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Thermodynamic analysis and experimental study of solid/gas reactor operating in open mode

Foivos Marias [a], Pierre Neveu [b], Gwennyn Tanguy [a,*], Philippe Papillon [a]

[a] CEA, Liten, LETh, F-73377 Le Bourget du Lac, France
[b] Université de Perpignan Via Domitia, PROMES-CNRS, Tecnosud, 66100 Perpignan, France

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ABSTRACT

Thermochemical storage with moist air is a promising way to achieve seasonal storage of solar heat. This paper investigates the link between outlet and inlet airflow conditions in the case of hydration/dehydration of thermochemical processes operating with moist air at atmospheric pressure. A thermodynamic analysis of a solid/gas reactor operating in open mode is performed. That leads to a thermodynamic relation called charge–discharge operating line. Experimental tests have been carried out with two different reactive salts in order to prove the validity of the charge–discharge operating line. Experimental results provide a close match between the theoretical approach of the charge–discharge operating line and the measurements. Based on this relation, a reactor performance criterion, called reaction effectiveness, is defined. Both operating line and effectiveness stand as efficient design tools to predict performances of the reactor and to guide R&D choices to enhance them.

1. Introduction

Reduction of greenhouse emissions is a priority action in order to limit climate change. To reach this target, energy conservation is essential. Process efficiencies have to be enhanced and the share of renewable energies has to increase. Thermochemical reactions have a key role in order to fulfil the two last objectives through, among others, chemical heat pumps and heat storage processes. The term thermochemical reaction can refer to a whole family of reactions [1]. This study focuses on chemical reactions of inorganic salts.

Indeed, the intermittent nature of most renewable energy sources and the mismatch between energy need and supply is an important difficulty for the development of renewable energies. Thermal Energy Storage (TES) is one of the key to overcome it [2]. Thermochemical storage presents two main advantages [1] in comparison to other technologies: highest storage energy density [3] and no heat loss during storage phase. It concerns both low and high temperature processes and consequently the storage applications are numerous: heat seasonal storage for household [4,5], thermodynamic solar power plants [6], heat/cold transportation [7], electrical load management [8]. Other fields of application of thermochemical reactions are also varied: heat pumps [9], air conditioning [10], cooling [11], industrial waste heat recovery [12], hydrogen production [13].

This paper concerns solid/gas reactor operating in the so-called open mode [4,14]. In classical thermochemical cycle, named closed mode, the reactor is feed with pure vapour (the reactive gas) produced by an evaporator, and, in a following phase, releases this pure vapour to a condenser (Fig. 1). The reaction heat is then exchanged through a heat exchanger, with a heat transfer fluid. In open mode, the rector is feed with a gas mixture, containing a certain among of reactive gas. In that case, the gas mixture acts both as heat transfer fluid and reactant source. . When air or flue gas is used as gas mixture, the reactant part can be CO_2 [15], H_2O or O_2 [16] depending on the reactive solid and the application.

Notice that R. Critoph investigated the heating/cooling of a reactive bed by using the pure reactant gas as heat transfer fluid in the late 90s [17]. He showed that very high heat transfer can be achieved with acceptable pressure losses [18]. When using a mixture, same behaviour could be expected, despite the fact that diffusion problem for the reactant gas through inert gas could appear.

This study focuses on seasonal solar heat storage, for which hydration/dehydration of reactive salt or adsorbent proceeding under open reactors seems a promising technology [4,14,19–21] and could enable to increase the solar fraction for household applications. However, theoretical analysis developed here could be

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* Corresponding author. Tel.: +33 4 79 79 21 22.
E-mail address: gwennyn.tanguy@cea.fr (G. Tanguy).

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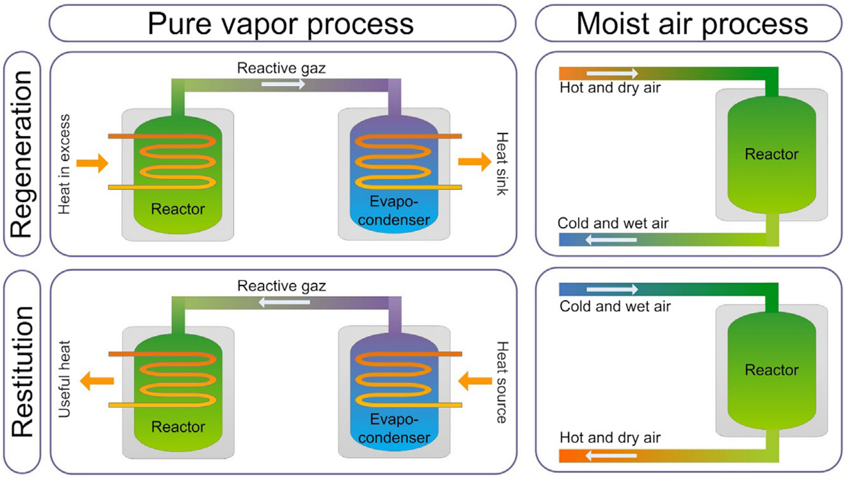

Fig. 1. Closed mode system (pure vapour process) and open mode system (example of moist air process).

easily applied to other thermochemical processes: CO_2 capture [22,23], high temperature heat storage [16].

