Aerosol Mineralization of Chlorofluorocarbons by Sodium Vapor Reduction

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This paper describes a new method for the destruction of chlorofluorocarbons (CFCs). The process consists of mixing vapor-phase CFCs and sodium at atmospheric pressure in an exothermic single-pass process leading to the mineralization of the carbon and halogen components. The process has demonstrated high destruction efficiencies for a surrogate CFC (CF_4) as well as high efficiency for the formation of the equilibrium-predicted products of reaction: benign salt-coated carbon aerosols, large enough to be filtered with existing filtering technologies, with no volatile products. The rapidity of the chemistry and condensation process and the low cost of sodium should enable the construction of industrial-scale reactors that are fairly small and economical to build and operate. The application of this chemistry would be toward destruction of CFC stockpiles and as a treatment of the effluent of plasma reactors used in semiconductor processing.

Introduction

Under strict guidelines of the Montreal Protocol, manufacture of chlorofluorocarbons (CFCs) ceased as of January 1, 1996 (*1*). Although billions of kilograms are currently in use or in stock, no mandate exists for the destruction of CFCs as the Protocol explicitly only addresses limiting the total amount of ozone-depleting substances entering the atmosphere. Certainly the existing stockpile of CFCs may cause serious damage to stratospheric ozone if allowed to escape into the atmosphere, so that a simple phase out of production may not be a satisfactory solution for the long run. Destruction may be a desirable approach for some CFC suppliers because phase over to replacements has been faster than expected and the floor tax on storage of CFCs by those other than the original manufacture can exceed $10.00 kg^{-1} yr^{-1}. Also, alternative refrigerants, foaming agents, and other CFC replacements are scheduled to be phased out within a few decades. These materials, although less dangerous to stratospheric ozone than the CFC counterparts, pose a threat to the environment as greenhouse gases. Finally, the microelectronics community is a large user of fluorocarbons for plasma etching operations and is working on a strategy for abating the effluent, which in many cases is primarily the unreacted starting CFC (*2*).

Currently, several processes exist for the destruction of CFCs, including those discussed in refs 1−7. Although theoretical destruction efficiencies exceeding 99.9% may be achieved through conventional incineration, there are some practical difficulties in maintaining the necessary time−temperature histories to destroy many of the more stable species. Furthermore, incineration has, at best, byproducts that are themselves toxic and must be removed (HF and HCl). Products of incomplete combustion are an even bigger concern since the potential to produce substances such as polychlorinated dibenzo-*p*-dioxins and dibenzofurans exist (*6, 8*). Plasma destruction is another possibility brought to attention by the electronic processing industry. This also results in volatile products, and high destruction efficiencies are not proven (*7*). Another novel method recently discussed (*3*) involves flowing the CFCs through powdered sodium oxalate, producing sodium chloride, sodium fluoride, and carbon dioxide. Another approach has also been recently reported in which solvated electrons produced by the reaction of sodium with anhydrous liquid ammonia are eacted with CFCs (*4*).

This paper discusses a new destruction method: aerosol mineralization. The CFCs are dehalogenated by reaction with sodium vapor with subsequent nucleation/condensation of the sodium halide salt(s) and elemental carbon:

$$(y)\text{Na} + \text{CX}_y \rightarrow$$
$$(y)\text{NaX(s)} + \text{C(s)} \text{ where X = F, Cl, Br, I} \quad (1)$$
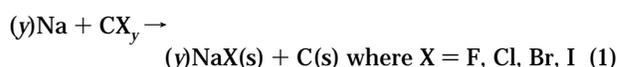
The chemistry is similar to that presented for the for production of nanoscale materials (*9−12*). The process discussed within has high conversion efficiencies (99+%), and byproducts are benign aerosols: sodium chloride, sodium fluoride, and elemental carbon. Furthermore, the carbon particulates may be of commercial importance because of zero hydrogen content, size, and state of agglomeration. The reactant, metallic sodium, is inexpensive (∼$3.00/kg), and we do not believe scale-up should present problems sufficient to prevent implementation.

