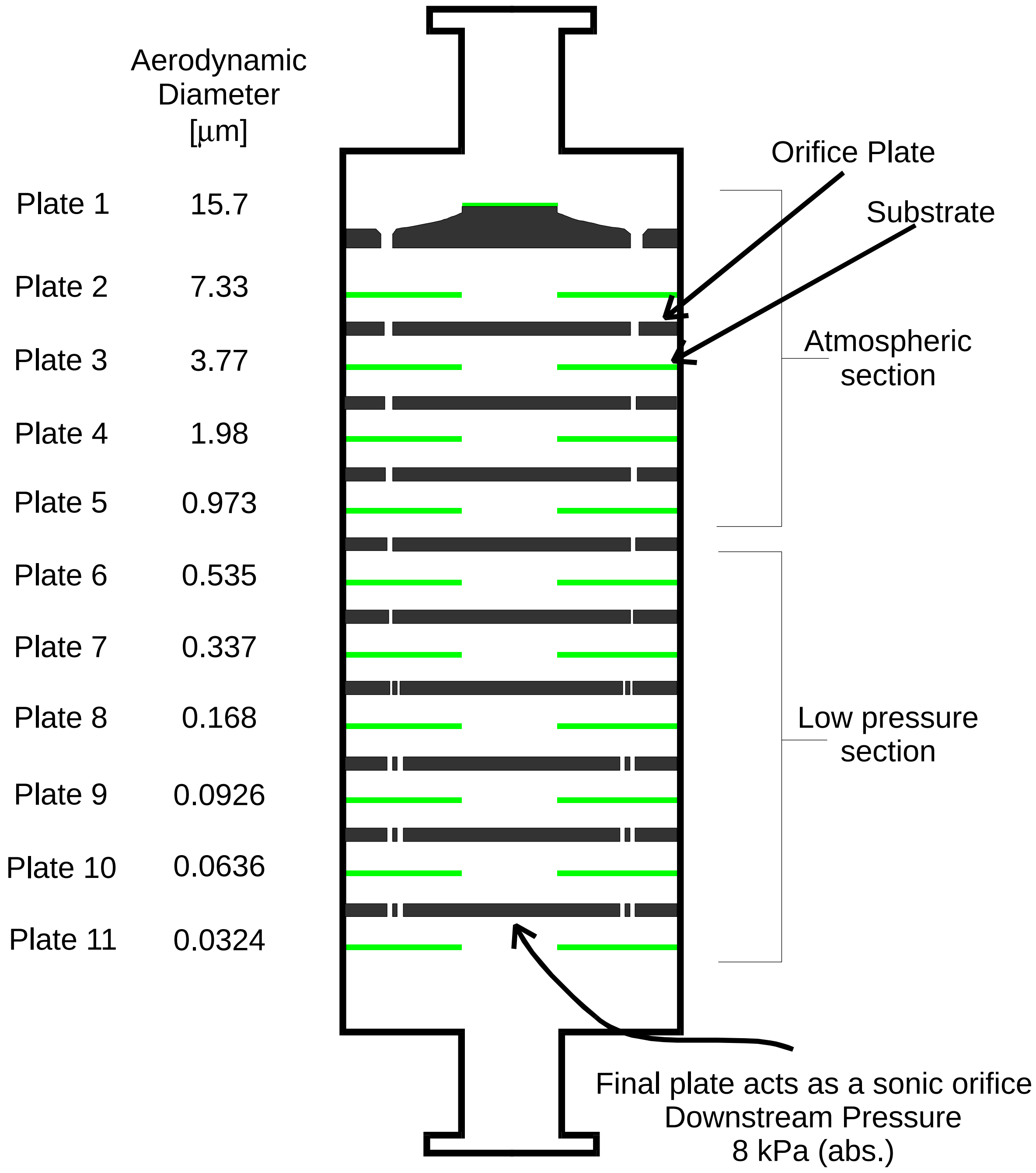

Figure 5: The Berner low pressure cascade impactor

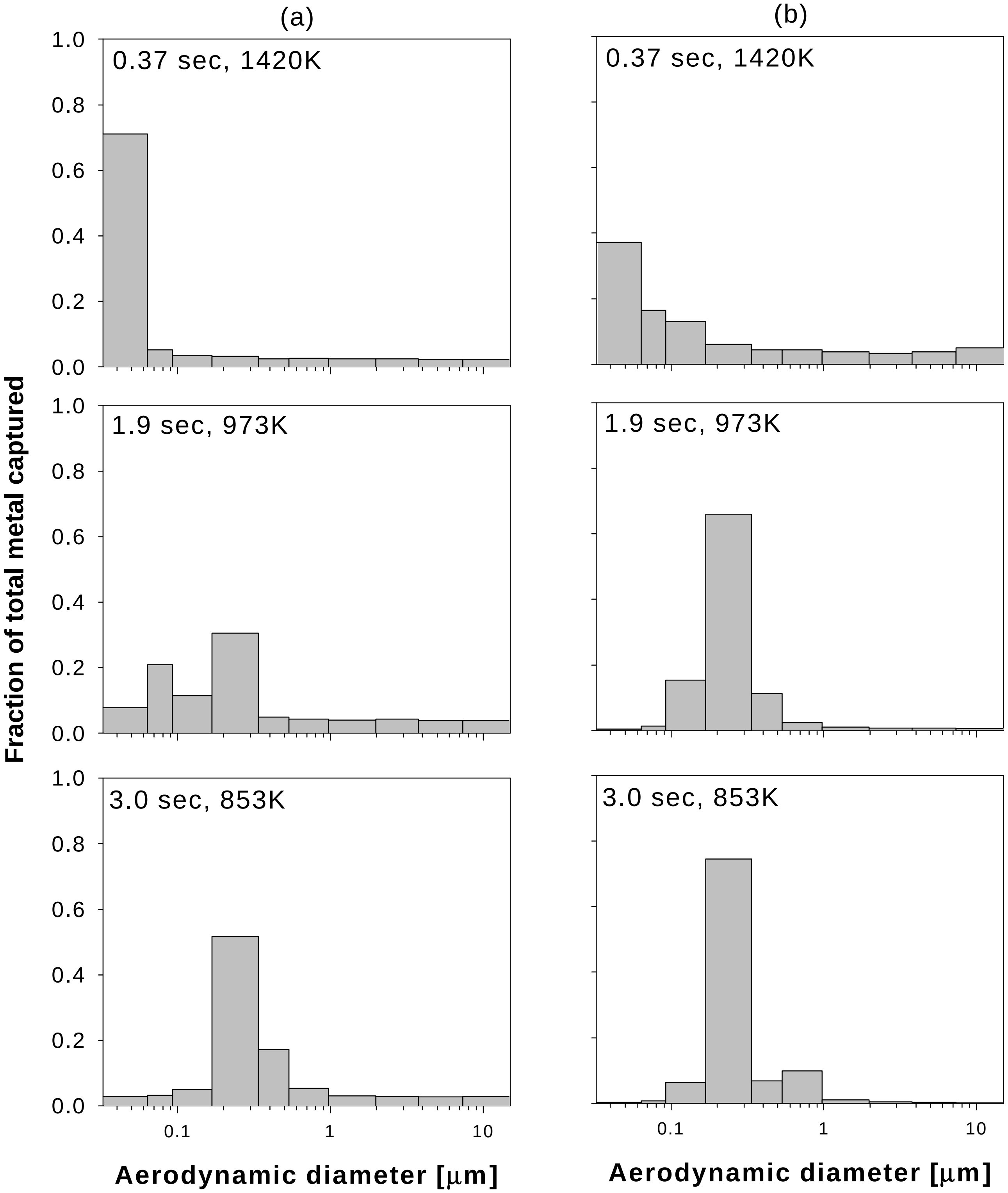

Figure 6: Aerosol evolution in downflow combustor
(a) sodium acetate injection, (b) cadmium acetate injection

