Techniques in Cryostabilized Additive Concentration

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A number of cryostabilized additives have been created in the past, but currently at levels too low to have engineering value. A variety of techniques for concentrating these impurities are discussed, centering on solution, recrystallization, and sublimation. Techniques vary with the matrix material and additive; concentrating impurities in solid hydrogen requires a different approach than is appropriate with the use of a solid oxygen matrix. Practical engineering techniques are suggested, together with the limitations of these techniques. Launch economics are found to justify cencentration processing. The most practical processes are found to be sublimation concentration and solution crystallization.

Nomenclature

Isp = Specific Impulse
k = Boltzmann's constant
K = Kelvins
M = Gram-molecular weight
$r_\#$ = Rate of evaporation in molecules or atoms per cm^2-s,
P_μ = Pressure in microns
T = Temperature
Θ_D = Debye temperature

I. Introduction

Cryostabilized Additives (CSAs)[1] are materials that although they are unstable at Standard Temperature and Pressure (STP), they can be stabilized at cryogenic temperatures and used to significantly enhance propellants. In isolation, all but the most energetic species can become CSA's, but only limited classes of these materials can be prepared in concentrations that have a macroscopic engineering use. Past reference work on CSAs centers on Cryochemistry[2] and Matrix Isolation Spectroscopy[3], with the latter being by far the more extensive of the two as a result of the available non-contact diagnostics and the richness of information that can be derived from the optical spectra of an isolated species in a solid, inert cryogenic matrix[4]. A more recent major effort in the development of CSA's has been the Air Force's High Energy Density Materials (HEDM) program (e.g. [5]). No practical CSA that is planned for use as a rocket propellant has arisen from this work at this time.

There are two primary classes of CSAs: those that are stable at 100% concentration at some cryogenic temperature, and those that can only be stabilized at a lesser concentration due to self-reaction. Generally, pure CSAs are the most easily stabilized, but self-reaction limited CSAs are potentially more useful, since they have a higher energy release per atom/molecule. At this time there are no well known examples of a pure CSA, and no self-reaction limited CSAs created at useful concentrations. For the HEDM program, CSA densities considered useful for major energetic fuel enhancement were on the order of 10 mole %[6]. Part of the present effort is to demonstrate that CSAs can be practically useful for propellant enhancement at significantly lower concentration.

A. CSA Stability

A stable material is defined as a material that will not spontaneously change state in response to its thermal environment at a specified temperature. Here the engineering definition of a stable material is used, often including materials that are more precisely metastable, but are stable on time scales that allow them to be useful as engineering

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materials.

Pure CSAs are those that have a potential barrier to reaction that is small enough such that immediate reaction takes place at STP conditions, but large enough that significant reaction does not occur in an appropriate cryogenic environment. It may be necessary that the cryogenic environment consist of a solid, inert, cryogenic matrix that isolates the CSA and prevents self-reaction, or it may be that the temperature alone (such as the 4 K of liquid helium (lHe)) is sufficient to stabilize these CSAs. There are a number of species (including radicals) of interest that have non-zero but small potential energy barriers to reaction. There are a smaller set of CSAs with potential barriers only in specific directions; these might be stabilized by an external field or by some other means in a van der Waals matrix.

Reaction potential energy surfaces in solids are complex and three dimensional. Although extensive work has been done to measure binary potentials (e.g. the H_2 potential[2]), and potential compilations exist for a variety of element pairs in their ground state (e.g.[3] for alkali-inert pairs), the problem of modeling many-body and long range effects in solid state compounds is as yet largely intractable computationally.

One can apparently define the approximate needed potential energy barrier height for a pure CSA to be cryostabilized in an inert matrix. Energy stability in the solid phase is quite different from that in the gas phase because there is no high-energy tail of the vibration distribution to initiate reactions. Transmission of lattice vibrations (phonons) implies an energy cutoff of approximately $k\Theta_D$, where k is the Boltzmann constant (10^{-16} erg/K) and Θ_D is the Debye temperature of the solid. This is an interesting result, since it is apparently not temperature dependent. Of the simple cryogenic gases[7], Kr has $\Theta_D = 75$ K, Ne has $\Theta_D = 75$ K, Ar has $\Theta_D = 92$ K, O_2 has $\Theta_D = 90$ K, and para H_2 has $\Theta_D = 118$ K[8]. For a propellant, this implies that Ne has the best combination of low molecular weight and low Debye temperature, but both para-H_2 and O_2 should be reasonable candidates. Actual Debye temperatures are somewhat temperature dependent. For Ne, the energy associated with its Debye temperature is 6×10^{-15} ergs or 0.004 eV, so species with this reaction barrier height will presumably be CSAs that can be concentrated to 100%. This is about a factor of 1000 below the normal chemical heat release/enthalpy difference between common reactant and product species; relatively small reaction barriers become important at cryogenic temperatures. This limit on barrier height does not define a duration of stability for lower barriers, where stability may be dominated by other thermal factors, such as diffusion.

It has been claimed that CSAs without reaction barriers cannot exist in useful concentrations because the probability of two reactive atoms being adjacent approaches unity as the reactive atom fraction in the host material approaches 10%[1]. When diffusion processes, particularly diffusion along grain boundaries, are taken into account, the estimated limiting concentration is estimated to fall to 1-2%, and work in radical trapping within solid matrices implies limiting concentrations of less than 1%. It is believed that this latter limit can be greatly exceeded by using CSA concentration techniques by creating more stable mixtures and crystals, and by avoiding limitations arising from path sensitive rather than state sensitive routes of cryogenic crystal formation.

II. CSA Formation Routes

For this work it is assumed that there exists a starting material that consists of some cryogenically inert matrix with a low concentration of CSA mixed into it. There are many ways to achieve these starting materials; the most well known are the use of thermal sources (e.g.[3]) and the use of laser ablation (e.g. [9]). A key aspect of the formation of these mixtures is that the concentration is an atomic-scale average. Concentrations of 0.1 mole-% probably imply that local atomic concentrations may reach 1 mole-%, depending on the degree of fluctuations in the deposition source.

