Characteristics of Silver Iodide Ice Nuclei Origination from Anhydrous Ammonia-Silver Iodide Complexes
Part I

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R. L. Steele [1] and F. W. Krebs [2]

Part I

Abstract:

Two methods of generating silver iodide ice nuclei have been investigated. Neither employs thermal processing. A 3000 liter isothermal cloud chamber controllable over the range of 0 to -200 $\pm$ 0.1 C was designed and fabricated to study nucleation processes along with other support equipment.

Anhydrous ammonia as the AgI carrier was employed since solution preparation is simple and direct, high concentrations (60%/AgI by mass) can be used, and corrosion and deposition problems are virtually nonexistent.

In a simple system in which the complex is sprayed into ambient air via a commercial nozzle the results are negative, 10^{12} nuclei per gram at -20C. Another system, using Dautrebande's principle of obligatory filtration, shows promise. Performance at -13C is 3 x 10^{14} nuclei per gram. The threshold temperature of both non-thermal systems is about 5°C lower than for other dispersion methods. Ultra pure silver iodide is a poorer nucleant than the commercial materials.

The electron microscope was used to study the effluents from both generators. The shape and physical characteristics of effective particles are quite different from those found in thermal generators. The marked difference in effectivensss between thermal and non-thermal systems is attributed to impurities.

Introduction

The development of silver iodide nucleating devices has been underway for a number of years. Most generators have used a solution of potassium and silver iodide in acetone. These have had varying degrees of success. Other devices using pyrotechnics and electric arcs have been employed. A review of the generator technology indicated a need for the development of simple and reliable generators of medium and high capacity. Furthermore, little seemed to be known about the influence of various generator performance parameters on nucleating effectiveness. The problems encountered in handling the solutions of AgI-KI in acetone indicated the need for another carrier of AgI.

The search for the new carrier began in 1962. It was found that anhydrous ammonia was indeed an excellent carrier of AgI. It can be complexed with ammonia in concentrations of as high as 60%. Information in the literature regarding the complex was scant. Tominaga did some preliminary work in 1954. He found that the complex when passed through an electric furnace produced a microaerosol of AgI. He did not report any information on its effectiveness as an ice nuclei. Bilz and Stollenwerk in the 1920's did some work on the physical properties of the complex. Corrin and his associates are currently working with the nucleating properties of ultra pure silver iodide which has been exposed to anhydrous ammonia in its preparation. Corrin's work and the work of others suggested that the NH_3-AgI complexes would have good nucleating properties.

The above preliminary work led to research activity aimed at developing a simple, reliable generator using anhydrous ammonia as a silver iodide carrier. In order to carry out this work effectively a program was outlined to determine the dominant variables effecting generator performance.

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Support-Apparatus

Apparatus was needed to carry out the experimental phases of the research project. The most critical need was a large cloud chamber controllable over a temperature range of about 0 to -20C. The design of this facility was undertaken with the following specifications:

1. Wall temperature - variance - ± 0.1C over the range of 0 to -20C.
2. Automatic control of temperature.
3. Volume -- 3000 liters.
4. Adequate multipoint cloud and wall temperature measurement.

A schematic diagram of the chamber showing all associated equipment is depicted in figure (1). The chamber is a closed double shell which is cylindrical in shape. The 4.5 feet diameter by 5 feet high inner shell is of 1/4 aluminum with 1" O. D. tubes at 6 inch spacing welded to the shell on 6" centers. The outer shell which is 5.5 feet diameter is of 10 GA steel. The annular space between shells is filled with polyurethane insulation. The close tube spacing, heavy inner shell and insulation thickness were required boundary conditions in the heat transfer analysis to maintain ± 0.1C variance on the walls of the chamber. The large tubes are necessary to maintain two phase flow throughout the circuit in order to avoid a hydrostatic temperature gradient.

Adequate controls were needed to maintain these wall temperatures. A L & N CAT controller with associated hardware was provided for this purpose. The refrigerant temperature is controlled rather than chamber air. This results in an air temperature higher than the controller indicates but this bias can easily be accounted for.

Monitoring of cloud and wall temperatures is mandatory. Two copper resistance thermometers which had been calibrated with a platinum resistance thermometer
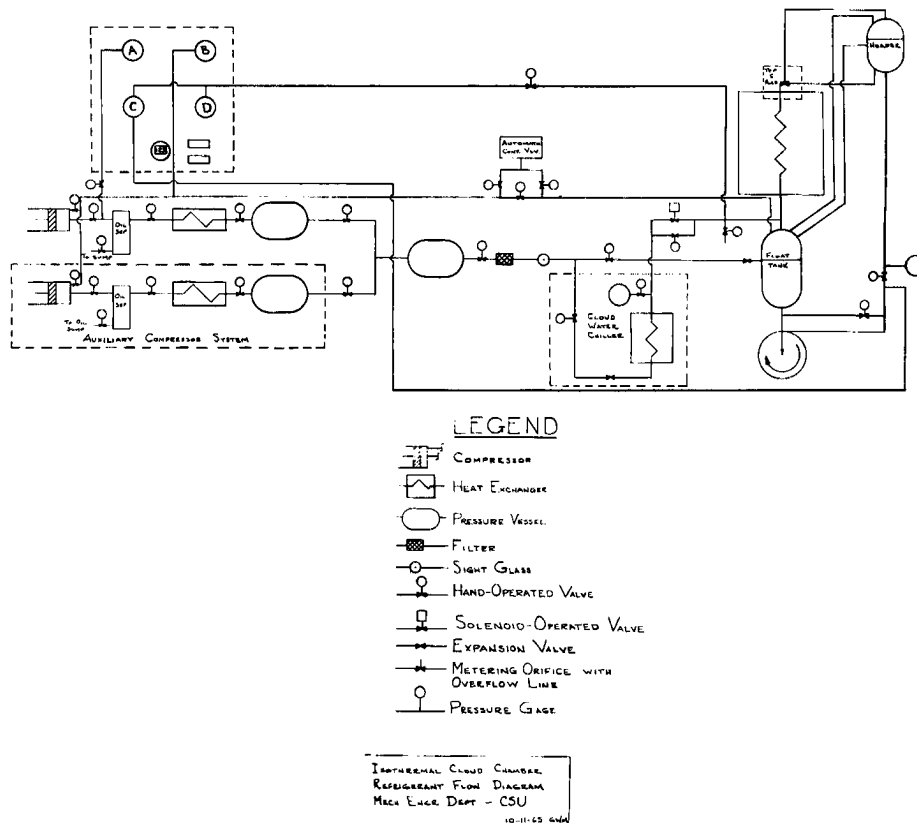

Figure 1
Schematic Flow Diagram - Isothermal Cloud Chamber

and bridge certified to 0.01C were used to calibrate 24 thermocouples of which 12 were later imbedded in the walls at random points. The remaining 12 were placed at predetermined points in the chamber proper to measure cloud temperature. The thermocouples were monitored with a L & N speedomax recorder which scans 12 points in approximately 15 seconds to an accuracy of about 0.1C.

The inner shell of the chamber is fitted with a velvet liner to minimize frost accumulation and shattering from the walls and to provide good visual inspection of the nucleation process. A fan is provided to facilitate cool down and warm up.

A continuous water droplet generator was designed and fabricated to supply the chamber with a cloud. The water for the generator is first chilled to about 1°C in a small tank which is fitted with a refrigeration coil. This is a part of the refrigeration system for the chamber proper. The chilled water is then passed through a commercial spray nozzle to produce small droplets which are thence passed through a Dautrebande obligatory filtration process. The effluent from this, a uniform cloud made up of particles about 10μ in diameter, is directed into the cloud chamber on either a time programmed or continuous basis via an aspirator supplied with chamber air.

Figure 2   Isothermal Cloud Chamber

Performance of the cloud chamber and associated equipment has been within expectations. Before a cloud is introduced, temperatures throughout are within ± 0.1C. When a cloud is introduced, a gradient of 2°C per meter develops due to the initial temperature difference between the cloud droplets and the chamber air. The temperature at a given point however remains to within ± 0.1C. A photograph of the chamber is shown in Fig. 2.

A dilution facility was needed to sample the effluent of generators for evaluation in the chamber. Along with this, a good air supply was provided for testing thermal generating systems. This is shown schematically in Fig. 3. A 5400 cfm blower is mounted in the enclosure into which the effluent is directed. High capacity generators of all types require pre-dilution to avoid agglomeration effects. An air supply is shown on the right which is used for testing thermal generators. This consists of a two stage axial flow fan fitted with an inlet control cone, honeycombs, nozzle and metering orifice.

A metering unit was needed in order to account for silver iodide consumption and other fuels or carriers used in producing nuclei. The unit is shown in Fig. 4. Provision is made for supplying and metering most any generator that uses liquid or gaseous fuels and liquid carriers.

The substance under study, i.e. silver iodide microaerosol, must be sampled in order to inject it in the cloud chamber and to process for later study in the laboratory. Samples were needed for chemical analysis. This was done with standard millipore filter apparatus. Samples for the chamber were taken in a 700 cc syringe and diluted as required. Samples for electron microscopy were taken with a thermal precipitator using a standard grid coated with collodion.

The above preliminary work permitted the study of nucleating characteristics of silver iodide microaerosols which is discussed in a subsequent section of this paper.

Preliminary Laboratory Work

Little information is available on the thermodynamic properties of silver iodide ammonia complexes. Certain of these were needed in order to carry out the research, in particular P-T data and Joule-Thompson coefficients. Other fluid characteristics were needed. The following results are reported.

Silver iodide complexes easily with anhydrous ammonia at ambient temperatures up to 60% concentration. The resulting solution is colorless and has about the same viscosity as anhydrous ammonia. It does not appear to attack ferrous materials and is incompatible with about the same materials as anhydrous ammonia, e.g. copper bearing alloys. The complex has a solid state which is unstable and white in color. The solid when exposed to ambient air decomposes to AgI and ammonia vapor in a short time.

The P-T data closely follows that of anhydrous ammonia as is shown in Fig. 5. The liquid complex is unstable in a concentration range of 10 to 14%. This is indicated in the figure. Point scatter below 80 psia was marked. This confirms the work of Biltz and Stollenwerk mentioned previously. The only apparent explanation of this behavior is a time rate of change in the number of AgI molecules bonded to ammonia molecules or an unstable state of the complex.

