COMPARISONS OF THE BEHAVIOR OF AgI-TYPE ICE NUCLEATING AEROSOLS IN LABORATORY-SIMULATED CLOUDS

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Abstract. A variety of commonly used ice nucleants have been tested for comparable simulated adiabatic parcel ascents in the Colorado State University dynamic cloud chamber. Atmospheric adiabatic expansion and cooling of a parcel of air is simulated by evacuation and wall temperature control within the working volume. Ice nucleation characteristics have been studied for the injection of nuclei preceding the formation of clouds at a temperature near 0°C and following nuclei injection directly into cooling cloud parcels.

A summary and comparison of the nucleation rates and mechanisms observed for four different ice nucleating aerosols is presented. In some cases, the results observed in the simulations of real cloud processes were quite different than found previously in the static conditions of the CSU isothermal cloud chamber containing an artificially generated cloud. In particular, complexed hygroscopic nucleating aerosols (2AgI·NaI and 2AgI·KI) display much higher nucleation rates during expansional cooling than for injection into supercooled isothermal cloud. Some implications of the experimental results to the expected results of seeding atmospheric clouds are discussed.

1. INTRODUCTION

New and significant informaton on the ice nucleating behavior of various nucleating aerosols used now and in past weather modification programs has been gained during concentrated testing at the Colorado State University Cloud Simulation Laboratory in the last several years. The isothermal supercooled cloud chamber (ICC) and the continuous slow expansion (dynamic) cloud chamber (DCC) have proved useful for the identification of the activities, rates and mechanisms (modes of nucleation) of various AgI-type aerosols for equivalent cloud conditions. Some of the findings have been discussed separately in recent weather modification conference proceedings. In this paper, the results for four common ice nucleating aerosols produced by solution combustion are summarized. These are silver iodide-silver chloride (AgI-AgCl), silver iodide-silver chloride-sodium chloride (AgI-AgCl-4NaCl), silver iodide-sodium iodide (2AgI·NaI) and silver iodide-potassium iodide (2AgI·KI) nucleating aerosols. The new insights into the complex and varied response of different ice nuclei to the cloud type and seeding method suggest careful evaluation of which nucleating aerosols are "best" for use in a particular field application.

2. FACILITIES

2.1 Isothermal Cloud Chamber

The CSU isothermal cloud chamber has been described in numerous publications (e.g., Garvey, 1975; DeMott et al., 1983). The chamber characteristics are described only briefly here. A cloud of known droplet concentration and liquid water content is physically continuously supplied to the 1000 L cloud chamber and a water saturated environment results at a constant cloud temperature for nucleation tests. The chamber has proved useful for the definition of the relative total yield (effectivity) of ice crystals per gram of nucleant dispersed (from actual field-type generators) as a function of cloud temperature for the conditions present. The constant conditions in the cloud chamber can be altered to the extent that cloud droplet concentrations can be varied at any one temperature or saturation ratio can be raised above water saturation by the purposeful introduction of humid air with aerosols. These features have proved useful for the delineation of the dominant nucleation mechanisms using observations of changes in ice crystal formation rates (kinetics) with changes in cloud conditions (DeMott et al., 1983; Blumenstein et al., 1987).

2.2 Dynamic Cloud Chamber

The CSU dynamic cloud chamber has been described in its current configuration, only in conference proceedings. Its primary characteristics relevant to the data presented here will now be discussed. A more technically detailed description is being prepared for separate publication.

The DCC and its support systems are shown schematically in Fig. 1. Adiabatic expansion is simulated in the DCC by the evacuation of a 2 m^3 volume surrounded by stainless steel. A 1.2 m^3 volume of air within the chamber is further isolated by a force-cooled copper liner that is only open to the outer 0.8 m^3 volume by small holes. The temperature of the inner liner is controlled empirically (by providing coolant

