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Deep freezing thermochemical storage for refrigerated transport applications

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Abstract:

Refrigerated transport is a cold chain key element. It is also responsible of high energy consumption. For this purpose, a feasible solution is to switch to autonomous containers which can be recharged more efficiently once having finished transport distribution. This work focuses on refrigeration transport for frozen products ranging between -20°C to -30°C. First, a comparison study on different available technologies is carried out. Technologies are ranged from their driving energy source, their performance and their ability to run autonomously. This comparison highlights systems coupled to batteries in order to be autonomous and systems intrinsically autonomous such as phase change materials (PCM), solid/gas adsorption or thermochemical sorption systems. The latter allows energy storage without losses, with large charge-discharge cycles and on demand production. Besides, ammonia-based thermochemical sorption systems appear as a suitable solution to fulfil requirements of deep freezing storage for mobile applications. A study of ammoniate salts selection is carried out to estimate feasible energy densities, mass and volumes of thermochemical reactors. Discarding cascade systems, best candidates for a single cycle appear to be MnCl₂ and FeCl₂.

Keywords: Energy storage; Sorption; Deep freezing; Transport applications;

1. Introduction

Nowadays, handle the cold chain has become a major issue in transport of sensitive medical products and perishable foodstuff. An important part of perishable foodstuff transport is done over long distances, while increasing, both, final distribution points and cold chain constraints. Moreover, multi-stop supply distribution results in an over solicitation of the refrigeration system. Indeed, the latter has to compensate heat transfer and temperature fluctuations resulting from frequent stops. Conventional refrigeration system based on compression cycles that are powered by the vehicle engine or a full-dedicated engine exhibits lower efficiency than large and optimised regimes systems, leading thus to extra energy and fuel consumption and more emissions of CO₂ [1], [2]. Thus, temperature fluctuations are a key determinant point for product quality. Therefore, an impeccable control of temperature is decisive to ensure the best quality of transported products. Real data and dynamic models [3] confirm how crucial is to have a precise control on the temperature in refrigerated products all along transport chain. It is a fact that to ensure an optimised temperature control, refrigerated container doors should be opened as less as possible. To attain this goal, a suitable solution could be an autonomous downsized refrigerated container which has to be opened only once having reached its final destination. Moreover, they can be recharged after delivery period with higher efficiency in a centralized manner. Hence, the refrigeration systems should run silently and without addition of greenhouse gases (GHG) rejection, even when vehicle engine is stopped. Standards for refrigerated transport are ruled by the "Agreement on the international carriage of perishable foodstuffs and on the special equipment to be used for such carriage (ATP)". It gives a framework for refrigerated transport by specifying the temperature range of each refrigerated transport class and for each group of perishable foodstuff [4]. Most of frozen foodstuff must be transported at -18°C or lower (within a tolerance of 3°C) [5]. Concerning medical sector, some products have to be kept at -25° C or -30° C.

2. Freezing technologies performances comparison

Focusing on autonomous freezing transport within a temperature ranging from -20° C to -30° C. A large range of technologies is reviewed, from commercially available to emerging ones. Their coefficient of performance (COP) with their cold temperature production and energy storage density for a given example are then compared. These values are summarised for each technology in *table* 2. The aim is to compare thermochemical systems with other existing technologies for the previously introduced application.

2.1. Systems description and classification

- *Vapour Compression Refrigeration (VCR)* : These technologies are mechanically driven (or electrically by mean of an electrical motor). They are the most extended systems, with highest COPs.

- *Air cycle* : is based on a mechanical compression cycle, with lower COP but using an environmental friendly working fluid: air. Furthermore, it brings the possibility to store the capacity to produce refrigeration effect from compressed air stored in tanks.

- *Ejection Cycle* : They are thermally driven and exploits the Venturi effect to drive the refrigerant loop. They present a low COP (under 0.2 for the targeted freezing applications).

- *Thermoelectric Refrigeration (TER)*: These compact systems are directly electrically driven. They lay on the Seebeck-Peltier refrigeration which consists in a solid state heat pump. They present low COP [6].

