# Production of powders and films by the rapid expansion of supercritical solutions

DEAN W. MATSON, ROBERT C. PETERSEN, RICHARD D. SMITH\* Chemical Methods and Separations Group, Chemical Sciences Department, Battelle, Pacific Northwest Laboratories, Richland, Washington, USA

A new process utilizing the rapid expansion of supercritical fluid solutions (RESS) is described for the production of fine powders and thin films by the rapid nonequilibrium precipitation of nonvolatile compounds from dense gas solutions upon expansion. A variety of the fluid solution expansion parameters, including solute and solvent identity, solute concentration, expansion temperature, and expansion nozzle configuration, has been shown to affect the product characteristics of materials formed during the RESS process. Conditions favouring thin film formation include very dilute solutions and short nozzles minimizing residence time during expansion. Particle formation is favoured by more concentrated solutions. The process has been demonstrated to produce products of widely varying morphology by the adjustment of RESS parameters, and examples of  $SiO_2$ ,  $GeO_2$ , and various polymeric materials are presented. Unique features of the RESS process relevant to other powder and film production methods are described and potential applications are discussed.

### 1. Introduction

A large number of techniques exist for the production of thin films or fine powders for use in a variety of applications. All such techniques, however, have limitations, either in the types of materials for which they can be used, or in the physical form or chemical characteristics of the products. New methods for the preparation of powders and films are needed; both to overcome the limitations inherent in existing techniques, as well as to address new problems arising in technological arenas relevant to the ceramics, electronics and pharmaceutical industries.

We present the initial results demonstrating a new technique which utilizes the rapid expansion of supercritical solutions (RESS) for the production of fine powders and thin films from any material which can be dissolved in a supercritical solvent. Our work to date has shown that fine control of the expansion parameters strongly influences the morphology of the various products. Thus, either fine powders, having a range of mean particle sizes, or uniform films can be produced from the same solute material by varying the conditions under which the expansion is allowed to occur.

In this initial report on the RESS process we briefly review its physical basis and present examples of RESS products. We also compare the RESS process with existing methods for powder and film production to highlight the similarities and, more importantly, its unique features which may provide the basis for the production of new classes of nonequilibrium materials.

### 2. Physical basis of the RESS process

A supercritical fluid is broadly defined as a substance

\*Author to whom all correspondence should be addressed.

0022–2461/87 \$03.00 + .12 © 1987 Chapman and Hall Ltd.

above its critical temperature, where it remains in a single fluid phase regardless of the applied pressure. Pressure does, however, strongly affect supercritical fluid densities, which may approach those of liquids [1-3]. Supercritical fluids are therefore characterized by greatly enhanced solvating capabilities compared to subcritical gases. In addition, however, supercritical fluids have higher diffusion coefficients and extended useful temperature ranges compared to their corresponding liquids. This unique combination of "gas-like" and "liquid-like" solvating properties has been exploited for a variety of specialized applications including extraction, fractionation, chromatography, and chemical reaction processes [1-3].

The enhanced solvating capacities of supercritical fluids allow the dissolution of many materials for which ordinary liquid solvents are inadequate. The transfer of supercritical fluid solutions to subcritical pressures results in the precipitation of nonvolatile solutes as the solution density drops. This phenomenon was first observed more than a century ago [4], and continues to attract attention as a method for powder production [5]. It is precisely this characteristic of solute precipitation from supercritical solution upon very rapid pressure reduction which provides the basis for the RESS process for powder and film formation.

A detailed understanding of the RESS expansion phenomenon and nucleation processes relevant to particle or film formation does not currently exist. Qualitatively, however, the RESS process can be described in terms of the nucleation and condensation of nonvolatile monomolecular solute species which are initially present in the supercritical solution. The



Figure 1 Temperature-pressure diagram for supercritical water showing lines of constant liquid/vapour composition after expansion to low pressures.

extent to which these processes occur during the RESS expansion is influenced by a number of factors and determines the nature of the RESS product. If nucleation and condensation of both the solute and solvent species can be minimized in the RESS jet, the result is the production of a "molecular spray" from which uniform thin layers of the solute can be deposited. When nucleation and condensation of the solute species are favoured by conditions of the expansion, small particles of the nonvolatile solute are formed, and the product is a powder. Variation of the expansion parameters, including solute concentration, allows control over the mean particle size of the resulting powders. The distinction between the RESS powder and film product modes is, however, somewhat arbitrary since films may consist of layers of ultrafine particles, and the total absence of nucleation phenomena is likely only at impractically low solute concentrations. The time involved in particle nucleation and growth within the RESS jet is estimated to be much less than  $10^{-5}$  sec.

