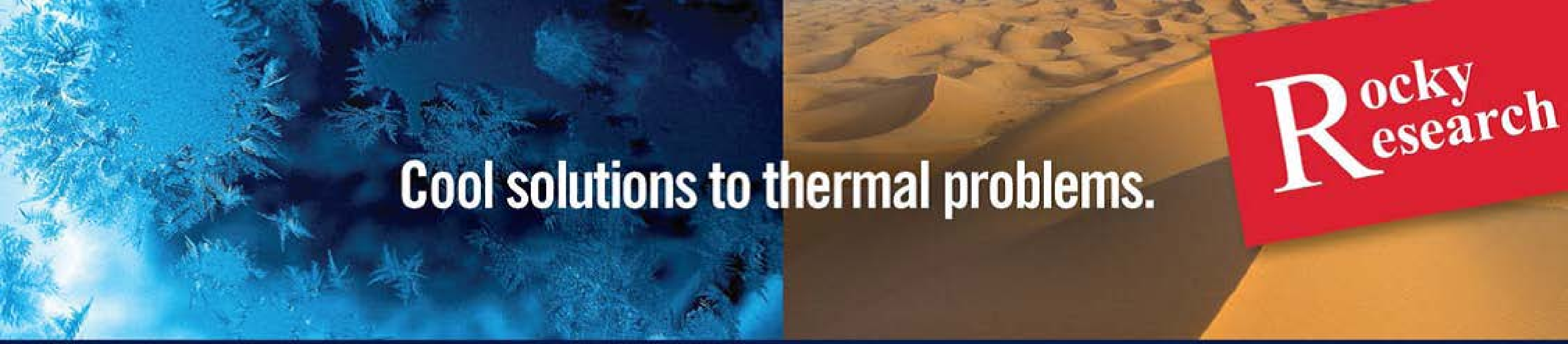


Complex Compounds

For more than 20 years, Rocky Research has been a pioneer in the field of sorption refrigeration utilizing complex compounds. Our technology earned special recognition from NASA in 1999. Now, with several key patents utilizing the technology, Rocky Research is poised to provide the most practiced, effective use of sorbent complex compounds for any number of applications.