The J-T data also closely resembles ammonia, as is shown in Fig. 6 for the range in question. The data taken is rough in terms of modern P-T and J-T measurements. However, it was sufficient to predict the behavior of the complex in various flow processes.
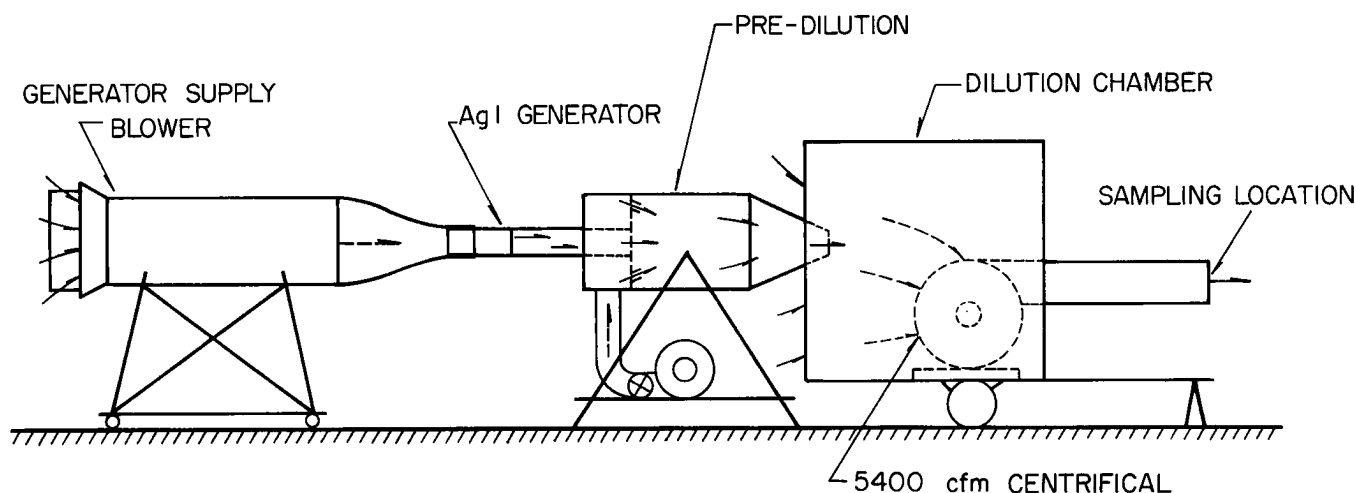

FIGURE 3   AgI GENERATOR DILUTION AND SAMPLING EQUIPMENT ARRANGEMENT
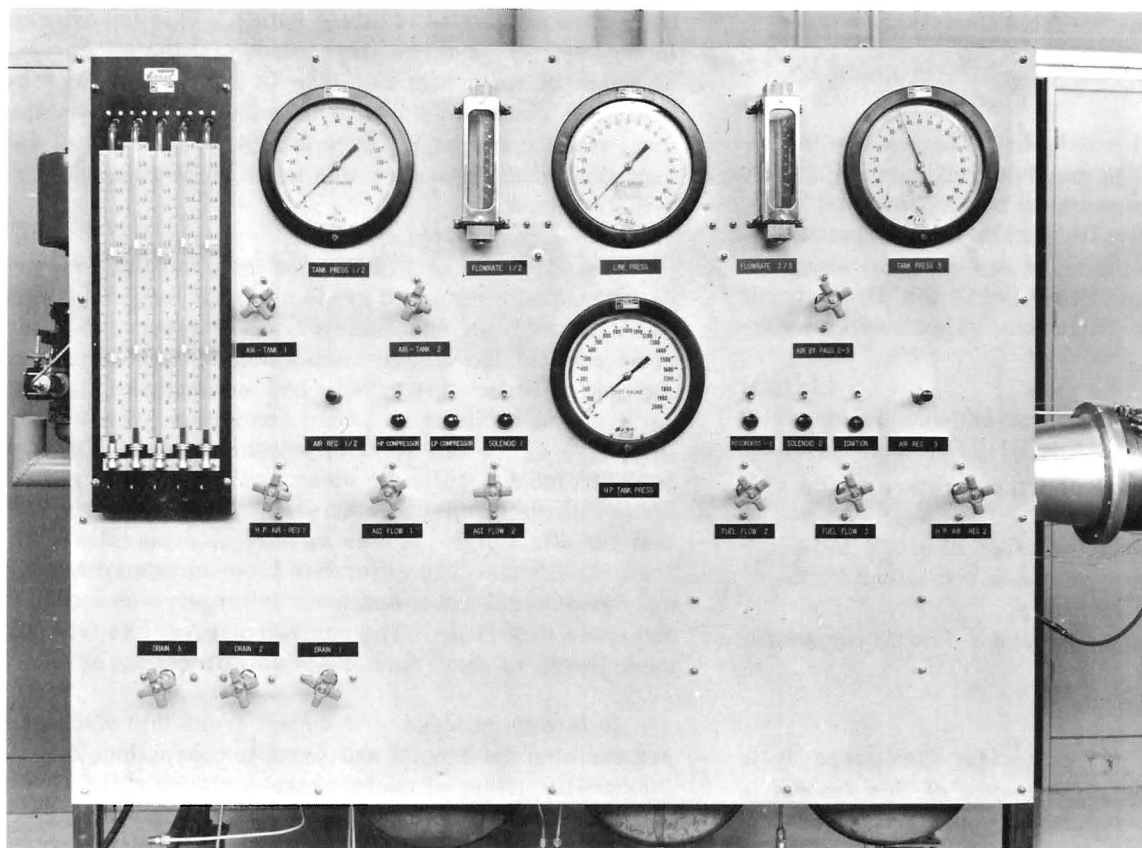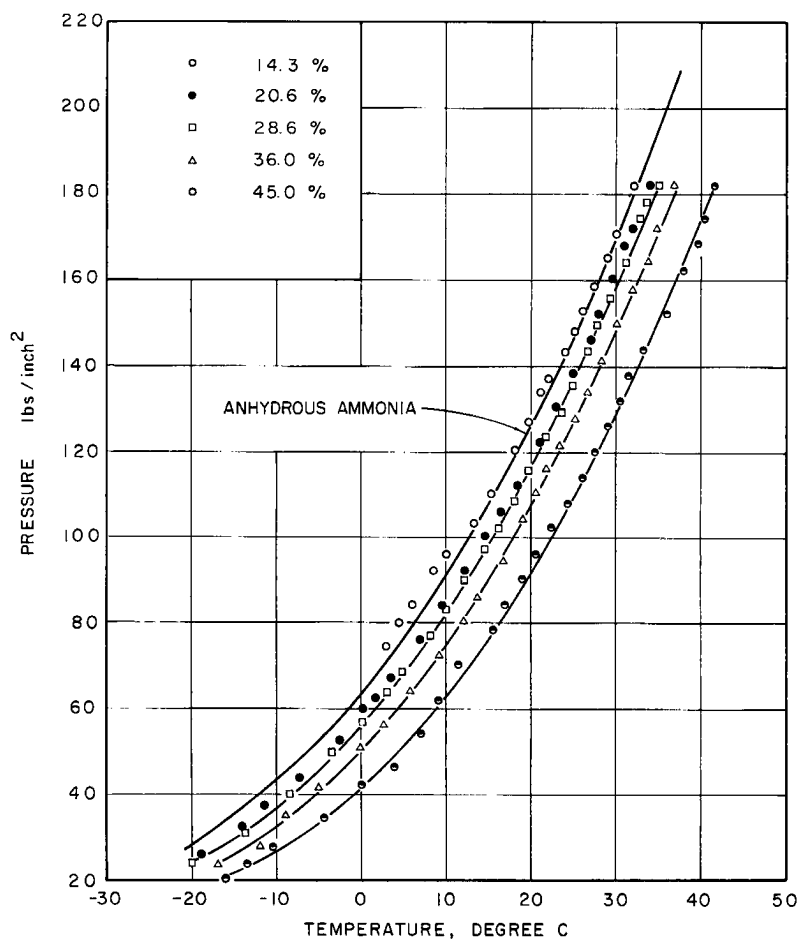
Figure 4
Universal Metering and Dispensing Unit

Figure 5
P. 7 Data for AgI-NH$_3$ Complexes
(Sample 2)

FIGURE 5   P.T DATA FOR AgI-NH$_3$ COMPLEXES (SAMPLE 2)

AgI Microaerosol Production from Complexes without Thermal Processing

Two systems were investigated. These were: (a) expansion of the complex at medium pressures (125-200 psia) at ambient temperature to atmospheric pressure via a commercial hydraulic nozzle. (b) expansion of the complex at medium pressure and ambient temperature to atmospheric pressure using the Dautrebande principle of obligatory filtration. These will be discussed separately.

The following performance variables were examined for system (a):
1. Effectiveness over the temperature range of 0 to -20C.
2. Concentration over the range of 0.03% to 24%.
3. Type of anhydrous ammonia and silver iodide.
4. Effluent droplet size data.
5. Effluent solid data (residue from evaporated droplet).
6. Threshold temperature.

The effectiveness of system (a) (Prototype I) is shown in Figure 7. The performance of this system is negative in that it is too low to be economical. A cost of $10 per 10^{15} nuclei is predicted. The general shape of the curves agree with Fletcher's predictions except for a shift in the origin.

However, other findings resulted from the effectiveness study which yield some insight into the nature of the nucleation process.

Effects of ammonia and silver iodide purity were observed. The complex prepared with agriculture grade ammonia and commercial silver iodide was more effective than when research grade ammonia was used with ultra pure silver iodide. The threshold temperature for the latter case was about $1^{o}C$ lower than for the former.

The ultra pure AgI was prepared by M. L. Corrin at the University of Arizona who is engaged in research on the surface properties of AgI. His material is prepared by reacting pure silver and iodine directly in a hard vacuum. Thus this material has no significant impurities. The substance was complexed with research grade ammonia to determine the change in effectivensss due to the absence of impurities which are thought to enhance the nucleation properties of silver iodide. This is borne out in Figure 7. It should be emphasized that the effect could be much more pronounced than is indicated. The pure substance could have been contaminated by the containment vessels and piping even though stainless steel was used throughout and care was taken to be sure the system was clean.

It was also found that when commercial AgI was complexed with research grade ammonia only hex plates were grown from the embryos. The other complexes grew rods at the higher temperatures, i.e. ultra pure AgI and research grade NH_3 and commercial AgI and agricultural grade NH_3. Only hex plates grew at temperatures of -8 to -9C with research grade NH_3 and commercial AgI while the other complexes grew rods at temperatures down to about -11C. This also suggests that the effect of impurities on surface properties is indeed significant. The difference between research grade and agricultural grade ammonia is largely water content and trace impurities. The commercial AgI was from the same batch so there was likely no differences here.

It is now necessary to depart from this discussion and examine the droplet and particle characteristics. A further discussion of nuclei characteristics will follow.

Effluent droplet data were taken to relate droplet and particle characteristics. The mass mean diameter of the droplets issuing from the simple hydraulic nozzle varies from 4.3 to 7.1μ for the 0.3% and 25% concentrations respectively. All droplets measured were less than 20μ in diameter. For the same nozzle conditions, the mass mean diameter of water droplets issuing from the same nozzle is approximately 20μ. It is not surprising that a volatile liquid such as the complex produces droplets. The expansion of the complex through the nozzle is meta stable. At some point down stream of the nozzle exit, the two phase flow rapidly changes to the stable state. The change of state occurs rapidly, causing the large droplets a small distance from the nozzle to "explode" into many small droplets.

