Safety in Supercritical Fluid operations

ABSTRACT

Most supercritical fluid operations do present specific hazards that operators shall take into account : Based on our long-term experience of operating and manufacturing supercritical fluid equipment, we present a list of these various hazards and how to avoid them :
-"Mechanical hazards" : high pressure explosion/rupture, corrosion, sintered disk, plugging ,...
-"Thermodynamic" hazards : dry ice formation, BLEVE phenomenon ;
-"Chemical" hazards : co-solvent, N_2O, corrosion, products,...
-"Biological" hazards : CO_2, co-solvent, product aerosols, bio-materials contamination,...
- "External" hazards : fire, electricity failure, control failure.
We will also describe some "traps" that must be avoided by an adequate design and wise operation : Pressure control before vessel opening, plugging of tubings, gauges/instruments or sintered disks, leak cure...

INTRODUCTION

Equipment handling supercritical fluids and liquefied gases present important hazards that must be taken into account both for equipment design and construction and for operation and maintenance. Safety considerations must influence any technical choice and operation and a detailed analysis of potential hazards must be specifically conducted for any case. In this paper, we would try to list the different classes of hazards and how to cope with them, so that both the process designer and the operator are informed.

MECHANICAL HAZARDS

Obviously, any pressure vessel presents a rupture hazard. However, both design standards and official tests that are enforced by state agencies (or equivalent), in combination with strict inspection procedures limit this hazard to a quasi-zero level, especially on large-scale units. But, some mechanical hazards are often underestimated, especially on R&D multipurpose equipment :

- **Corrosion** : as many products are handled, it might happen that some of them do induce corrosion causing cracks and local weakness of the metal.

- **Plugging** : most solid-fluid extraction equipment use baskets closed by sintered disks ; on large scale units, sintered disk plugging causes breakage on decompression but, on lab or pilot-scale equipment, the sintered disk may not break : then, even if the autoclave decompression seems effective, compressed CO_2 may remain in the basket ; on autoclave opening, the basket may be brutally ejected and/or may explode.
  So, we strongly recommend to be extremely prudent when the treated material could lead to sintered disk plugging : polymers, "sticking" materials, highly viscous extracts,....

Anyway, in all cases, especially on lab or pilot scale units, it is better to wait around 5 to 10 minutes after autoclave decompression before opening the autoclave, so that CO_2 have time to exit from the basket, even through a plugged sintered disk.

- **Tubing connection rupture** : Double-ring connections (like SWAGELOK ®, GYROLOK ® or SAGANA ®) are commonly used on most small scale equipment, when the service pressure is below 400 bar. These connections are perfectly safe and reliable when the screwing procedures are strictly followed. Otherwise, the rings are not strongly attached to the tubing and a brutal rupture may occur on pressurization.
  We recommend to always verify the good setting of the connections rings prior to high pressure use.

- **Metal fatigue** : The life duration of high pressure vessels is linked to the number of pressurization / depressurization cycles. Commonly, autoclaves are authorized for 10 000 to 20 000 cycles, depending on their design.
  On large scale units that are intensively used, a leaded counter must be installed to verify the cycle number and to stop any operation after the limit number is reached.

- **Metal fragilization** : As carbon steel exhibits much better mechanical properties than stainless steel, large-scale pressure vessels are commonly built in carbon steel covered by an internal stainless steel cladding. As carbon steel may be subject to phase transition, it becomes brittle when temperature decreases below -20°C ; so it is absolutely necessary to avoid such low temperature "exploration" during depressurization. In fact, adiabatic CO_2 decompression to atmosphere leads to very low temperature and CO_2 ice formation. So hot fluid circulation in the autoclave jacket and a "controlled" decompression could easily eliminate this hazard. However, it is recommended to set a temperature captor inside the autoclave wall near the autoclave bottom where the lowest temperatures may occur, so that the temperature limit fixed by the autoclave design be not reached ; otherwise, the autoclave must be replaced.
  Another hazard might also appear on these stainless steel cladded autoclave if this cladding is perforated or cracked and CO_2 corrodes the carbon steel (in presence of water) ; so a strict inspection must be made frequently to ensure that no such cladding perforation occurs.

THERMODYNAMICAL HAZARDS

- **Dry ice** : As said earlier, CO_2 handling often leads to drastic temperature decrease and tubing plugging by water, products or dry ice itself. This plugging might be dangerous when occurring in basket sintered disks, captors tubing, or vent line from safety valves/rupture disks to atmosphere. In order to eliminate this vent line plugging that, in fact, cancels safety devices operation, it is necessary to over-estimated this vent line diameter and design it carefully.