Thermochemistry

A generic reaction for the mineralization of CFCs by sodium vapor reduction may be written as

$$\text{C}_x\text{Cl}_y\text{F}_z(v) + (y+z)\text{Na}(v) + \text{inert} \rightarrow$$
$$x\text{C(s)} + y\text{NaCl(s)} + z\text{NaF(s)} + \text{inert} \quad (2)$$
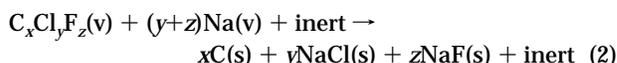
and the specific reaction for the CFC used in most of our experiments is

$$\text{CF}_4(v) + 4\text{Na}(v) + \text{inert} \rightarrow \text{C(s)} + 4\text{NaF(s)} + \text{inert} \quad (3)$$
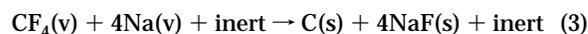
A limited number of experiments were also conducted on CF_3Cl.

Thermodynamics can be used to provide information on the operating parameter space for efficient mineralization of the CFCs. Thermochemical computations were conducted using thermodynamic data from the JANAF tables (*14*) and the NASA thermodynamic equilibrium code (*13*). The system described by eq 3 was chosen as the specific case to be investigated because of the high thermodynamic stability of CF_4 relative to all other CFCs, making it the most difficult to mineralize. The inert used for the computations is Ar. It should be noted that molecular nitrogen as a diluent could potentially lead to sodium cyanide.

The overall heat of reaction is highly exothermic. At 1000 K for example, the heat of reaction is 1750 kJ/mol, which at 1 atm and no inert gives an adiabatic temperature of 3350 K. The exothermicity comes about, however, when the products condense. This is clearly illustrated in Figure 1, which shows the free energies and enthalpies for the global reaction of

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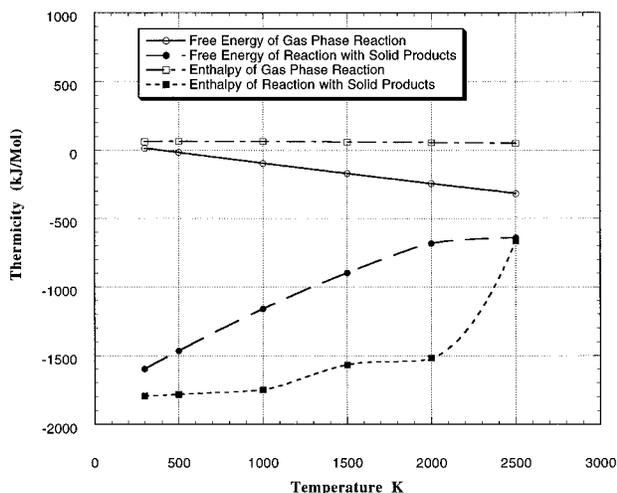
FIGURE 1. Free energies and enthalpies for the global reaction of Na + CF$_4$ → C + NaF (kJ/mol).

CF$_4$. The overall process to gas-phase products is in fact slightly endothermic, and since the elementary steps in the chemistry will be gas phase, the gas-phase chemistry will be the energetically limiting steps. While we do not know the exact steps of elementary gas-phase reactions for the reduction of CF$_4$, we can speculate that it involves processes as follows:

$$CF_4(g) + Na \rightarrow CF_3(g) + NaF(g) \tag{4}$$

$$CF_3(g) + Na \rightarrow CF_2(g) + NaF(g) \tag{5}$$

$$CF_2(g) + Na \rightarrow CF(g) + NaF(g) \tag{6}$$

$$CF(g) + Na \rightarrow C(g) + NaF(g) \tag{7}$$
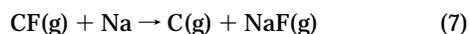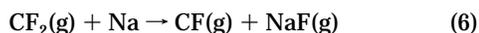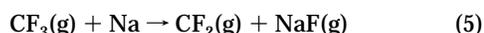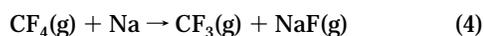
This mechanism is written assuming that the chemistry is primarily a sequential stripping of a halogen atom by sodium (12), and while certainly not the only reactions occurring in the chemistry, they do provide some insight. Calculation of the enthalpy of reaction shows that at 1500 K reactions 4, 6, and 7 are in fact endothermic by approximately 63, 41, and 68 kJ, respectively, and would require some thermal activation. The results are summarized in Table 1. Assuming that the activation energy for the elementary steps is approximately equal to the endothermicity (the endothermicity is a minimum energetic barrier) and A factors of about 10^{14}, which is reasonable for this class of abstraction reaction (12), we can estimate characteristic reaction times as a function of temperature and concentration. For example, at 1500 K and