- *Magnetocaloric Refrigeration (MR)*: This electrically driven technology works with the reversible magnetocaloric effect of certain materials. It exhibits a promising and advantageous theoretical COP [7] with magnitudes equivalent or higher than VCR systems. But, real system shows lower COPs than VCR [8].

- *Thermoacoustic Refrigeration (TAR)* : This technology can be electrically driven (to power a loudspeaker) or by an acoustic engine (reaching an overall COP of 0.21 [9], so exhibiting lower COP than VCR). It is based on an acoustic wave transit producing a temperature gradient along a stack.

- *Phase Change Materials (PCM)* : Typically cold storage is done by PCM. Three types of latent storage can be used to generate low temperatures. Latent heat of fusion (S/L) where the most commonly used is eutectic water-salt solutions. Vaporisation (L/G) with liquefied gases, i.e. CO_2 or N_2 permits a rapid freezing because of their very high heat transfer coefficient (20 kW/m².K) [10]. To finish with sublimation (S/G) where typically, CO_2 ice is used to maintain cooled spaces for a few days long. Its low heat transfer coefficient counteracts its low sublimation temperature (almost -80°C at atmospheric pressure).

- *Liquid absorption* : This technology presents one of the best COPs for thermally driven refrigeration systems. Storage is possible by drying the absorbent down to the crystallisation point to increase energy density of the storage unit [11]. But such crystallisation application are not still available for subzero applications.

- *Solid sorption :* enclose adsorption and thermochemical processes. They are thermally driven and work in two different phases, allowing thermal storage. This technology is further developed in part 3.

As one of the purposes of the present work is to set up a performance comparison between autonomous refrigeration systems, *table 1* sorts them by their energy source while producing the refrigeration effect.

Mechanically/Electrically driven	Thermally driven	Autonomous		
VCR	Ejection Cycle	РСМ		
TER		Air cycle		
MR	Absorption	Thermochemical		
TAR				

Table 1: Described refrigeration technologies sorted by their driving energy source while running.

Systems driven mechanically, electrically or thermally operates when they are respectively coupled to an engine shaft, alternator or waste heat. But they are not autonomous and cannot work when engine stops. They need a storage system, which is a battery system. A comparison is dressed up between the different systems. Thermally driven ones are excluded since they cannot be autonomous even coupled to batteries. Third column of *table 1* lists systems which can work autonomously during the refrigeration period.

2.2. Comparison of performances model

COP is the ratio between the energy taken from the cooling space and the driving energy input to the refrigeration system (mechanical, electric, thermal or several simultaneously). Each system is driven by its own energy source. Therefore, COPs cannot be used roughly to compare systems performances correctly. In an energy consumption limitation context, it seems wise to take in consideration the primary energy source. For this purpose, it has been chosen to use a standard conversion coefficient from final energy to primary energy which is established at 2.58 in France [12]. To take into account work (W) or electricity consumption from primary source, this conversion coefficient permit to draw out Primary Energy Rate (PER). The latter is calculated as follows [13]:

$$PER = \frac{PE}{E_{frace}} = \frac{2.58}{COP_{comp}}$$
(1)

Thus, the lower is the PER the more efficient is the system using a primary energy source to produce the refrigeration effect.

For PCM charging, the most performing system, which is VCR, is considered. The PCM related COP is calculated as it follows:

$$COP_{PCM} = \frac{L_{v}}{W_{comp}} = \eta_{stock} \cdot COP_{comp} \qquad (2)$$
with $COP_{comp} = \frac{L_{v} + C_{p} \cdot (T_{amb} - T_{cold})}{W_{comp}} \qquad (3) \quad \text{and} \quad \eta_{stock} = \frac{L_{v}}{L_{v} + C_{p} \cdot (T_{amb} - T_{cold})} \qquad (4)$

Where W_{comp} is the work done by the compressor, L_v the latent heat of change of state, C_p the thermal capacity of the PCM, and η_{stock} the efficiency of PCM storage, taking into account the energy required for its sensible cooling from ambient to phase change temperature.

