CLOUD SEEDING POTENTIAL OF INDUSTRIAL PARTICULATES

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Abstract. Bulk nucleation testing of kiln and stack effluent from several mineral processing facilities near Calgary, Alberta indicates the presence of anthropogenic ice nuclei. Many of the samples tested activate above -7.7°C and have a theoretical crystal chemistry similar to that of silver iodide and natural ice. Stack effluent captured by pollution control devices is considered to be a waste product but may have potential for use in directed cloud-seeding operations.

1. INTRODUCTION AND BACKGROUND

At Exshaw, Alberta, 80 km west of Calgary and only minutes from the eastern entrance to Banff National Park, there is a large mineral processing complex (Figure 1). In operation since the late 1800's and pre-dating the park, the complex currently includes four facilities that produce cement, quicklime and magnesium oxide from local mineral deposits. These

Figure 1. The mineral processing complex at Exshaw, Alberta.

industries also emit large quantities of waste heat, water vapour and airborne particulate matter, including ice nuclei (IN) as discovered during *ad hoc* Alberta Research Council airborne particle sampling flights in 1985 (Heimbach, 1986).

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In a subsequent climatological impact study (O'Dowd, 1994) it was postulated that such nuclei, likely from the cement producing facility, may modify the weather downwind at Calgary (Figure 2) and emission rates were correlated with regional precipitation anomalies. Results, however, were inconclusive as to the role of ice nuclei from the cement plant - the statistical significance of differences between measured and predicted precipitation amounts at Calgary varying according to the testing technique. T-test results were indicative of no differences at a 0.05 significance level, whereas Mann-Whitney U-test results were supportive at the same significance level.

It was further postulated (O'Dowd, 1994) that these results could be the consequence of additional sources of ice nuclei, unidentified during the original airborne investigations. To explore this hypothesis further, a physical experiment to test nucleating ability of Exshaw aerosols was designed. The experiment made use of factory supplied kiln and stack effluent samples obtained in June and July of 1994, and followed the procedures used by Murty and Murty (1972,1974) in establishing the effectiveness of Portland cement and quick lime as ice nucleants.

2. EQUIPMENT AND TECHNIQUE

The highest (warmest) temperature at which a particle acts as an ice nucleator is considered to be its activation temperature. This threshold value at which nucleation occurs is commonly used in comparing the effectiveness of various suspected nucleators. Much of the classical work in this field explores contact nucleation (collisions between supercooled cloud droplets and suspect ice nucleating agents), and uses some form of cloud chamber (e.g. Mason and Hallett, 1956; Fukuta, 1958; Langer and Weickmann, 1971; Mason, 1971). Bulk freezing (immersion of suspect nucleating agents in progressively cooled droplets) has also been explored (e.g. Price and Gornick, 1967; Vali, 1971), but to a far lesser extent.

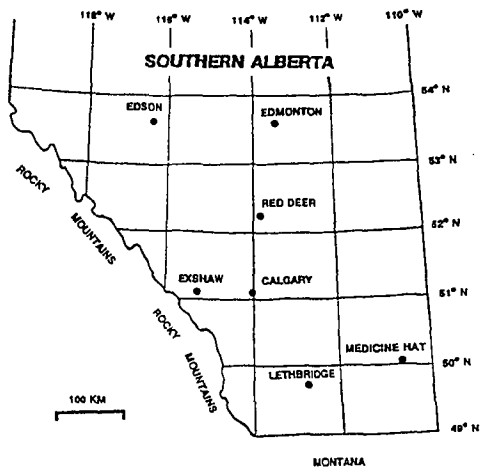

Figure 2. *Map of southern Alberta. Exshaw is located 80 km west of Calgary.*

The advantages of bulk freezing experiments are twofold: the experimental equipment required can be fairly unsophisticated, inexpensive and robust, and where only activation temperatures are sought, experiments can be quickly run and repeated easily. The primary disadvantage of such experiments is that it is often difficult to produce droplets of identical size, particularly where the surface tension of the droplet is effected by differing water soluble nucleating agents. A second disadvantage is that bulk freezing of larger droplets (e.g. 2 mm diameter) is not representative of actual cloud nucleation situations, where the largest cloud droplet rarely exceeds 0.2 mm in diameter, and where most are closer to 0.02 mm (Dennis, 1980).