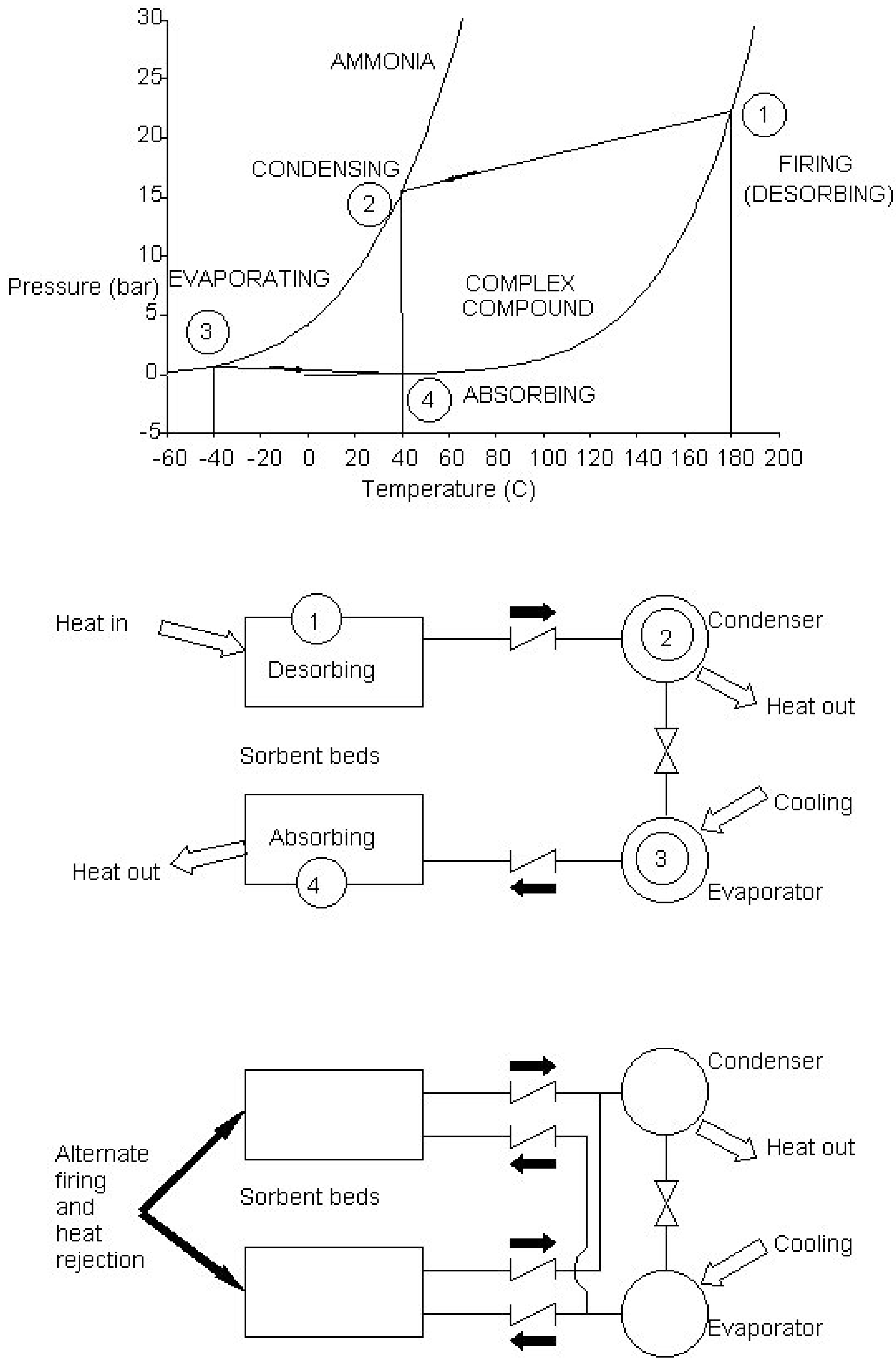
Background of Complex Compound Technology

Sorption refrigeration and thermal storage systems produce refrigeration through the sorption of a refrigerant by some sorbent media. Complex compounds are one class of solid sorbent media and they provide many advantages over other liquid and solid sorbents. Included herein is a brief description of sorption refrigeration, followed by an explanation of complex compounds and their advantages in sorption refrigeration.

The enabling principle for sorption refrigeration and chill storage is that zeotropic mixtures of pure substances exhibit a vapor pressure between that of the constituents. Thus the mixture vapor pressure is lower than the pressure of the more volatile component; this is often referred to as vapor pressure suppression. The most volatile substance is the refrigerant. Ammonia-water mixtures are one useful example. Ammonia is the refrigerant, and water is the absorbent which provides the vapor pressure suppression. Refrigeration is produced by allowing a lean sorbent to draw in refrigerant vapor from the evaporator. The sorbent and evaporator are at essentially the same pressure, so evaporation occurs at a much lower temperature than the solution temperature. The more vapor pressure suppression, the larger the temperature difference possible between the evaporator and the solution or absorber. As the solution becomes richer in refrigerant, it must be regenerated; that is refrigerant must be driven off. This is accomplished by heating the sorbent to drive off refrigerant vapor, and letting the vapor condense, typically near ambient temperature. Lean sorbent is then cooled and allowed to again absorb refrigerant from the evaporator.

The same processes are used for sorption refrigeration whether the sorbent is liquid or solid: (1) sorption of refrigerant from the evaporator, (2) heating the sorbent to an elevated temperature, (3) desorption of refrigerant to the condenser, and (4) cooling the sorbent back to absorption temperature. These processes are executed in a continuous manner for liquid-vapor sorption, with the liquid solution being pumped between the absorber and generator (desorber). Solid sorbent systems are periodic, with each sorber undergoing these processes sequentially.