The problems of generating, cooling, and trapping CSAs are not addressed in this work in general, but they are a major factor in determining the starting concentration of the CSA and the distribution of the CSA in the host material. The route to formation of the CSA/matrix mixture influences the techniques and the economics of CSA concentration.

Almost all previous techniques used to form a CSA/matrix combination involve high differential energy at the deposition interface. In other words, these previous techniques cool and trap the energetic CSA species in a very thin region at the surface of the cold, inert matrix. This region is termed the accretion zone, and it may consist of a thin layer at the top of a liquid, a thin liquid non-solid layer on the surface of a solid, or a thin solid surface layer. In any case, the accretion layer is often the limiting factor in creating higher concentrations of CSA, rather than any inherent concentration limit in the inert matrix.

III. Economics of CSA Concentration

The basic justification for work on CSA concentration may be two-fold. In the best case the increase in I_{sp} gained by using a CSA may permit radical transformations in launch technology such as single-stage-to-orbit vehicles. The more likely justification, at least in the short term, is that the cost to add and concentrate a CSA in a propellant is more than paid for by a reduction in payload cost per unit mass resulting from the use of an enhanced propellant.

Based on today's launch technology, one can estimate what sort of propellant processing cost is justified. Typical payloads today are in the range of 500 to 20,000 kg, and fuel mass is typically about 50 times payload mass. As of the year 2000, payload costs were about $10,000/kg[10]. For a RP-1/LOX propellant combination, a 1% improvement is I_{sp} leads to a 2% increase in payload mass to Low Earth Orbit (LEO)[11]. Thus for a 1,000 kg payload, a 1% improvement in I_{sp} decreases the payload cost by 2%, or about $200,000. A 1000 kg payload would require 50,000 kg of propellant, and allow an increased cost of propellant by about 4 $/kg of propellant. Given that the current cost of LOX is about 0.15 $/kg, it would seem that comparable processes to concentrate CSA's would be economically justified – assuming that full percentage increases in Isp could be achieved.

At least initially, costs will be dominated by the facility cost, with some personnel costs. Given the large quantities of propellant that must be processed for even a single flight, facilities costs can be readily amortized to a reasonable extent. Time and thermal costs should be not be large, compared with the cost of the liquefied propellant, since the concentration processes are not energy intensive, and involve recycling rather than absolute cooling. Economics also dictates that there be a generic facility that works with many propellants; the temperature processing should not be a material-specific technique. Significant further payload cost gains will be achieved for air-breathing vehicles. Also, double gains can be obtained for rockets if both the oxidizer and fuel contain CSAs. There is some question as to whether there will be added handling costs of the CSA-laden propellants, but since the CSAs are stable, these costs should be minimal.

Based on these arguments, any CSA concentration that provides significant cost savings in payload costs is worth developing, assuming that the future development (vs. manufacturing) costs are relatively small. At current cost levels of 10M$/launch, 1% cost savings is significant, so the initial target level for CSA concentration will be the profitable 1 mole-%, rather than the dramatic improvements of 10 mole-% sought in the HEDM program.

IV. CSA Phases

CSA's will almost certainly be generated in the gas or plasma phase, where high-energy processes can be used to create isolated energetic species. These species must be cooled to an appropriate cryogenic temperature, where *afterward* they can be concentrated from the cold gas, liquid, and solid phase. The concentration process itself takes place only at a low temperature. The low temperature may not be sufficient for stability – a stabilizing host matrix may be required – but a low temperature is required to prevent diffusion and other destabilizing thermal effects. The CSA will be a solid because all known CSA materials will crystallize at the cryogenic temperatures needed for stability, so in all cases the goal of CSA concentration is to create a stable, increased-I_{sp}, solid propellant.

Producing and storing the solid propellant is not a major technical problem. Using the solid propellant may also not be a problem, but it is inconsistent with the current predominant practice of using either a liquid propellant or a solid, room-temperature booster. The options for using a CSA solid propellant include using the solid in a slurry (e.g.[12]), using the solid as the charge of a hybrid rocket (e.g. [13]), or using it as a solid monopropellant (e.g.[13]). All of these options are in various stages of development, and all have undergone some experimental validation. Small commercial efforts have been undertaken to use these types of propellants.

The most likely commercial scenario seems to be the use of CSA-laden propellants as a slurry, where the slurry can be pumped as a liquid[12]. In this case it is necessary to be able to maintain a stable particle size. The particles must not strongly agglomerate or grow through some sintering or recrystallization process. Wetted particles will tend to stay separate, and low temperature will minimize sintering diffusion processes. Significant research has been done in this area[13].

The most intriguing possibility is that of developing a pure CSA that is fully soluble in a standard cryogenic liquid propellant such as lH_2 or LOX. There is no physical reason to believe that such a CSA does not exist. Certainly lH_2 would cryostabilize some unstable materials, the question is whether a CSA can be developed that provides sufficient solubility and sufficient gain in I_{sp}.

V. Concentration of Pure CSAs

Although there are many possible techniques for concentrating pure CSAs, the techniques that appear most promising without extensive preliminary experimental research are dictated by the nature and status of cryogenic fluids as they are currently used. The key to creating a pure CSA is to trap and cool each individual molecule/atom in isolation. Once this is accomplished, the CSA can be concentrated by a variety of means. The coldest, totally non-reactive material that can be used to cool a CSA is lHe. It maintains its temperature of about 4 K in spite of heat input (from condensing CSAs) because it is a boiling liquid – evaporative cooling balances deposition heating. Liquid He also provides another important advantage for pure CSAs: it can be used to easily transport the isolated CSA species to a location away from the trapping zone, where the CSA can be concentrated at a uniformly low temperature.