90% argon dilution, the CF$_4$ half-life is on the order of 10^{-5} s for a stoichiometric amount of Na and CF$_4$. The subsequent reactions should be at least as fast based on heat of reaction considerations. At any but very high temperatures, gas-phase carbon will be highly supersaturated and nucleation/condensation will proceed on the order of a few microseconds (15, 16). This nucleation process also serves as a product sink for the gas phase and implies that the elementary reactions will be essentially irreversible, even thought they are endothermic. These rates suggest that residence times on the order of tens of milliseconds should be sufficient for the mineralization process.

Results obtained from the equilibrium calculations show that high conversion efficiencies can be achieved under a broad temperature range. Using typical operating conditions of 5 mol % tetrafluoromethane, 22 mol % sodium, and the balance argon, conversion efficiency remains in excess of 99.999% (efficiency is defined as the percentage of CFC-bound halide converted to sodium halide) up to a temperature of 2000 K. It should be noted that 22 mol % sodium is in excess of the stoichiometric value by 10% (20 mol % is stoichiometric). This value is justified below. High conversion efficiencies at low temperatures offer the advantage of lower energy and reactor material costs and can be obtained by the addition of inert.

Another concern is reactant stoichiometry. Equilibrium calculations for 1 atm, 70% argon, and 2000 K show that the conversion efficiency drops from over 99.999% with 10% excess sodium to slightly over 99.9% at the stoichiometric value to under 90% at a 10% sodium deficiency. One would clearly wish to conduct the chemistry under excess Na conditions. Practically, this does not present a problem because the products of reaction are solid phase and the sodium may be condensed downstream of the solid removal and reused. Indeed, industrial implementation of the chemistry would be in a fully closed-loop configuration where the particles are removed from the gas phase (cyclone, electrostatic precipitation, etc.), and the remaining unreacted sodium is condensed out and recycled along with the carrier gas (Ar).

Experimental Section

To demonstrate the process, tetrafluoromethane (R-14) was injected into a laboratory-scale sodium reactor. As mentioned, CF$_4$ was chosen as the model compound because it should be the most difficult to destroy.

The apparatus, shown in Figure 2, is based on the familiar co-flow diffusion flame and similar in design to that used by DuFaux and Axelbaum (11). All construction materials are type 316 stainless steel unless otherwise noted. The burner is composed of four concentric tubes. The inner tube was

TABLE 1. Heat and Free Energies of Formation for Gas-Phase Sequential Steps in Halogen Stripping Reactions[a]

gas-phase reaction	free energy of reaction (kJ) enthalpy of reaction (kJ)					
	298 K	500 K	1000 K	1500 K	2000 K	2500 K
CF$_4$ + Na → CF$_3$ + NaF	45.1 / 65.9	31.3 / 66.1	−1.9 / 64.8	−33.7 / 62.5	−64.5 / 59.9	−94.4 / 57.1
CF$_3$ + Na → CF$_2$ + NaF	−121.3 / −109.1	−129.4 / −108.9	−148.8 / −109.9	−166.9 / −112.1	−184.1 / −114.7	200.5 / −117.3
CF$_2$ + Na → CF + NaF	28.7 / 39.9	21.2 / 40.6	2.4 / 41.1	−16.2 / 40.7	−34.4 / 40.2	−52.3 / 39.7
CF + Na → C + NaF	61.1 / 64.9	58.9 / 65.8	52.7 / 67.4	45.8 / 68.5	38.7 / 69.4	31.5 / 70.3