When the particles produced from vaporization of the complex at ambient temperatures are examined the following is observed: (a) The number of effective ice nuclei per droplet is a function of the concentration. At very low concentrations (0.03%) only 0.15 effective nuclei are formed per drop. This increases with concentration to a value of 15.4 nuclei per drop at 25% con-
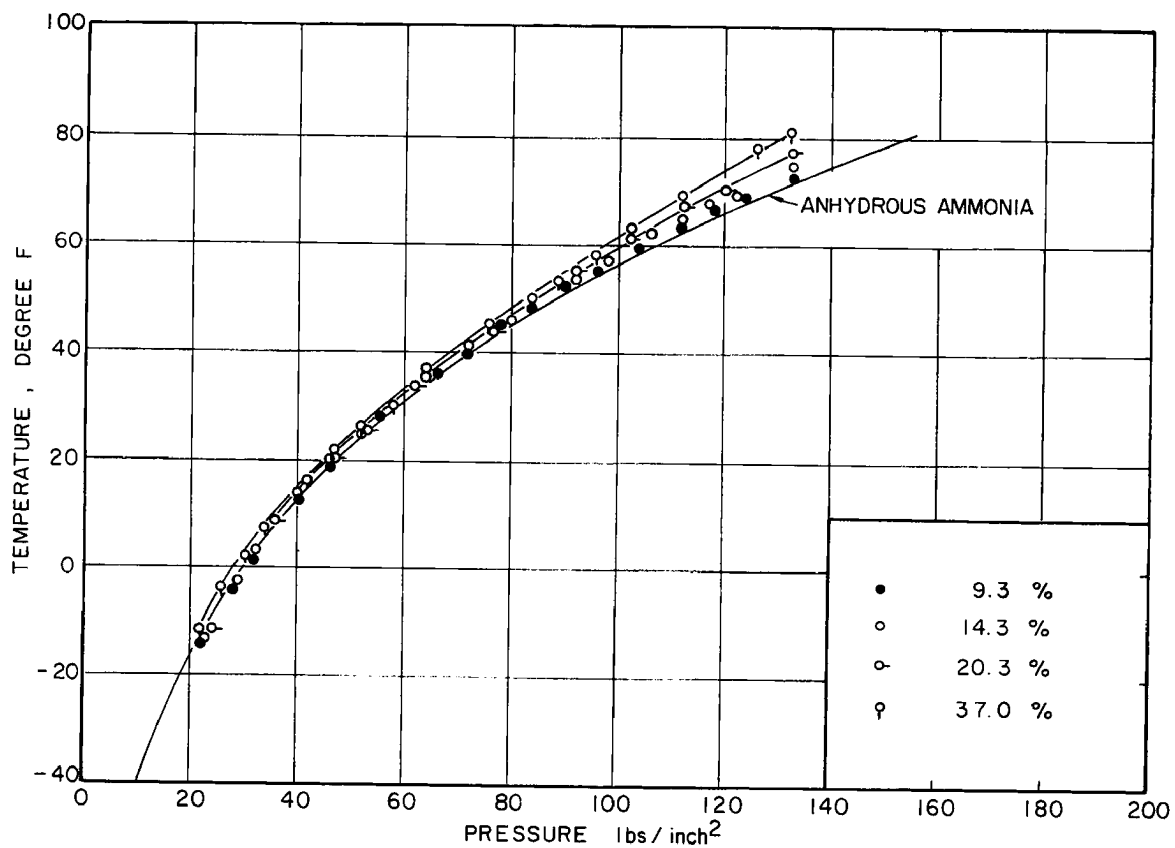
FIGURE 6   JOULE — THOMSON EFFECT IN AGI—NH₃ COMPLEXES
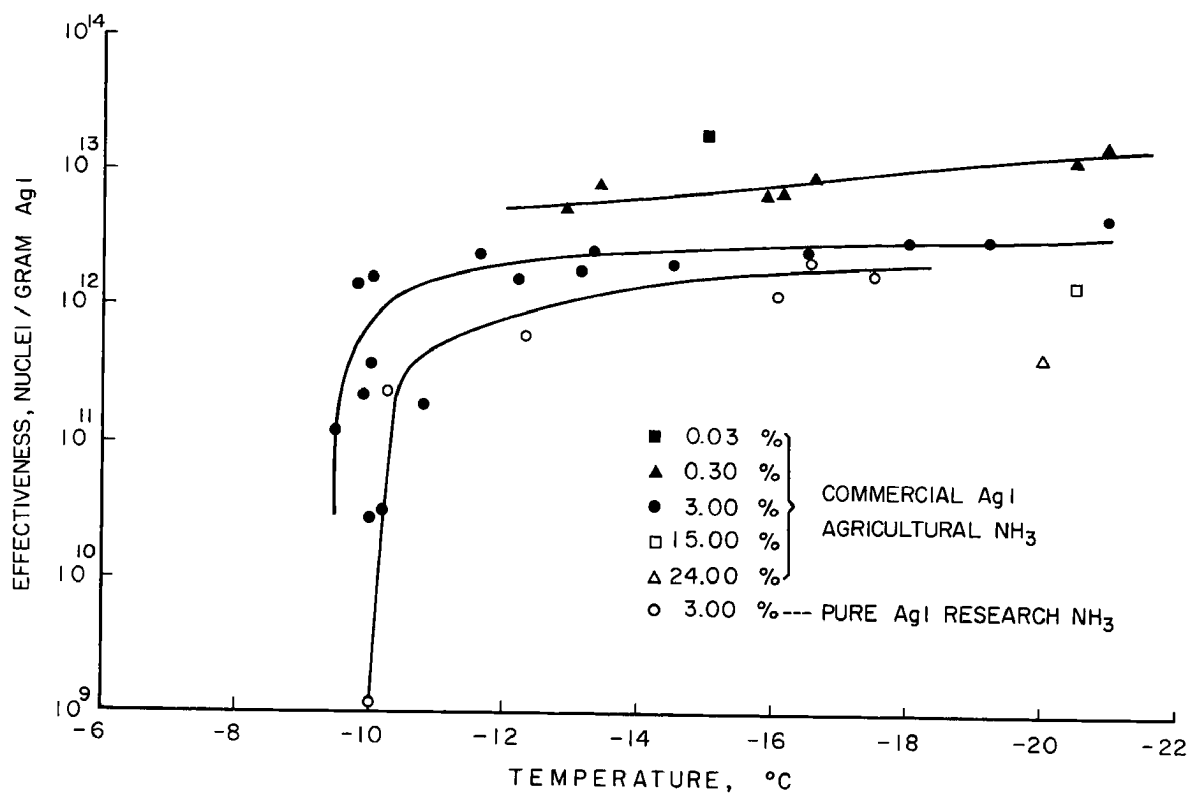

FIGURE 7   PERFORMANCE CURVES FOR THE PROTOTYPE I GENERATOR

centration. This result together with the number of drops per gram of AgI which decreases with concentration explains the peak in the effectiveness of the system as a function of concentration, which was a maximum at a concentration of 0.3%.

Electron micrographs were taken of the AgI from the complex. One of these is shown in Figure 8 and is typical of those taken for concentrations of 3 and 25%. Note the two distinct forms. The large generally spherical particles are probably hollow. The small particles are solid. One explanation of this geometry is as follows: The surface of a complex droplet vaporized first leaving a shell of AgI or solid complex with a liquid complex center. However, the liquid in the drop is not in stable equilibrium so the pressure and temperature rise due to a heat interaction with the surroundings. When the pressure is higher than the solid shell will support, a hole is blown in the shell and the liquid complex is expelled. This material then reaches the stable state of small solid particles and ammonia vapor. Holes were observed in the shells in some cases which support this explanation.

From the above analysis it would seem that the number of nuclei per drop would be essentially constant. However, the shell of AgI or AgI-NH$_3$ may change in physical properties with concentration. The thickness of the shell formed may vary with concentration as could the thermal properties. These changes in turn would influence the number and size of small droplets expelled. The net effect could be a change in nuclei per drop at different concentrations.

The remaining item for discussion in this section is nucleation characteristics. The effectiveness curve shows that the threshold temperature for this system is about 5° lower than for nuclei that has been thermally processed. The electron micrograph (Fig. 8) is needed to examine this. In general the particles ranged from a maximum of 2μ to a minimum of about 0.01μ. The larger particles represent most of the mass while the smaller ones represent most of the numbers. According to Fletcher the large particles should be effective down to about -4C, yet the effectiveness was too low to measure at -8C.

One could argue that there were too few large particles, yet the small particles were also not as effective

as usual. This is borne out by the flatness of the effectiveness curve at the low temperatures. In fact the curve obtained is quite similar to a Fletcher theoretical curve for a single particle size if a shift in the origin is made.

Finally, the poorer performance could be attributed to the presence of ammonia. This is not indicated (see other pertinent remarks). The question of photolytic activation should also be considered. However, no measurable change in effectiveness was observed when samples were taken at night. This is a subject of continuing investigation but its effect in this case is not significant.

We are still left with a question regarding the reasons for the behavior of the AgI particles from the non-thermal system.

Before pursuing this it is necessary to discuss the microscopic characteristics of particles which do produce numbers of nuclei which are an order of magnitude higher. An electron micrograph of an AgI particle originating from the NH$_3$-AgI complex which has been thermally processed is shown in Figure 9. The effectiveness of this system is 1.2 x 10^{14} at -10C or about an order of magnitude higher than the non-thermal system. The threshold temperature for thermally processed AgI is normal. The particle size varies from 0.02 to .2 μ. The structure of these particles is markedly different from the non-thermal system. Most important is the nebulous material surrounding the particle, the nature of which is not known at this time. There is also no question that the impurities are different in quantity and species due to the different environments. Carbonaceous material and traces of sulphur oxides present at high temperatures are in the environment of the particle in the thermal system and are absent in the non-thermal system. Using these particles for comparative purposes also tends to bar the influence of photolytic action since the particles were processed through a radiant flame and high temperatures in one case and high temperatures only in the other. The effectiveness depended almost entirely on gas temperatures.