A fundamental problem in the trapping and cooling of a CSA is the possibility of reaction in the accretion layer where the CSA particles are slowed and cooled. Fig. 1 shows the process schematically. The CSA particles have directed momentum that causes them to penetrate the surface of the liquid (or solid) in a path determined by the direction of entry and the slowing forces of the liquid. Although the CSA does not react with the cooling liquid, it will react with any other CSA particle that it comes in contact with as it passes through the liquid. Due to a natural dispersion in direction and momentum, particle tracks will overlap as the density of CSAs in the liquid increases. Thus the density of CSA particles must be kept low enough to minimize the probability of reaction. This can be done using either a batch or a flow method. In a batch method when a predetermined concentration is reached, the deposition is turned off until the matrix can be refreshed by physical displacement. The deposition surface is continually refreshed in the flow method.

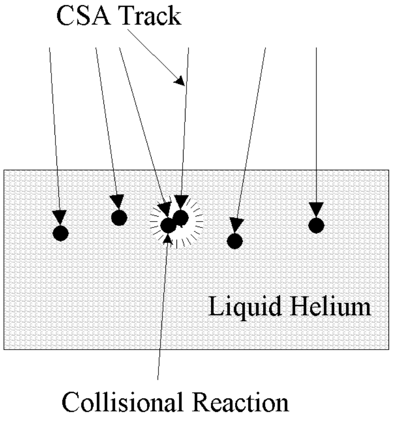

Figure 1. Schematic of CSA accretion layer.

The more efficient technique is to present a continuously refreshed liquid surface to the incoming CSA particles to limit the buildup of CSAs at the surface. The required speeds of the flow of a liquid bath to achieve this imply that the CSA beam must be narrow and deposition rates restricted. This limitation is avoided by using co-flowing CSA beams and helium sprays. Much higher helium flow velocities can be achieved in this way, and the reduced volume density of the spray allows penetration of the CSA beam into the spray core. Furthermore, the droplets in the spray will be rotating and have internal motion, continually presenting fresh surface to the CSA beam.

A conceptual schematic of a pure CSA concentration machine is shown in Fig. 2. The principal is to collect cooled and trapped CSA material in lHe then crystallize the CSA, removing the lHe for recycling. Helium vapor generated by the CSA cooling is also collected, reliquefied, and reused. The only inputs to the device are CSA material and power. The entire apparatus is insulated and in vacuum. A thermal or beam source provides the isolated CSA species. The geometrical configuration of the CSA trapping in lHe is dictated by the reaction concentration limits discussed above. The solid, cold CSA would be scraped or broken off of the substrate for use. Smaller particles could be generated by continuous scraping of a thin film as it builds up.

An estimate of the scale of a potential CSA production plant is as follows. A typical current launch to Low Earth Orbit (LEO) uses on the order of 50,000 kg of propellant. Assuming a 5 mass % CSA implies that 2500 kg of CSA must be produced for the launch. Production capacity support of one launch per week (6×10^5 s) implies a CSA production rate of about 4 g/s. The critical factor then becomes the flow rate of lHe that is required to supply this CSA mass flow rate. A 1000/1 volume ratio implies a lHe flow rate of 4 kg/s, but this implies 1 CSA atom in a cube of lHe that has 10 atom on each side. This is a high enough concentration to imply a significant collision reaction rate. A 100 atom cube would be a lower limit, implying a 4000 kg/s. A reasonable compromise would be 400 kg/s. A droplet field with a 0.5 m x 1 m cross section and a mass flow rate of 10 kg/s is readily achievable, implying a 40 m long facility to produce the CSA mass generation rate required. For an average droplet size of 0.1 mm, and an average speed of 20 m/s, this would imply a volume flow rate of 20 m^3/s, at a volume loading of 0.1%. These are numbers that can be achieved with standard technology, but the actual case should require a somewhat smaller facility.

The deposition profile is also credible. For a 0.1% volume loading, there are about 2000 drops/cm^3, so that approximately 1.6% of the frontal area of a cubic cm is blocked by droplets. An approximately 100% blockage (on the average) would then occur at a depth of about 60 cm, which is the depth of the droplet field.

This is also a reasonable CSA generation rate. For a 40 m long facility generating a total of 4 g/s of CSAs, 0.4 g/s per m length must be generated. Typical growth rates for vapor deposition are on the order of 100 nm/s, which, for a 1 m x 1 m area implies 0.1 cm^3/s, or 0.4 g/s for a double sided deposition system as shown in Fig. 2, and assuming only a CSA specific gravity of 2.

It seems thus that a pure CSA generation facility is a feasible project, once an appropriate pure CSA is found. The current problem with pure CSAs is that no pure CSA that provides sufficient benefits to a propellant has yet been found.

