

A Problem in the Use of AgI-NH₄I-Acetone Solutions in Cloud Seeding

BRIANT L. DAVIS AND RICHARD A. SCHLEUSENER

Institute of Atmospheric Sciences, South Dakota School of Mines and Technology, Rapid City 57701

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1. Introduction

In our cloud seeding activities during the past two years, we have used acetone solutions containing AgI and NH₄I in addition to the more widely used solutions containing NaI. Our purpose in the use of these solutions was to eliminate the chemical complexing variable. The seeding solution desired consisted of 85.2% acetone, 9.9% AgI, 3.1% NH₄I, and 1.9% water (all weight percentages). The 9.9% solution was approximately double the concentration used in the previous year. The higher concentration was used to obtain larger particle sizes from the higher solution strength to yield nucleation at warmer cloud temperatures (Donnan *et al.*, 1970).

The first indication of trouble came after the solution had been stored approximately two weeks in the generator tanks. During a seeding operation clogging of the generator mechanism was encountered which resulted in failure of the generator to ignite. During cleaning and subsequent reassembly of the generator, it was noted that a very large quantity of blue crystalline sediment had accumulated at the bottom of the tank and the remaining solution was a deep red color. A laboratory study was initiated immediately in an attempt to determine the chemistry of the problem, and inquiries were made to determine if similar problems had been encountered by other groups in the past.

A review of our own experience for the 1970 summer field season in which one of our projects used a 4%

solution (also with NH_4I) on a temporary basis indicated that little trouble had been experienced until near the end of the summer when clogging and stoppage of the lines and nozzle had taken place. At the time of the difficulty, this had not caused much concern since it was not unusual to experience occasional trouble of this type.

A check was made with other groups that had experience with ammonium iodide solutions. It was learned that during the seeding season of 1970 a private project in North Dakota (Wilbur Brewer, personal communication) had used the NH_4I -bearing solutions. In their 1970 project a 4% $\text{AgI-NH}_4\text{I}$ -acetone solution remained continuously in their generator tanks for about two months, at which time it was found to be necessary to drain and clean the tanks in order to re-establish the proper burning functions. Solid material had precipitated in the solution. The precipitate consisted of the blue crystalline material. Further examinations by this group in May 1971 revealed that the generators that had been used in the 1970 summer season had suffered serious deterioration of copper lines in the interior of the tank and that in one case the copper lines had been corroded to the extent that the generator failed completely.

Another university group (August Auer, personal communication) had used a 2½% $\text{AgI-NH}_4\text{NO}_3$ solution. This group had experienced no mechanical problems or corrosion to date. They used generators composed of stainless steel with either copper or stainless steel tubing, and they reported no greater problems with plugging of the generators than had been experienced earlier with use of sodium iodide solution.

Pending a complete definition of the problem and recommendations for a cure, our field operations continued using the temporary expedient of leaving the solution in the tanks only for the minimum time period required during the seeding flights. After draining the tanks following each flight, they were further flushed with acetone.

2. Identification of the cause of the problem

A laboratory analysis of the problem consisted of a number of separate tests which are described below.

The blue crystalline material was analyzed in the laboratory by means of x-ray diffraction, x-ray spectrometry, and infrared absorption. The most prominent interplanar spacings as obtained by x-ray diffraction are presented in Table 1. Qualitative x-ray fluorescent spectroscopy revealed the presence of silver, iodine and a smaller amount of copper, whereas the infrared absorption analysis indicated an NH bond at about $3.2\ \mu$ wavelength, but no OH bond. There appears to be no corresponding set of x-ray data in either the ASTM powder files or in the National Bureau of Standards file.

Artificial mixtures of AgI , NH_4I , acetone, and copper foil resulted in etching of the copper foil and associated deposition of pure metallic silver. In one test, about

TABLE 1. X-ray analysis of copper-silver-amine-iodide complex* using peak-height measurements.