Drops of 2.4 mm diameter, produced from a freshly prepared aqueous suspension of 2 grams of oven-dried sample in 200 ml of distilled, de-ionized water, were placed on an ordinary glass (50 x 75 mm) slide. A 1.0 mm pipette was used to produce the drops. The slide was transferred to the Styrofoam and Plexiglas insulated stage of a commercial Peltier-effect cold plate, and a thermistor lowered into contact with the slide (Figure 3). To ensure representative contact and to limit sensor lag, the thermistor was lowered into a pre-cooled (0°C) droplet of ethylene glycol and water (1:1). The glycol insured that the sensor droplet would not freeze. The droplets were continuously observed visually with a magnifying glass through crossed polarizing filters during the cooling process, and the temperature (calculated from thermistor resistance) and time of both the first and last freezing events were noted. Unfrozen droplets would appear dark, whereas frozen droplets, due to birefringence, would appear bright and coloured. The experiment was repeated at least five times, and the droplets were under observation for up to ten minutes, subject to whether total nucleation occurred or not. The aqueous suspension was then stored for one full day, and the experiments repeated to test the effect of "aging" (hydration or dissolution or chemical recombination).

Fluctuations in stage temperature, acute during the positioning of the slide and thermistor, were partially dampened by the use of a 6 mm thick brass plate on the stage. The stage was allowed to come into thermal equilibrium before each experiment, and it was subsequently found that a measured slide temperature of -7.7°C was the cooling limit for this particular apparatus, confirmed by glass thermometer and thermocouple means. Below this limit, the measured temperature would oscillate, and sustained cooling was no longer guaranteed. The thermistor was calibrated for 0°C in an ice water bath at the start of each experiment.

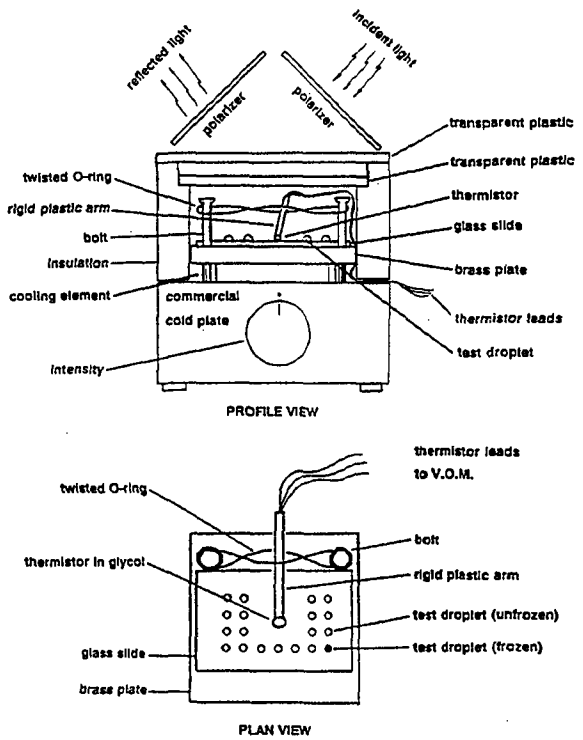

Figure 3. *Schematic of equipment used in bulk nucleation experiments.*

3. TESTED MATERIALS

At the time of the airborne sampling missions, three separate mineral processes took place at Exshaw, each under the auspices of a separate company: Lafarge Canada Inc. (Lafarge) producing cement, Baymag (Baymag) producing magnesium oxide using the

former Lafarge kiln 3, and Continental Lime Ltd. (Continental) producing quicklime and crushed limestone. A fourth facility has since been built by Baymag to produce magnesium oxide through electric arc furnaces. This facility was not in operation at the time of the Alberta Research Council sampling flights.

For the purpose of inadvertent weather modification investigation, only stack samples were considered important, although both kiln and stack samples were tested. Stack samples consisted of particulates trapped by factory emission control equipment (electrostatic precipitators (ESP) and wet-process scrubbers), and were not samples taken from the stacks themselves. Emission control equipment was in operation at the time of the 1985 sampling flights. Fugitive dust of kiln composition, rarely released and then only during loading and shipping operations, was evaluated as an ice nucleating agent for comparison with the results for Portland cement and quick lime (CaO) obtained by Murty and Murty (1972,1974). All samples were "aged" for 24 hours and then re-tested. All facilities liberate significant quantities of water vapour and coupled with high exhaust gas temperatures, solid particles could be expected to undergo accelerated hydration or dissolution during release.