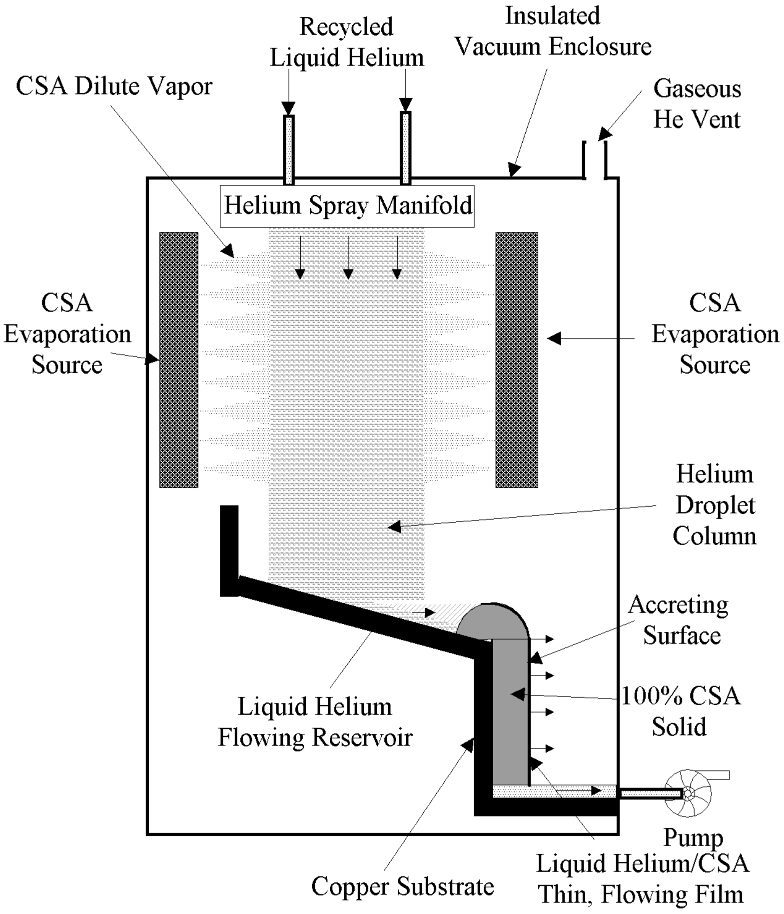

Figure 2. Concentration machine for creating a pure, cryogenically stabilized CSA.

VI. Unstable CSA Concentration

Fractional Purity/Unstable CSAs are those with zero reaction barriers, where the CSA species cannot come into contact (overlapping potentials) with another identical CSA molecule without reacting with itself. In this case there are a number of well known and well researched CSA candidates, such as the individual atoms of all of the lighter elements, lithium (Li), beryllium (Be), boron (B), carbon (C), oxygen (O), nitrogen (N) and fluorine (F). These elements have formed the core of work in the HEDM program, but the HEDM efforts have not met with successful production of significant mole fractions of these species. Computational efforts, however, have indicated that at least some of these CSAs (B) are stable at useful concentrations (e.g.[15]). One purpose of the present work is to find techniques for concentrating samples to commercially useful target concentrations.

A. Concentration Techniques

CSAs are assumed to be formed in the gas or plasma phase. The final product of the concentration technique for an unstable CSA is a CSA-doped solid propellant with a CSA concentration of at least 1 mole-%. All of the combinations of state changes can be considered for concentration. Concentration can be done in or from the gas, liquid or solid phase, followed by formation or condensation into the necessary final solid state. It should also be stated that the final CSA/inert solid may either be a mixture or a true compound.

B. Concentration Fluctuations

The fundamental difficulty of concentrating unstable CSA's is the avoidance of self-reaction, and elimination of the enhancement capabilities of the CSA by this self-reaction. Self-reaction can also have a more serious effect: it can destabilize the entire matrix, leading to potentially catastrophic results. The transition from isolated reaction to general instability is dependent on the details of the solid and will not be considered here, where the goal is to avoid significant reaction.

One fundamental problem associated with the avoidance of self-reaction, and the consequent necessity for avoiding spatial proximity of CSA species, is the natural fluctuations of the CSA. In the gas and liquid these fluctuations exist in both position and velocity space, whereas in the solid the fluctuations are dominated by variations in the CSA atom position relative to a totally uniform distribution within the inert matrix. In previous work CSA-doped inert matrix concentrations were limited by a number of effects, including energetic reactions in the accretion layer, CSA diffusion, the local concentration fluctuations. All of these factors can be reduced to a certain extent, and all are important for CSA concentration and limitations in CSA concentration.

As a preface to considering CSA concentration, techniques to avoid limits imposed by energetic reactions in the accretion layer and CSA diffusion must be briefly addressed. It is critical to avoid the formation of any kind of high mobility layer associated with the accretion process. In the case of para-hydrogen (para-H_2), due to the quantum nature of the solid there is a thin, highly mobile layer on the surface of all para-H_2 crystals at temperatures greater than about 3 K[16]. Thus, all accretion should be performed at lower temperatures, although experimentally this has not been done in the past. To minimize CSA diffusion, low temperatures and high crystal perfection (single crystals with few defects) are the key elements. Some elements (such as oxygen (O_2) have an inherent difficulty in forming high quality single crystals, due to the constraints of the necessary phase changes associated with cooling the sample to liquid helium temperature.

The issue of fluctuations in local CSA concentration must be addressed in the formation stage, and there are techniques available to do this. By reducing CSA atom/molecule position fluctuations, higher levels of CSA concentration can be achieved.

VII. Gas Phase Concentration

In the gas phase, atoms/molecules have positional and velocity fluctuations arising from the standard Maxwellian velocity distribution associated with an equilibrium temperature. This velocity distribution and the associated position distribution can be modified by constraining the atoms with body forces (electrical or magnetic) or through the use of external boundary conditions such as physical walls. Some experimental techniques of direct use to allow increased concentration by reducing gas phase fluctuations can be discussed.

One technique for concentration in the gas phase is by charging the CSA, the inert carrier gas, or both, and then manipulating the charged species using electromagnetic fields. One species can be separately charged by taking advantage of the different ionization potentials of the different species; excitation by electron beam or optically below a specific energy level will lead to the ionization of the species with the lower ionization potential. Optical ionization of either species irrespective of ionization potential can often be done using multiple photon excitation of appropriate energy levels. A more complex technique, however, usually implies a higher cost.

The charged species can then be moved in relation to the uncharged species. In the case of a collisionless mixture at low pressure, if the inert matrix gas is uncharged, it can be removed from the charged CSA simply by electromagnetically turning the flowing CSA, allowing the inert gas to separate by inertia. The concentration of the inert gas surrounding the charged CSA can be reduced by allowing it to expand normally while the CSA is constrained by the electromagnetic fields. The concentrated CSA/inert gas mixture would then be collected in a more standard fashion by co-condensation. This is more a technique for increasing area deposition rates rather than absolute concentration, since gas phase concentration limit result from high interdiffusion rates.

At higher pressures, similar effects are achieved in what are termed “drift tubes,” where the charged species does not undergo significant charge exchange and is moved on average relative to the carrier gas in spite of numerous collisions with the carrier gas (not other CSA atoms). Thus, in a similar manner to the collisionless case, the inert carrier gas can be expanded and its relative concentration reduced while the CSA is constrained by the electromagnetic fields. Co-condensation again completes the process.