Figure 1 *Refrigeration system schematic.*



Complex compound refrigeration uses fixed sorber beds containing solid complex compounds as the sorbent. An example flow schematic is illustrated in Figure 1. In this example, two sorber beds with complex compounds are used. The vapor pressure of the pure refrigerant (in this case ammonia) and the complex compound are plotted versus temperature. State point numbers on the pressure-temperature diagram and schematic can be used to trace the cycle. At state point 1, one sorber bed is heated until the pressure in the sorber is greater than pressure in the condenser, shown as state point 2. Consequently, ammonia vapor is driven off the complex compound and flows to the condenser, and becomes a liquid. In this example, the sorbent is heated to about 180 C to drive ammonia to a 40 C condenser. Liquid refrigerant then flows from the condenser through an expansion valve to the evaporator which is at much lower pressure. Figure 1 shows the evaporator at -40 C and about 0.7 bar (state point 3). Evaporator pressure is maintained by the second sorbent bed which is cooled to a low enough temperature for the sorbent pressure to be below evaporator pressure. Thus refrigerant vapor is drawn from the evaporator into the sorbent.

Absorption and desorption processes last from 5 to 30 minutes. When an absorption process is complete, that bed is heated for regeneration (desorption). When the desorption process is complete the bed is cooled for absorption. Thus two sorbent beds operate out of phase to produce continuous refrigeration. Unequal absorption and desorption periods can be used to avoid time periods with no suction on the evaporator.

The desorption reaction is endothermic, so energy is required to drive the desorption as well as heat the sorbent beds. Heat is the energy source which drives the cycle. Heat from many sources can be used, such as gas combustion, waste heat, electrical resistance heat, or solar. Integration of heat into the cycle is accomplished with pumped loops, heat pipes, thermosyphons, cartridge heaters, or other appropriate means.

Maintenance of low evaporator temperature and pressure during absorption requires that the sorbers be cooled and maintained near ambient temperature. The absorption process is exothermic so heat removal is required for the entire absorption period. Cooling is achieved by forced air flow, pumped loops, phase-change refrigerant, or other means depending on the application.

The mechanical schematics of Figure 1 illustrate how two sorbent beds are integrated into a refrigeration system. The portion of the system comprising the condenser, expansion valve, and evaporator is identical to the portion of a vapor compression refrigeration system. The pair of sorbent beds substitute for the compressor. In this example, each sorbent bed is fitted with a pair of check valves (non-return valves) just like a cylinder on a compressor. These check valves direct vapor exiting the sorber to the condenser, and only allow inflow from the evaporator. Thus flow of ammonia vapor to and from the sorber beds follows passively from heating and cooling of the sorbent.