Interplanar spacing (Å)	100(I/I ₀)**
11.44	5
9.89	19
9.52	39
9.09	100
8.38	11
7.92	7
6.89	2
5.94	5
5.29	3
4.85	7
4.60	2
4.40	2
4.18	4
3.943	5
3.745	13
3.565	21

* MoK radiation, zirconium filtered; 1° divergence; and scatter slits.

** I_0 is the strongest peak in the pattern ($d=9.09\ \text{Å}$).

0.5 ml of water was added to tubes of this solution with the result that in a period of 72 hr small blue needle crystals precipitated and fell to the bottom of the tube. X-ray diffraction revealed this to be the same material as that observed from the reaction with the generator parts. No water was added to the other test tube and no crystals formed, but CuI gradually built up into a dense red suspension.

Treatment of the blue crystalline material with HNO_3 and HCl released the ammonium molecule and reduced the solid to pure silver iodide as identified by x-ray diffraction. Treatment of the residual solution from the generator tank with HNO_3 and boiled down resulted in a release of NO_2 gas as well as pure iodine. The red color of the original residual generator solution also indicated a high concentration of either CuI or iodine.

The most important aspect of the reaction involved the presence of water. In the dry solution, absolutely no blue crystalline material was precipitated, whereas with water there was profuse precipitation of this compound. The etching of the copper and coating of it by pure silver occurred to some extent in both cases.¹ This reaction took place within a few minutes of the addition of copper to the solution.

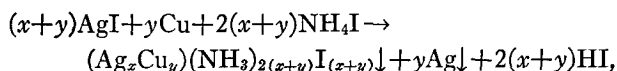
3. Chemical reaction involved

Because of the position of copper, iron and zinc relative to silver in the electrochemical series for aqueous solutions, it appears that the addition of the water provides the electrical bridge necessary for solution of copper and deposition of silver on internal copper-bearing parts of the generator tank.

The silver and copper diamine complexes, $\text{Ag}(\text{NH}_3)_2^+$ and $\text{Cu}(\text{NH}_3)_2^+$, appear to be the prevalent ion species

¹ The replacement of Cu by Ag in "dry" acetone solutions may be due to traces of water as well as the polar nature of the acetone molecule.

in these solutions. Both copper and silver appear to be in the univalent state. Immediately upon the introduction of metallic copper to the initial solution containing AgI, NH₄I, and H₂O, all dissolved in acetone (CH₃CO CH₃), a surface layer of copper is dissolved and replaced by metallic silver. After a certain amount of copper has dissolved, the complex diamine compound precipitates as the blue crystalline material. We suggest the reaction to be



which describes a solid solution diamine complex of Cu and Ag with both cations in the reduced (monovalent) state. Here x/y is probably about 4. The crystallites precipitated out are stable indefinitely out of solution. The process will continue as long as copper ions are able to diffuse through the deposited silver layer and initiate the crystal precipitate. Since the reaction is also dependent upon the presence of water, the rate of the reaction is a function of the concentration of water within the solution.

We have also tested various types of stainless steel, iron and zinc in these same solutions. The only observable reaction within the two-week period of the tests is severe corrosion of the iron. However, silver solder yields a white flocculent precipitate of unknown composition over a period of several days and is therefore not recommended for use in construction of the generator.

4. Effect of the problem on cloud nucleation properties

The primary effect of the above chemical reaction on the generators was the plugging of the lines caused by

the formation of the precipitate. In addition to this problem, it can be noted from the above reaction that the formation of the precipitate will result in a reduction of the concentration of silver iodide in the solution and will therefore tend to create a deleterious effect on the nucleation ability of the generator output.

5. Recommendations

It is our recommendation that field programs involving the use of these solutions take the following precautions:

- 1) The water concentration within the solution must be kept to the absolute minimum required for the solid components to dissolve (2% H₂O in the case of 10% AgI and 3% NH₄I in acetone).
- 2) All parts including the solution tanks and flow lines should be constructed of stainless steel.
- 3) It is advisable that solutions not be stored in the generator tanks for long periods of time (weeks). Even with stainless steel, corrosion may slowly take place.

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