Solid boundary walls can be used to aid concentration in a number of ways. The cold walls of a tube can be used to trap CSAs that have any transverse velocity, reducing velocity fluctuations in two of the three dimensions that determine the movement of the CSA molecules. For the case of CSA’s co-flowing with an inert gas that forms its stabilization matrix, if the transverse velocity is reduced enough the lateral concentration fluctuations of the CSA are reduced, so that it can be condensed in higher concentrations.

A special use of walls is the expansion of a gas through a nozzle. This process changes the thermal energy of the gas into directed kinetic energy at greatly reduced temperature. This is a common technique used to “freeze” the properties of a gas. Direct deposition using this technique leads to large concentration fluctuations due to collision-induced concentration fluctuations. However, if this atomic beam were charged and slowed in a electromagnetic field, concentration fluctuations would be greatly reduced and the concentrated co-deposition could take place. In this case, the elimination of particle tracks in the surface layer allows higher concentrations to be laid down. Charged particle slowing is common to many techniques that extract energy from a charged gas. Overall deposition rates would be lower due to limits on densities in a charged-particle beam.

The importance of low temperature deposition is indicated by data that shows that whereas thermal sources depositing into solids have multiple substitutional sites within the solid lattice, laser ablated material deposits in a single site, due to the narrower range of energies associated with laser ablation[17]. The fewer the number of types of substitutional sites, the more regular the crystal, the less the diffusion in the crystal, and the more controllable is the entire process.

VIII. Liquid Phase Concentration

Concentration techniques that only involve the liquid are limited by the relatively high diffusion rates of the CSAs in the liquids. However, an inert cryogenic liquid is an excellent tool for rapidly cooling CSAs impinging on its surface. Internal flows redistribute the CSAs within the liquid, allowing greater deposition per unit area, but overall concentration limits per unit volume are much lower than those for solids.

Cold CSAs in an inert liquid, in spite of their low concentration, could be deposited and concentrated in a manner analogous to crystal growth from solution. The process would begin by trapping both the CSA and the inert matrix molecules in a liquid that is a third, different material. Trapping in the liquid state of the inert matrix by itself would not allow controlled crystal growth of that matrix at temperatures well below the melting point of the solid, since solidification would be rapid and uncontrolled. This implies that both the CSA and the inert matrix molecules must be soluble in the third, carrier liquid. The carrier liquid must, of course, remain a liquid at the crystallization temperature of the inert matrix. The key to this technique is the fact that the CSA atoms/molecules will join themselves to the solid preferentially at certain sites, rather than randomly on the surface. This will tend to create the high quality crystals that are necessary to prevent CSA diffusion and reaction at higher concentration. The overall concentration of the CSA relative to the inert solid matrix would be determined by their relative concentrations in the liquid. The primary problem with this process for engineering purposes is the slow rate of deposition. It certainly appears to be an excellent vehicle for creating high concentration CSAs, and may also eventually prove to be a practical commercial process.

Experimentally, there are not many liquid carrier/inert matrix combinations to choose from. Liquid He/solid H_2 is probably not appropriate, since H_2 is not soluble in lHe and floats on its surface[14]. There may also be a problem with the solid solubilities of the different candidate materials. As solids, Ne and H_2 are not soluble; during attempted solidification, Ne crystals form on surface[18]. In liquid form, however, there are broad temperature and concentration ranges where H_2 and Ne have complete solubility[4]. No other liquids appropriate to sH_2 growth at 10 K exist.

The other major inert solid matrix of propellant interest is O_2. The difficulty with solid O_2 is that there is a major volume change associated with the phase change from the rhombohedral β-phase that exists in the temperature range from 43.8 K to 23.9 K (sp. gr. = 1.50), to the monoclinic α-phase that exists at temperatures below 23.9 K (sp. gr. = 1.55)[19]. This volume change leads to crystal defects that cannot be annealed out if an O_2 crystal is cooled from melt temperatures to below 24 K. Two liquid carrier/sO_2 combinations are thus available: lNe as a carrier liquid at 27 K crystallizing β-phase solid O_2, and lH_2 as the carrier liquid at 20 K, crystallizing α-phase solid O_2 as the inert matrix. The lower temperature process using lH_2 would be preferable in terms of diffusion in the solid, but as a practical experiment, the inertness of lNe is much preferable as a liquid to use for trapping the possibly hot CSA atom/molecules. This appears to be a very promising technique.

An intriguing addition to the crystallization technique is the use of optical excitation to dissociate reaction products generated from CSA contact back into the original CSA form. The surrounding cold liquid would absorb the energy from this dissociation reaction. This process has long been used to create atomic species in solids for matrix isolation studies (e.g.[20]). This technique might allow high concentrations of the CSA to be formed in the liquid and thus the deposited solid.

IX. Solid Phase Concentration.

All of the solid phase techniques considered here are surface processes; it is believed that bulk solid processes are too intractable to be commercially useful. Although sublimation concentration, the initial concept developed by the author for solid phase concentration, is a surface process, it assumes that the structure of the surface of the solid is similar to that of the bulk, which is not usually the case. Other concentration techniques that use surface properties will be discussed below.

A. Sublimation Concentration

Sublimation concentration refers to the process by which a condensed van der Waals gas that provides a matrix for the CSA can be sublimed to concentrate the CSA at the surface. The surface-concentrated CSA is then harvested in some way or buried by unconcentrated material and the process is repeated.

B. Sublimation Concentration Machine

Figure 3 shows a schematic of a sublimation concentration machine designed by the author. It uses three stations to perform the basic sublimation concentration functions.

At station #1 the CSA and inert gas are co-deposited at low concentration – but at the highest stable concentration that the deposition process can tolerate. Deposition takes place on a cooled substrate that stabilizes the mixture, and it takes place on top of a thin layer of pure inert matrix.