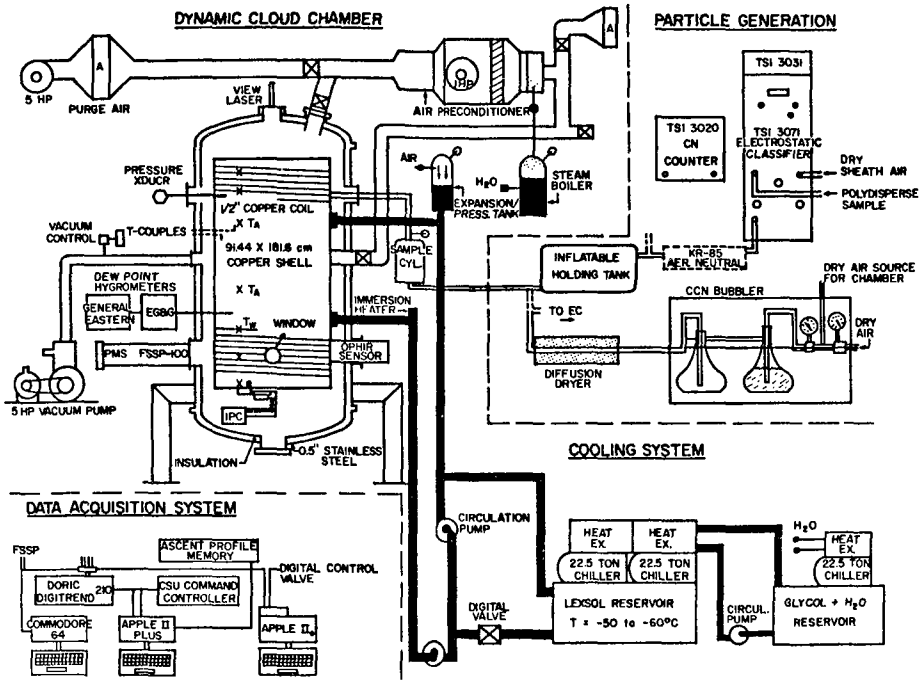

Fig. 1. Schematic diagram of the CSU dynamic cloud chamber facility, including particle generation, cooling and data acquisition systems. Additional descriptions and discussion of capabilities utilized are in the text.

through a digital flow valve) to follow as closely as possible the simulated adiabatic cooling from evacuation. Thus, the cloud that forms is contained within the inner liner. Temperature, pressure, humidity, cloud droplet sizes and concentrations, and the number of ice crystals settling from the volume are measured in time, within the inner volume.

Temperature is measured continuously using an array of ten Cu-Constantin thermocouples located on the inner liner and two faster response thermocouples located ten inches into the air volume from the inner wall. Pressure is measured using a transducer. Humidity is measured using a optical condensation-type dewpoint hygrometer. A differential-absorption infrared hygrometer (OPHIR Corporation) has recently been installed, but was not employed in these studies. Cloud droplet spectra are measured with a Particle Measuring Systems FSSP-100. A specially designed sampling inlet protrudes into the chamber to draw cloud in, accelerate it to 25 m s^{-1}, and focus it in the laser beam. Ice crystals are detected by a laser-based extinction device (~ 20 μm size threshold) similar to that of Lawson and Stewart (1983) that has been calibrated versus ground truth measurements on microscope slides. This is denoted as the ice particle counter (IPC) in Fig. 1. The device depends on the settling of ice crystals from the cloud for measurement. This causes a slight measurement lag because crystals must both grow and settle. Pulse nucleation tests using CO_2 have shown this time to be between 30 and 60 s. Since a transfer function has not been determined yet, ice counts were adjusted 30 s back in time to determine their nucleation temperature. A PMS 2D-C ice crystal sensor has also been used in the DCC (see, for example, DeMott et al., 1984), but all results reported here are from the IPC.

Concentrations of CCN (ammonium sulfate aerosols) and initial temperature and dewpoint temperature can be specified to form a cloud of known characterisitics at a desired temperature and pressure. Evacuation control, cooling control, and data acquisition are currently done by three microcomputers. One (Commodore 64) is devoted to cloud droplet measurements, one to cooling control (Apple IIe), and the other (Apple II+) handles data acquisition, display and control. Data are recorded at 15 s intervals. Simulated ascents are programmed based on equations for dry adiabatic expansion to cloud point and moist adiabatic expansion in cloud. Ice nucleus aerosols can be vented into the DCC and mixed briefly at any point during expansion. The DCC thus permits a large variety of comparative studies of nucleation by different aerosols for cloud conditions that are more like atmospheric cloud conditions than the conditions in the isothermal cloud chamber. Ice nucleus aerosol generation was done within a vertical dilution wind tunnel (Garvey, 1975) and samples were transported by syringe to the DCC. The mass of nucleating material in each sample was determined by standard procedures.

