COMMUNICATIONS TO THE EDITOR

Freezing Droplets of Aqueous Solutions for the Cryochemical Process

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A cryochemical method has been described employing solution techniques originally developed for preparing ceramic oxides (*1*, *2*). Essentially this consists of freezing and then freeze drying droplets of analyzed aqueous salt solutions of the starting materials. The principal merits of this development are that: 1. freeze drying is simple and clean, 2. precise formulation is achieved with the use of high purity reagents, 3. minor components can be added with assurance of uniform distribution, 4. the powder particles are homogeneous in composition, and 5. fine powders with controlled, large surface area can be readily produced.

It was soon realized that the process could be used advantageously to produce a variety of other products. Filter beds, catalyst beads, and abrasives have been suggested previously (*3*). Pigments, fillers, and desiccants are other obvious possibilities. In similar work at the Bureau of Mines (*4*) the applicability of freeze drying techniques to the preparation of dispersion strengthened alloys has also been demonstrated. Still another interesting study was that of Tseung and Bevan (*5*) who found that the process could be usefully employed to prepare a catalyst composed of relatively volatile lithium oxide reacted at low temperatures with refractory nickel oxide.

More recently this philosophy has found interest in the field of metals treatment and finishing. Potentially attractive economical advantages have been recognized in our industry in the recovery of metals from spent plating baths.

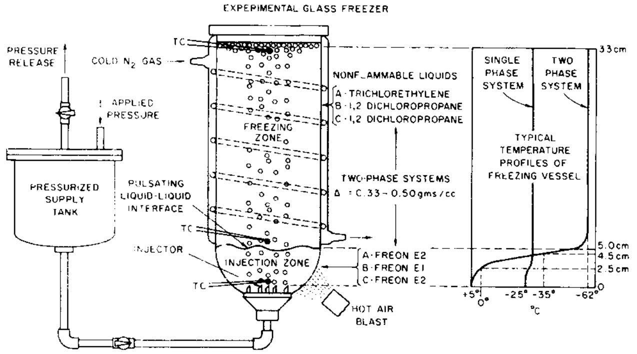

Fig. 1. Freezing of aqueous solutions of salts for the cryochemical process.

In a further application in this field, similar benefits may be realized in the solution of such specific ecological problems as the safe disposal, in solid form, of phosphates and other pollutants in etching and pickling baths.

In one freezing technique (*1*, *2*), a fine broken stream of solution impinges upon the inner wall of the vortex of a cold, rapidly stirred immiscible hexane refrigerant. Hexane is less dense than the solution, thus the frozen small spherical droplets sink to the bottom of the freezing vessel. They are then recovered by a screening operation, freeze dried without alteration of geometrical shape, and subsequently calcined to the oxide.

FREEZING INNOVATION

In a new freezing method, Figure 1, droplets of aqueous salt solution are introduced into the lower region of the freezer.* They rise through an immiscible, nonflammable refrigerant of higher density than the solution, freeze and float as individually identifiable spherical droplets to the top of the liquid column. This technique can be successfully practiced if the temperature of the refrigerant in the close environment of the injector is maintained slightly above the freezing point of the salt solution to prevent freezing in the nozzle of the injector, and if a sharp negative temperature gradient exists immediately above the injector in order to encourage rapid freezing and to prevent coalescence of the droplets.

This is accomplished in a two-phase liquid system in which the interface is a natural barrier to free convection and to uncontrolled heat transfer, phenomena which would occur in a single-phase refrigerant. The short injection zone is heated in the neighborhood of the injector, while the much longer freezing zone is cooled over its entire length. This establishes a temperature differential between the zones, and a sharp negative temperature gradient in the injection zone. The gradient is maintained by a balance between heat transferred by conduction in narrow zones, or "boundary layers," adjoining the vessel walls and the

* To illustrate the process, a solution of $Al_2(SO_4)_3 \cdot 17H_2O$ was used.

interface between the two fluids. The same qualitative description applies with even greater force to the single-phase case; but convection makes it impossible to maintain the bulk of the fluid at a suitably low temperature if the temperature at the injector is maintained above the freezing point. The appearance of striations, due to large temperature gradients in the flow, also confirms the presence of temperature boundary layers and makes the circulating flow in the lower fluid visible.

The most prominent feature of the flow is the pulsating motion of the interface between the two fluids, which plays an important role in the transfer of heat and momentum across the interface. As one would expect, when the densities of the two fluids are almost equal, the interface becomes unstable and the motion so violent that the interface may actually break up. At the opposite extreme, when the interface is almost stationary, the interfacial boundary layer is thickened and cooled to the point where the droplet stream may have difficulty penetrating it. There is thus an optimum operating range where the interfacial disturbance keeps the boundary layer thin, but is not so pronounced that the interface breaks up.