Experimental limitations for laboratory-scale work, discussed in greater detail below, have dictated that the expansion nozzle used in our initial studies of the RESS process consist of short lengths of capillary tubing. Some insight into the RESS process can be gained by comparing the RESS expansion in a capillary-type nozzle with the flow of a compressible fluid through a pipe [6]. As a first approximation, the expansion of a supercritical fluid through a short nozzle can be considered to be adiabatic, such that the phase behaviour of the expanding fluid can be predicted for dilute solutions from available thermodynamic data. The fraction of liquid produced during the expansion of supercritical water from various pressures and temperatures has been plotted in Fig. 1. The Joule-Thomson coefficient,  $(dT/dP)_{\rm H}$ , is positive for the expansion of supercritical water and for most other solvents under conditions relevant to the RESS process, and net cooling results during expansion within the nozzle. By controlling the temperature and pressure of the fluid solution at the entrance to the nozzle, the two-phase solvent region can be avoided during the expansion, and solvent clusters or droplet formation can be effectively precluded. The expansion of supercritical water from 600 bar and 550° C avoids the two-phase region, whereas the corresponding expansion from 600 bar and 500° C must result in droplet formation. In general, for reasonable pressures (less than five times the critical pressure) a reduced temperature of greater than 1.3 will avoid intersection of a two-phase region during an adiabatic expansion of most pure solvents.

Between the end of the capillary nozzle and the point at which the RESS jet interacts with background gases in the expansion region, an isentropic expansion phase occurs in which the jet can attain supersonic velocities. Interaction between the jet and background gases produces a shock front perpendicular to the jet axis (the Mach disc), which is characterized by collisional processes serving to heat and break up small solvent clusters (but probably not larger droplets) which may have formed during the earlier stages of the expansion [7, 8]. The distance from the tip of the nozzle to the Mach disc is determined by the system pressure, background pressure, and diameter of the nozzle opening and can be approximated as  $0.67D(P_f/P_b)^{1/2}$ , where D is the nozzle diameter and  $P_f$  and  $P_b$ 



Figure 2 Appearance of the RESS jet (H<sub>2</sub>O) with increasing temperature ( $T_e$ ) of the pre-expansion fluid and at a constant system pressure (~600 bar).

are the respective fluid and background pressures [9]. Under typical operating conditions for the RESS water system, the Mach disc is less than 1.0 mm from the tip of the nozzle, corresponding to an extremely short ( $\ll 10^{-5}$  sec) isentropic expansion period. Beyond the Mach disc there is significant mixing between the RESS jet and the background gas in the expansion region.

Visibility of the RESS jet, resulting from solvent droplet formation, decreases dramatically as the preexpansion fluid conditions approach those for which only a single solvent phase is expected on the basis of the adiabatic approximation (Fig. 1). This effect is illustrated in Fig. 2, which shows the RESS jet produced with a system pressure of 600 bar and various preexpansion fluid temperatures ( $T_e$ ). Formation of the RESS jet under conditions at which only a single solvent phase is produced allows for the deposition of a dry, rapidly quenched solute product.

### 3. Practice of the RESS process

Our initial investigations of the RESS process have utilized high-pressure equipment on a small laboratory-scale to facilitate the study of different solute materials and supercritical solvents. A schematic representation of a typical RESS experimental apparatus is shown in Fig. 3. Although the exact configuration of the system varies, depending on the product (powder or film) or the solvent-solute system, the basic components as shown are common to each RESS apparatus. Solvent is introduced via a pump capable of attaining pressures at least several times that of the fluid's critical pressure. In many studies a high-pressure autoclave containing the solute is maintained at the system pressure, and temperature is used to control solubility. The temperature within the autoclave may be kept above the critical temperature of the solvent, although this is not a requirement for the RESS process. Many systems investigated used subcritical or even ambient autoclave temperatures, depending on the solubility of the solute and the concentration desired. Supercritical conditions must, however, be maintained in the region leading to the expansion nozzle so that the solution is elevated to supercritical temperatures prior to expansion into a low-pressure environment.