In addition to industrial products and by-products, two other materials were tested: silver iodide and pure water. Commercially available purified silver iodide (AgI) was used as a warm temperature control, having a high activation temperature. For bulk freezing, Murty and Murty (1972,1974) found this to be -4.2°C, and it was anticipated that none of the tested materials would induce freezing at temperatures above this. For a cold temperature control, distilled and de-ionized water was used. Pure water, lacking nucleation sources, can be strongly supercooled, and for small cloud droplets (e.g. smaller than 10 μm) can reach temperatures as low as -40°C before homogenous nucleation occurs (Mossop, 1955). Murty and Murty (1972) found that 2.2 mm diameter double distilled water droplets would not freeze at temperatures as low as -9.8°C and Mason (1971) noted that 2.0 mm droplets could be supercooled to as low as -35°C.

4. RESULTS

The results for pure water (distilled and de-ionized) were consistent with those of Murty and Murty (1972), with no initial nucleation observed in the course of maximum droplet cooling. However, in an earlier series of preliminary test runs using pure water drawn from an open beaker, an average activation temperature of -3.9°C was observed. This value may be attributable to either accidental mechanical nucleation due to hoar frost or scratches on the cooling surface, or to contamination by atmospheric dust particles. Vonnegut (1947) speculated that airborne silver particles caused by sparks at silver or silver-bearing copper electrical contacts may be naturally present in laboratory air. To minimize this possibility, all mixtures were prepared and drawn from covered erlenmeyer flasks. The failure of pure water to freeze in these experiments provides confidence that accidental laboratory-sourced nucleation was not occurring. Nucleation results are presented in Table 1.

The results for silver iodide (AgI), one of the most commonly used commercial cloud seeding agents, were initially puzzling. Nucleating at an average temperature of +1.8°C, the results indicated equipment response lag - specifically the inability of the thermistor to cool rapidly enough to match the temperature fall of the slide containing the sample droplets. Inspection of the cooling curve (Figure 4) suggests that this lag was most pronounced during the first two minutes of cooling from room temperature to -5.0°C. Murty and Murty (1972, 1974) found the average activation temperature for bulk freezing of AgI to be -4.2°C, suggesting a possible 6.0 C° equipment lag. Consideration was given to adjusting all measured values by this lag value, but rejected due to (1) uncertainty of AgI particle size information believed to effect bulk nucleation temperature (Fletcher, 1959), (2) strong confidence in measured values below -5.0°C, and (3) a design objective that stressed the rank of potential Exshaw nucleators in light of inconclusive results from an earlier study (O'Dowd, 1994). Measured activation temperatures above -5.0°C are likely to be too warm, but the majority of readings fall

TABLE 1: Nucleation Results

Fresh Sample Results			Aged Sample Results		
Rank	Particle	Average Activation	Rank	Particle Type	Average Activation
1	AgI	+1.8	1	AgI	+1.3
2	Continental Scrubber	-4.9	2	Baymag Kiln	-4.3
3	Baymag ESP	-6.1	3	Baymag ESP	-4.7
4	Lafarge ESP A	-6.1	4	Lafarge Kiln	-5.1
5	Lafarge Kiln	-6.4	5	Continental Scrubber	-5.4
6	Lafarge ESP B	-6.7	6	Lafarge ESP A	-6.3
7	Baymag Kiln	-7.3	7	Lafarge ESP B	-7.0
8	Continental Kiln	-7.5	8	Continental Kiln	< -7.7
9	Pure Water	< -7.7	9	Pure Water	< -7.7

below this, supporting all rank and most absolute activation values for the Exshaw particulates.

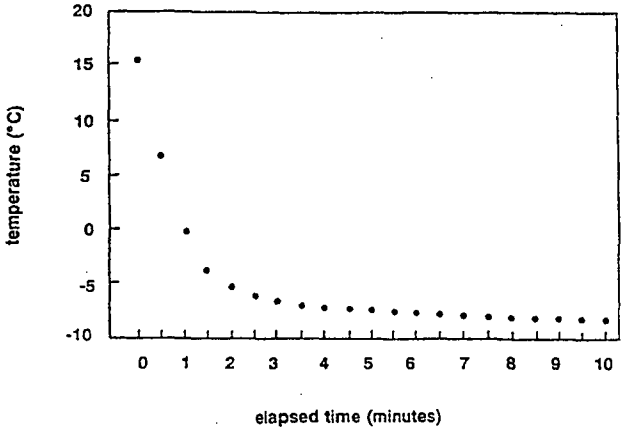

Figure 4. Bulk nucleation apparatus cooling curve.

In cases of identical temperatures, samples were further ranked by the number of test runs that failed to induce nucleation, where applicable.