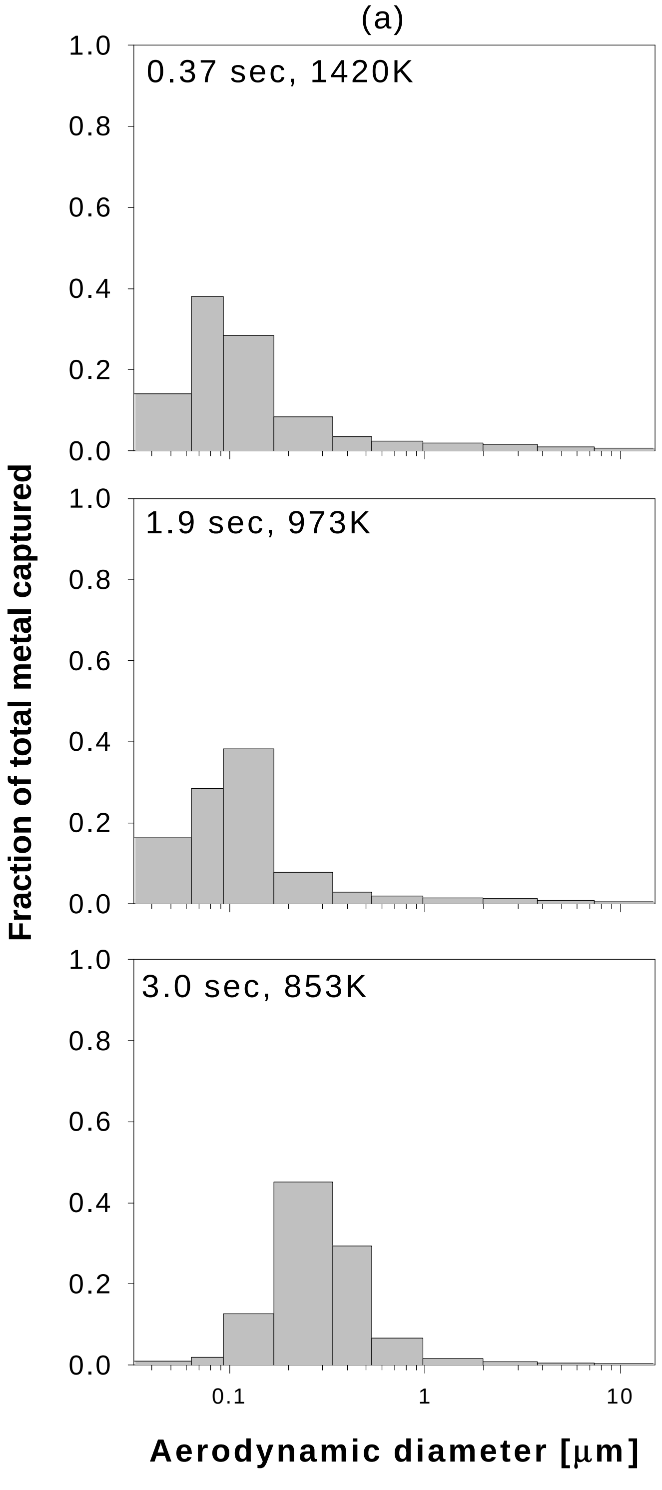

Figure 7: Aerosol evolution in downflow combustor (a) lead acetate injection

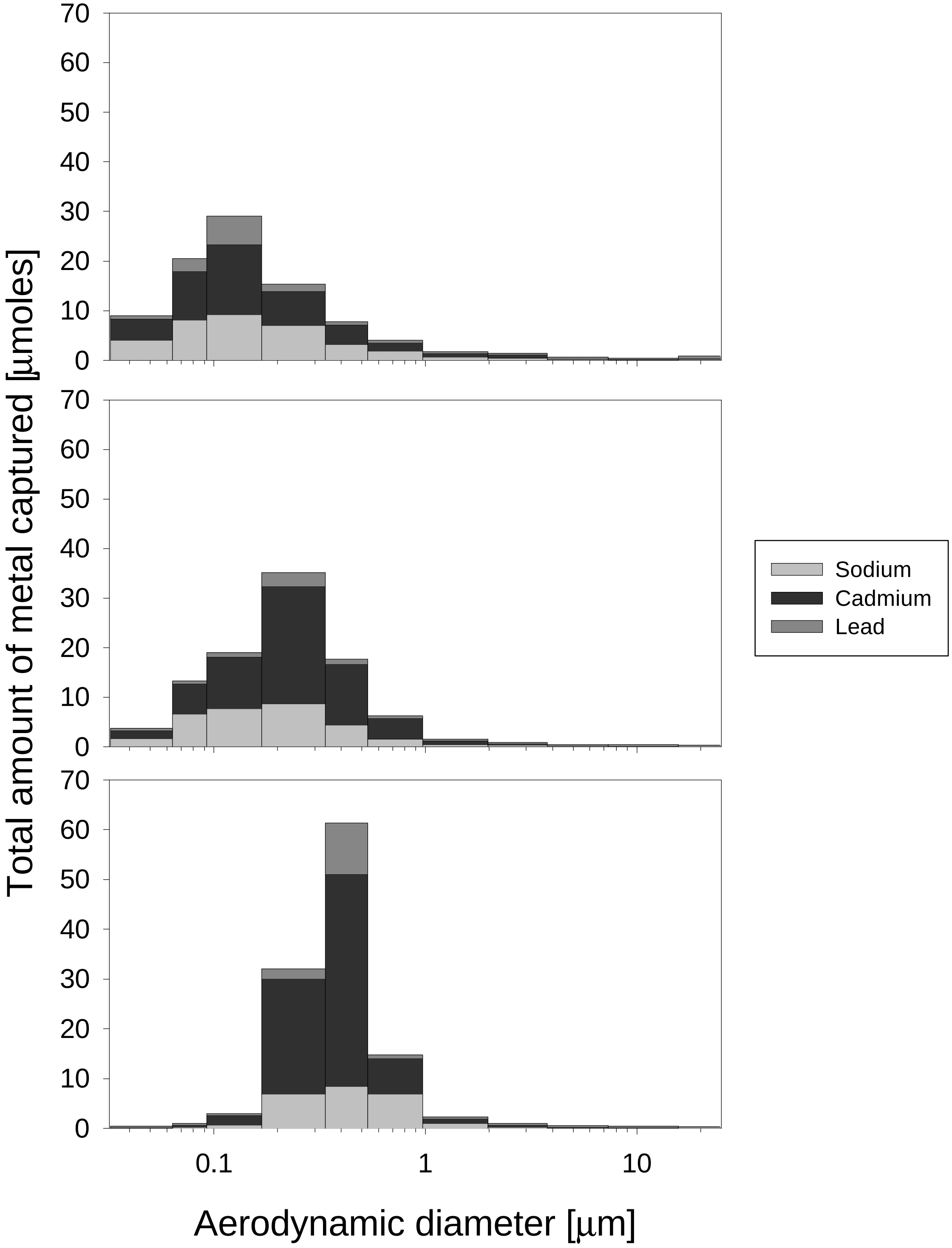

Figure 8: Evolution of metal oxide aerosol produced by the simultaneous injection of sodium, lead, and cadmium acetate