Ice in the Capillaries of Solid Particles and its Effect on their Nucleating Ability[1]

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ABSTRACT

The ice forming ability of solid particles was tested at −2 to −3C after first cooling them to −35 to −78C. During the cooling process, the water vapor pressure over the solid particles was kept below ice saturation, in order to avoid any ice formation on them. All of the treated samples of nine test materials showed ice-forming ability at −2 or −3C which is much warmer than their ordinary threshold temperatures. This ability was lost after warming above 0C.

1. Introduction

Many kinds of wettable or partially wettable solid particles can allow condensation of water in their capillaries even when the ambient humidity is below the saturation value; this, of course, is predicted by the well known Kelvin formula. It was expected from the experimental study on freezing of water sorbed on silica gel (Barnes, 1962) that condensed water in the capillaries might freeze at a temperature lower than −35C. Once frozen, the ice in the capillary might remain to act as an embryo for ice crystal growth even after warming the particles to a temperature near 0C, as has been discussed by one of the authors (Fukuta, to be published).

Since the formation of ice crystals on the particles is not necessary in this case, this can be regarded as a different activation process of ice forming nuclei from the 'pre-activation' reported by Fournier d'Albe (1949), Mossop (1956), Mason and Maybank (1958) and Serpolay (1959) where various substances acted as ice forming nuclei after having an ice crystal formed on them. But, it seems to be related to the activation of a frost-point hygrometer reported by Dobson (1949). Some experiments were carried out to study this activation process, and will be described in this paper.

2. Experiments

Relative humidity of air over silica gel. In order to make clear the difference between the activation process in this case and that reported by Fournier d'Albe and others, any ice formation on the solid particles should be avoided during cooling. Silica gel has the property of keeping the relative humidity nearly constant during cooling, since the radius of curvature of a water surface in a capillary does not change much with temperature. This property was confirmed by measuring the amount of water vapor in air passed through silica gel by the use of a Moisture Monitor (Type 26-303 of Consolidated Electrodynamics Corporation).

The samples of silica gel were tested after keeping more than a week in a desiccator where the relative humidity was kept at 40 per cent at room temperature by the use of sulfuric acid of known concentration. Silica gel prepared in this way was used in the experiments described in the following section. Although the ratio of the volume of water vapor to that of air changed from 2.2 ppm at −60C to 2666 ppm at +2C, the relative humidity was nearly constant with respect to water during the cooling process, and constant with respect to ice during the warming process, as seen in Fig. 1. It is certain, therefore, that the relative humidity did not reach ice saturation during cooling to −60C, or after keeping the sample at −78C for over 10 hours. This property of silica gel thus provides a method of cooling the solid particles without ice forming on them.

Activation of solid particles by cooling below −30C. The ice-forming ability of solid particles was tested at −2 to −3C after first cooling them to −35 to −70C. During the cooling process, the water vapor pressure over the sample was kept below ice saturation, the solid particles being kept in a small air-tight plastic box containing silica gel in a small silk bag.

The following samples were tested qualitatively; illite, kaolin, mica, montmorillonite, silica gel, stony meteorite, volcanic ash, clay and soil. All of the treated samples of these materials showed ice forming ability at −2 to −3C, a temperature much warmer than their ordinary threshold temperatures. This ability was lost after warming above 0C. It was also confirmed that the treated samples retained their ice forming ability for more than two months when kept at a temperature below 0C and a humidity below ice saturation.

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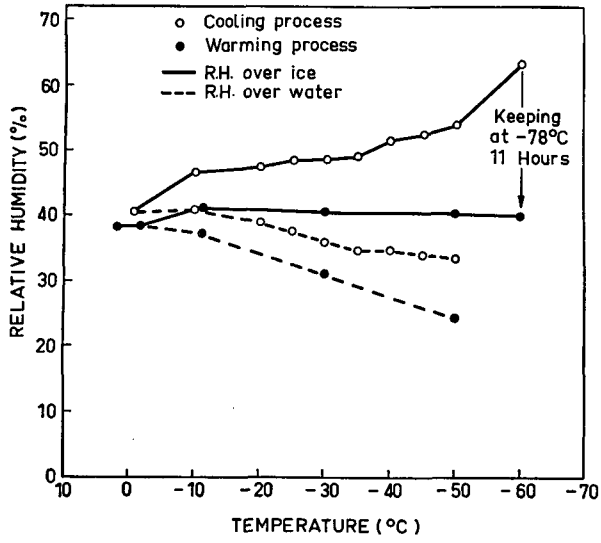

FIG. 1. Relative humidity of air passed through silica gel which had been kept in a desiccator at a relative humidity of 40 per cent and room temperature.

A further study was made to determine the percentage of solid particles activated by this treatment. After dispersing the particles into a big beaker, the solid particles were collected at the bottom of the beaker on thin metal foil 3 cm in diameter which had been deactivated with paraffin wax. The period of sampling selected was 3 min, measured 30 sec after dispersal, in order to select the larger particles suitable for counting under a microscope. A millipore filter, set among the metal foil samplers, was used for microscopic sizing and counting the particles. The particles used in the following experiments ranged from 1 to 10 μ in diameter.