3. YIELDS, MECHANISMS AND RATES OF NUCLEATION

Ice nucleation yield, mechanism and rate are intimately related for a given set of cloud conditions, as shown in the referenced isothermal cloud chamber studies. A population of ice

nucleating aerosols has an inherent yield by a given nucleation mode, that can only be measured experimentally. However, this yield can be a function of time due to the kinetic details of the mechanism (e.g., how nucleation rate depends on temperature, cloud droplet distribution and saturation ratio). These interactions vary for different ice nucleants and together define the utility of an ice nucleus for weather modification by cloud seeding. Four examples of nucleating aerosol systems are discussed in this paper. All were generated using the CSU standard generator, which functions by aerosolizing acetone-based solutions into a propane flame.

3.1 AgI-AgCl Aerosols

AgI-AgCl (silver iodide-silver chloride) aerosols are produced by the combustion of solutions of AgI, acetone, ammonium iodide, ammonium perchlorate and water. These have been found to act predominantly as contact-freezing ice nuclei at temperatures warmer than -15°C in the isothermal cloud chamber (DeMott et al., 1983). This was noted by the fact that the kinetic rate of ice crystal production in the chamber was linearly related to the cloud droplet concentration at any temperature. Thus, although they are highly efficient ice nucleating aerosols (see Fig. 2), the potential efficiency of the AgI-AgCl aerosols in the atmosphere may be controlled by the existing droplet concentrations and sizes, and the time available to scavenge the aerosols. An exception to this behavior may occur when solutions are burned in propane flame within cloudy air (see, for example, Finnegan and Pitter, 1987). In this case, high transient supersaturations may force a rapid nucleation mechanism, despite the hydrophobic nature of these aerosols. In any case, it is clearly difficult to attempt to generalize or predict nucleation effects a priori in particular atmospheric conditions. Pure AgI aerosols have these same characteristics.

Comparative simulations of in-cloud and below-cloud (before cloud formation at warm temperatures) seeding using AgI-AgCl nucleating aerosols were performed in the DCC by DeMott et al. (1984). Similar clouds were formed close to 0°C during simulated 2.5 m s^{-1} parcel ascent and nuclei were introduced before or after cloud formed, as appropriate. In-cloud seeding was done at -7°C, the temperature at which ice was first detected in the pre-cloud seeded tests. The essential results of this research are displayed in Fig. 3 and Fig. 4. Fig. 3 shows the cumulative yield of ice crystals at various temperatures during adiabatic cooling at near 1°C min^{-1} (in-cloud). The AgI-AgCl nuclei, are strongly sensitive to the seeding method. When introduced before cloud formation, much time is available for collision with cloud droplets and the immersion-freezing nucleation mechanism must be considered in addition to contact-freezing nucleation. The immersion-freezing mode is apparently much less efficient for these aerosols than for a direct contact-freezing mode at supercooled cloud temperatures. It is also shown (Fig. 4) that the rate of ice crystal generation by AgI-AgCl aerosols is dependent on the cloud droplet concentrations present in the cloud. Lower droplet concentrations result in fewer ice crystals in the same time period. Finally, it is notable that the

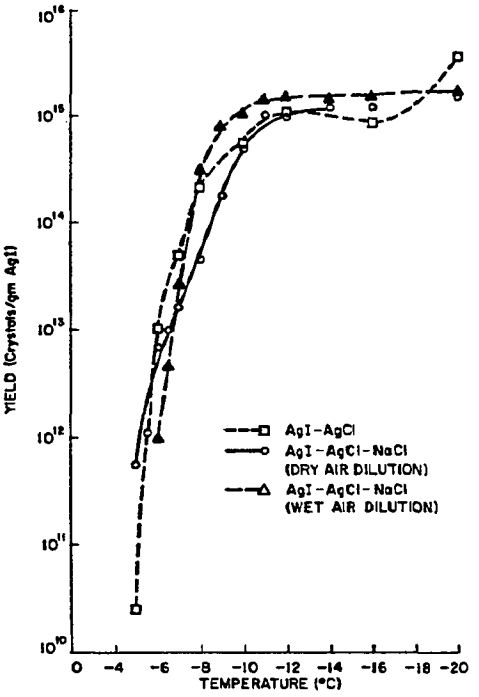

Fig. 2. Comparison of total yield as a function of isothermal cloud chamber temperature for AgI-AgCl versus AgI-AgCl-4NaCl ice nucleating aerosols. Data for injections with humid air are denoted as "wet air dilutions".

cumulative yield during cooling approaches the yield in the ICC only at the coldest temperatures. This is consistent with the nucleation mechanisms hypothesized.