5. DISCUSSION

The ability of any of the Exshaw particles to induce freezing is a function of a number of particle properties. These properties, summarized by Thangaraj et al. (1988), include (1) lattice match and crystal morphology, (2) solubility, (3) particle size, (4) polarizability, (5) hydrophobicity and hydrophilicity, (6) surface charge, and (7) number and strength of surface sites capable of adsorbing water molecules.

In the classic work carried out by Vonnegut (1947), lattice match was investigated, with silver and lead iodides (AgI and PbI_2) determined to be similar to ice and consequently have nucleating potential. When water freezes it forms a hexagonal crystal with an a-axis length of 4.523 Å, a c-axis length of 7.367 Å, and an a:c axis ratio of 1:1.629 (Pounder, 1965). AgI occurs in three forms at standard temperature and pressure - hexagonal iodyrite, hexagonal silver iodide and cubic miersite, the latter weakly soluble in water (Weast, 1989). The a:c axis ratios for the hexagonal forms are 1:1.635 and 1:1.633 respectively, and both have a unit crystal size approximating that of ice. Crystal and chemical considerations are discussed below on a source-by-source basis.

5.1 Continental Discussion

The isometric Periclase group crystal lime (CaO), formed during the calcination of limestone ($CaCO_3$), is believed to be the primary mineralogy in Continental kiln and stack samples. CaO is a non-ideal ice nucleator. Its size and symmetry differs from that of ice and its activation temperature is low. On hydration, the nucleating potential of CaO decreases even further and may be attributable to a reaction with dissolved carbon dioxide (CO_2) in which some of the CaO reverts back to a hydrated parent calcite ($CaCO_3 \cdot nH_2O$) form. Although the $CaCO_3$ substrate is hexagonal and a potential nucleator at -7 °C (Mason, 1971), it appears that the sheath of water molecules increases the crystal size and changes the axis ratio sufficiently to impair its nucleation as observed.

5.2 Baymag Discussion

The isometric crystal periclase (MgO) is believed to be the primary mineralogy of Baymag kiln and stack samples. Formed through the calcination of magnesite ($MgCO_3$), MgO unit cell crystals are smaller than ice crystals, and like CaO are non-ideal ice nucleators. On hydration, however, their nucleating ability improves significantly. This change is most likely attributable to the formation of the intermediate hydration product brucite ($Mg(OH)_2$). Brucite is hexagonal and forms clusters of thin platelets. Base crystals are smaller than ice, but have a similar a:c axis ratio. In time, however, brucite will react with periclase and dissolved carbon dioxide to form the hydration product hydromagnesite (e.g. Deer et al. 1967). Hydromagnesite occurs in several orthorhombic and monoclinic forms according to the number of bound water molecules, and is likely a non-ideal nucleator.

5.3 Lafarge Discussion

Unlike Continental and Baymag, the kiln and stack samples of Lafarge are highly heterogeneous in terms of chemistry and morphology. The nucleation improvement on hydration observed for the kiln product, near-Portland cement, and the decay in nucleation observed for both types of Lafarge stack sample also suggests a compositional difference between these two particulate streams.

Unhydrated Portland cement has four main constituents (Bye, 1983):

1) tricalcium silicate	Ca_3SiO_2
2) dicalcium silicate	Ca_2SiO_2
3) tricalcium aluminate	Ca_3AlO_3
4) tetracalcium aluminoferrite	Ca_4AlFeO_3

Of these constituents, dicalcium silicate has the best crystallographic potential as nucleator, with two stable hexagonal forms (Donnay, 1963). With an average a:c axis ratio of 1:1.238 and an a-axis length of 5.460 Å, the unit cell dimensions are similar although not identical to that of ice and AgI.

On cement hydration, or, more properly, hydrolysis (Bye, 1983), the tricalcium and dicalcium silicates

slowly form calcium hydroxide (portlandite) and several poorly crystalline calcium silicate xerogel hydrates. Portlandite, the calcium-substituted parallel of brucite, is a hexagonal layered mineral and forms flat platelets (Bye, 1983) resemblant of snowflakes. However, portlandite unit crystals are smaller than AgI or ice crystals and have, like dicalcium silicate, a slightly different a:c axis ratio (1:1.332). Tricalcium aluminate also forms intermediate crystalline hydration products of hexagonal symmetry. Resembling portlandite, these form very quickly (within hours) during a strong exothermic reaction but ultimately convert to a more thermodynamically stable cubic form (Ramachandran, 1984). This intermediate hexagonal phase is believed to be responsible for the nucleation results observed. The di- and tricalcium parented portlandite crystals take up to a year to form (Eglington, 1987) and are unlikely to have contributed to nucleation.