All the performance parameters used below are related to the cold production phase. Concerning the autonomous mode, $PER_{autonom}$ is the PER of the system when operating in autonomous mode. It is estimated taking an energetic efficiency of 0.8 for systems coupled to batteries. Best achieved COP examples are given for each autonomous refrigeration system.

For this performance comparison a case study is established consisting in a commercial vehicle refrigerated container (2.6m length, 1.6m width, 1.76m height accounting for $7.3m^3$). This example is taken to extend the comparison to the autonomous energy supply unit. For such refrigerated space and according to ATP standards for class C [4], the reference case considers an outside temperature of 30°C, a refrigerated space maintained at -20°C with a global heat loss coefficient of 0.4 W/m²/K. Maintaining this cold space temperature for 12h gives an amount (Q_{freeze}) of 5.5kWh of cold production. This value is taken as reference to estimate a storage volume of autonomous driving energy source (V_{5.5kWh}). For that, a typical Li-ion battery with an energetic density of 400kWh/m³ is taken for systems needing to be plugged to a battery. An energetic density of 90kWh/m³. Operating cold temperatures (T_{cold}), systems performances and an energy storage volume is estimated for each system, taking in consideration the established energy need.

PCM volume calculation:

$$V_{PCM} = \frac{Q_{freeze}}{L_{v} \cdot \rho_{PCM}}$$
(5)

(B . Dailery, L. Taleni neal, CA. compressed all, A. sorption) and storage source volumes (V 5.5kWh).									
Refrigeration system	T _{cold}	COP	PER	COP _{autonom}	PER _{autonom}	Energy source	$V_{5.5kWh}$ (dm ³)	Ref.	
VCR	-40°C	2.41	1.07	1.93	1.34	В	7.1	[14]	
TER	-33°C	0.27	10	0.22	12.5	В	62.5	[15]	
MR (*)	-26°C	0.23	11.11	0.18	14.28	В	76	[7],[8]	
TAR	≈ -35°C	≈ 0.8	≈ 3.23	≈ 0.64	≈4	В	21.5	[16]	
PCM (melting)	-33°C	1.13	2.27	1.13	2.17	L	67	[17], eq. (2)	
PCM (evaporation)	-196°C	≈ 0.12	≈ 20	≈ 0.12	≈ 20	L	123	eq. (2)	
PCM (sublimation)	-58°C	0.85	3.03	0.72 (**)	3.57 (**)	L	19	[18]	
Air cycle (***)	-20°C	0.86	3.03	0.86	3.03	CA	320	[19], [20]	
Adsorption- Thermochemical	-30°C	0.34	2.94	0.34	2.94	А	61	[21]	

Table 2: Performances comparisons for different freezing systems with their energy sources (B: battery, L: latent heat, CA: compressed air, A: sorption) and storage source volumes ($V_{5.5kWh}$).

(*) Data from experimental works exhibits a 16,8K span for a COP of 0,69 from a hot reservoir temperature at 297,7K [8].

(**) As far as sublimation is considered, 15% of weight loss is supposed when storing [22].

(***) Performances of the compressed air storage are considered to be the same as the air cycle. Nevertheless, for high energy density storage, compressed air pressure in a tank should be the highest permitted, reducing substantially the COP of the cycle.

Table 2 exhibits ranged systems with the different previously defined COPs and PERs. From PER_{autonom} column, best performing systems are compression cycle coupled to batteries, followed by PCM, thermochemical sorption and compressed air. Penultimate column in *Table 2* shows storage volume magnitude for each system working autonomously. For systems running on batteries the higher the COP is, the lower is the storage volume, increasing the compactness of the overall system. Nevertheless, systems based on PCM or thermochemical storage exhibits a storage volume which accounts essentially for the overall refrigeration system. A deeper comparison to compare systems compactness should take into account the overall refrigeration systems volume.