At station #2 sublimation of the inert part of the matrix occurs, concentrating the remaining CSA at the surface. The sublimation process is an evacuation process that can be heat-driven externally as shown in the figure, or using heat conducted through the substrate. The volume around the surface of the deposited mixture is evacuated to drive the sublimation. Heating is performed to maintain the sample temperature and pressure, replacing the heat lost to the subliming inert matrix material. External heating is preferred over substrate heating to avoid thermal gradients in the sample. Optical heating can be done by broadband excitation in the UV or IR (most inert matrix materials are transparent in the visible), or by wavelength-specific absorption. Excitation of the CSA must be avoided to avoid any excitation of the molecule that may result in such effects as enhanced diffusion. Sublimation can be initiated or stopped at any time by controlling the heating. The substrate is then returned to station #1 for addition of another layer to be concentrated.

At station #3 the multilayered, concentrated CSA material is collected for formation into its final shape, either as particles in a pumped slurry, or as large segments for use in a hybrid rocket. Figure 3 shows a sloughing technique being used, where a very thin layer is loosened from the substrate by slightly warming the substrate. This assumes that many concentrated surface layers have been built up, so that the thin pure layer at the base is a small fraction of the overall volume collected.

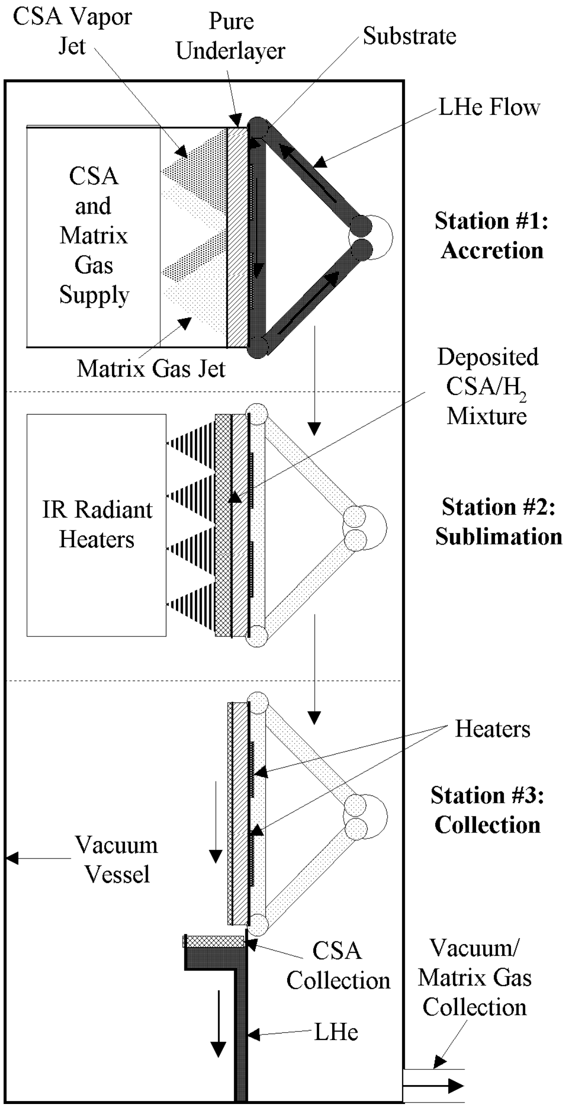

Figure 3. Schematic of a sublimation concentration machine for use with unstable CSAs.

C. Sublimation Concentration Feasibility Calculations

To demonstrate the practicality of sublimation concentration, a worst-case scenario of CSA sublimation concentration was examined; the case of a solid matrix of H_2 at 3 K. Sublimation at 3 K is necessary to avoid the high mobility layer that forms on sH_2 at higher temperatures[16]. This is a worst-case example due to the extremely low working vapor pressure of H_2 at this temperature that must be used for sublimation. Calculations have been done to show that the process is feasible, at least on a laboratory scale.

The parameters associated with the sublimation of solid H_2 are reasonably well known. Solid H_2 has a vapor pressure of 5×10^{-11} torr at 3.0 K[21], so the sublimation of H_2 at this temperature would require a vacuum pumping system that supplies this level of vacuum. A 10^{-11} torr, vacuum can be and has often been achieved with care using a hard-sealed vacuum system and either a cryopump, a cryosorption pump, an ion pump, or a variety of gettering techniques. An external vacuum pump must supply a base pressure of about 1×10^{-11} torr to provide the sublimation pumping. A simpler technique is to use local cryosorption pumping or to use the chamber walls as high speed cryopumps by keeping them at 3 K.

In order to practically concentrate a widely dispersed CSA in H_2, enough lattice layers of solid H_2 must be removed to greatly increase the surface concentration of the CSA. If, for instance, the CSA is present in volume concentrations on the order of 0.1%, there will be one CSA atom/molecule for every 1000 H_2 molecules, assuming that the CSA specie is not large compared with the H_2 molecule. There is thus one CSA atom/molecule somewhere in each cubic volume of H_2 that has 10 H_2 molecules on a side. To achieve CSA densities on the order of 10%[1] optimal for major fuel enhancement, concentration by a factor of 50 would be required. To create a 5% concentration surface layer from a material with a 0.1% volume concentration would require the removal of 55 lattice layers on average. Each 10 molecule layer set that was sublimed would bring 1 CSA molecule to a 10 x 10 H_2 molecule area at the surface.

Assume, for laboratory experiments, that a circular surface film of H_2 5 mm in diameter is grown. This film has an area of about 0.2 cm^2. The effective cubic lattice spacing for H_2 is about 3.5×10^{-8} cm. This can be deduced from the density of solid H_2 of 0.088 g/cm^3, which implies a volume density of $0.088/(3.3 \times 10^{-24})$ molecules/cm^3 or 2.5×10^{22} H_2/cm^3, and a lattice spacing as estimated. This lattice spacing is also consistent with the hcp Van der Waals radius for H_2 of 1.9 A. A surface area of 0.2 cm^2 thus contains about 1.7×10^{14} H_2s in each lattice layer. The time taken to sublime 50 lattice layers and concentrate the impurity is then determined by the pumping rate, or, in the case of cryopumping, by the heat absorbed in the cryosurfaces.