The RESS nozzle constitutes a key component in determining the fluid expansion characteristics and, ultimately, product morphology and quality. In the initial RESS studies the nozzle dimensions have been constrained by fluid flux and pumping capacity limi-



Figure 3 Schematic diagram of a typical RESS apparatus.





tations imposed by the laboratory-scale operation. In addition, the type of expansion nozzle which could be used for the supercritical water RESS system was limited by the relatively high pressure and temperature required and the corrosive nature of the solvent. Typically, short lengths (<5mm) of capillary  $(<100 \,\mu\text{m i.d.})$  stainless steel or crimped platinumiridium tubing were used as nozzles with the supercritical water system. The crimped Pt-Ir tubing  $(<5\,\mu\text{m i.d.})$  likely more closely resembled a "pinhole" orifice than the lengths of stainless steel capillary, but are difficult to reproduce and prone to plugging. Short lengths of fused silica capillary tubing (5 to  $50\,\mu\text{m}$  i.d.) were used as expansion nozzles for the lower pressure and less corrosive organic solvent RESS systems. It is anticipated that larger pilot-scale operations of this process will allow the use of more "ideal" machined nozzles. Machined orifices will likely lead to improvements in powder product quality due to reduced particle agglomeration which occurs under some conditions and appears to be an artefact of nozzle wall effects. This should also facilitate more reproducible operation and modelling of the RESS process.

The SiO<sub>2</sub>-H<sub>2</sub>O solute-solvent system was among those chosen initially for investigation of the RESS process for inorganic materials because the solubilities of various polymorphs of SiO<sub>2</sub>, including silica glass, have been extensively investigated and reported in the geochemical literature [10–12]. A solubility diagram of SiO<sub>2</sub> quartz in the near-critical and supercritical regions for water is shown in Fig. 4. The basic features of this diagram represent the solubility characteristics of a large number of materials with respect to variations in pressure and temperature. Solubilities gradually increase with temperature nearly independent of pressure below the critical point. Near the critical point, however, densities change rapidly with small pressure and temperature variations. This density dependence is reflected in the extreme silica solubility variations evident near the critical point of water (374°C and 221 bar) shown in Fig. 4. At elevated pressures ( $\geq 600$  bar) the temperature effect on SiO<sub>2</sub> solubility is less dramatic, and at pressures in excess of 750 bar no solubility drop is observed with increasing temperature above the critical temperature. SiO<sub>2</sub> glass, which was used as the feed material in our  $SiO_2-H_2O$ system, has two to three times the solubility of quartz under the same autoclave conditions, but its solubility characteristics with respect to changes in temperature and pressure are basically the same as those shown in Fig. 4 [11]. To avoid potential complications resulting from the complex solubility behaviour near the critical point, most RESS studies to date have been conducted at pressures several times those of the critical pressure.

## 4. Initial characterization of RESS products

Insight into the potential applications of the RESS process may be gained by observing some of the variety of materials which have been produced to date using this technique. Representative samples are given below to illustrate not only the various types of products that have been produced, but also some of the effects observed by variation of expansion parameters.

### 4.1. Production of inorganic films and powders

At least two distinct modes of RESS film production from inorganic oxides have been identified. Fig. 5 shows scanning electron micrographs of an assortment of silica surfaces which were produced utilizing a crimped piece of platinum-iridium capillary tubing as the expansion nozzle (effective i.d. estimated to be  $\sim 3 \,\mu$ m) under various RESS expansion conditions. These surfaces range from essentially smooth (Fig. 5a) to a highly textured "plate-like" product (Figs 5c, d).



*Figure 5* Scanning electron micrographs of various silica surfaces (films) deposited by expansion of a supercritical water solution using a short length of pinched Pt–Ir capillary tubing as an expansion nozzle. The characteristics of surfaces deposited under these conditions range from essentially smooth (upper left) to having an irregular textured surface (lower right).

The smooth surfaces (or films) were obtained using low silica concentrations (<10 p.p.m.) and low fluid flow rates (<100  $\mu$ l min<sup>-1</sup>). The more textured surfaces were produced using higher fluid flow rates (>150  $\mu$ l min<sup>-1</sup>) and solutions having higher silica concentrations (>400 p.p.m.).