3.2 AgI-AgCl-4NaCl Aerosols

The AgI-AgCl-4NaCl ice nucleating aerosols were synthesized (Finnegan et al., 1984; Feng and Finnegan, 1985) as a way of producing an uncomplexed and hygroscopic nucleant that forms ice rapidly by condensation-freezing nucleation at water saturation and also retains nearly the effectivity of the AgI-AgCl system in the isothermal cloud (see Fig. 2). Comparative simulations of in-cloud versus below-cloud seeding with the AgI-AgCl-4NaCl aerosols in the dynamic cloud chamber were also performed by DeMott et al. (1984) and the primary results appear in Figures 3 and 4. In-cloud injection was made at -9°C, the temperature at which ice was first detected in the pre-cloud seeded tests. These condensation-freezing nuclei appear to function in the same way whether introduced before or after cloud formation. This implies that the freezing step is rate determining for nucleation and also that the occurence of the condensation step at warmer temperatures during cooling does not decrease yield due to potential dissolution effects. No dependence of nucleation rate or yield on droplet concentrations present was found in the simulated adiabatic parcel ascents (see, for example, Fig. 4). This is consistent with the nucleation mechanism envisioned and the ICC results of Feng and Finnegan (1985). In general, the AgI-AgCl-4NaCl aerosols would be expected to act in a more consistent manner in a wide variety of atmospheric cloud conditions than AgI-AgCl aerosols based on this information.

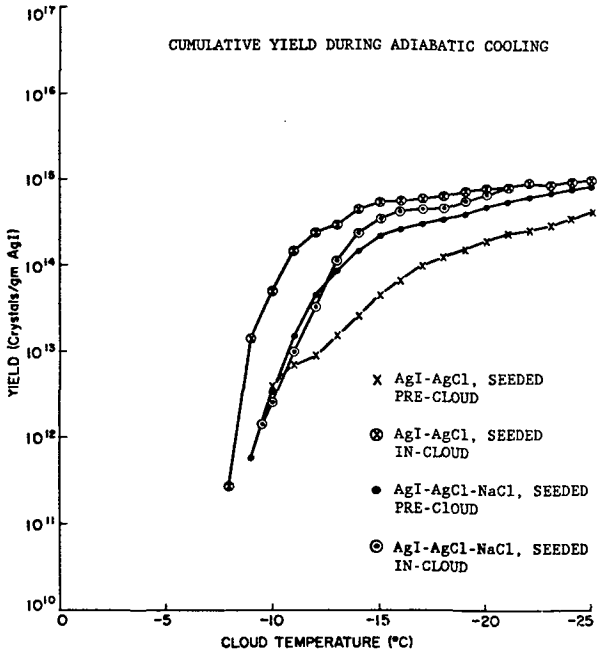

Fig. 3. Cumulative yields of ice crystals formed as a function of cloud temperature during simulated adiabatic cooling in four equivalent dynamic cloud chamber tests for AgI-AgCl and AgI-AgCl-4NaCl aerosols. Cooling rate in-cloud was approximately 1°C min in these tests. Cloud was formed at 0°C in each case (except -x- formed at +5°C). The AgI-AgCl aerosols were introduced at -7°C in the in-cloud seeding test, while the AgI-AgCl-4NaCl aerosols were introduced at -9°C.