In view of the foregoing, it may be concluded that impurities are necessary to cause silver iodide to act as an ice nuclei, especially at warmer cloud temperatures.
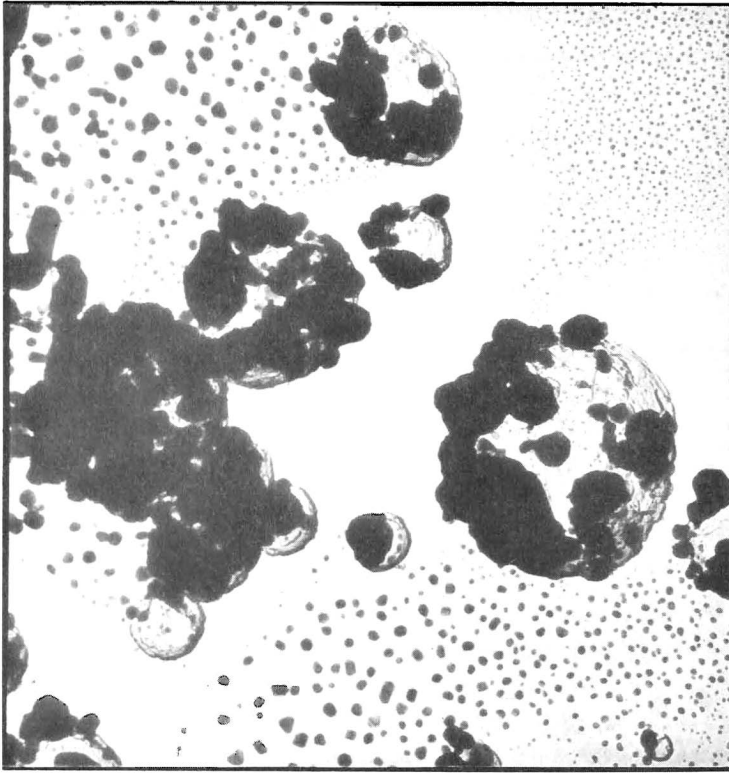
Figure 8 – Typical Electron Photo-micrographs of
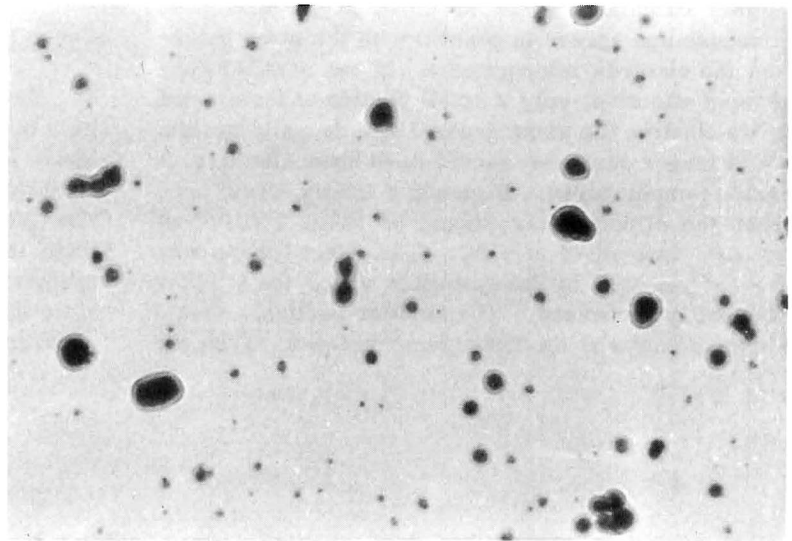the output of the Prototype I Generator

Figure 9 – Typical Electron Photo-micrograph of
the output of a Thermal Generator

Dautrebande System

Recall that in this system the complex is expanded from medium pressure and ambient temperature to atmospheric pressure using the Dautrebande principal. A schematic diagram of this system is shown in Fig. 10. The liquid complex is first expanded through a commercial nozzle into the filtering column which is nothing more than a laboratory "spine type" distillation column. The large droplets stopped by the spines form layers and act as filters for the other droplets. Thus, the drops are forced through successive liquid layers. Vapor is also released in the process. Only the smallest drops emerge since only those carried in a vapor bubble can get through. The length of the column and the liquid flow rate are the dominant variables in effluent droplet size and rate of flow.

The effluent from system (b) was significantly smaller than for system (a). The droplets could not be seen with an optical microscope (The droplets from system (a) were about 5μ). Electron micrographs of the solid residue reveal a structure which is quite similar to system (a), i.e. relatively large hollow spheres and relatively small individual solid particles. However, the size of the large particles are roughly an order of magnitude smaller than in system (a) or about $0.1-0.2 \mu$ in diameter. The smaller particles were in the order of 0.05μ.

The effectiveness of system (b) is as shown in Fig. (11). This unit could be economically attractive. The flatness of the curve can be explained by the essentially flat particle size distribution if one ignores the smaller particles. Assuming only the larger particles close to the measured size were effective, 2×10^{14} shells of 0.25μ diameter would be formed per gram of AgI. This calculated value is close to the measured effectiveness and agrees in general with the sizes measured on the electron micrographs. If the smaller particles were effective, only a small portion of them were. Again we observe the same general effects as in system (a). The larger particles should have been effective at the higher temperatures. Fletcher's theory would predict that the effectiveness should be about 2×10^{14} at $-8C$ to $-10C$ instead of at $-13C$. The effectiveness was $x \ 1.2 \times 10^{14}$ at $-10C$ in the system in which the simplex was thermally processed. The smaller particles should have been effective at the lower temperatures. Thus the

data from the Dautrebande system is also in agreement with the hypothesis that impurities are essential to the nucleating process. The increase in effectiveness compared to system (a) is due solely to the increase in particle numbers.

It should be emphasized that system (b) is still in the laboratory stage of development. The capacity of the unit described was only 1.5 mg of effluent AgI per minute. Additional development work is needed if the unit is to be used in field. This would include increasing the capacity by at least 4 orders of magnitude and changing the size distribution from flat to normal for most field applications.

Other pertinent Remarks -- Systems (a) and (b)

It has been reported that ammonia increases the effectiveness of silver iodide. This was confirmed at $-20C$. It was found that addition of ammonia in the cloud chamber after all the ice crystals had fallen out produced about the same number of nuclei as for the original sample. However this effect was not observed at temperatures above $-15C$.

System (a) was not sensitive to the flow rate of silver iodide. This was varied from 2 to 850 grams per hour with no noticeable change in effectiveness at a given temperature.

Conclusion

Two non-thermal silver iodide ice nuclei generators have been examined. The first of these is not economically feasible. The second, though promising needs additional development before it is usable in the field. The physical characteristics of the aerosols issuing from non-thermal systems are different than in thermal systems and are not as effective as ice nuclei particles from thermal generators. This is probably due to trace differences in impurities.
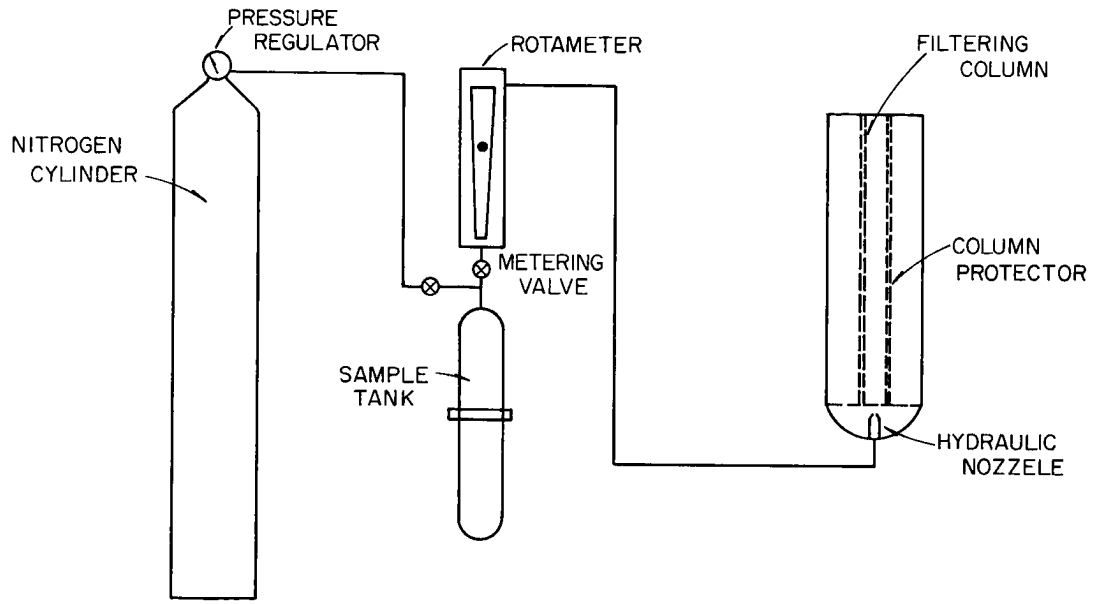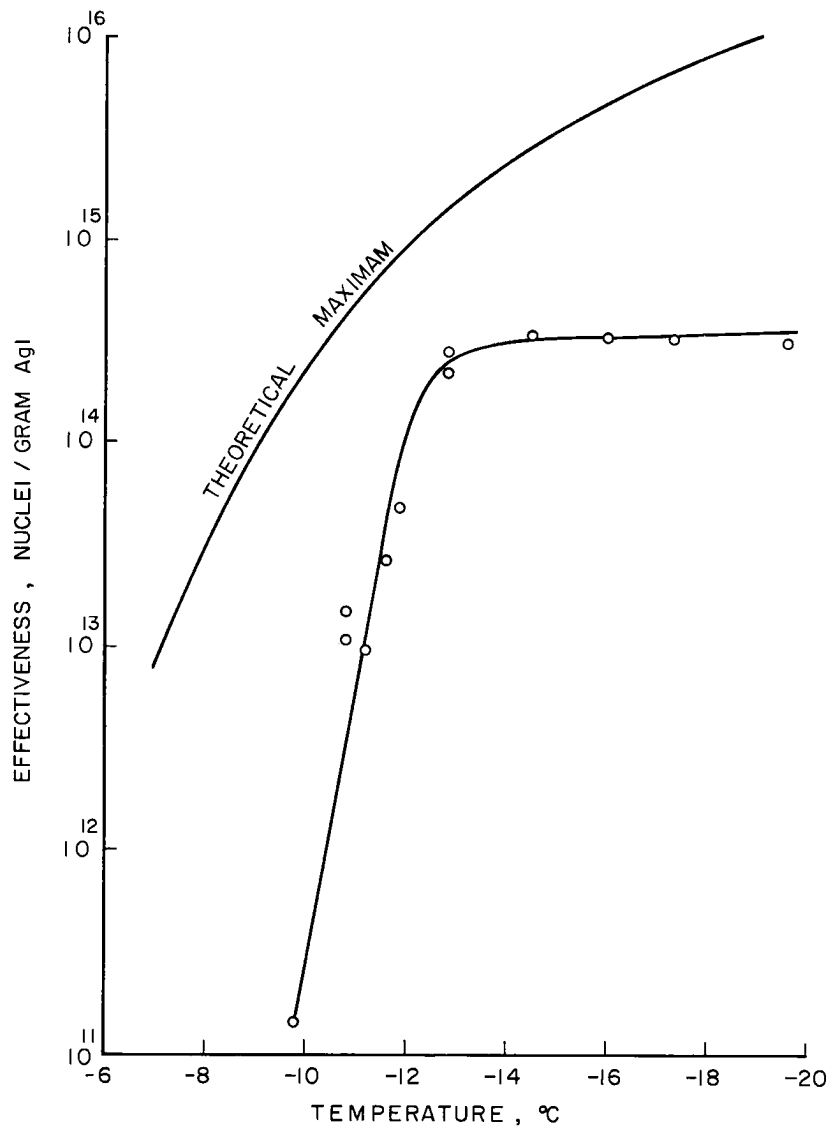
FIGURE 10 SCHEMATIC OF SYSTEM B

FIGURE 11 PERFORMANCE CURVE FOR SYSTEM B

Acknowledgements

References

1. Corrin, M. L., Edwards, H.W., and Nelson, J.A.: The Surface Chemistry of Condensation Nuclei: II. The Preparation of Silver Iodide Free of Hygroscopic Impurities and Its Interaction with Water Vapor. Journal of the Atmospheric Sciences, Vol. 21, pp. 565-567, September 1964.

2. Corrin, Storm, N. S.: The Surface Chemistry of Condensation Nuclei I. The Sintering of Silver Iodide. Journal of Physical Chemistry, Vol. 67, pp. 1509-1511, July 1963.