[a] Also included are the global energies for gas and condensed products.
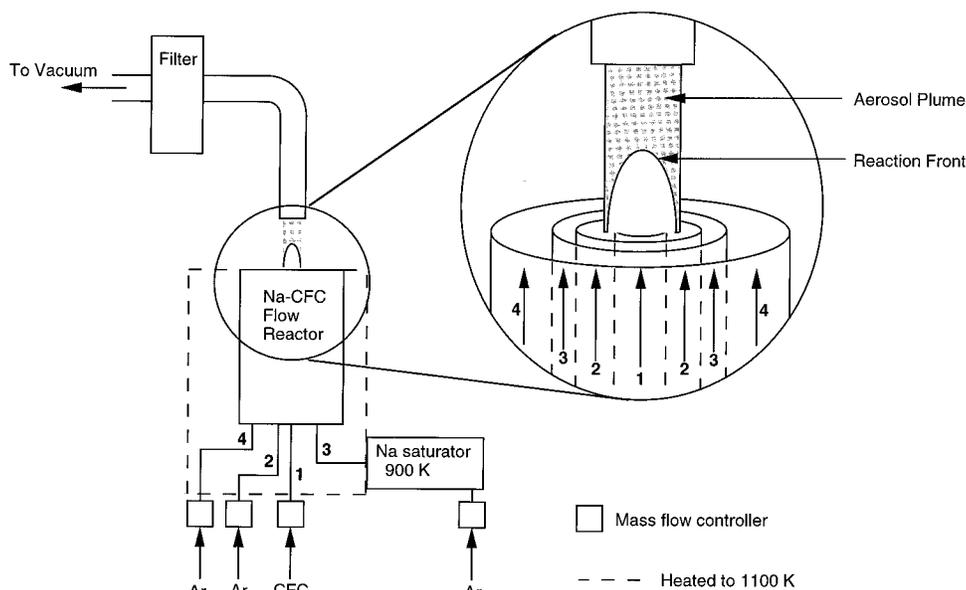
FIGURE 2. Schematic of Na/CFC reactor.

machined from solid graphite round stock with an i.d. bored to 3.2 mm and the outside of the injector varies from 5.0 to 12.5 mm. The variation in the outside diameter ensures flow uniformity and minimizes recirculation at the reactor exit. The next three tubes are stainless steel having dimensions of (i.d./o.d.) 12.6/15.9, 25.4/31.8, and 95.3/101.6 mm. The outermost tube can be extended above the reactor exit to reduce radiation heat loss from the reactor exit. In these experiments, the tube was extended 100 mm and heated to 1100 K. To reduce recirculation at the reactor exit, the tubes are tapered near the burner, and to ensure flow uniformity, honeycomb flow straighteners are located in both the second and third annular regions.

The innermost tube (graphite injector) supplies the halide/inert mixture (CF_4 or CF_3Cl). The first annulus, created by the graphite injector and first tube, contains a flow of inert. This inert flow is a practical requirement due to formation of solid products that build up on injectors. This flow separates the two reactants thereby preventing buildup and potential reactor clogging. The second annulus supplies the sodium vapor/inert mixture, and the outermost annulus supplies an inert flow, isolating the reactions from the atmosphere. Argon and tetrafluoromethane flow rates are controlled by calibrated mass flow controllers. Sodium vapor is produced by passing preheated argon through a high-temperature sodium saturation device operated at temperatures up to 950 K. Sodium vapor concentration can be varied by adjusting the operating temperature of the saturation device or by adding diluent argon. All lines from the saturation device to the reactor are maintained at 1000 K to ensure that sodium remains in the vapor phase. The reactor is operated at 1100 K so that radiative heat loss at the reactor exit does not reduce the temperature such that sodium condensation would occur. The reactant gases exit the burner with a uniform temperature of 1000 K. The inner and outer flows of argon are preheated before entering the burner. All temperatures are measured with type k thermocouples and maintained at operating temperature with PID-controlled heaters.