Some combinations of nonflammable liquids, or liquids which do not sustain combustion at normal ambient temperatures, and which perform well are listed in Figure 1. For example, in the *A* combination, Freon E2 occupies the injection zone, and trichloroethylene, the freezing zone. For these liquids, the range of differential density is about 0.3 to 0.5 g./ml. Also in Figure 1 a typical, useful, and controllable temperature profile is shown for a two phase refrigerant in this experimental freezer. Thermocouples were located as indicated along the vertical axis of the two phases. The profile was determined by probing both phases axially along the entire length of the freezer. A temperature of +5°C. is maintained adjacent the injector; about 1 in. above it, the temperature is 0°C. From this point upward the temperature decreases rapidly to the freezing zone temperature of −62°C. In the operation of this facility it has been found that a freezing zone temperature of −30°C. is usually sufficient to obtain complete freezing and to protect against agglomeration of the floating droplets. The temperature profile included in Figure 1 for a single phase refrigerant in this glass system exemplifies the effect of uninhibited convection and uncontrolled heat transfer while attempting to attain an above freezing temperature at the injector. The temperature of the frozen nozzle is −25°C.; in the freezing zone it is only −28°C., a 3° temperature differential. A baffle for impeding free convection was installed between the injection zone and the freezing zone without appreciable benefit.

The freezing zone is cooled by passing cold nitrogen gas through the annulus of a double-walled zone. The injection region is maintained above the freezing point of the solution by a hot air blast in the lower region of the injection zone or by an electrical heater attached to the injector. The rate of injection of droplets is monitored by varying the pressure of the liquid in a pressurized supply tank. A neoprene "O"ring supports a 5-orifice injector in the neck of the freezer. The dimensions of the extended stainless steel orifices are 0.015 cm. × 1.6 cm. An 18-orifice injector of the same over-all dimensions has been found useful only for low injection rates, at which the droplets are quite large and uniform in size, although shearing forces in the circulating refrigerant cause some variability in diameter. As the rate is increased, the droplets become smaller. At high tank pressures, the droplets are formed by the breakup of a stream of solution forced into the refrigerant. These are much smaller and less uniform in size.

Figure 2 is a pictorial view of the variations in size of freeze-dried aluminum sulfate [$Al_2(SO_4)_3 \cdot 17H_2O$)] droplets with pressure (rate of injection) for the 0.015 cm. orifice. Here the range is from about 2 mm. to 0.5 mm., although it can be extended in the direction of smaller size. The high degree of uniformity of a random sampling of the large droplets is indicated in the histogram of Figure 3 by a narrow frequency distribution. The smaller droplets, Figure 4, exhibit a broader distribution. The variation of average droplet size with injection pressure for two orifice sizes (0.015 cm. and 0.025 cm. in diameter) is shown in Figure 5. As would be expected, the larger orifice provides the larger droplets at any given pressure.

CONVECTIVE BOUNDARY LAYER FLOW

As we have already remarked, it is the combination of interfacial motion maintaining the balance of momentum and energy, together with boundary layers separating the freezing zone from the injection zone, which make the two-phase freezer possible (see Figure 6). By the same token, such boundary layers make a single phase freezer impractical, for they confine the effect of cooling to thin layers near the wall, the bulk of the circulating fluid remaining relatively warm. An estimate of the Grashof number, giving the relative magnitude of buoyant and viscous forces, con-

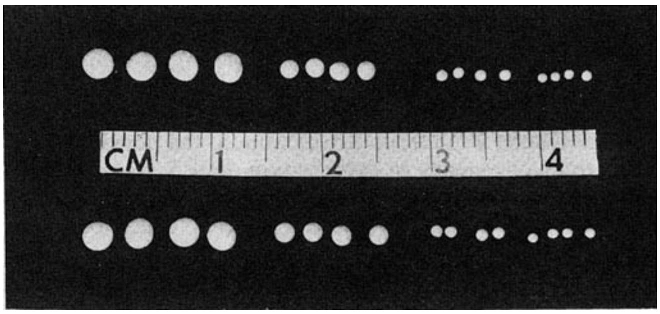

Fig. 2. Freeze dried $Al_2(SO_4)_3$ droplets.

TABLE 1. FLUID PROPERTIES

Freon E2	
Density	1.66 g./cu.cm. (25°C.)
Viscosity*	1.1×10^{-2} poise (25°C.)
	5.0×10^{-2} poise (0°C.)
	2 poise (−50°C.)
Coefficient of thermal expansion	1.5×10^{-3}/°C.
Specific heat	0.24 cal./g.-°C.
Thermal conductivity	2.5×10^{-4} cal./(cm.)(sec.)(°C.)(25°C.)
Trichlorethylene	
Density	1.47 g./cu.cm. (15°C.)
Viscosity†	0.57×10^{-2} poise (20°C.)
	0.64×10^{-2} poise (0°C.)
	0.82×10^{-2} poise (−50°C.)
Freezing point	−86.8°C.
Aluminum Sulfate Solution	
Density	1.1 g./cu.cm.

* Low temperature values found by exponential interpolation between 25°C. and pour point at −123°C.