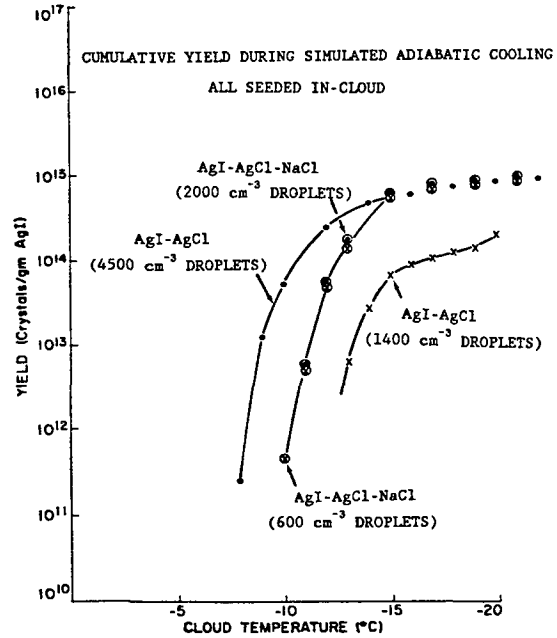

Fig. 4. Results from experiments in the DCC as shown in Fig. 3, but for different droplet concentrations at the point of ice nuclei injection. Droplet concentrations are indicated in parenthesis. All injections shown were directly into cloud. AgI-AgCl aerosols were injected at -7°C, while AgI-AgCl-4NaCl aerosols were injected at -9°C.

3.3 2AgI·NaI and 2AgI·KI Aerosols

The 2AgI·NaI and 2AgI·KI ice nucleating aerosols are grouped together here due to their similar chemistry and ice nucleation behavior. 2AgI·KI aerosols are fully complexed upon generation and the 2AgI·NaI aerosols are fully complexed upon the formation of a tri-hydrate. The 2AgI·NaI aerosols have been used in the Climax and Israeli weather modification programs among others and the 2AgI·KI aerosols are most familiarly associated with Project Whitetop. The yield curves for 2AgI·NaI in the isothermal cloud chamber are shown in Blumenstein et al. (1987). The ICC results for 2AgI·KI aerosols are shown in Fig. 5 (unpublished, from a study by Rilling et al., 1984). Nucleation rate constants for standard water saturated conditions are typically as low as 0.05 min^{-1} (47 minutes for 90% of the the total ice crystals formed to nucleate at one temperature) for both aerosols. The slow rates are apparently the result of the multiple stage process leading to ice formation (Blumenstein et al., 1987). The complexes must first be broken within a solution droplet, freeing the AgI, before nucleation can occur. Recognizing that the isothermal cloud does not truly simulate atmospheric clouds where water saturation is probably a more transient state and water supersaturations can occur, and realizing that the effect of intermediate stages to nucleation might be eliminated when supersaturations exist, Blumenstein et al. induced transient supersaturations in the isothermal cloud chamber by injecting the 2AgI·NaI aerosols with varying amounts of moisture. Nucleation yield was markedly increased and nucleation rate was faster than the fallout rate of ice crystals, so it could not be measured. The implications of this potentially fast and efficient mechanism to the quantity and location of ice formed in 2AgI·NaI seeded clouds

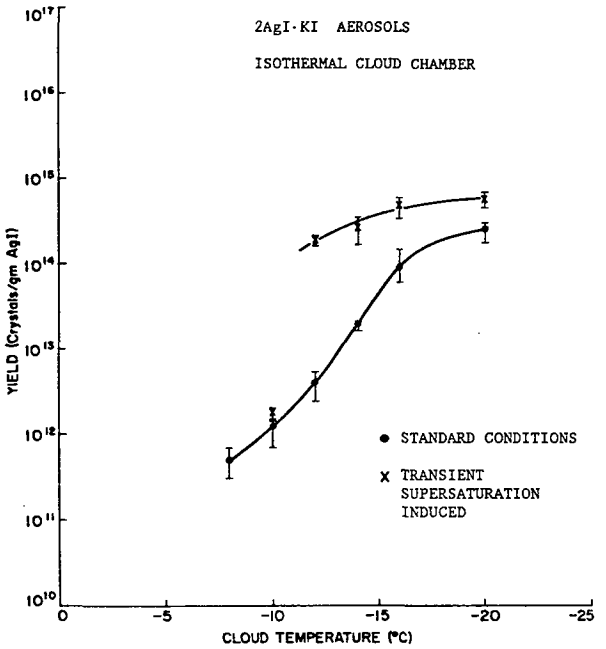

Fig. 5. Average total yields of ice crystals for 2AgI·KI aerosols in the CSU isothermal cloud chamber (data courtesy of Mr. Robert Rilling). Error bars display one standard deviation from mean values (6-10 tests for each set of conditions). These errors are typical for most ICC data.

was demonstrated, using a simple 2-D orographic cloud model, by Blumenstein et al. The 2AgI·KI aerosols displayed similar results to the 2AgI·NaI aerosols when transient supersaturations were induced in the isothermal cloud chamber tests (Fig. 5). The only questions that have remained concern the magnitude of the induced supersaturations and their validity to atmospheric conditions.