The plume emanating from the reaction is a well-defined stream of particles that were collected with a 2.5 cm diameter stainless steel flexible tube positioned over the center of the burner, approximately 8 cm above the burner exit (<1 s flow time). Suction is adjusted such that the stream of particles is directed into the collection tube and onto a 10-μm porous stainless steel filter. After collection, powders are analyzed

TABLE 2. Flow Rates and Conversion Efficiencies for CF_4/Na Reaction[a]

exp no.	flow rates (sccm)[a]						conversion efficiency[b]
	CF4 (1)	Ar (1)	Ar (2)	Ar (3)	Na (4)	Ar (4)	
1	12.6	40	150	2000	99.4	35000	0.972
2	12.6	40	150	2000	99.4	25000	0.968
3	6.1	15	164	2000	96.6	35000	1.007
4	3.1	18	164	2000	96.6	35000	0.996
5	9.4	12	164	2000	96.6	35000	0.968
6	6.1	15	164	2000	63.1	35000	0.862

[a] Number in parentheses corresponds to injection region of Figure 2. [b] Conversion efficiency is computed as the fraction of halogen atoms mineralized to salt.

using the following techniques: (1) measurement of fluorine ion concentration in water solutions with a fluorine ion selective electrode (FISE), (2) X-ray diffraction (XRD), and (3) elemental analysis on sodium and fluorine.

For the FISE technique, powder collected over a specified amount of time was mixed with a known amount of water, well in excess of saturation (if all CFC was destroyed). Because the pH is very high due to the excess sodium collected during the experiment (which produces NaOH), the pH was adjusted by adding buffer solution to the specifications of the probe manufacturer The probe was calibrated using three standard solutions: fluoride ion concentrations of 100, 500, and 1000 ppm. From the fluorine ion concentration measurements, we determined the amount of NaF produced (assuming that C−F bonds would not dissociate in water) and compared them to the theoretical value of complete reduction.

Results and Discussion

Because the laminar flow reaction system used here involves a mixed control reaction/diffusion system sensitive to parameters such as flow rates, concentrations, and temperature in a non-intuitive and non-linear fashion, a detailed study of conversion efficiency with respect to these parameters is beyond the scope of this paper. The object here is to present the method, demonstrate its effectiveness, and discuss important practical issues.