Moreover, systems coupled to batteries are not adapted for long-term use as batteries exhibits a drop of performances after a limited number of cycles, even if growing [23]. The other mentioned autonomous systems allow perdurable cyclability. On one hand, PCM are limited in the storing duration as they may encourage heat transfers even when well thermally insulated. On the other hand, sublimation and fusion PCM have low heat transfer coefficient. Furthermore, they may present low reactivity to a temperature fluctuation. Compressed air application for refrigeration allows higher temperature control, but need voluminous overall systems and moving parts. Thermochemical systems store on demand freezing production with precise temperature regulation and without significant losses when not in use. After having worked out the previous comparison, thermochemical systems are a good candidate for specific requirements of a controlled low temperature, autonomy and adaptable to mobile applications.

3. Thermochemical systems

In its simplest configuration they involve two elements and two stages. One element, the reactor, contains the reactive salt that absorbs or desorbs chemically the gaseous refrigerant. The other element is where refrigerant fluid condenses or evaporates. In subzero applications the most common refrigerant fluid used is ammonia but other working fluid are being developed [24]. Such systems are intrinsically proper to use for energy storage applications as their discharge and regeneration phases are not simultaneous. Commercial applications already exists for both main criteria: refrigeration and energy storage [25].Various working pairs can be implemented in thermochemical processes [26]. CO₂ adsorption in activated carbon exhibits low COP [27]. On the other hand, metal hydrides exhibits high volumetric density, but their specific cooling power (SCP) is lower than ammonia-metal chlorides working pairs [28]. For these mentioned reasons ammonia-metal chlorides are considered in the following section. Thermochemical systems are based on the reaction type:

$$SG_{\varepsilon} + v \cdot G \leftrightarrow SG_{\varepsilon+v} + v \cdot \Delta h_r^0$$
(6)

Where *s* is the reactive salt, *G* is the reactive gas, Δh_r^0 is the enthalpy of reaction, *v* is the stoichiometric coefficient and ξ is the gas number of moles always present in the reactive salt.

The equilibrium conditions of such systems are defined by Clausius-Clapeyron equation:

$$\ln\left(\frac{p}{p_0}\right) = -\frac{\Delta h_r^0}{R \cdot T} + \frac{\Delta s_r^0}{R}$$
(7)

These conditions are schematically plotted Fig. 1 b).

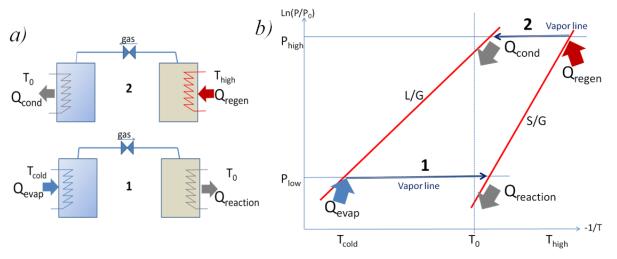


Fig. 1. a) Working principle schema and b) Clausius-Clapeyron diagram with its equilibrium curves (red).

Figure 1 describes the working principle of a simple thermochemical cycle. Phase 1 is the cold production phase when heat is absorbed to evaporate the refrigerant at low pressure. The reactor absorbs the refrigerant vapour in an exothermic reaction. The resulting heat has to be evacuated to ensure performing refrigeration as reaching the equilibrium temperature may stop the reactions and therefore no more gas will be absorbed. Phase 2 corresponds to the regeneration of the system at high pressure. That means heating the reactor desorbs the gas which condensates in the condenser, evacuating the corresponding heat in a heat sink.

3.1. Working conditions

First, salts selection within Clausius-Clapeyron diagram is done referring to the operating conditions for deep freezing transport defined by the ATP and for the mentioned application. In addition, technological and security limitations are taken in consideration for the regeneration phase. Thus, a working conditions framework is defined as follows:

 $T_{ev_NH3} = -38 \text{ °C}$; $T_{react max} \le 220 \text{ °C}$; $T_{min_react} \ge 70$; $p_{min} 0.8 \text{ bars}$; $p_{max} = 25 \text{ bars}$.

All salts selected in the established temperature and pressure conditions are shown in Fig.2 within their proper equilibrium temperature curves.

Drawn curves correspond to the convenient ammoniate salts, meaning that their equilibrium reaction point is upper than 0.8 bars and 70°C for the synthesis phase and lower than 25bars and 230°C for their regeneration phase. Names of selected salts appear followed by their stoechiometry as $(v + \xi)/\xi$. Interesting candidates can be those having high stoechiometries v.