3. Dautrebande, L.: Microaerosols – Physiology, Pharmacology, Therapeutics: New York. Academic Press, 1962.

4. Beltz & Stollenwerk: Halogen Silver Ammoniates, Zeitschrift fuen Anonganische Und Allengenmeine Chemi 114, pp 174-202, 1920.

5. Fletcher, N. H.: Size Effect in Heterogeneous Nucleation. The Journal of Chemical Physics, Vol. 29, No. 3.

6. Fletcher, N. H.: Nucleation by Crystalline Particles. The Journal of Chemical Physics, Vol. 30, pp. 1476-1482, June 1959.

7. Fletcher, N. H.: Entropy Effect in Ice Crystal Nucleation. The Journal of Chemical Physics, Vol. 30, pp. 1476-1482, June, 1959.

8. Rowland, Layton and Smith: Photolytic Activation of Silver Iodide in the Nucleation of Ice. Journal of Atmospheric Sciences, Vol. 2.

9. Robertson, Charles E.: Analytical Methods for Determining Silver Iodide Smoke Characteristics (Paper presented at National Meeting of American Meteorological Society on Cloud Physics and Severe Storms, October 1965).

10. Tominaga, H. and Kinomaki, S.: Note on a Method of Spraying AgI-in-Liq. NH_3 Solution for the Purpose of Artificial Seeding. Tohoku University, Science Report, 5th Series Geophysics, Vol. 6, pp. 39-42, August, 1954.

Characteristics of Silver Iodide Ice Nuclei Originating from Anhydrous Ammonia – Silver Iodide Complexes
Part II – Thermal Systems

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CHARACTERISTICS OF SILVER IODIDE ICE NUCLEI ORIGINATING FROM ANHYDROUS AMMONIA - SILVER IODIDE COMPLEXES

PART II - THERMAL SYSTEMS

by R. L. Steele [1] and F. W. Sciacca [2]

Abstract

   The characteristics of Silver Iodide Ice Nuclei originating from a complex of silver iodide and ammonia without thermal processing is discussed in a companion paper. Reported here are the effects of thermal processing. This is accomplished by burning the ammonia in the complex in a supporting flame of No. 1 fuel oil using highly preheated air. The process releases the silver iodide from the complex by rapid evaporation without decomposition of the AgI. Silver iodide particles ranging in diameter 100 to 700°A are produced. The effectiveness measured in an isothermal cloud chamber varies from 1.5 to 10^{14} to 2×10^{15} at -10 C and -20 C respectively for an output rate of 133 gms/hr. At an output of 500 gms/hr. the effectiveness is about 8×10^{13} nuclei/gm.

   The influence of various combustion parameters on effectiveness are discussed. It is shown that the stoichiometric ratio is a dominant variable in effectiveness which falls sharply at stoichiometric ratios of greater than 1.15. Dissociation of the AgI and the ammonia were investigated and this was found to be minimal. The influence of temperature is examined with regard to effectiveness. This increases exponentially with temperature and reaches a maximum at about 2750°F.

   The thermal and non-thermal processed AgI are compared using effectiveness data and electron micrographs. The thermally processed AgI has a different structure and composition than the same material dispersed without thermal action. The effectiveness of the former is greater than the latter.

   The paper closes with a comparison of thermal and non-thermal AgI-NH$_3$ complexes and AgI-KI-Acetone systems. Also mentioned is an isopropylamine-AgI system which has many similarities to the anhydrous ammonia system but is much simpler. Both systems show markedly better effectiveness than the AgI-KI-Acetone systems, especially at the higher temperatures.

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Introduction

The non-thermal dispersion of AgI from a complex AgI and NH_3 by non-thermal means is described in another paper (1). The effectiveness of this system is too low to be economic. This finding led to the development of a thermal system. It was believed that if the complex of $AgI-NH_3$ were burned, the effectiveness would be improved. This opinion was based on the success of other thermal systems (2) (3) (4) (5). Such systems are thought to be more effective due primarily to the chemical environmental effects of the combustion process.

In order to carry out the combustion of ammonia in air it is necessary to burn it in a supporting flame. Various combustion processes were investigated. It was found that a system using No. 1 Fuel Oil as the supporting fuel showed promise. It was further concluded that the use of preheated air enhanced the combustion of the combination fuel, i. e., No. 1 Fuel Oil and a complex of NH_3-AgI. The advantages of preheat are well documented in the literature for many diverse combustion processes. An analytical and experimental feasibility study demonstrated the need for preheat to improve generator effectiveness.

Combustion System

The experimental work referred to in the introduction permitted design of the prototype preheat generator. The system is depicted in Fig. (1). The combustion air passes through the outer annulus to the exit end of the generator, turns and passes back to the inlet end. The air is preheated by the heat interaction with the hot gases passing through the central core or combustion section. Liquid fuel is admitted through the lower nozzle; the complex is admitted in the upper nozzle. Cooling NH_3 is admitted in the chamber surrounding the nozzles to prevent vaporization of the complex in the line. A swirl plate and a convergent cone encompass the nozzle section so that the high temperature air flow will enter the combustion section as a highly turbulent vortex to promote rapid mixing of fuel and air. This rapidly vaporizes the fuel so that it will ignite and burn in an intense short flame. Fuel flows of 15 gal/hr have
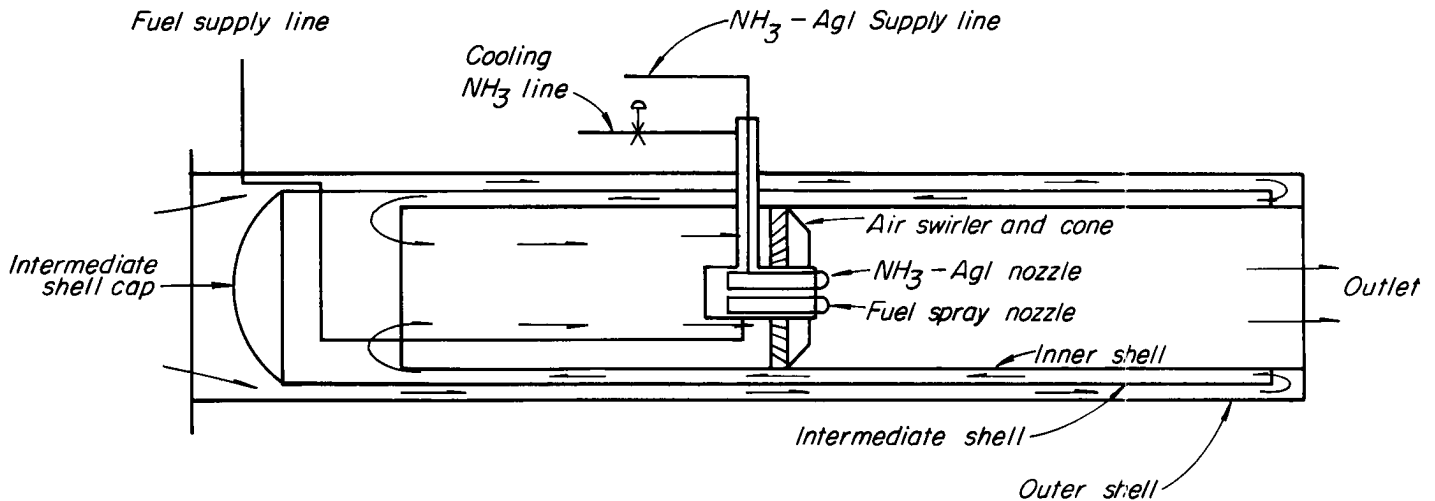

FIG. I   PREHEAT   GENERATOR

Fig. 2

been processed by the unit with complete combustion. Flame temperatures of 3000°F have been measured. A photograph of the preheat unit in operation is shown as Fig. (2). Other photos of the generator are shown in Fig. (3).

Combustion Variables Effecting Nuclei Effectiveness

The dominant variables which effect the nucleating characteristics of silver iodide particles which have passed through a combustion process are for the most part unknown, (4) (6). The more important independent variables (and there may be others) may be listed as follows:

1. Geometrical Configuration of Combustion Chamber
2. Temperature (Reaction Zone)
3. Supporting Fuel
4. Atomization
5. Quench rate
6. Stoichiometric ratio

Another related variable is the effect of temperature alone, i.e. particle characteristics resulting when the silver iodide is exposed to a high temperature, non-reacting gas stream.

Items one and two in the list are essentially fixed by a given prototype. The literature search coupled with the experimental feasibility study led to the design described in the previous section. The maximum temperature achievable is also largely fixed by the geometrical configuration as well as the heat interaction
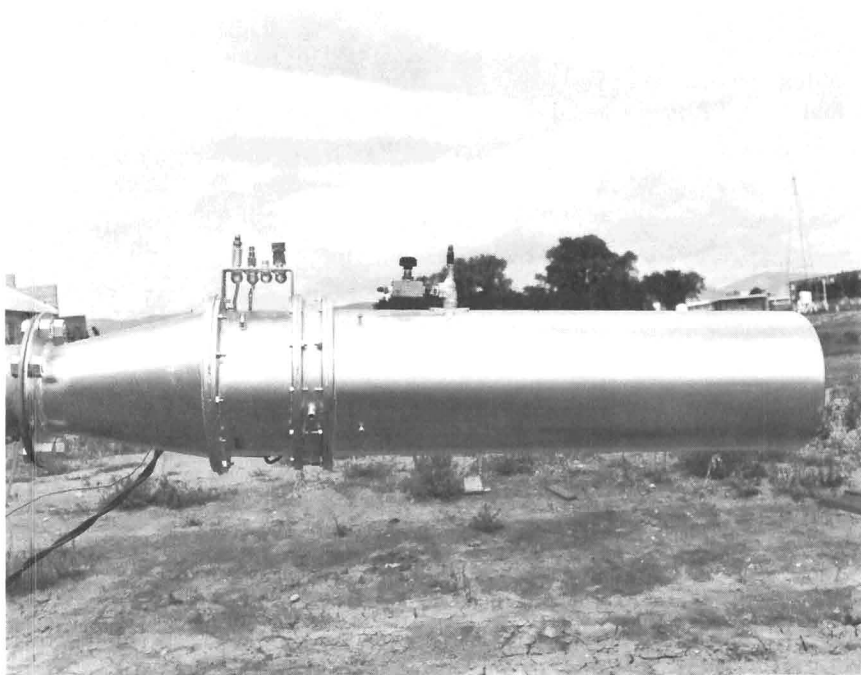
Fig. 3

barriers and the fuel used. The maximum temperature is variable to an extent by a change in the stoichiometric ratio but it is a dependent variable in this sense. The chosen prototype provided a means for investigating the effect of the remaining variables.

Fuel – A detailed study of fuels to support the combustion of the ammonia was not undertaken. A given fuel effects all of the variables listed. The preliminary work was done with #1 fuel oil. This material when used with ammonia produced good results in the cloud chamber. It was chosen due to this and its low cost, simplicity, safety, and availability. Other fuels are under investigation.