An alternate mode of RESS SiO<sub>2</sub> film deposition is illustrated by the product shown in Fig. 6, where a relatively thick film (> 1.0  $\mu$ m) of silica has been deposited on a Millipore filter. This material was deposited using a capillary-type nozzle (typically 60  $\mu$ m i.d., 5 mm length, and 40 ml min<sup>-1</sup> flow rate) and under pre-expansion conditions that produced a transient two-phase jet. This constitutes a much faster film deposition mode than shown in Fig. 5, and deposition rates of several  $\mu m \min^{-1}$  appear feasible in this mode. The film shown in Fig. 6 was cracked by flexing the substrate, demonstrating the continuous and nonporous nature of the original SiO<sub>2</sub> surface.

Typical examples of  $SiO_2$  particles (powders) deposited from the RESS spray are shown in Fig. 7. The effect of silica concentration in the supercritical fluid solution prior to expansion on the size of particles produced is graphically illustrated in Figs 7a and b. In general, the individual mean particle size increases with solute concentration in the solution prior to expansion. Maximum SiO<sub>2</sub> concentrations of the solutions used to deposit samples shown in Figs 7a and b were estimated to be 200 and 1000 p.p.m. respectively. These concentrations were achieved by maintaining



Figure 6 Film of amorphous SiO<sub>2</sub> (>  $1.0 \,\mu m$  thick) deposited on Millipore filter.

the temperature of the autoclave containing the silica glass feedstock at 75 and 225° C [11] prior to pumping the solution into the supercritical region (where the solution was heated to ~470° C before expansion). The highly agglomerated "snowlike" mass of very small particles ( $\leq 0.10 \,\mu$ m) shown in Fig. 7c was produced at ~600 bar and ~470° C expansion temperature, and with a dilute KI solution ( $10^{-3}$  M) replacing deionized water as the supercritical solvent. Each of the products shown in Fig. 7 was produced using a short length (~ 5 mm) of ~60  $\mu$ m i.d. stainless





steel capillary tubing as the expansion nozzle with a 30 to 50 ml min<sup>-1</sup> flow rate. X-ray diffraction analysis of powders representative of those shown in Fig. 7 indicates that these products are totally amorphous, reflecting the extremely fast quench rate inherent in the RESS process. The BET measured surface area of a powder sample collected under the same conditions used to produce the sample shown in Fig. 7b was found to be  $13.7 \text{ m}^2 \text{g}^{-1}$ . Using this value, a surfaceaverage diameter of these particles can be calculated on the assumption that they exist as a solid sphere having a density of  $2.2 \,\mathrm{g \, cm^{-3}}$  [13]. The calculated diameter (0.2  $\mu$ m) is consistent with the mean particle diameter for this sample estimated from electron micrographs, indicating that the assumptions are valid, and that the SiO<sub>2</sub> particles produced under these conditions have a very low porosity.

Further insight into the range of phenomena related to the RESS particle production process can be obtained by examination of the  $GeO_2-H_2O$  system.

Figure 7 Examples of silica particles deposited from supercritical water solutions under different experimental conditions. (a) SiO<sub>2</sub>-water system with the autoclave operating at 75° C, (b) SiO<sub>2</sub>-water system with autoclave at 225° C and (c) SiO<sub>2</sub>-0.001 M KI in water with the autoclave at 385° C. For each of the above samples, the pre-expansion fluid temperature was maintained at ~470° C, the system pressure was 600 bar, and the background pressure was ~10 torr. A 5 mm long, ~ $60 \,\mu$ m i.d. capillary-type expansion nozzle was used to produce each of the samples.





Figure 8 GeO<sub>2</sub> particles deposited under identical conditions (25° C autoclave, ~ 580 bar) except fluid temperature at the expansion nozzle, which was ~475° C for (a) and ~445° C for (b).

The solubility of crystalline GeO<sub>2</sub> is approximately three times that of quartz under similar conditions (8700 p.p.m. compared to 2600 p.p.m. at 500° C and 1000 bar) [14]. A product consisting of highly agglomerated ultra-fine (<0.02  $\mu$ m) GeO<sub>2</sub> particles is shown in Fig. 8a. This product is very similar in appearance to those produced in the SiO<sub>2</sub>-salt system (Fig. 7c), although no electrolyte was present in the GeO<sub>2</sub>-H<sub>2</sub>O system. The product shown in Fig. 8b consists of somewhat irregular rounded "beads" exhibiting a range of particle sizes from less than 0.1 to greater than 1.0  $\mu$ m. The two GeO<sub>2</sub> samples shown in Fig. 8 were collected sequentially under identical conditions except for fluid temperature, which was reduced from 475° C (Fig. 8a) to 445° C (Fig. 8b).