- **B.L.E.V.E.** : This means "Boiling Liquid Expanding Vapor Explosion" and characterizes the physical explosion of a liquefied gas/supercritical fluid that is brutally decompressed to atmospheric pressure, in case of pressure vessel rupture or opening. Catastrophic BLEVE occurred when liquefied petroleum gases vessels burst (Mexico, Feyzin,...), followed by the "chemical" explosion due to gas cloud inflammation. In fact, this hazard is directly linked to metal weakening in case of fire around the vessel(s). It is the reason why it is recommended to install fire detectors that could order immediate depressurization of the whole plant in case of fire.

- **Safety valves/Rupture disks** : The safety system design is often poor as very few experimental validation with liquefied gases/supercritical fluids have been published until now. We did operate some measurements of flash discharge of liquid/supercritical CO_2 from pressure vessels and proposed a simple model for mass flux evaluation [1] ; these results can be used for safety systems design.

CHEMICAL HAZARDS

- **N_2O** : As no consensus has been yet driven among the scientific community regarding N_2O comburant behavior under high pressure, in relation with explosions possibly linked to organic compounds oxidation by supercritical N_2O, we recommend to use N_2O with extreme case when contacted with flammable products.

- **Flammable fluids, co-solvents, products** : Explosion proof equipment, buildings and procedures must be enforced when flammable fluids are handled, especially for light hydrocarbons. Explosion atmosphere sensors have to be installed, and connected to high power fans and to fluid reservoirs stop valves.

- **Corrosion** : As said earlier, this hazard must be evaluated prior to treating any fluid/co-solvent/raw material in the equipment. A considerable corrosion hazard is related to supercritical water oxidation equipment, where special alloys are required.

BIOLOGICAL HAZARDS

- **Asphyxia** : Most supercritical fluid equipment use CO_2 : non toxic, non flammable, it is particularly safe. However, CO_2 build-up in closed rooms could lead to people asphyxia. It is the reason why all possible CO_2 emissions (exit valves, safety valves, rupture disks,...) must be collected in a "over-dimensioned" vent line ensuring a good dispersion of the gas in the outside atmosphere. Moreover, it is highly recommended to install CO_2 detectors in the equipment room but also in any connex room, for action on high power fans and operators information. Anyway, it is preferable not to operate equipment in rooms located over other rooms, especially underground cellars, where CO_2 that is heavier than air may accumulate.

- **Chemical and biochemical toxicity** : Handling any co-solvent or raw material or fluid that presents a danger in terms of chemical toxicity or pathogenic agents must lead to drastic care as supercritical fluid equipment work at high pressure with possible leaks at any moment. It is to be noticed that fluid leakage often leads to aerosol formation (droplets of extract, co-solvent, fluid in the gas flux) that are easily absorbed when breathing. In particularly dangerous cases, it is necessary to isolate the equipment in a closed room with operation through a remote automation system. Moreover, in these cases, environment must be protected by liquid and gaseous effluent treatment and equipment cleaning and/or sterilization.

SOME FINAL ADVICES

As far as supercritical fluid equipment is concerned, safety must be taken into account at any moment : equipment design, building and installation, operation, inspection and maintenance,....
But we would stress on the fact that a key for a safe and reliable operation of a supercritical fluid equipment consists of a very cautious training of the operators, in close relation with the equipment designer and supplier.
Such training should avoid that they fall in various "traps" that could lead to accidents, among which we could cite :

- Be prudent after vessel decompression if exists a risk of plugging ; wait several minutes before opening a decompressed autoclave ;
- Never "over-screw" a leaking nut, as CO_2 leakage causes a very sharp temperature decrease and leak cure is not possible, with potential risk of nut break and metal piece ejection ;
- Verify the reliability of the instruments (especially pressure gauges) ; be prudent on instrument indications especially if "plugging" materials are handled ;
- Always check what could happen in case of electric power or instrument air failure ; be sure that in case of electric power/instrument air recovery, nothing hazardous will occur ;
- Never modify an equipment without the consent of the original manufacturer and never introduce "new" type of spare parts without his approval !

CONCLUSION

Supercritical fluid technology is potentially hazardous and should not be used by "beginners" ; very often, home-designed and home-made equipment do not incorporate all the safety levels that are required, according to us ; moreover, it is extremely important that operators be trained by specialists prior to work on supercritical fluid equipment.

A detailed information exchange between the equipment supplier and user should be the key for a reliable and safe operation, both for lab/pilot scale versatile equipment and for large scale dedicated units.