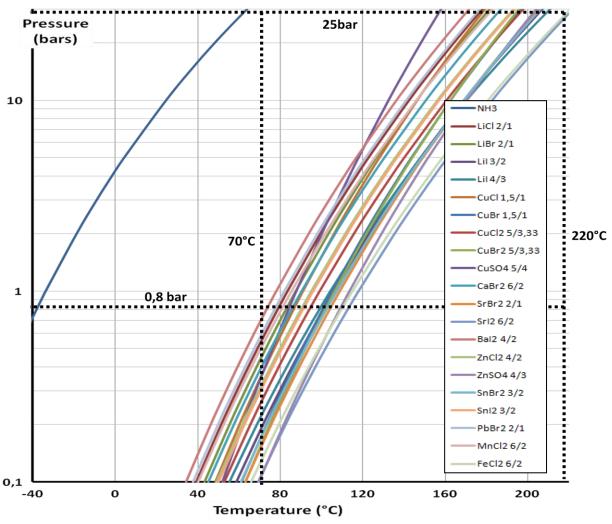


Fig. 2. Clausius-Clapeyron diagram within constraints framework. Enthalpy and entropy data from [29].

3.2. Energy densities

Secondly, a selection criterion is examined within physical quantities energy density (DE). DE is taken as the rate of energy "pumped" from the cooled space to the volume of the whole reactor. The latter is mainly composed from reactive salts, to absorb gas, mixed with Expanded Natural Graphite (ENG) which increases thermal conductivity and prevents from salt agglomeration but lower the reactive gas permeability in the composite compound [30]. This mixture is characterized by the ratio w_s that defines mass of reactive salt in the composite and the apparent density $\tilde{\rho}_{GNE}$ that determines the ENG mass compared to the overall composite volume. The ratio and quantity of each compound define the reaction behaviour. All is contained in a stainless steel sealed volume. Disposition of gas diffusers through the composite or around relies on reactor design. Thus, energy densities comparison is obtained by (8):

$$DE = \frac{Q_{freeze}}{\frac{1 - w_s}{w_s} \cdot \frac{n_{NH 3}}{\upsilon \cdot \Delta X_{max}} \cdot M_s}$$
(8)

For this reason two cases are studied:

- maintain of a targeted temperature ($\tilde{\rho}_{GNE} = 60 \text{ kg/m}^3$; $w_s = 0.9$). The purpose is to maximise the the energy density and thus the storage duration.

- powerful refrigeration application ($\tilde{\rho}_{gNE} = 120 \text{ kg/m}^3$; $w_s = 0.7$). In this case, the goal is to maximise the heat and mass transfer to increase the thermal power.

Targeting a powerful cooling system or a long duration cooling system (higher energy density) has not the same effect on the reactor configuration. Indeed, for high cooling power, higher heat and mass transfers are required. Consequently, higher porosity and heat conductance in the reactor is necessary. This is obtained by increasing the amount of ENG [31].

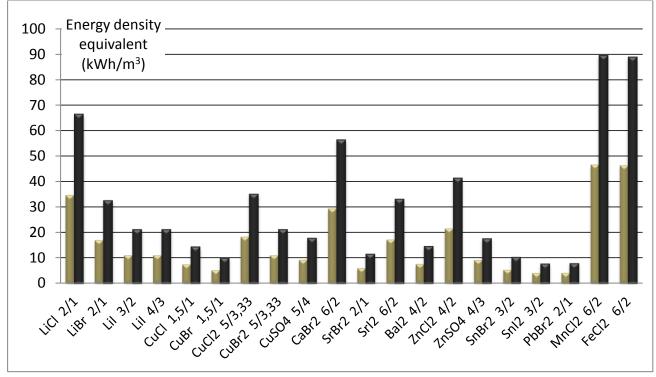


Fig. 3. Equivalent refrigeration energy density for selected ammonia metal salts ranging from energy density for powerful design (lighter grey) to energy density for long time temperature maintenance (black).