### 4.2. Application to organic and polymeric compounds

A variety of non-aqueous solvents has been applied to the RESS process, including carbon dioxide, propane, butane, pentane, ethanol and ammonia. In particular, low molecular weight alkanes are excellent solvents for many organic and organometallic polymers [15]. Fig. 9 illustrates several examples of RESS polymer products generated using supercritical pentane as the solvent. In general, the solubilities of polymers in organic solvents are considerably higher than those of the inorganic oxides in water, with a corresponding increase in the efficiency of the process. This results, at least in some cases, in the formation of relatively large particles (e.g. Figs 7c, e). In other particles instances smaller individual and/or agglomerates of small particles (Figs 9a, b, f), or polymer films (Fig. 7d) can be produced. Fibres having aspect ratios well in excess of 100 have also been made from some of the polymers under the appropriate conditions [16].

The relatively high solubility of polymeric materials in organic solvents allows, in many cases, straightforward preparation of "premixed" liquid solutions. This permits the use of controlled solute concentrations, and in some cases more dilute solutions than

would otherwise be practical using an autoclave system. Although the solvating characteristics of supercritical fluids are not utilized for dissolution in these instances, the solutions are still pressurized and heated to supercritical conditions prior to expansion. The premixing procedure has been utilized for the preparation of polycarbosilane (Fig. 9f), a ceramic precursor of the refractory silicon carbide [17, 18]. The generation of ultrafine polycarbosilane particles with diameters in the 0.01 to 0.08  $\mu$ m size range and a relatively narrow size distribution has been demonstrated [16]. Processing this material to the silicon carbide refractory may provide an improved green material for the formation of ceramic products. Powder and fibre production from very high molecular weight polymers using supercritical fluids, where conventional liquid solvents are inadequate, may also present viable technological opportunities.

#### 4.3. Effects of expansion parameters on RESS product morphology

As shown above, a number of variables exist for manipulation of the physical properties of RESS products, although the details of their effects remain to be investigated. Some of the factors which have been shown in the examples above to affect RESS product morphology include the solute concentration, configuration of the expansion nozzle, expansion flow rate, solvent composition and parameters affecting the solvent phase behaviour in the expansion jet.

In the case of dilute solutions, and with the nozzle operating at a sufficient temperature to avoid intersection of the solvent two-phase solute region during the expansion, a "molecular spray" is produced in which solute-solvent and solute-solute molecular interactions are minimized. Placement of a suitable substrate in the path of such a jet allows deposition of the solute on the surface in the form of monomolecular species or very small clusters, resulting in the formation of a thin uniform film as is illustrated in Figs 5a and b. Shorter capillary nozzles and low fluid flow rates are expected to enhance the "molecular spray"



*Figure 9* Examples of polymer materials produced from supercritical fluid solutions and their pre-expansion conditions. (a) Polypropylene (isotactic) from a pentane solution, 170 bar, 225° C; (b) polyphenyl sulphone from a propane solution, 170 bar, 300° C; (c) polyvinyl chloride (77 300 molecular weight,  $M_w/M_n = 1.95$ ) + potassium iodide from an ethanol solution, 170 bar, 250° C; (d) polystyrene (300 000 molecular weight,  $M_w/M_n = 1.06$ ) from a pentane solution, 280 bar, 200° C; (e) same material and solvent as in (d), 170 bar, 350° C; (f) polycarbosilane from a pentane solution, 240 bar, 250° C. A 25  $\mu$ m fused silica capillary expansion nozzle and a background pressure of 1 bar were used to produce each of the above examples.

mode of operation and the production of thin films, since solute nucleation phenomena would be minimized within the nozzle.