It should be noted that Lafarge stack ESP particles are not necessarily of the same composition as kiln products and may even differ from the actual solids released as stack effluent. There is evidence that cement ESP capture is enriched in hygroscopic alkali chlorides and sulphates (Portland Cement Association, 1992), whereas calcination stack emissions (e.g. Baymag and Continental) are likely to contain limestone, dolomite and clay impurities found in both source rocks and kiln product.

5.4 Commercial Applications

It has long been recognized that for directed cloud-seeding operations insoluble particles are among the best nucleating agents (e.g. Fukuta, 1958; Dennis, 1980). Unlike soluble particles, they theoretically remain isochemical and isomorphic and react in a predictable manner. The results of this study, however, suggest that kiln and stack waste products from some of the Exshaw operations, despite being polychemical, polymorphic and in some cases, exothermically reactive and partially soluble, could be employed as low cost alternative cloud-seeding agents.

The apparent usefulness of the Exshaw industrial particulates, kiln and stack alike, is evident from the ranking shown in Table 2. These values are based on the average activation temperatures from Table 1 but with the additional requirement that *every* test run exhibit activation. Baymag aged kiln results (-4.3°C), for example, are not included as one-third of the trial runs failed to show any nucleation and freezing. In support of this ranking system, it was noted that an alternative ranking based on the highest (rather than the average) initial nucleation temperature produced virtually the same results, with only minor switching at the scale extremes. From the results in Table 2, the more chemically and morphologically predictable Baymag and Continental kiln and stack products would be the best commercial ice nucleating choices.

While the preceding discussion is in relation to cold, continental-type cloud processes in which ice nuclei are effective, it should be reiterated that cement ESP capture is potentially enriched in hygroscopic salts and may be useful as a cloud seeding agent in warm, maritime-type clouds. Today, hygroscopic flares are being used operationally in a number of rain-enhancement projects world-wide, including Texas, particularly where the ice-nucleation process is absent or limited or where benefit from a combined seeding process above *and* below the freezing level is merited.

TABLE 2: Ranked industrial nucleation potential

Rank	Type	Average Nucleation Temp. (°C)*
1	Baymag ESP (hydrated)	-4.7 (-3.7)
2	Continental scrubber (dry)	-4.9 (-3.1)
3	Continental scrubber (hydrated)	-5.4 (-4.1)
4	Lafarge ESP A (dry)	-6.1 (-4.8)
	Baymag ESP (dry)	-6.1 (-5.6)
5	Lafarge kiln (dry)	-6.4 (-6.3)
6	Baymag kiln (dry)	-7.3 (-6.1)

* Highest Initial Nucleation Temp. in brackets.

Well documented ice nucleating materials such as AgI, PbI_2 and biogenic nucleators such as *Pseudomonas syringae* activate at temperatures warmer than those measured for the Exshaw particulates. *Pseudomonas syringae*, for example, has been documented to trigger activation at temperatures as warm as -2.0°C (for a comprehensive summary see Szyrmer and Zawadzki, 1997). However, the low cost of the tested kiln and stack products and the virtual ubiquity of calcining and cement operations around the world makes these products an attractive cloud-seeding option. Injected into existing industrial exhaust stacks (e.g. power plants, steel mills) upwind of target areas, solid particle injection seeding (SPINSEED) offers significant cloud-seeding benefits, especially where aircraft operations are constrained by night-time, weather or airspace limitations.

6. CONCLUSION

The key objective of these activation experiments was to rank the ice nucleating abilities of anthropogenic Exshaw particulates to help determine whether the ice nuclei detected in the 1985 aerial sampling flights (Heimbach, 1986) were from a single industrial source. Results suggest that all Exshaw industries produce anthropogenic IN, supporting bias in an earlier study (O'Dowd, 1994) where anomalous downwind precipitation was inconclusively correlated with

upwind cement plant production. Output from Lafarge and Baymag stacks would seem to have about the same nucleating potential, although in terms of overall mass, the Lafarge facility produces more than twice as much particulate material as Baymag and ten times as much as Continental.

The secondary objective of this study was the quantification of the nucleating potential of the Exshaw particulates for comparison with well known commercial ice nucleators. Activation temperatures suggest that some of the stack and kiln products have potential as commercial cloud-seeding agents. If mechanically injected into existing high velocity gas streams, the SPINSEED process may offer weather modification advantages in terms of both material and application cost.

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