In the case of cryopumping, higher pumping speeds are possible even at very low pressure, only limited by the surface area that can be cooled to below 3 K. It will be better to use cryopumping because there is greater flexibility in temperature; a cryopanel at 2 K can provide a potential base pressure in H_2 of 4×10^{-18} torr, which is unattainable in real systems with small vacuum leaks. Taking the heat of sublimation of H_2 to be 240 cal/mole, a heat input of 4×10^{-22} cal is required to sublime each H_2 molecule. For each lattice layer considered above, 1.2×10^{-10} cal/s is required for sublimation. The heat of vaporization of LHe at 3 K is 22 cal/mole, so 10 times as many molecules of helium must be vaporized to provide the cooling to condense each H_2 molecule. For the case defined above the amount of heat and pumping mass involved is very small, since the total amount of H_2 sublimed is small. It is easy to provide a pumping surface 100 times as great as the surface area of the H_2. Another factor to be considered in cryopumping is the thermal shielding effect of the condensed gas on the metal cryopump surface. Solid H_2 has a low thermal conductivity, so pumping speeds become limited by the rate at which heat can be removed through the H_2 to maintain its temperature. Again, this is not a problem for a small volume of H_2 sublimed relative to large surfaces, and no thick layer is built up to hamper the pumping process.

Assuming that the cell is used as a cryopump, one can estimate the time to perform a concentration experiment. The sample surface is 5 mm diameter; a cryopumping area 100 times larger would consist of a 4 x 4 cm area, somewhat smaller than the cell internal surface area. Assuming the deposited sample to be about 100 lattice layers thick, or 200 A, implies only a 1 A layer of H_2 condensed on the cell. The thermal diffusivity of solid para-H_2, α_{H2} is 8.25 cm^2/sec, such that temperature equilibrium (90% T) in a 100 A thick layer would be reached in a time, t, such that $x/[2(\alpha_{H2}t)^{0.5}] = 1$, or $t = x^2/16$ seconds, where x is in cm. This implies that the surface of the cryopumped H_2 reaches 2.5 K very rapidly; the experiment time will be determined by the time it takes to cool the helium bath from 3 K to 2.5 K by pumping on it. This will probably be on the order of 30 min, given the vacuum setup. It is expected that a typical sublimation concentration process will take on the order of 30 min, not limited by the fundamentals of the process and an overall test, including deposition, will probably take a few hours.

Further consideration of the sublimation process at the surface implies that a much higher sublimation temperature can be used in the case of H_2. The key is to be sure that the material loss rate from the surface is high enough that the any liquid layer that forms on the surface does not have sufficient time to provide mobility to the CSA species at the surface of the solid. This mobility should be small, given the small mass of the H_2 molecules compared with the CSA. The practical sublimation temperature should be a much higher temperature than 3 K.

D. Sublimation Concentration Engineering

Sublimation concentration is basically a surface process. The use of surface processes for large-volume production is common in the chemical/materials processing industry. A commercial effort in sublimation concentration would begin with a pilot plant to produce 1 m^3 of the propellant in a minimum time on the order of a week. Concentration by a factor of 10 (0.1% to 1%) implies that a volume of about 10 m^3 of solid must be pumped away. Deposition of the film is rapid; pumping away the solid matrix molecules to concentrate the film is the rate limiting process. Operation over a week and a half (10^6 s) implies a volume rate of 10^{-5} m^3/s, or 10 cm^3/s of the solid must be carried away.

Again, assuming a worst case of a H_2 inert matrix, for a lattice spacing of about 3×10^{-8} cm, there are about 3×10^{22} molecules in a cubic centimeter of H_2. For a needed evaporation rate of 10 cm^3/s, 3×10^{23} molecules/s must be evaporated. Based on a standard evaporation rate, $r_{\#}$, the rate of evaporation in molecules or atoms per cm^2-s, Log

$r_{\#} = 19.5458 - \log P_{\mu} - 0.5 \log (MT)$, where, P_{μ} is the pressure in microns, M is the gram-molecular weight, and T is the temperature (K). Evaporating from a 10 m^2 area (10^5 cm^2) implies a vaporization rate of an average of about 10^{18} molecules/cm^2-s is required. This implies a vapor pressure on the order 4 microns and a temperature of between 6.3 K.

E. Surface Concentration Processes

Material properties change at their surfaces; atoms rearrange to compensate for the lack of bonds beyond the boundary of the material. Analogous effects allow a substrate to control a material forming on top of it. One key element of creating a highly concentrated CSA is the perfection of the created crystal mixture. Deposition from the gas phase normally results in surface layers that are disorganized and have higher diffusion rates, often resulting in porous solids. If a high concentration crystal is to be grown, it must be grown using low energy deposition and careful growth of the crystal surface.

Epitaxial growth techniques are suggested, using the carefully chosen substrate to induce a crystal pattern that will continue once formed. In many cases the CSA and inert gas matrix have significantly different sizes that suggest both a specific crystal structure and a substrate, such as B and H_2. This concept has been investigated previously by the author[1] , indicating that ionic solids may be one promising substrate. The present work, however, indicates that low energy deposition, such as from a doped liquid, will be required, rather than the gas-phase deposition used in the semi-conductor industry. Some materials may be useful as substrates as a result of their unusual surface chemistry: diamond, for instance, is usually capped with hydrogen at its surface.

Another aspect of surface control is the creation of strong electromagnetic fields at the surfaces of many materials. O_2 is strongly magnetic, and B is strongly polarizable; the growth of a combination of these elements should be strongly affected and perhaps controllable by bulk or surface electromagnetic fields.

These techniques will require more foundation work than the others discussed above, since they require a greater knowledge of the details of the atomic-scale interactions, rather than more globally physical effects, such as sublimation.