The situation for concentrated solutions is more complex due to the increased interactions between solute molecules early in the expansion process, and consequently the nucleation and particle growth. Nucleation and condensation processes leading to particle formation may begin within a capillary-type nozzle due to a density gradient existing along its length. An estimation of the pressure and temperature conditions just inside the tip of this type of nozzle can be made [6] if the initial system conditions are known. For example, if the fluid is assumed to expand adiabatically from 600° C and 575 bar through a nozzle 6 mm in length and having a 100  $\mu$ m i.d., the fluid conditions just prior to exiting the capillary will be roughly 450° C and 200 bar, corresponding to a density drop of 40% through the nozzle. Depending on the initial solute concentration and its solubility in the fluid under the initial and final density conditions during expansion in the capillary, particle nucleation within the nozzle may be significant. Thus, relatively concentrated solutions and the use of capillary-type expansion nozzles favour the formation of particles, with solute concentration clearly affecting the mean particle size (Fig. 7).

Films produced using solutions having relatively high  $SiO_2$  concentrations (e.g. Fig. 6) are believed not to have been formed by the "molecular spray" discussed above. We speculate that the mechanism for the "thick film" deposition involves the formation of

highly saturated droplets of  $SiO_2-H_2O$  solution produced by intersecting the solution two-phase region during the RESS expansion. Supersaturated liquid droplets impact the substrate, where a uniform  $SiO_2$  film is produced upon solvent evaporation (presumably) at the surface.

The examples given above illustrate the variety of particle sizes and morphologies that can be produced from the RESS systems. The presence of the salt should have little or no effect on the solubility of the silica glass [19, 20], although it clearly has a striking effect on the product morphology (Fig. 7c). It is speculated that the presence of the electrolyte retards individual particle growth but encourages the simultaneous nucleation of large numbers of particles and contributes to the agglomeration of smaller particles, perhaps by inter-particle bonding through the ionic species [21]. Particles produced from the  $H_2O-SiO_2$ system in the absence of electrolyte species, but under autoclave and expansion conditions similar to those used to produce the particles shown in Fig. 7c, are similar in morphology, but somewhat larger than, the SiO<sub>2</sub> spheres shown in Fig. 7b. The "snow-like" characteristics of oxide products deposited from systems using deionized water solvent, but having relatively high solute concentrations (e.g. Fig. 8a), undoubtedly also results from simultaneous nucleation of large numbers of solute particles early in the expansion process. It appears that very high SiO<sub>2</sub> concentrations may also contribute to the formation of highly porous products, as SiO<sub>2</sub> deposits produced with the autoclave operated at temperatures in excess of 400° C tend toward similar agglomeration characteristics. Differences between the GeO<sub>2</sub> products shown in Fig. 8 likely result from differences in the relative liquid-vapour phase distribution in the expansion jet due to the pre-expansion fluid temperature. We speculate that the lower temperature results in production of intermediate particles incorporating significant liquid solvent, yielding both larger particles and a larger particle size distribution.

### 5. The production of unique materials and other potential applications of the RESS process

The RESS process for particle formation and film deposition has potential applications for the production of novel materials, or where existing technologies for the preparation of powders and films are currently inadequate. Specific applications of the process remain largely unexplored, although our work suggests that the technique has potential in several technological arenas. The RESS process belongs to a broad class of methods which involve nucleation from an initial monomer population for the production of nonequilibrium powders or films. It is different from the other methods, however, in the range of materials to which it is amenable, as well as the mechanism of monomer generation and condensation. These differences give the RESS process unique capabilities, and may also allow formation of products having unique characteristics. Specific advantages of the RESS process over others used for powder and film production include the relatively low temperatures involved (as opposed to sputtering or plasma processes) and the elimination of a need for a solvent evaporation step (as opposed to conventional spray techniques). The RESS process is also unique in that it can be used to produce a variety of nonequilibrium products from the same material by utilizing subtle variations in expansion parameters. Application of the RESS process is limited only by the availability of a suitable supercritical solvent for the material of interest.

Because the RESS process involves extremely rapid product formation and quenching, it allows for the production of intimately mixed nonequilibrium materials having highly uniform microstructures. Such materials can be produced from a system in which two or more components are dissolved in a common autoclave and the solution expanded through the same nozzle. For a greater control over the product composition, multiple systems, each containing a single component and operating at different temperatures, could be used to feed a common nozzle. Highly uniform particles of SiO<sub>2</sub>-GeO<sub>2</sub> have been produced by this technique in preliminary studies of the process. Materials dissolved in incompatible supercritical solvents could also conceivably be combined in the RESS spray after being expanded through independent nozzles operated in parallel.