Atomization – In order to achieve complete vaporization the ammonia and the fuel must be broken up into a spray of uniform small droplets ($\approx 50\mu$). The spray envelope must be geometrically compatible with the combustion chamber. The correct atomizing nozzle must be chosen. This is not a problem though choice of such variables as spray angle and type, (hollow or solid cone) are best determined by experiment. Complete vaporization of the fuel was assumed to be a necessary condition for the production of effective nuclei. Fuel which does not vaporize will not undergo a chemical reaction of significance in the flame zone. This results in a lower flame temperature which reduces the evaporation of the ammonia spray. Poor spray characteristics of the ammonia reduces the number of resulting AgI particles. The nozzle type chosen provided good atomization of fuel and ammonia. The flame was smokeless at normal stoichiometric ratios with no carbon monoxide detectable at ratios greater than 1.1.

Quench Rate – The rate at which a gas containing silver iodide is quenched strongly effects the nuclei effectiveness. This was established by Fuquay (5) and others. A satisfactory explanation of this necessary condition is needed. The history of the interaction of the AgI and the burning fuel must be known. At about 146°C AgI α transforms to AgI β which melts at 558°C and boils at 1506°C. The flame temperature is considerably higher than the melting point temperature of β AgI. The following questions arise: (a) Does the AgI dissociate in the flame to Ag and I_2 ? (b) Is there sufficient time for this reaction to occur? (c) Does a passive resistance prevent this? If item (a) does not occur and if there is insufficient time and a passive resistance, the AgI can pass through the reaction zone as AgI in a meta stable state. This argument supports the need for a rapid quench rate.

Experimental evidence supports the meta stable state hypothesis. The effluent from the thermal system was sampled for analysis by means of a high temperature water cooled gas probe. The sampled gas was thus very rapidly cooled to ambient temperature in an attempt to "freeze" the chemical composition prevailing in the gas stream. The particulate matter was collected on a millipore filter and chemically analyzed. No detectable amount of silver as metallic silver or oxides of silver were found. This was also the case for iodine. This

data leads to the conclusion that the silver iodide passes through the reaction zone as the compound AgI and that it is therefore in a meta stable state in the reaction zone.

The above discussion raises the related question – if the AgI passes through the reaction zone as AgI how are small particles formed? This will be discussed in the section on microscopic aspects.
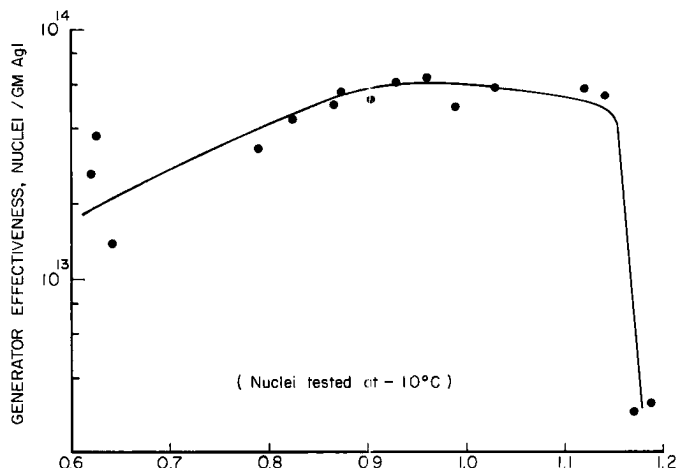

FIG. 4   VARIATION OF GENERATOR EFFECTIVENESS WITH STOICHIOMETRIC RATIO

Stoichiometric Ratio

The effect of stoichiometric* ratio on generator effectiveness was evaluated at 8% complex concentration and at a temperature of -10C. This temperature was chosen since nucleation parameters are more sensitive than at -20C. The effectiveness was measured in the isothermal cloud chamber designed for evaluating ice nucleating devices (1). A plot of effectiveness vs. stoichiometric ratio is shown in Fig. 4.

Certain hypotheses can be drawn regarding the effect of air-fuel ratio. This ratio can affect the environment of the silver iodide in at least two ways. First, the temperature will vary to a degree. Second, the chemical constituents of the environment will vary. At stoichiometric fuel ratios of less than 1.0 a reducing atmosphere prevails. The constituents of this atmosphere could conceivably interact (but not necessarily react) with the silver iodide particles in a way which would influence their nucleation characteristics. From the data presented above, this interaction appears to be detrimental. Alternately, or possibly in addition, the temperature of the products issuing from the generator is lower in the range of .6 to 0.8 than it is in the range 0.8 to 1.0. This very likely influences the characteristics of the particles produced.

Optical pyrometer measurements indicated that the flame temperature was highest near stoichiometric

*The ratio of actual air required to the theoretical amount used for combustion of the fuel oil and ammonia.
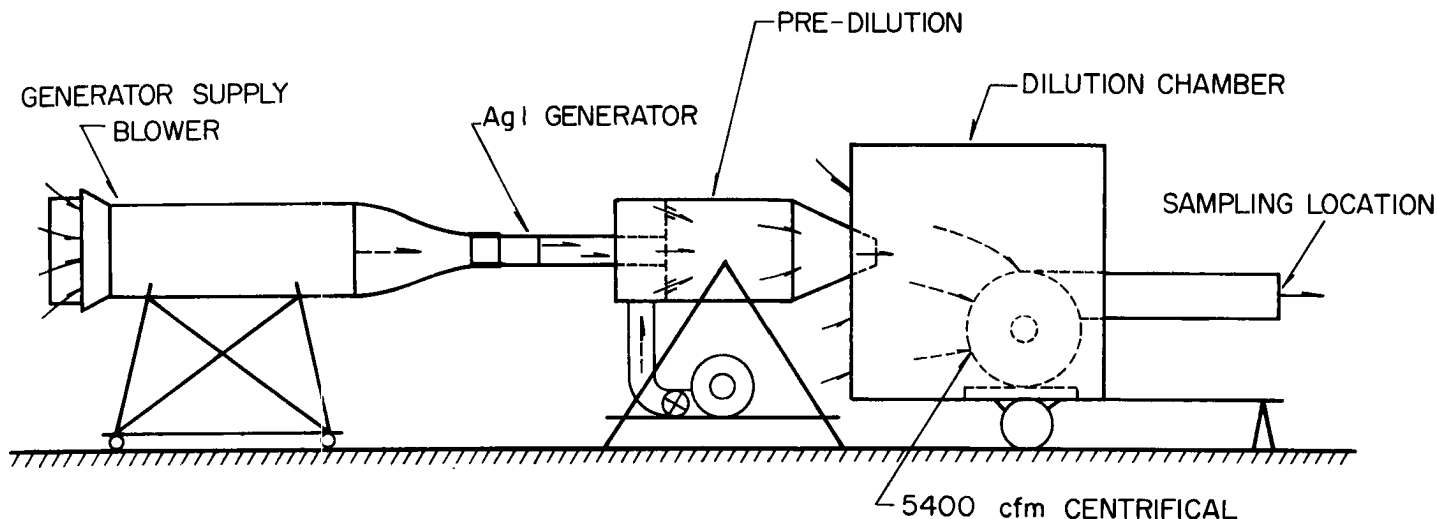
FIGURE 5   AgI   GENERATOR   DILUTION   AND   SAMPLING   EQUIPMENT
ARRANGEMENT

conditions, being approximately 2400°F. Also, at these operating conditions the most complete combustion was obtained.   Fewer possible contaminants were present. In light of the above discussion, the following statements are purported:

1. High temperatures (at least up to 2400°F) are conducive to the formation of large numbers of active silver iodide nuclei.

2. A reducing atmosphere (of the nature produced by incomplete combustion) is somewhat detrimental to the formation of active ice nuclei.

3. The environment produced by the use of air-fuel ratios above 1.15 times stoichiometric sharply reduces generator performance.

Analysis and discussion of the above items are a subject of continuing investigation. The mechanism of nucleation must be better understood to pursue this. If impurities must be present in the form of hydrophillic sites to provide the free energy necessary to trigger the nucleation process, then the nature of the chemical environment surrounding the particles could well contribute to the formation of the hydrophillic sites.

Effect of Temperature Alone

Experiments were designed to give insight into the influence of temperature alone on active silver iodide production in the absence of a chemical reaction. A high temperature gas stream was produced by burning fuel oil only in the generator. The temperature of the gases (mainly CO_2, H_2O and N_2) were varied by introducing cold air into the stream with the dilution apparatus shown in Fig. (5). The complex was introduced into the gas stream at temperatures of 2750, 1300 and 680°F respectively. The concentration of the complex was held constant at 8%. Nuclei effectiveness was measured in the cloud chamber at -10C.

The results of these tests are shown in Fig. 6.

The curve shows a sharp increase in effectiveness with increases in temperature in the 1000°F range with a definite flattening trend as the temperature approaches 3000 F. It is probable that the effectiveness would decrease if even higher temperatures were used. Other investigators have found this same trend for other silver iodide generating systems. For one particular system employing acetone and potassium iodide as the silver iodide, D. M. Fuquay found that optimum performance was obtained using temperatures of about 2200°F. The
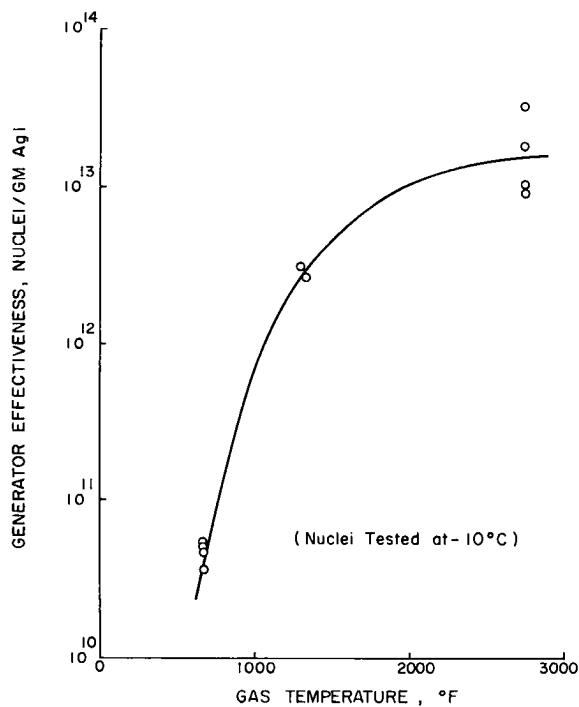

FIG. 6   VARIATION OF GENERATOR EFFCTIVENESS WITH TEMPERATURE
OF AgI ENVIRONMENT

difference in the thermodynamic properties of the carrier employed could account for the difference in optimum temperatures. Some of the difference probably can be accounted for in experimental error in temperature measurement.

The results shown in Fig. (6) tend to confirm the hypothesis that the AgI does not decompose in the flame at the temperatures prevailing when ammonia and fuel oil were burned. Fuquay (5) found that the performance decreased after a certain temperature was reached or that effectiveness as a function of temperature was not monotonic. Dissociation of the AgI at higher temperatures is likely. Metastability of the AgI would certainly be a function of temperature. Discussion of the rising portion of the curve is presented in the next section.