X. Conclusions

The analysis of this work implies that cryostabilized additive (CSA) concentration is practical with respect to the physics, the engineering, and the economics of the various processes that can be used to perform the concentration. Concentrated CSA propellant mixtures provide sufficient increase in I_{sp} and sufficient decrease in payload cost to orbit to justify the expense of creating the CSA. The limiting factor in the use of CSAs is rather the need to use them in the form of solids; the necessary techniques of slurry fuelling, cryogenic hybrids, or cryogenic mono-propellant rockets have not yet been developed to the point of commercial use.

An economic analysis based on current launch costs indicates that CSAs with concentrations of as low as 1 mole-% are practical and justified. This motivates various efforts to concentrate such atomic species as boron, and to develop CSAs that have reaction barriers that allow them to be cryogenically stabilized at 100% concentration.

In particular the following experimental efforts to validate the CSA concentration approach appear to be practical and will be pursued according to their probability of success in the following order:

1) Sublimation concentration: where progressive layers of CSAs/inert matrix deposition have the matrix material sublimed away to concentrate the CSA.

2) Growth of a high concentration, high quality CSA/inert matrix solid crystal from a solution of CSA and inert matrix atoms/molecules dissolved in a third inert liquid.

3) Creation and purification of a CSA that is stable at a 100% concentration and which can enable a significant increase in I_{sp} when added to a propellant.

Key elements in achieving high concentration of CSAs include only low temperature processing, high crystal quality, and the proper choice of materials and inert propellant matrices; specifically H_2 and O_2.

References

[1] S.C. Bates, "Cryostabilized Propellant Additives," AIAA-2003-5213, (2003).

[2] M. Moskovits and G.A. Ozin, *Cryochemistry*, J. Wiley & Sons, New York, NY, (1976).

[3] Matrix Isolation Spectroscopy, A.J. Barnes, W.J. Orville-Thomas, A. Muller, and R. Gaufres Eds., Reidel, Dordrecht, (1981).

[4] V. A. Schwentner, and S. N. Apkarian, "Molecular Photodynamics in Rare Gas Solids," *Chemical Reviews*, Vol. 99, No. 6, p. 1481 (1999).

[5] Proceedings of the High Energy Density Matter (HEDM) Conference, M.R. Berman Ed., 12-15 April 1992, Lancaster, CA, USAF Phillips Report, (1992).

[6] P. G. Carrick, "Theoretical Performance of Atomic and Molecular HEDM Additives to Solid H_2 ," Proc. of the HEDM Conf., T.L. Thompson, Ed., 6-8 June 1993, Woods Hole, MA, USAF Phillips Lab Report,PL-TRS93-3041, (1993).

[7] R. B. Scott, *Cryogenic Engineering*, Met-Chem Research, Boulder, CO, (1959).

[8] *Physics of Cryocrystals*, V. G. Manzhelii and Y. A. Freiman, Eds., Amer. Inst. of Physics, Woodbury, NY, (1996).

[9] M. E. Fajardo, "Matrix isolation of metal atoms generated by laser ablation. II. The Li/Ne, Li/D_2 and Li/H_2 systems," *J. Chem. Phys.*, Vol. 98, No. 1, p. 110 (1993).

[10] *Space Transportation Costs: Trends in Price Per Pound to Orbit 1990-2000,* [Corporate White Paper], Futron Corporation, Bethesda, MD 20814, URL: http://www.futron.com/pdf/FutronLaunchCostWP.pdf, (cited May 17, 2004).

[11] "Introduction ," Proc. of the HEDM Conf., T.L. Thompson, Ed., 6-8 June 1993, Woods Hole, MA, USAF Phillips Lab Report,PL-TRS93-3041, p. 15., (1993).

[12] R. O. Voth, P. R. Ludtke, D. E. Daney, and J. A. Brennan, "Production, Characterization, and Flow of Slush Hydrogen," NASP Technical Memorandum 1165, NASA Langley Research Center, (1992).

[13] J. Polk, “An Overview of JPL's Advanced Propulsion Concepts Program,” Jet Propulsion Lab, Pasadena, CA, [online notebook] URL: http://www.islandone.org/APC/, (cited May 17, 2004).

[14] B. Paleszewski, "Solid Hydrogen Experiments for Atomic Propellants: Image Analysis," AIAA-2001-3233, NASA/TM-2002-211297, 1 (2002).

[15] S. J. S. a. V. G. A. Jang, "Quantum Molecular Dynamics Simulations of Low-Temperature High Energy Density Matter: Solid p-H_2/Li and p-H_2/B," *J. Phys. Chem. A*, Vol. 103, p. 9512 (1999).

[16] P. Leiderer and U. Albrecht, "Investigation of Quantum Systems with Surface Plasmons and Surface State Electrons," *J. Low Temp. Phys.*, Vol. 89, p. 229 (1992).

[17] J. K. T. E. J. a. K. H. Ahokas, "Theoretical analysis of alkali metal trapping sites in rare gas matrices," *J. Chem. Phys.*, Vol. 112, No. 5, p. 2420 (2000).

[18] C. S. Barrett, L. Meyer, and J. Wasserman, "Crystal Structure of Solid Hydrogen and Deuterium, and of Neon-Hydrogen and Neon-Deuterium Mixtures," *J. Chem. Phys.*, Vol. 45, No. 3, p. 834 (1966).

[19] S.C. Bates and T.L. Altshuler, "Shear Strength Testing of Solid Oxygen," Cryogenics, Vol. 35, p. 559 (1995).

[20] V.A. Benderskii, D.E. Makarov, and C.A. Wight, *Chemical Dynamics at Low Temperature,* J. Wiley & Sons, New York, NY, (1994).

[21] ASRDI Oxygen Technology Survey, Thermophysical Properties," H. M. Roder and L. A. Weber, Eds., Volume1, NASA SP-3071, Available From NTIS, (1972).