The nucleating behavior of 2AgI·NaI and 2AgI·KI aerosols in the presence of realistic atmospheric supersaturations has now been examined using the dynamic cloud chamber. The aerosols were introduced to the cloud chamber either at temperatures of +2°C or -7°C during simulated adiabatic ascents at 2.5 m s^{-1}. Cloud was set to form at 0°C in concentrations comparable to the tests discussed in sections 3.1 and 3.2. The results of the cumulative yield of ice crystals formed as a function of cloud temperature for characteristic tests of the two nucleating aerosols are shown in Fig. 6. Comparing to Figure 2 in Blumenstein et al. and Fig. 5 here, these results can certainly not be explained by the inefficient nucleation mechanism noted for standard ICC conditions. This is particularly true since the nucleation rates were very slow in the standard (no supersaturation induced) ICC tests. With slow nucleation at any given temperature and given the approximately 1°C min^{-1} cooling rates in the DCC tests, the standard ICC yields would never be achieved. Clearly the nucleation mode is different in the DCC. The results agree more with the higher yields and fast rates noted when transient supersaturations were induced in the isothermal tests. These results agree with findings in warm cloud base seeding tests of 2AgI·NaI aerosols, produced by burning solution-impregnated coke samples, reported by DeMott et al. (1985). Those tests also demonstrated the potential of long survival times through warm cloud for these aerosols. In-cloud seeding tests of the 2AgI·NaI and 2AgI·KI nucleating aerosols in the DCC show a slightly higher activity compared to the pre-cloud seeding results. The significance of this is not known at this time.

The 2AgI·NaI and 2AgI·KI complex nuclei are far more efficient than previously thought for the clouds and seeding method simulated, particularly in comparison to the two uncomplexed aerosols. Figures 7 and 8 show the cloud characteristics and ice crystal flux (from the chamber volume) in the below-cloud seeding simulations with similar concentrations of 2AgI·KI and AgI-AgCl aerosols respectively. Ice flux is determined from the number of ice crystals settling from the chamber in each 15 s interval divided by the time and the mass of aerosol injected (based on generator burn rate and sample dilution factors). The scale factors for the ice flux differ due to different generator burn rates (different solution densities). Normalization was not done because the differences were small. The comparison of results in Figures 7 and 8 clearly shows the higher efficiency of the complexed 2AgI·KI aerosols for equivalent seeding simulations. The ultimate activity of the 2AgI·KI aerosols is probably underestimated at temperatures below -14°C, as cloud was completely consumed. This also occurred for 2AgI·NaI aerosols.

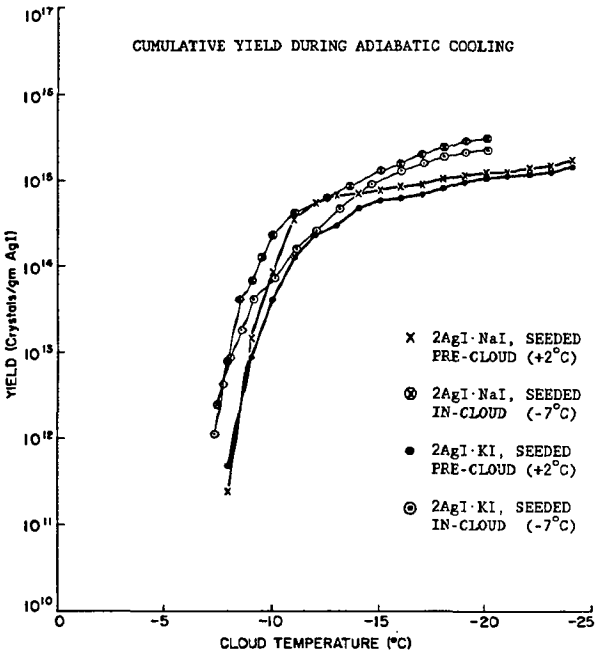

Fig. 6. Cumulative yields of ice crystals formed as a function of cloud temperature for equivalent adiabatic ascent simulations in the DCC using 2AgI·NaI and 2AgI·KI aerosols. The nucleating aerosols were injected at +2°C or -7°C as indicated. Cloud formed at 0°C in all cases, and the cooling rate was ~ 1°C/min (2.5 m s ascent) in cloud.