† Low temperature values found by linear extrapolation from values at 20° and 80°C.

firms that the flow is indeed of boundary layer type. For fluid density $\rho \sim 1.7$ g./cu.cm., viscosity $\mu \sim 5 \times 10^{-2}$ (0°C.) to 2 (−50°C.) poise, thermal expansion coefficient $\alpha \sim 10^{-3}$/°C. (See Table 1), typical length $h \sim 5$ cm., typical temperature difference $\Delta T \sim 50$°C., and acceleration of gravity $g = 980$ cm./sec.^{2},

$$Gr = \rho^2 h^3 \alpha \Delta T g / \mu^2 \sim 10^6 \text{ to } 10^5,$$

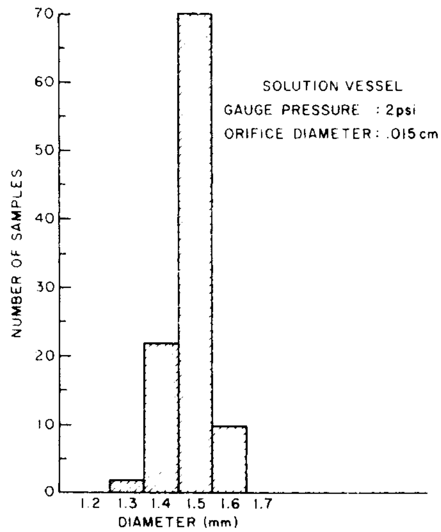

Fig. 3. Droplet size frequency distribution.

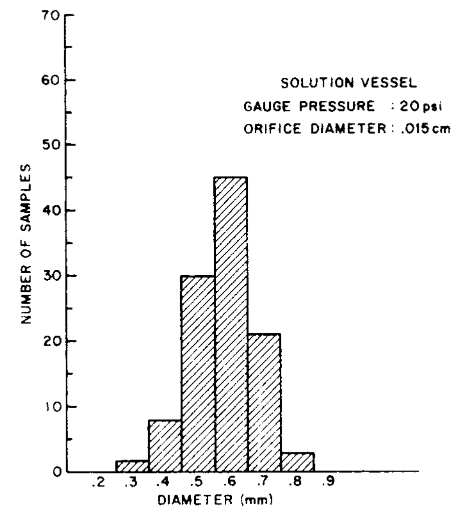

Fig. 4. Droplet size frequency distribution.

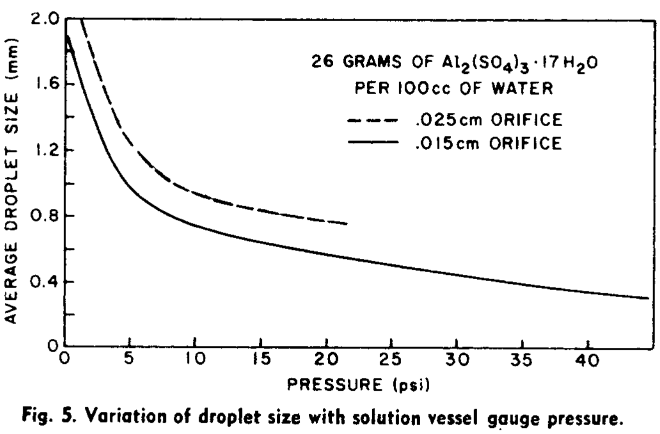

Fig. 5. Variation of droplet size with solution vessel gauge pressure.

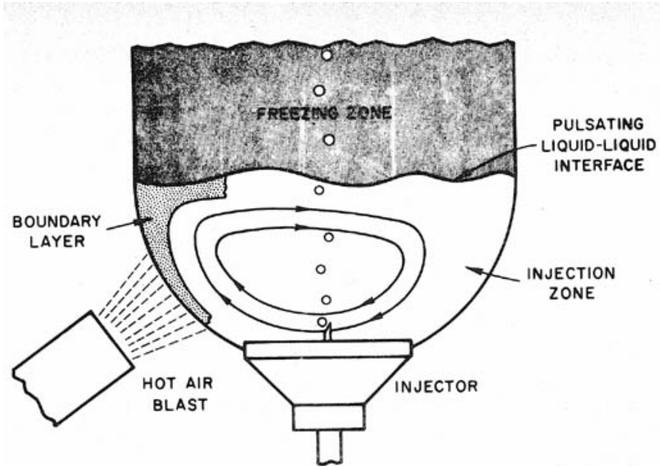

Fig. 6. Convection pattern in injection zone.

certainly large enough for convective boundary layer flow and perhaps even for transition to turbulence. It is the magnitude of Gr which characterizes the flow, so that in scaling one should maintain Gr roughly of the same magnitude.

CONCLUSION

In the cryochemical process for preparing ceramic oxides a new technique has been developed for freezing droplets of aqueous salt solutions. Injection and freezing are conducted in a two-phase liquid refrigerant. The droplets rise in the refrigerant, freeze, and float at the top. The flotation feature in which the droplets can be continuously floated off, readily adapts this method to a continuous process, which could include the drying step, and which can be scaled to plant production.

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NOTATION

g = acceleration of gravity, cm./sec.^{2}
h = typical injector zone dimension, cm.
α = volume coefficient of thermal expansion, °C.
ρ = fluid density, g./cu.cm.
μ = fluid viscosity, poise
ΔT = temperature difference in fluid, °C.
Gr = Grashof number

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