Microscopic Aspects

The electron microscope was used to examine the effluent of the thermal system. A typical electron micrograph is shown in Fig. (7). The dark particles were identified as AgI by treating the electron microscope grid with microdol developer which causes "silver whiskers" to grow on the particle.

The nebulous surrounding the individual particles and connecting the multiparticle groups has not been identified nor is a hypothesis regarding its identification offered.

Methods of identification are under study. It is planned to burn the complex with hydrogen. If the nebulous disappears, it is probably carbonaceous. The possibility that the phenomena is merely an artifact has been considered. The AgI aerosol from the non-thermal system is shown in Fig. (8). Note the absence of the nebulous on even the smallest particles. The nebulous seems to be related to the agglomeration characteristics which are severe unless the particle density is about 10^5 particles per cc. It appears to be the nexus for the particles. Typical agglomerates are shown in Fig. (9).

The particles range in size from 30 to over 700 °A. Most of the individual particles are roughly sperical (determined from shadowing at 30°). Some have a plate or disc geometry. There is no apparent difference in the particles from 3 or 8% solutions, though this is based on a limited number of samples.
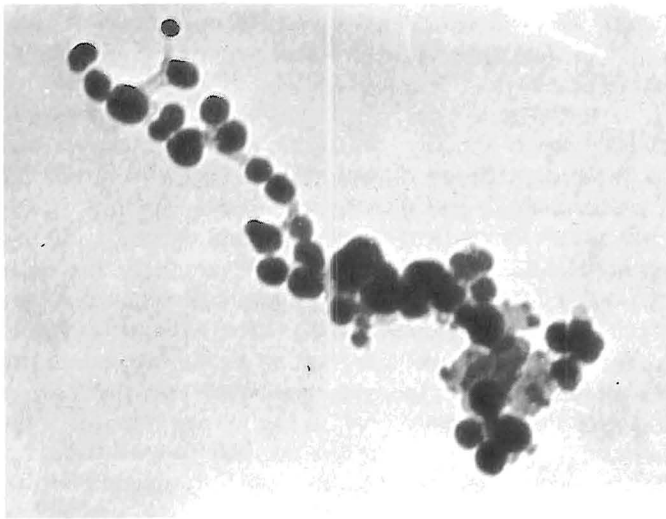

1000°A

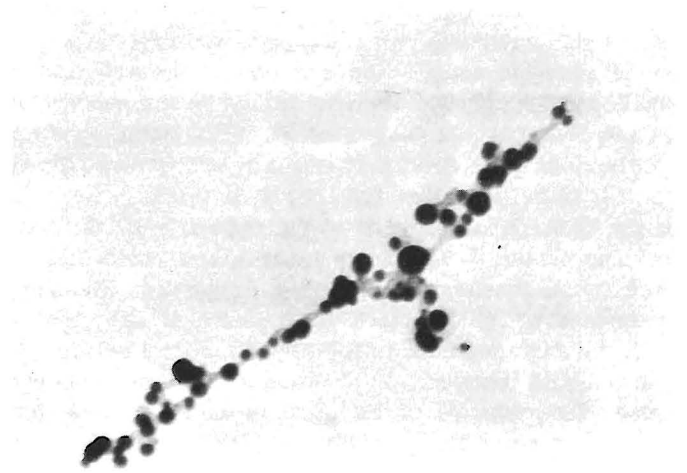Figure 7 - Typical Electron Photo-micrograph of the output of a Thermal Generator

|◀──────── 1μ ────────▶|
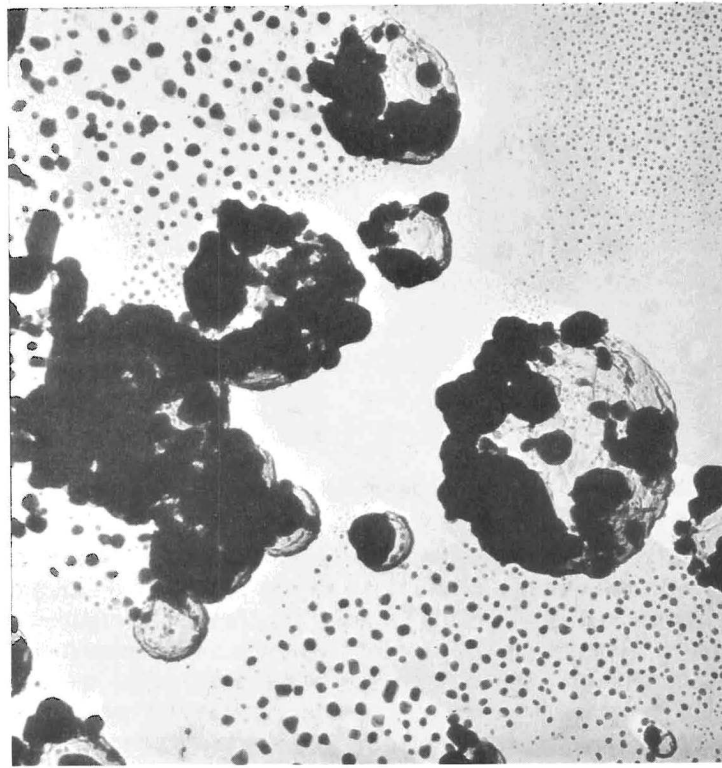
Figure 8 – Typical Electron Photo-micrographs of
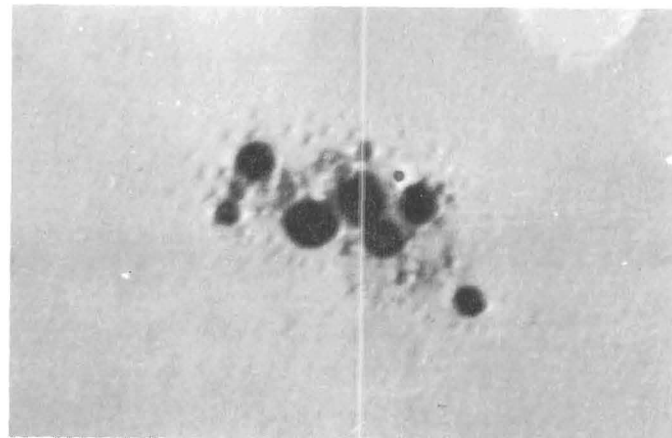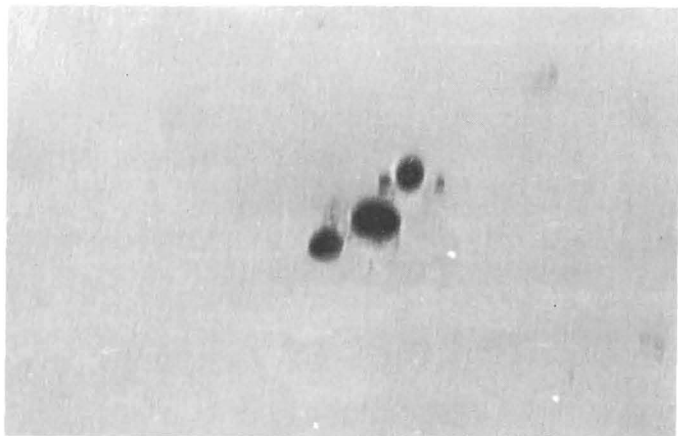the putput of the Prototype I Generator

1000°A

1000°A

Figure 9 – Electron Micrographs of Typical Agglomerates

◉◀ 1000°A   Fig. 10 Electron Micrographs of AgI Particles from Ice Crystals   ◉◀ 1000°A

Electron micrographs of AgI particles from ice crystals nucleated at -12C were collected and are shown in Fig. (10). Note the various shapes and sizes. This is in disagreement with the theory of Fletcher (2) (7), as regards the size-temperature relationship. According to the theory, the particles should be larger than 720°A to be effective. There is also disagreement in geometrical considerations. However, the thermal system performance agrees closely with Fletcher's theoretical maximums except for a shift in the origin.

No other quantitative and theoretical quantitative analysis is available to the writer's knowledge. The work of Corrin (8) (9) strongly suggests a different mechanism which is based on the mechanism mentioned in a previous section. This is also implied in the work of Rowland, Layton and Smith (10) where it was found that AgI must be photolytically activated to be effective. This observation also suggests that photolytic change of a particle changes the chemical potential of certain sites on the particle surface.

The remaining item to be discussed in this section is the hypothesis regarding meta stability of the AgI in the reaction zone. The question of the mechanism small particle production was raised in the section on Quench Rate but was not answered. This same question was implied in the section of effect of temperature alone.

It is believed that the answer to this question lies in the electron micrograph of the aerosol from the non-thermal system. The large spheres are really hollow shells. See discussion in Steele & Krebs (1). The shell is formed by initial rapid evaporation of the carrier from the surface of the droplet resulting in a solid shell with a liquid interior. Interaction with the environment causes the pressure of the liquid in the interior to rise. Interaction between the shell and the interior has the result of dissolving the shell due to the escaping tendency of the ammonia relative to the AgI in the shell. These interactions cause failure of some point in the shell at which point the liquid in the interior is expelled.

Holes have been observed in some of the larger shells which supports this argument.

The above argument may be applied to the thermal system. This same process can occur but more rapidly since evaporation rate from the droplet is much higher in the thermal system due to the higher temperature. This would mean that the shell would form sooner on the drop or when it was larger, since the initial evaporation rate of NH_3 from the drop is quite likely much greater than the NH_3 diffusion rate in the droplet. (The initial complex droplet size is approximately 20μ. These are smaller then the fuel oil droplets due primarily to the Joule-Thomson expansion through the nozzle.)

If we conclude that the shell forms sooner, it is seen that the AgI would be essentially prevented from decomposing due to the cooling effect of the evaporation process and the protection of the shell. Now suppose that the shell fails as in the non-thermal system and expels the liquid in the interior. These droplets are much smaller than the parent shell (see Fig. 8) and are much larger in number. The droplets from the parent shell would in turn form their own shells and rupture again as above and so on. These processes all require time.

In the meantime, the liquid phase is increasing in concentration rapidly. At some point the complex will be in the solid phase. This state has been observed (1). This is unstable and decomposes to NH_3 and AgI. Thus even after all the ammonia has been driven from the liquid droplet, it must also be driven from the solid phases before silver iodide as such is exposed to the flame. As long as ammonia is present, the temperature of the droplet will remain low due to the evaporation of the ammonia. It is therefore proposed that particles of the size range encountered in Fig. 7 are formed in the manner described above due to insufficient time for evaporation. They would thus escape dissociation and would pass through the reaction zone as AgI and not as Ag and I_2.