The general form of solid/gas reactions used in such processes writes:

$$S_0 + \nu G \leftrightarrow S_1 + \Delta h_r^0 \tag{1}$$

Thence, a solid/gas reactor constitutes a monovariant system, for which thermodynamic equilibrium is given by the Clausius–Clapeyron equation. Assuming constant heat of reaction Δh_r and pure ideal gas phase, it results in the Van't Hoff equation [24,25]:

$$\ln\left(\frac{p_{eq}}{p^0}\right) = -\frac{\Delta \boldsymbol{h}_r^0}{R \cdot T_{eq}} + \frac{\Delta \boldsymbol{s}_r^0}{R} \tag{2}$$

with p_{eq}: equilibrium pressure (Pa). $\Delta \boldsymbol{h}_r^0, \Delta \boldsymbol{s}_r^0$: enthalpy (J/molw) and entropy (J/K molw) of reaction at reference pressure p^0 (Pa), respectivley. R: ideal gas constant (J/mol K).

Eq. (2) normally stands for pure vapour system. In that case, the equilibrium temperature can be easily deduced according to the vapour pressure submitted to the system:

$$T_{eq}(p) = \frac{\Delta \boldsymbol{h}_r^0}{R \ln\left(\frac{p}{p^0}\right) - \Delta \boldsymbol{s}_r^0} \tag{3}$$

Equilibrium temperature allows evaluating the temperature swing experimented by the reactor during the whole cycle and consequently to perform the energy and exergy analysis of the process [26,27]. For a reactor working with gas mixture, composed of one or more inert species and one reactant, the system is no longer monovariant, and Eqs. (2) and (3) have to be modified. However, it can be easily shown that Eq. (1) is still valid if total pressure is replaced by the partial pressure of reactant (see Appendix). Nevertheless, as the reactive gas composition and temperature evolve when it flows across the reactive bed, the outlet conditions have to be determined to evaluate the performance of the system. This paper is aimed to determine these outlet conditions of the reactive gas according to the inlet conditions and the reactive pair thermodynamic properties.

2. Thermochemical storage with moist air

A seasonal storage system designed for household applications must satisfy the following constraints: (i) very low thermal losses, (ii) high energy density, and (iii) no toxicity. Therefore thermochemical reaction seems to be the most appropriate solution for seasonal storage from a practical point of view [28,29] as well as regarding thermodynamic aspects [30,31]. Indeed, the energy density can be up to ten times higher than water latent storage. Another interesting feature of such system is that thermal losses remain weak during storage phase because the heat is stored as chemical energy. As far as hydration/dehydration reactions of inorganic salts are concerned, the no toxicity constraint is respected; water being the only reactant flowing in/out of the system. Nevertheless, an environmental friendly reactive salt should be preferred, although that the solid material stays confined in the reactor for normal operations.

For atmospheric pressure systems, also called open cycle [4,14], the air has two features: (i) matter source for the chemical reaction (water vapour) and at the same time (ii) heat transfer fluid. Indeed, moist air is composed of dry air, which is inert, and water vapour which is the reactant.

The equilibrium curve (Eq. (2)) of solids/moist air system can be represented in the well-known psychometric chart. As an example, Fig. 2 displays the strontium bromide mono- /hexahydrate equilibrium line in such a diagram.

In an open air system, the exothermic reaction of hydration induces simultaneously water vapour consumption (i.e decrease of

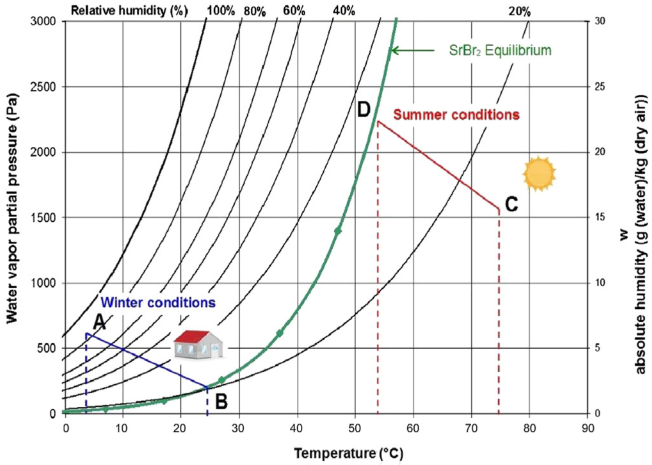

Fig. 2. Strontium bromide mono/hexa-hydrate equilibrium curve in a psychometric chart.