Each metal foil sampler was put into a small air-tight plastic box containing silica gel, and cooled slowly by dry ice in a big vacuum jar. After cooling, the samples were allowed to warm up in a cold box. When enough time had passed to ensure thermal equilibrium between the samples and the air in the cold box, the metal foil samplers were transferred from the plastic box to a metal tray deactivated by paraffin wax. The ice forming ability of the particles was then detected after supplying water vapor from a wet filter paper or a water bag of sausage skin. The ice-coated particles are then easily counted by pouring a super-cooled solution of polyvinyl alcohol or sodium silicate over them as in the usual method of developing millipore filters (Bigg *et al.*, 1963).

Montmorillonite, volcanic ash from Mt. Agung, Bali, and kaolin were used as samples because of their suitable particle size for dispersal. When the samples were developed at −2 to −3C, the number of the particles retaining their activation acquired by cooling to −45C to −70C was roughly one particle per thousand, or 0.1 per cent. This value is an order of magnitude higher than the concentration of ice crystals produced at this

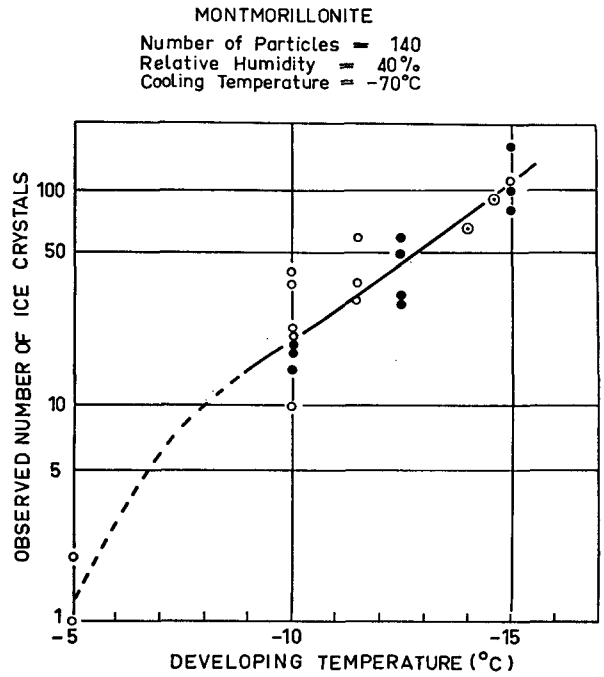

FIG. 2. Dependency of retention of activation of montmorillonite particles on the developing temperature used for detection of their ice forming ability.

temperature by the most effective natural ice nuclei (Mossop, 1963), but still fairly low in comparison with expectation on the basis of the many capillaries in the solid particles.

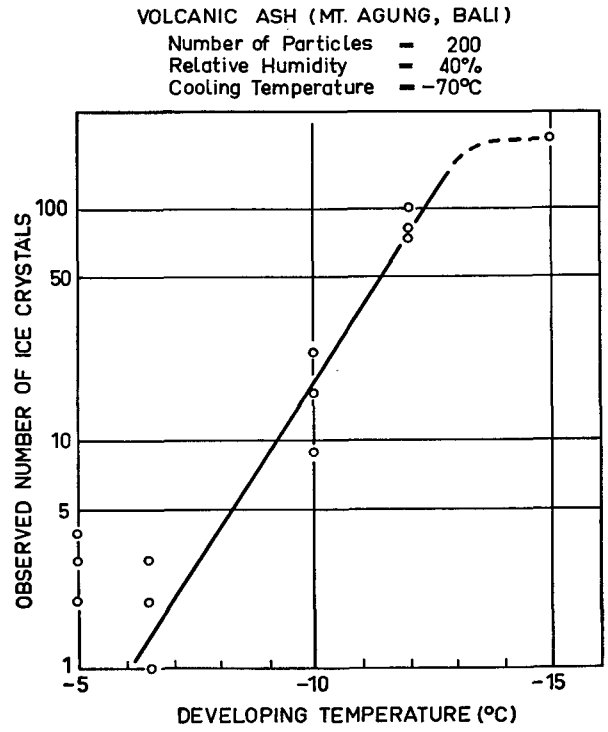

FIG. 3. Dependency of retention of activation of volcanic ash particles on the developing temperature.