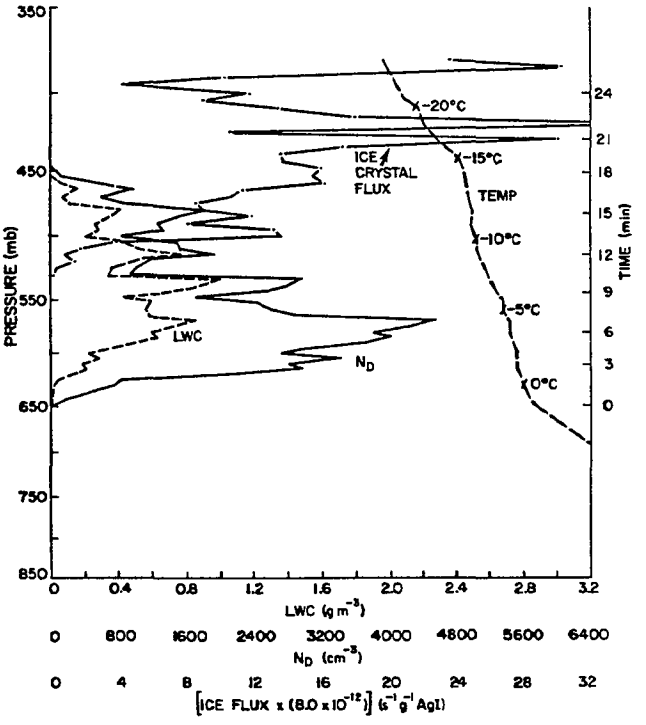

Fig. 7. Temperature, pressure, cloud droplet concentration (N_D), liquid water content (LWC) and ice crystal flux as a function of time after cloud forms in a simulated adiabatic ascent in the DCC seeded with 2AgI·KI aerosols at +2°C.

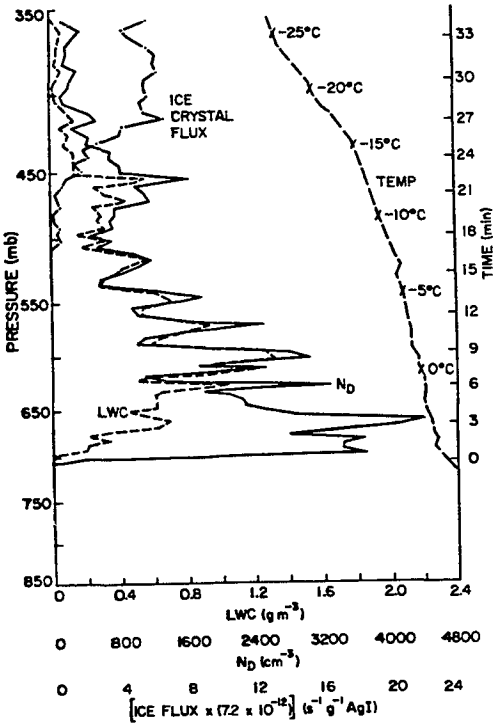

Fig. 8. As in Fig. 7, but for seeding with AgI-AgCl nucleating aerosols prior to cloud formation. The scale factor on ice crystal flux differs slightly due differing mass generation rate.

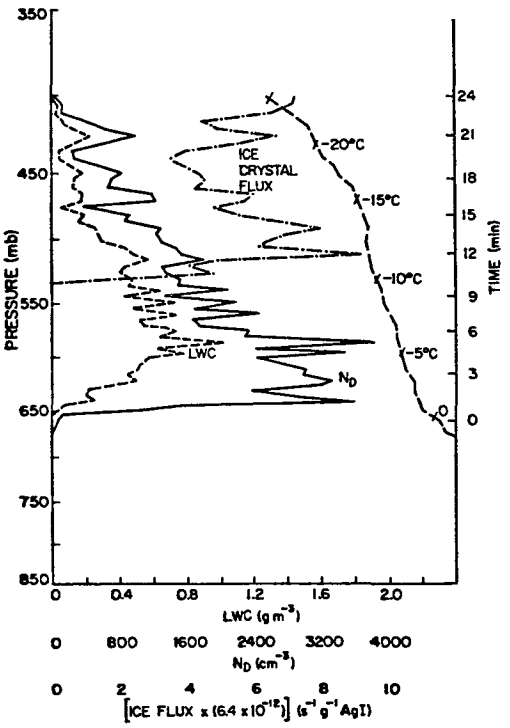

Fig. 9. Same type of data as shown in Fig. 7, but in this case AgI-AgCl-4NaCl nucleating aerosols were injected into cloud in the DCC at -9°C.