Complex Compound Sorption Media

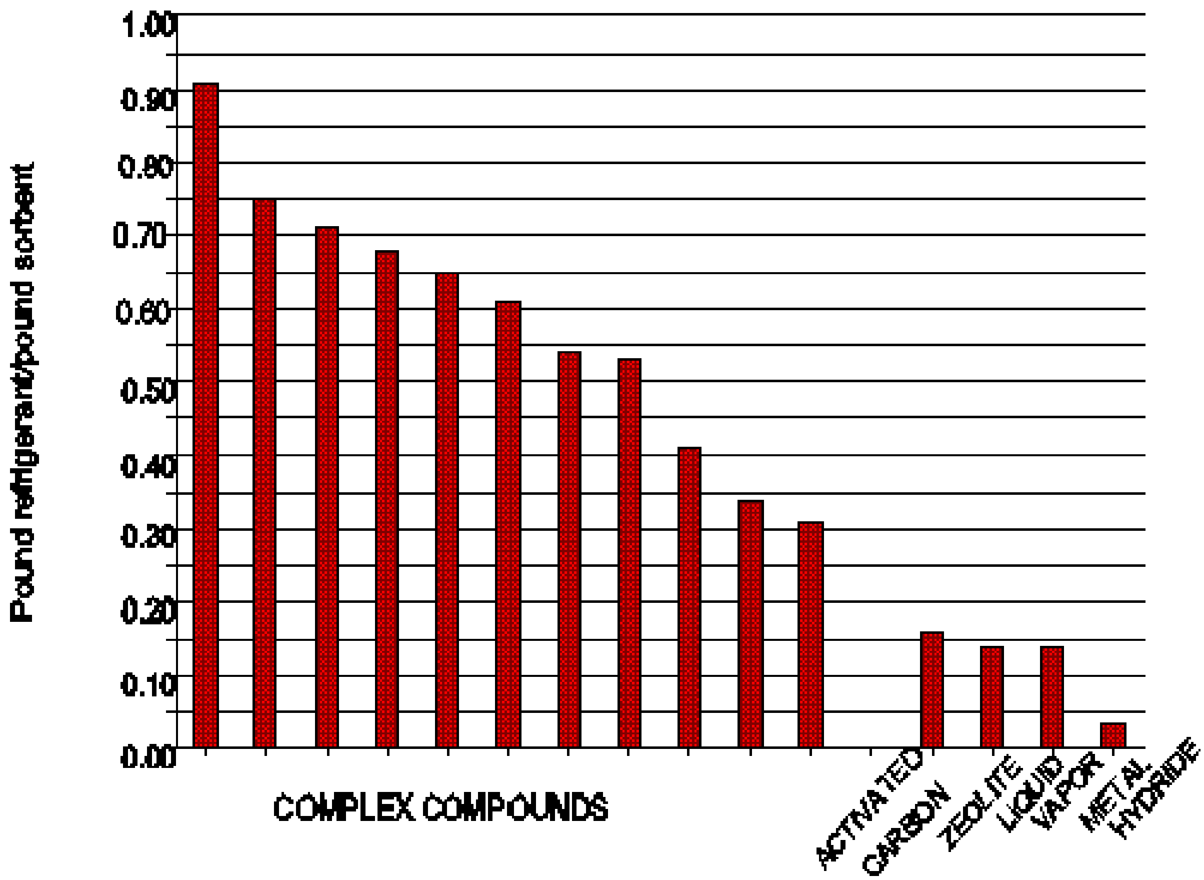
A coordination complex compound is a compound formed by an inorganic salt that bonds to several small molecules acting as complexing agents, better known as ligands. The complex compounds as used in sorption thermal energy systems consist of solid simple inorganic salts which serve as absorbents and ammonia as the ligand. Such complexes are examples of the chemistry studied by Alfred Werner 100 years ago. The absorbent salts complex the ammonia vapor directly from the gas phase, and this reaction is accompanied by a large release of heat. The reaction is reversible, where with the input of heat the ammonia can be made to desorb or release from the absorbent. Thus, the ammonia functions as a refrigerant, and cooling systems can be designed taking advantage of this reversible chemistry. Coordination complex compounds have two intrinsic features which make them superior media for sorption refrigeration, monvariance and high refrigerant holding capacity.

Monovariance: Monovariance refers to the independence of vapor pressure and absorbed refrigerant concentration. The complexes are crystalline both as absorbed and as desorbed compounds, and only certain definite well-ordered and well-defined lattice structures are preferred. Thus as the salt absorbs ammonia, one solid crystalline phase with a small amount of ammonia converts microcrystal by microcrystal to another crystalline phase which contains a higher fixed amount of refrigerant. As a consequence of the presence of the two solid phases, and the Gibbs Phase Rule, "plateau" behavior of the pressure results (also seen in metal hydride systems), in which the refrigerant is held at one vapor pressure up to a certain absorbed concentration. Then, the pressure increases in nearly a step function to a higher vapor-pressure plateau with a new set of two solid absorbent phases. These phases are the relatively more absorbed crystal lattice from the former step, and a new crystal lattice, one that incorporates an even higher number of ligands.

Monovariance is important for the application of a sorbent to a refrigeration system because absorption and desorption pressures and temperatures remain fixed during the sorption process. Referring back to the example of Figure 1, full desorption occurs at the temperature and pressure indicated by state point 1. If vapor pressure decreased as refrigerant concentration decreased, the desorption temperature would have to continuously increase during the desorption, thereby negatively impacting the energy efficiency of the cycle and amount of refrigerant desorbed. Likewise, without monovariance the absorption conditions would vary as refrigerant absorption continued, and eventually the vapor pressure would rise above evaporator pressure and absorption would cease. Monovariance enables the pair of sorber beds to maintain constant suction and discharge pressures. The pair of sorbers provides nearly a direct substitute for a mechanical compressor.