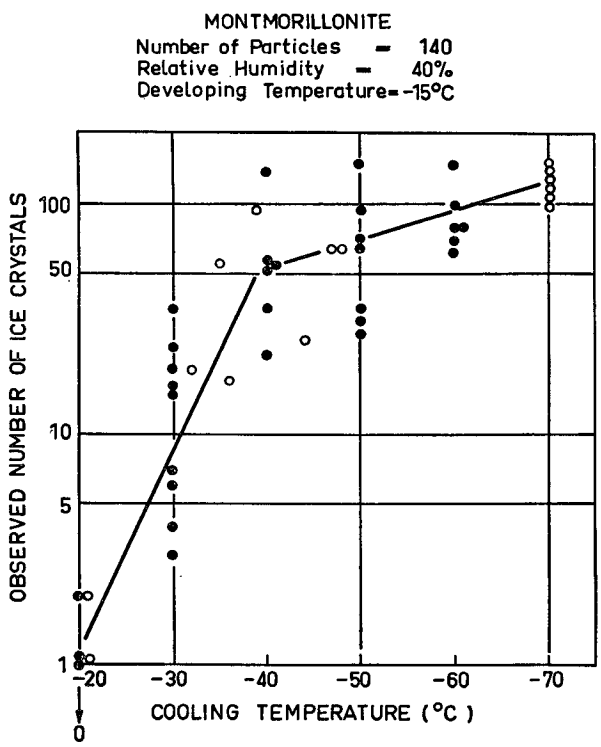

FIG. 4. Dependency of activation of montmorillonite particles on the cooling temperature.

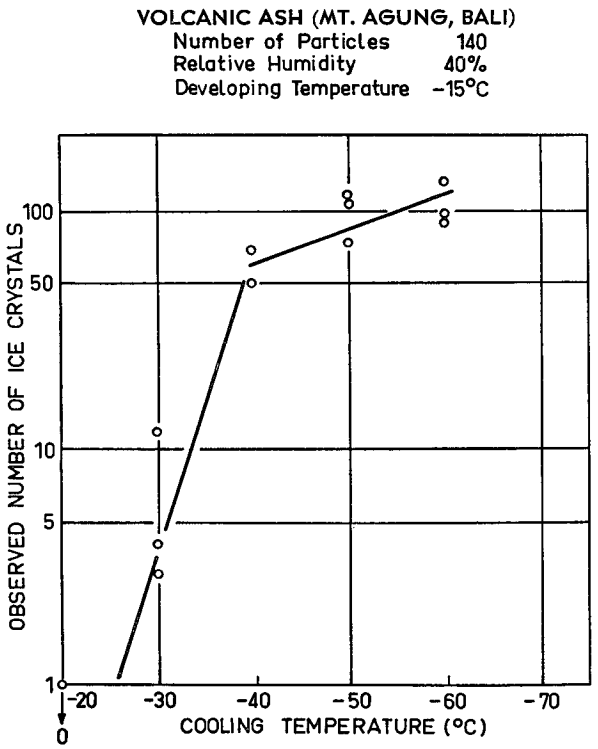

FIG. 5. Dependency of activation of volcanic ash particles on the cooling temperature.

It was decided, therefore to develop the treated samples at various temperatures. Fig. 2 shows the results for the case of montmorillonite. As seen in this figure, when the particles are cooled to −70C and developed at −15C nearly 100 per cent of them retain their activity, but the proportion decreases sharply at warmer temperatures.

The white circles with center point represent development after the samples had been kept at that temperature for over three days, and show how their activity is retained. Similar results were obtained with volcanic ash, as shown in Fig. 3. But, in the case of kaolin, this tendency was more pronounced than for the other two substances. When kaolin particles are cooled to −70C, nearly 50 per cent of them retain their activity at the developing temperature of −20C, but only 10 per cent at −15C. The reason for such a remarkable dependency of retention of activation on developing temperature is not at present clear, but may be due to the lowering of the melting point of ice in the capillaries because of capillary effect (Fukuta, to be published) or the existence of some impurity in it.

It was for this reason that the dependency of activation on cooling temperature was tested using a constant developing temperature of −15C. During the cooling process, some samples were transferred from the vacuum jar to the cold box for development at −15C, when the temperature of the samples reached −20C, −30C, etc.

The results in the case of montmorillonite are shown in Fig. 4, in which "cooling temperature" means the temperature when the samples were taken out. As easily seen in this figure, the number of activated particles increases sharply between −20 and −40C, with a gradual increase to the maximum value of nearly 100 per cent at −70C. Fig. 5 shows the results in the case of volcanic ash.

In order to check the effect of change in the cooling treatment, some samples were developed after keeping them at a constant temperature over 11 hours. The results, shown by the white circles in Fig. 4, were not much different from those obtained by the cooling process described above.

3. Conclusion

The results demonstrate the existence of an activation process of the ice forming ability of solid particles under rather dry and very cold conditions. Such activated particles can retain their ice forming ability for a long time, thus differing from what Day (1958) showed to be a brief retention of the 'preactivation' described by Fournier d'Albe and others.

Since ice in the capillaries of the solid particles is the source of their ice forming ability, this activation process might not depend on the property of the particles, but only on their surface characteristics, such as low contact angle, existence of capillaries, pores, crevices or even gaps between the primary particles of an aggregate.

We can expect the occurrence of this activation process in the upper atmosphere where the temperature is below −40C and relative humidity over 40 per cent. It may be reasonable, therefore, to consider that a

number of activated solid particles exist in the air at levels where the temperature is below 0C.

Such particles would not be detected by the established technique for counting of ice forming nuclei in sub-zero air, in which the air is first heated above 0C to avoid ice particles, formed possibly on the intake tube, being carried into the equipment.

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