Fig.3 shows these two cases for each salt previously selected. Best energy densities are exhibited for $MnCl_2$ and $FeCl_2$ ranging between $46kWh/m^3$ and $89kWh/m^3$, depending rather if reactor configuration is for powerful or for long duration maintenance refrigeration. In comparison a salt solution PCM presents DE in this range, but doesn't permit a precise temperature control nor an adaptable cold production rate.

3.3. Reference example

To proceed to a mass and volume comparison of reactors design for each salt, the previously defined reference of 5.5kWh is taken. For that, a general equation to evaluate the mass of reactors is set up as:

$$m_{reactor} = \left(\frac{\gamma \cdot w_{s} + 1}{w_{s}}\right) \cdot m_{s} + \frac{n_{NH 3}}{\upsilon \cdot \Delta X_{max}} \cdot \xi \cdot M_{NH 3}$$
(9)

And volume of reactor is defined as:

$$V_{reactor} = \frac{V_{composite}}{1 - \tau_{dv}} + V_{inox}$$
(10)

With a stainless steel mass to reactive salt mass ratio $\gamma = \frac{m_{inox}}{m_x} = 3$; percentage of dead volume in the total internal volume of reactor: $\tau_{dv} = 10\%$; and considering a maximum extent of reaction of: $\Delta X_{max} = 0.8$. For each selected salt, Fig.4 shows mass and volumes of reactor necessary to the sorption of evaporating ammonia corresponding to the defined need of 5.5kWh of cooling energy.

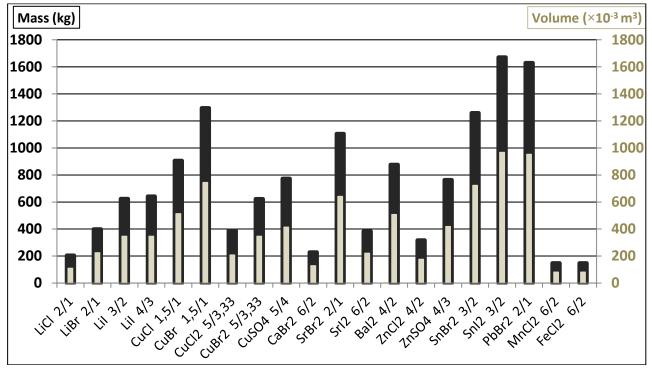


Fig. 4. Reactors masses and volumes for 5kWh deep freezing by thermochemical process

Figures 4 and 5 bring out LiCl 2/1, CaBr₂ 6/2, MnCl₂ 6/2 and FeCl₂ 6/2 with their respective volumes 110L, 130L, 82L and 82L, and their respective masses 204kg, 228kg, 147kg and 148 kg, as the most appropriate reactive salts for the previously mentioned requirements. Notice that even if these values seem considerable, they account for a substantial part of the overall refrigeration system.

3.4. Cascading thermochemical system

The challenge consists in reaching low temperature from ambient temperature with a single cycle. Thus, cascading systems should be considered since experimental prototypes have successfully achieved temperatures below -20°C [32].

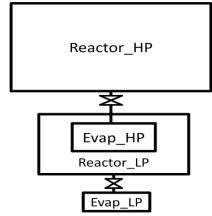


Fig. 5. Simplified schema of cascading a thermochemical system

For that, a reactor adsorbs gas from low pressure evaporator and the former is cooled down by the high pressure evaporator. That implies, to have a high pressure system nearly twice heavier than the low pressure one, as it has to adsorbs roughly twice the amount of gas from the low pressure evaporator. Indeed, compared with evaporation energy, energy of reaction is around twice higher when considering ammonia (L/G) and ammonia salts (S/G), with 23.37 kJ/mol and 40-60 kJ/mol respectively. Consequently, nearly twice more mass is necessary compared with achieving it with a single evaporator and reactor system. Thus, ideally, a deep freezing thermochemical systems for transport should target a simple reactor in order to reduce the overall mass of the system and its compactness.