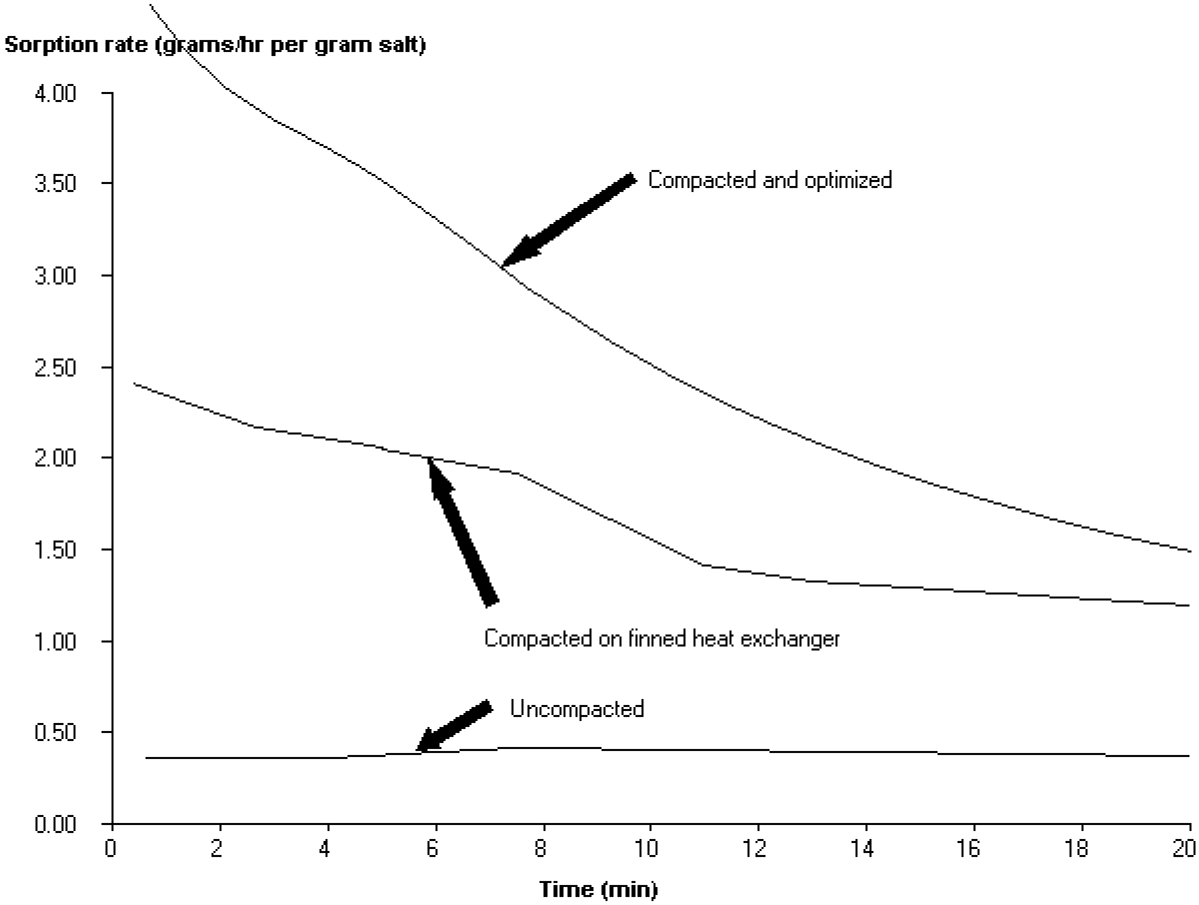
High refrigerant holding capacity: Refrigerant holding capacity of complex compounds is very high, often as high as 70% of the absorbent dry weight. Several moles of ligand can be bonded to a single mole of salt. This allows the amount of ligand mass which can be bound by complex compounds to be four to five times greater than the mass found for either other absorbent systems or from adsorption including zeolite, activated carbon, and liquid-vapor media such as aqua-ammonia or LiBr-water. Figure 2 shows relative refrigerant holding capacity for several complex compounds contrasted to other sorption media such as liquid solutions and zeolite or activated carbon. Data for all media are at identical thermodynamic conditions. High refrigerant holding capacity is especially Many complex compounds are shown in Figure 2 because different complex compounds have different vapor pressures, and are therefore used to provide different evaporator pressures. The most suitable complex compound is selected for each application.