Powders can be produced from highly labile materials not otherwise suitable for mechanical grinding or other conventional powder formation processes. Furthermore, powders formed by the RESS process tend to have a much more uniform particle size distribution than those produced by mechanical milling. Areas in which the production of fine powders having uniform size distributions is desired include the ceramics and pharmaceutical industries. Pharmaceutical applications include many labile materials which preclude the use of high-temperature methods. The RESS process may also prove invaluable for the preparation of finely powdered explosive materials, where i size reduction by mechanical grinding is hazardous. The production of high surface area catalysts is an additional area of potential RESS application.

Potential uses for RESS-deposited films include optical coatings, semiconductor applications, and thin corrosion protection barriers. Films of nonvolatile or thermally labile materials can be deposited on temperature-sensitive substrates (e.g. polycarbonate lenses) because of the relatively mild deposition conditions of this process as opposed to chemical and physical vapour deposition or sputtering techniques.

The element of control over the RESS process and its product characteristics allows the potential to produce a variety of unique products, for which only a limited number of applications have been explored. Extensive research remains to be performed in order to fully understand phenomena occurring in the RESS expansion, the effects of process variables on its products, and the practical limitations of the RESS process.

### Acknowledgements

This work was supported by Battelle, Pacific North-

west Laboratories and Battelle Memorial Institute through Corporate Technical Development Project 2322247110/B-03330-4250.

### References

- 1. G. M. SCHNEIDER, E. STAHL and G. WILKE, "Extraction with Supercritical Gases" (Verlag Chemie, Deerfield Beach, Florida, 1980).
- 2. U. VAN WASSEN, I. SWAID and G. M. SCHNEIDER, Agnew. Chem. Int. Ed. Engng 19 (1980) 575.
- 3. M. E. PAULAITIS, J. M. L. PENNINGER, R. D. GRAY and P. DAVIDSON (eds), "Chemical Engineering at Supercritical Fluid Conditions" (Ann Arbor Science, Ann Arbor, Michigan, 1983).
- 4. J. B. HANNAY and J. HOGARTH, Proc. R. Soc. (London) 30 (1880) 178.
- 5. M. E. PAULAITIS, V. J. KRUKONIS, R. T. KURNIK and R. C. REID, Rev. Chem. Engng 16 (1983) 179
- 6. C. E. LAPPLE, Trans. Amer. Inst. Chem. Engng 39 (1943) 385.
- 7. O. F. HAGENA and W. OBERT, J. Chem. Phys. (1972) 1793.
- 8. L. G. RANDALL and A. L. WAHRHAFTIG, Rev. Sci. Instrum. 52 (1981) 1283.
- H. ASHKENAS and F. S. SHERMAN, "Proceedings of the 4th International Symposium on Rarefied Gas Dynamics", Vol. II, edited by J. H. deLeeuw (Academic, New York, 1966) p. 84.

- 10. G. C. KENNEDY, Econ. Geol. 45 (1950) 629.
- 11. R. O. FOURNIER and J. J. ROWE, Amer. Mineral. 62 (1977) 1052.
- 12. J. V. WALTHER and H. C. HELGESON, Amer. J. Sci. 277 (1977) 1315.
- 13. R. K. ILER, "The Chemistry of Silica" (Wiley, New York, 1979) p. 465.
- 14. G. W. MOREY, Econ. Geol. 52 (1957) 225.
- 15. L. H. BANGERT, J. L. LUNDBERG, J. D. MUZZY, G. H. HOYAS, L. H. OLSON and W. D. FREESTON Jr., "Advanced Technology Applications in Garment Processing", NSF Technical Progress Report, NSF/RA-770428, 1977.
- 16. R. C. PETERSEN, D. W. MATSON and R. D. SMITH (Abstract) American Chemical Society, 191st National Meeting (1986).
- 17. S. YAJIMA, Y. HASEGAWA, J. HAYASHI and M. IIMURA, J. Mater. Sci. 13 (1978) 2569.
- 18. Y. HASEGAWA, M. IIMURA and S. YAJAMI, ibid. 15 (1980) 720.
- 19. S. A. GREENBERG and E. W. PRICE, J. Phys. Chem. 61 (1957) 1539.
- R. SIEVER, J. Geol. 70 (1962) 127.
  R. K. ILER, "The Chemistry of Silica" (Wiley, New York, 1979) pp. 372-96.

Received 19 May and accepted 23 September 1986