Droplet evaporation rate is mentioned in the preceeding paragraph. This rate should be estimated since if it is too high, the above explanation will not stand scrutiny. The instanteous rate is given by the equation:

$$\frac{dr}{dt} = \frac{\rho r c \frac{dT}{dt} - h_r (T_o - T_o)}{P_o - \frac{2\sigma}{r} + \rho h_{fg}}$$

Where:

$\frac{dr}{dt}$ = Time rate of change of radius

ρ = Droplet density

r = Droplet radius

$\frac{dT}{dt}$ = Time rate of change of droplet temperature

h_r = Heat transfer coefficient

T_o = Temperature of surroundings

T_o = Temperature of drop

P_o = Pressure of surroundings

σ = Surface tension

h_{fg} = Heat of vaporization

Examination of the equation permits insight into the time required to remove the ammonia from the complex droplet. Suppose that we consider the time required to remove all the ammonia from a droplet with an initial concentration of 3% AgI by mass. The initial droplets are about 20μ in diameter. The size when all of the NH_3 is evaporated is about 1μ. For simplicity and to be conservative in the analysis, the effects of shell formation may be neglected (this produces a delay in the evaporation). In determining $\frac{dr}{dt}$ one can neglect several of the terms for this particular case. $\frac{dT}{dt}$ and $\frac{2\sigma}{r}$ are very small compared to the other terms. The term containing $\frac{dT}{dt}$ is also small for an evaporating liquid. Furthermore neglecting this term has the conservative effect of increasing the evaporation rate.

Insertion of the dominant variables in the equation gives an evaporation rate of about 40μ/sec. The droplets are in the high temperature zone about 0.5 seconds. This rate of evaporation is therefore compatible with the hypothesis that all of the ammonia does not leave the drop before it leaves the system, in which case the AgI does not break down.

The non-dissociation hypothesis should also be discussed from the temperature only effects (Fig. 6).

The decrease in effectiveness with temperature results from fewer particles being formed. The evaporation rate decreases with temperature so the concentration of AgI at the surface also increases at a lower rate. The shell then forms at a later time in the reaction due to the lower evaporation rate. As the temperature is lowered, the shell formation-fracture cycle does not occur as many times. The result is fewer, but larger particles, hence the lower mass efficiency. At the low temperatures, the situation compares to the non-thermal system.

Other arguments against dissociation to any degree can also be given. These are developed as follows: The concentration of the AgI in the gas stream is about 3.5×10^{-2} mols AgI per mol of gas. Now suppose that the AgI dissociates into iodine gas and solid silver. The concentration of the iodine will also be 3.5×10^{-2} mols/ mol gas if all of the AgI dissociates. If the total pressure of the stream is one atmosphere, the partial pressure of the I_2 will also be 3.5×10^{-2} ATM. By contrast, the concentrations of water vapor, carbon dioxide and nitrogen are orders of magnitude higher. The collision frequency of the I_2 with Ag is thus much lower than with the other constituents present.

Now consider the silver. If the temperature of the gas stream is $2300^\circ F$, the silver will not vaporize since the boiling point is about $3540^\circ F$. Thus the silver will be in the liquid phase in the gas stream.

The recombination probability now becomes even smaller. The iodine is in the gas phase. A single collision of an I_2 molecule with a silver particle may produce a molecule of AgI. Furthermore, the reaction will probably stop when a monolayer of AgI forms on the silver particle. All of this must occur in a short time as the material passes through the combustion chamber. If there is dissociation, there is insufficient time for the reaction:

$$Ag + 1/2\ I_2 \rightleftharpoons AgI$$
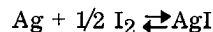
to reach equilibrium.

This explains why, as mentioned previously, detectable amounts of Ag, AgO or I_2 were not found in the exit gas stream. One can counter that a mono-layer of AgI on a particle may be enough for the particle to act as a nucleus. However, if this were the case, there would have been insufficient AgI in the particle to grow the silver whiskers mentioned previously.

Effectiveness of the Thermal System

The effectiveness of the thermal system is shown in Fig. 11 for a complex concentration of 3% and an output rate of 133 gms/hr. Not shown is the 500 gm/hr curve which corresponds to 8% concentration. The output is somewhat lower, e.g. 8×10^{13} nuclei per gram at -10C. The performance of the thermal ammonia system is quite attractive, however, the system is too complex in its present state to employ in the field. The IPA system shows as much promise (11) and is much simpler. This is designated IPA after the carrier, isopropylamine, $(CH_3)_2CH\,NH_2$. This complexes readily with AgI and is similar to ammonia in many respects. It has the added advantage of having a much higher boiling point (31^oC @ 76mm) than ammonia and is a good fuel. These features eliminate the complexities of the ammonia system.

Conclusion

The effect of some dominant variables on ice nuclei effectiveness in systems employing thermal processing have been presented. When a complex of ammonia and silver iodide are burned with No. 1 fuel oil the effectiveness is very sensitive to stoichiometric ratios above 1.15. The optimum ratio is about 0.95. Lower stoichiometric ratios lower the effectiveness. An explanation of these effects is the subject of continuing investigation.

The effect of temperature alone on the formation of nuclei was also investigated with the finding that the nuclei effectiveness increases exponentially as the temperature is increased to about 3000^oF.

It is hypothosized that the AgI does not decompose when it is thermally processed using NH_3 as the carrier. This is confirmed by chemical analysis. The thermodynamics of a complex droplet passing through a flame do not favor dissociation of the AgI as long as NH_3 is present.

The effectiveness of the thermal system using the NH_3-AgI complex is higher than acetone-KI-AgI systems over a wide temperature range, but the system is too complex for field use. A new system employing IPA as carrier is developed to the point that it may be used in the field.
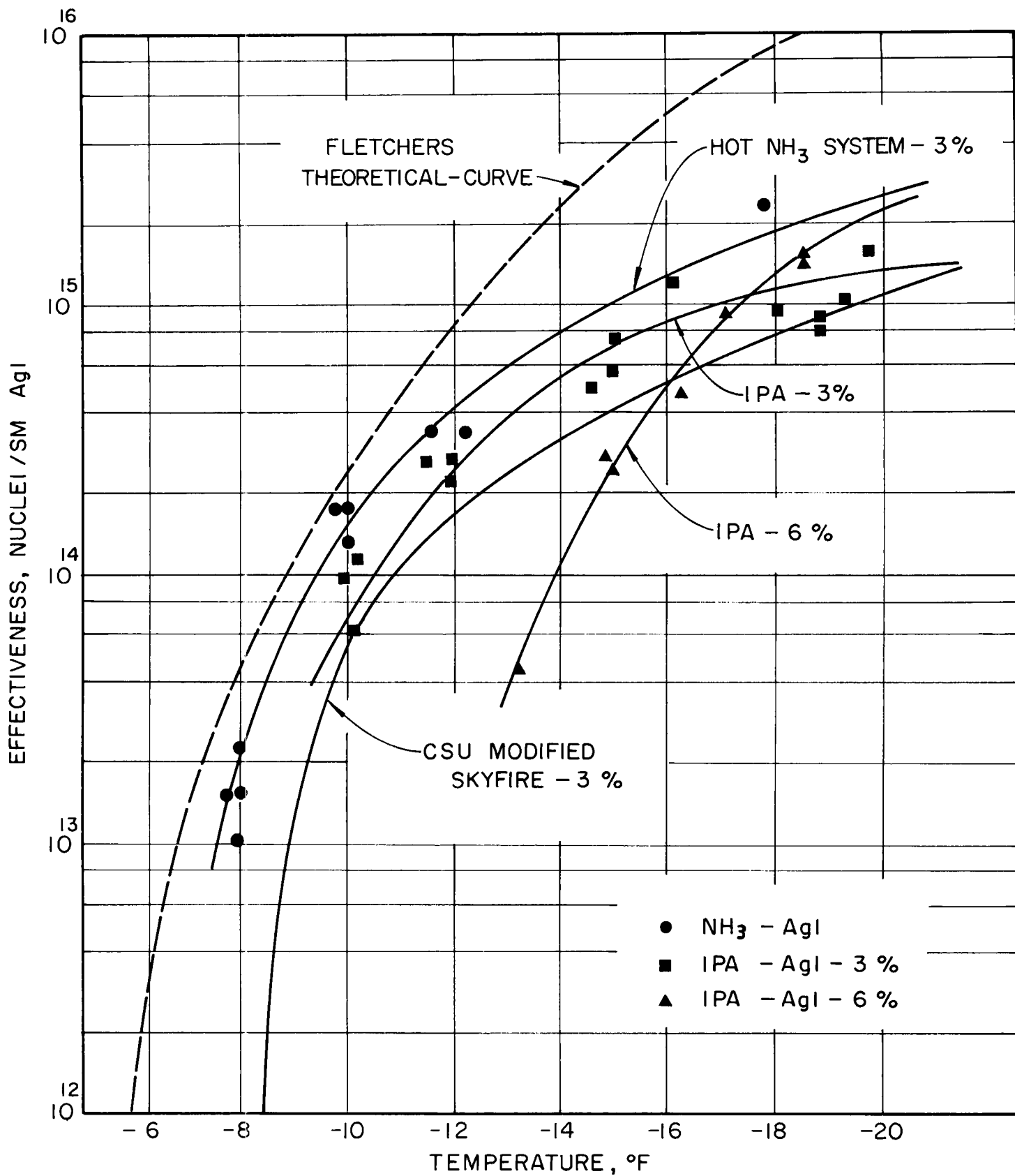
FIG. 11 COMPARISON OF IPA GENERATOR EFFECTIVENESS

References

1. Steele, R. L. and Krebs, F. W.: Characteristics of Silver Iodide Ice Nuclei Originating from Anhydrous Ammonia-Silver Iodide Complexes. Colorado State University, Mech. Engr. Tech. Paper No. 66-1, Atmospheric Science Tech. Paper No. 73.

2. Fletcher, N. H.: The Optimum Performance of Silver Iodide Generators. Journal of Meteorology, pp. 385-387, August 1959.

3. Vonnegut, B.: Early Work on Silver Iodide Smokes for Cloud Seeding. Final Report of the Advisory Committee on Weather Control, Vol. II, pp. 283-285, Washington: Government Printing Office, 1958.

4. Vonnegut, B.: Techniques for Generating Silver Iodide Smoke. Journal of Colloid Science, pp. 37-48, February 1950.

5. Fuquay, D. M. and Wells, H. J.: The Project Sky-fire Cloud Seeding Generator. Intermountain Forest and Range Experiment Station U. S. D. A., Research Paper No. 48, 1957.

6. Robertson, Charles E.: Analytical Methods for Determining Silver Iodide Smoke Characteristics (Paper presented at National Meeting of American Meteorological Society on Cloud Physics and Severe Storms, October 1965).

7. Fletcher, N. H.: Size Effect in Heterogeneous Nucleation. The Journal of Chemical Physics, Vol. 29, No. 3.

8. Corrin, M. L., Edwards, H. W., and Nelson, J. A.: The Surface Chemistry of Condensation Nuclei: II. The Preparation of Silver Iodide Free of Hygroscopic Impurities and Its Interaction with Water Vapor. Journal of the Atmospheric Sciences, Vol. 21, pp. 565-567, September 1964.

9. _____, Storm, N. S.: The Surface Chemistry of Condensation Nuclei I. The Sintering of Silver Iodide. Journal of Physical Chemistry, Vol. 67, pp. 1509-1511, July 1963.

10. Rowland, Layton and Smith: Photolytic Activation of Silver Iodide in the Nucleation of Ice. Journal of Atmospheric Sciences, Vol. 2.

11. Steele, R. L.: Preliminary Investigation of a New Generating System for Silver Iodide, Proceedings, Western Snow Conference, Seattle, Washington, 1966.