***Figure 2** Refrigerant holding capacity of complex compounds compared to other sorption media.*



These favorable equilibrium properties of complex compounds--monovariance, high refrigerant holding capacity, and available media with good vapor pressure suppression--can only be exploited if rapid sorption (reaction) rates are achievable. Because complexing reactions are energetic, high rates can be maintained only if sorber beds are designed to provide very effective heat and mass transfer. Rocky Research has developed proprietary sorber designs and processes which enhance heat and mass transfer significantly. The traditional method of conducting solid-vapor sorption reactions is to place a thin layer of absorbent on flat heat exchanger surfaces. Refrigerant vapor enters the absorbent from above, and heat is conducted to the heat exchanger below. As the sorption process proceeds, many sorbents--especially complex compounds--increase in volume and swell away from the heat exchanger. The low density solid is an effective thermal insulator, and heat transfer limits the sorption rate. During solid-vapor complex-compound sorption reactions as practiced by Rocky Research, the space for expansion of the solid is limited and the tendency to swell creates a dense mass with enhanced thermal conductivity. Heat exchangers are designed such that the mass diffusion and thermal conduction path lengths can be independently selected. Optimization of sorption rate is accomplished by selecting an ideal density of the complexed sorbent, and ideal thermal and mass diffusion path lengths. Due to the complex nature of the process and variability of material properties with temperature and refrigerant uptake, this optimization is usually performed experimentally rather than analytically. Figure 3 shows reaction rates achieved by the conventional methods, by use of early Rocky Research procedures, and finally the results after optimization. All three curves were generated for the same sorbent at identical temperatures and identical refrigerant pressures. The new system resulted in fourfold rate increase over conventional technology, and optimization provided nearly another doubling of the rates. The same system of enhancing heat and mass transfer also provides increased stabilization of the salt.

Figure 3 *Sorption rates showing improvements with the compaction system and further optimization.*



In summary, advantageous properties of complex compounds include:

1. Large amounts of refrigerant can be absorbed, sometimes equal to the weight of the absorbing salt.
2. Many compounds are available; vapor pressure nearly ideal for many applications can be selected.
3. Vapor pressure is independent of refrigerant concentration, over very broad concentration spans.
4. The compounds are solid and immobile. Solution pumps are not required to circulate solutions between pressure levels, and the sorption processes are not gravity sensitive.

Development Status of Complex Compound Sorption Technology

Complex compound sorption technology has advanced well beyond a laboratory curiosity, and is in an early stage of commercialization. One product for ammonia pumpout of large refrigeration systems is commercially available. Industrial thermal energy storage systems have been field tested, and an industrial heat pump will be field tested in 1996.

Small complex compound refrigeration systems with refrigeration capacities of 20 to 100 W are being fabricated in low volumes by an OEM manufacturer. Following successful field tests and design for manufacturer, units will be marketed in consumer appliances.

Many other applications of complex compound sorption are being prototyped and the economics evaluated. These included HVAC, commercial refrigeration, transportation refrigeration, and medical appliances to name a few.

COMPLEX COMPOUND REFRIGERATION MODULE FEATURES

- Wide Temperature Range -60 C to +300 C
- Scalable from 3W to Several Hundred Watts
- No Moving Parts Except Check Valves
- No Noise
- No Vibration
- No CFC/HCFC/HFC
- Compact Designs
- Thermal Storage Options (runs w/o power if desired)
- Portable
- Orientation and G-Force Insensitive
- Fast Pull-Down Possible at Multiple Capacity of Nominal
- Improvements Expected