4. Conclusion and perspectives

This work introduces a comparison between different refrigeration technologies. Their energy sources can be either mechanical, electrical or thermal. The focus is placed on their ability to store on demand a freezing production within a precise temperature control. For that, performances of different autonomous systems have been compared. Highlighting that a compression cycle coupled to batteries have better PER_{autonom} and need lower energy storage volume. PCM presents interesting DE, but are not suitable for precise temperature control. In long-term running thermochemical freezing processes may have a better performance than VCR and PCM. Indeed, they work autonomously, don't suffer from limited cyclability life expectancy, are compact and allow a precise temperature control. For that, ammonia metallic salts are chosen by considering their energy density, their masses and volumes. MnCl₂ and FeCl₂ result as the most appropriate salts for this application ranging their DE from 46 to 89 kWh/m3, depending on if design targets high cooling power or the maintain of cold space temperature. An example gives that a 82L and 147kg reactor would be necessary to maintain during 12h a 7.3m³ container at -20°C with an exterior temperature of 30°C. Hence, once having discarded cascading as they may enlarge the system, single thermochemical cycle systems appear appropriates for refrigerated transport at controlled temperature and deserve to be further studied for such application.

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Appendix

Energy density DE calculation:

$$Q_{freeze} = n_{NH 3} \cdot \Delta H_{vap} \qquad m_{s} = \frac{n_{NH 3}}{\upsilon \cdot \Delta X_{max}} \cdot M_{s} = w_{s} \cdot m_{composite} \qquad m_{GNE} = \frac{1 - w_{s}}{w_{s}} \cdot m_{s}$$

$$\widetilde{\rho}_{GNE} = \frac{m_{GNE}}{V_{composite}} \qquad V_{composite} = \frac{1 - w_{s}}{w_{s}} \cdot \frac{n_{NH 3}}{\upsilon \cdot \Delta X_{max}} \cdot M_{s} \cdot \frac{1}{\widetilde{\rho}_{GNE}}$$

$$DE = \frac{Q_{freeze}}{V_{composite}} \qquad DE = \frac{Q_{freeze}}{\frac{1 - w_{s}}{w_{s}} \cdot \frac{n_{NH 3}}{\upsilon \cdot \Delta X_{max}} \cdot M_{s}}$$

Mass calculation:

$$m_{reactor} = m_{s} + m_{\xi} + m_{inox} + m_{GNE} \qquad \qquad m_{\xi} = \frac{n_{NH-3}}{\upsilon \cdot \Delta X_{max}} \cdot \xi \cdot M_{NH-3}$$

$$m_{reactor} = \left(\frac{\gamma \cdot w_{s} + 1}{w_{s}}\right) \cdot m_{s} + \frac{n_{NH 3}}{\upsilon \cdot \Delta X_{max}} \cdot \xi \cdot M_{NH 3}$$

Volume calculation:

$$V_{reactor} = V_{reactor_int} + V_{inox}$$

$$V_{dv} = \tau_{dv} \cdot V_{reactor}$$
 _ int

- C_p specific heat at constant pressure, J/kg.K
- *G* reactive gas
- L_v latent heat of phase change, J/kg
- *M* molar mass, g/mol
- *m* mass, kg
- *n* number of moles
- *p* pressure, bars
- *R* gas constant, J/mol.K
- *s* reactive salt
- T temperature, °C
- *V* volume, m³
- W work per mass unit, J/kg
- w_s mass ratio reactive salts-composite
- ΔX extent of reaction
- Δh_r^0 Enthalpy of reaction, J/mol
- Δs_r^0 Entropy of reaction, J/mol K

$$V_{reactor} _{int} = V_{dv} + V_{composite}$$
$$V_{reactor} = \frac{V_{composite}}{1 - \tau_{dv}} + V_{inox}$$

Greek symbols

- γ stainless steel to reactive salt ratio
- η efficiency
- v number of reacting gas moles
- ξ gas moles number always in reactive salt
- τ percentage

Subscripts and superscripts

comp compression cycle dv death volume ev evaporation expanded natural graphite GNE stainless steel inox NH_3 ammonia prim primary energy *react* reaction anhydrous reactive salt S stock storage gas g HP high pressure LP low pressure

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