In-cloud seeding with AgI-AgCl-4NaCl mixed particle aerosols and the 2AgI·KI aerosols are compared in Figures 9 and 10. The only differences between the two experiments shown were the somewhat lower drop concentrations present with 2AgI·KI (should not matter for condensation-freezing) and the difference in seeding temperatures (-7°C for 2AgI·KI and -9°C for AgI-AgCl-4NaCl). The 2AgI·KI aerosols outperform even the rapid nucleating AgI-AgCl-4NaCl aerosols for this seeding situation. All results were repeatable.

4. CONCLUSIONS

A review of studies of the ice nucleating behavior of various artificial ice nucleating aerosols made during the past several years at the CSU Cloud Simulation and Aerosol Laboratory indicates that the judgement of the potential utility of the aerosols cannot be based on one set of test conditions. The potential mechanisms and rates of nucleation and how these change with cloud conditions must be known in order to quantify or even assess the behavior and ultimate utility of a given ice nucleant in weather modification.

Four nucleating aerosol systems have been discussed to demonstrate the specious nature of a one-dimensional characterization of artificial ice nuclei. AgI-AgCl aerosols show high effectivities as contact-freezing ice nuclei, but long nucleation time constants (due to details of the "contact" step) can prevent this yield from being achieved in real clouds. Also, an immersion-freezing nucleation process which appears to be much less efficient than contact-freezing on these

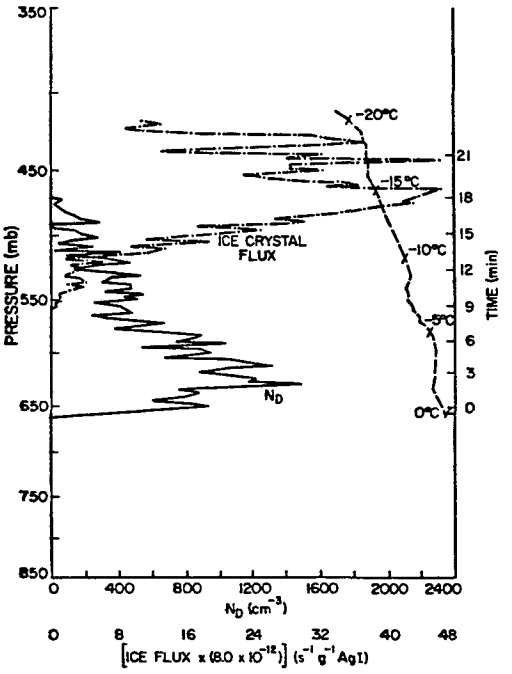

Fig. 10. Same as in Fig. 9, but for 2AgI·KI aerosols injected into cloud in the DCC at -7°C.

aerosols, is active during parcel ascent and cooling in cloud. There was no evidence of rapid nucleation on these hydrophobic aerosols, induced by the naturally occurring supersaturations generated in the DCC. AgI-AgCl-4NaCl aerosols appear to always function by a rapid freezing mechanism at water saturation and above. Although the rate of ice crystal formation is somewhat temperature dependent, yield in atmospheric clouds during parcel ascent (and at least water saturated conditions) might justifiably be approximated as a simple function of temperature. 2AgI·NaI and 2AgI·KI aerosols, once considered inferior ice nucleants based on their low effectivities and slow nucleation rates in standard ICC tests, appear to be ideal for seeding in dynamic cloud conditions. Specific experiments have now been defined to quantitatively characterize the function of all these common ice nucleating aerosols over a broad range of simulated atmospheric conditions. This will allow the most accurate evaluation of seeding effects using numerical cloud models and should help to guide field studies to detect seeding effects.

5. ACKNOWLEDGEMENTS

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