Figure 3 shows a picture of the reaction zone for a CF_3-Cl/Na system. The reaction zone looks very similar to the well-studied laminar diffusion flame (16). The chemistry is similar to that summarized in Table 2 except that a much
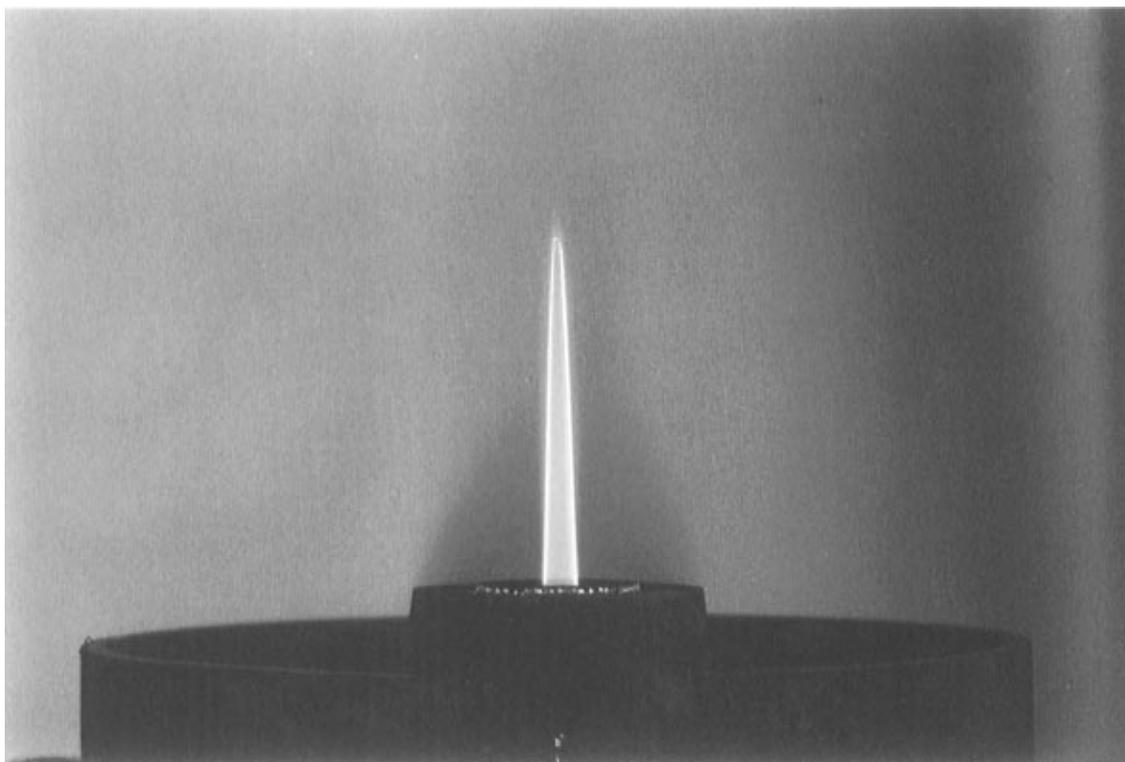
FIGURE 3. Photograph of reaction zone for $CF_3Cl + Na$.
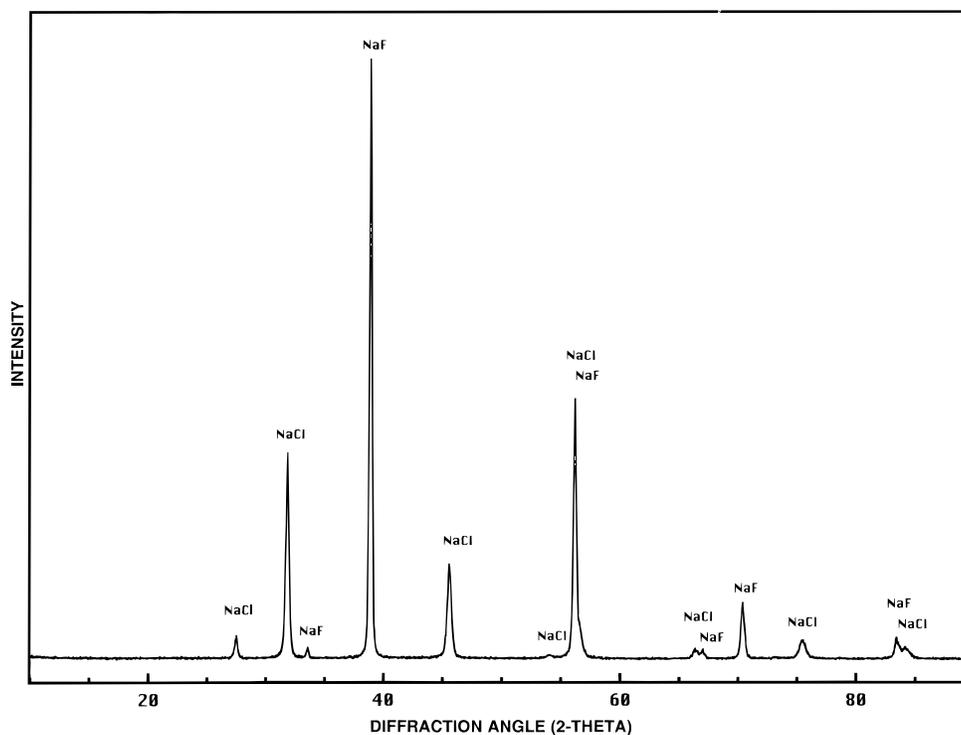
FIGURE 4. Example of X-ray diffraction pattern of products of reaction.

higher argon flow is mixed with the CFC, providing a high velocity jet through the inner injector. This jet produces the well-defined lines seen in the photograph. The bluish color surrounding the flame is caused by the strong absorption at the sodium D-lines (589 nm). Condensed sodium can be seen on the exit of the reactor injector tubes; this lower temperature region results from radiation heat loss to the surrounding. In normal operation the burner is surrounded by a heated shroud, reducing radiation loss and thereby maintaining the burner exit at sufficient temperatures to avoid condensation.

An XRD spectrum of powder collected from a CF_3Cl/ Na reaction is included in Figure 4. Powder from a CF_4/Na reaction produces a spectrum less the NaCl peaks. Carbon does not appear in the spectrum due to its amorphus nature. To determine if fluorine was present in the carbon matrix either as trapped NaF or bound fluorine for the experiments with low conversion of CF_4, elemental analysis was performed. Experiment 6 of Table 2 was run under conditions such that insufficient sodium was available to completely reduce the tetrafluoromethane. The collected powder was twice washed with water and centrifuged. This washed powder was sent
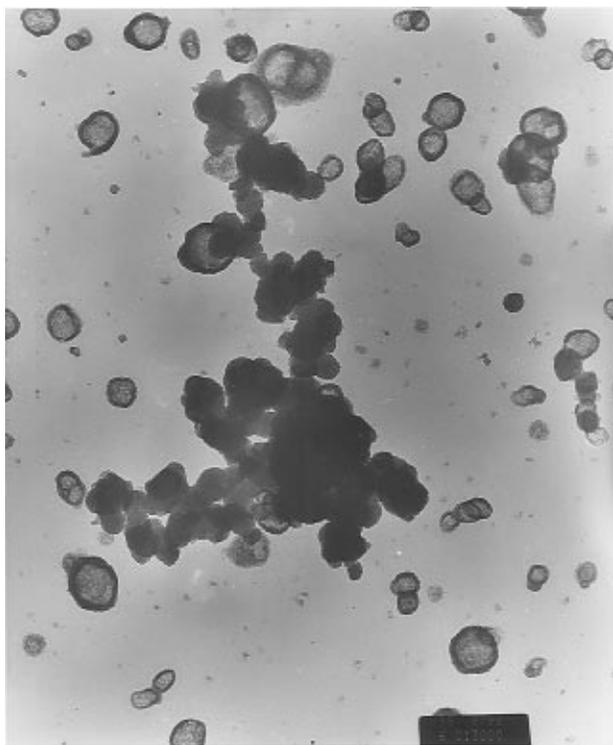
FIGURE 5. Transmission electron micrograph of products.

to a commercial laboratory for sodium and fluorine analysis. The results show 0.28% fluoride and 1.94% sodium, on a mass basis. The low value for fluorine indicates that the solid carbon component is essentially fluorine free and that any incomplete conversion of CF_4 presumably results in a gas-phase species or very small cluster that passes through our particle filtration system. The higher concentration of sodium may be the result of the formation of sodium peroxide, which has low cold-water solubility, residual sodium hydroxide from the wash, or direct sodium contamination of the carbon particles.

A TEM micrograph of the particles produced in experiment 2 of Table 2 is shown in Figure 5. This material was collected by inserting a carbon-coated TEM grid into the reaction zone for approximately 0.1 s and a location corresponding to approximately 0.5 s flow time. Particles deposit on the substrate through thermophoretic forces developed between the hot process stream and the cold grid (*18*). The micrograph shows individual and agglomerated structures consisting of 200−500 nm particles encapsulated in a coating of salt. EDS indicates the particles are composed of sodium, fluorine, and carbon. At this time, we do not know if the carbon component within the salt shell is a single particle or a matrix of carbon and salt. It should be noted that because of the sampling technique, the powder shown in the micrograph of Figure 5 is expected to be smaller than that in the bulk powder because the particles will spend a longer time at high temperatures causing further agglomeration. From an industrial prospective, the particle sizes produced are amenable to separation from the gas phase by standard methods.

Table 2 shows process parameters and conversion efficiencies for several different reactor conditions for a Na/ CF_4 system. Injection regions for the summarized flow rates are detailed in Figure 2. From Table 2, we see what can be achieved. In the thermochemistry section, it was noted that excess sodium is required to effectively mineralize the CFC. It should be pointed out here that sodium flow rates (Table 2) are well in excess of the amount discussed above. This is due to radial diffusion losses associated with this type of laminar flow reactor, which cannot be accounted for in the equilibrium calculations previously presented that are for a well-mixed system. However, the nature of such a lamanar diffusion flame configuration is that at the reaction front the local stoichometry will be that for the overall reaction. This is because the chemistry is a balance between the reactive and diffusive fluxes, such that the reaction front adjusts itself spatially in order to satisfy the balance between these two fluxes. In our case, the reaction front adjusts itself such that the sodium vapor envelopes the CFC feed as seen in the photograph. In fact, this is a very effective method for determining that one is operating under conditions of excess sodium. Naturaly, for industrial application, flows would be turbulent rather than laminar, and the enhanced mixing would minimize the amount of excess sodium required.

In these experiments, temperature effects are not expected to influence the process because of the low reactant concentrations. The adiabatic reaction temperatures are all below 1550 K and, as discussed previously, not high enough to influence the process. Also, due to radiation heat loss from the solid products to the surroundings, the actual reaction temperature will be lower.
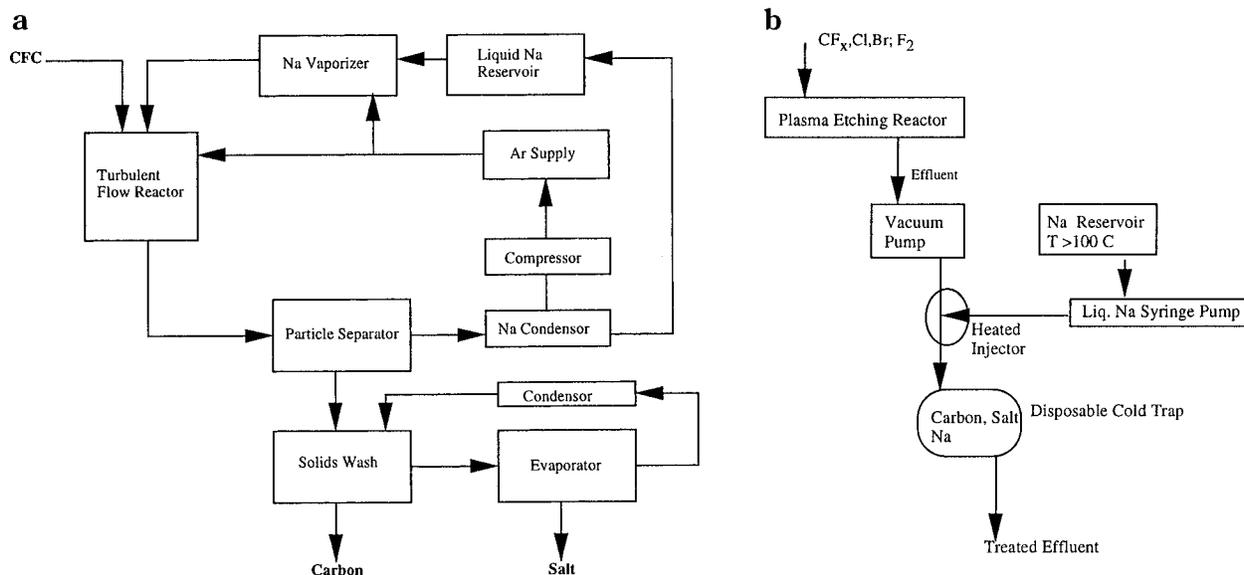
FIGURE 6. Schematic of a potential closed-loop Na/CFC aerosol mineralizer.

The rapidity of the chemistry and condensation process should enable the construction of industrially relevant reactors that are fairly small and therefore economical to build and operate. A continuous closed-loop system would be efficient and cost-effective and should be scaleable in a relatively straight-forward manner for the destruction of large quantities of CFC stockpiles. Such a system might have the components described in Figure 6. For application to the semiconductor industry small reactors, considerably simpler systems to that shown in Figure 6b could be placed downstream of vacuum pumps on the output of plasma reactors. Particle separation may take place with electrostatic precipitators or cold traps, without the need to seperate the salt from carbon. Because of the low volumes of sodium required for this particular application, sodium could be simply removed from the process stream with a cold trap rather than recycling.

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