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Preparation & characterization of sodium sulfide hydrates for application in thermochemical storage systems

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Abstract

Bottlenecks for realizing a commercial system for thermochemical heat storage (TCS) with hygroscopic salts are the chemical, physical and mechanical stability of the salt under operation conditions. Hence, improved knowledge of thermochemical materials (TCMs) is critical to spur progress in TCS system development. Sodium sulfide hydrates ($Na_2S.nH_2O$, n=0-9) are highly interesting as TCMs because they exhibit a high energy density under operation conditions and are potentially readily available and affordable. Preparation methods for well-defined nonahydrate and pentahydrate crystals of Na_2S were developed and the resulting samples were subjected to cycling experiments under conditions representative for TCS. Before and after cycling, crystal samples were taken and characterized using techniques like SEM/TEM, XRD. Mechanical strength was evaluated using a salt bed stability test. Based on the extensive characterization of sodium sulfide hydrate salts, a method has been proposed to improve the stability of the salt by blending it with cellulose. First trials on these composites yielded promising results with respect to improved material stability.

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1. Introduction

As Europe and the US move more and more towards low and zero-carbon buildings, challenges arise in the management of building-integrated renewable energy technologies. Electricity generating renewable energy sources have the benefit of electrical connection and financial mechanisms allowing feed-in to the network. Thermal technologies do not have such general interconnectivity and therefore rely on sizing typically meeting 90% of thermal demands in the summer in moderate climates. This approach provides little benefit in winter, e.g. for space heating purposes. Wouldn't it be nice to be able to store the summer heat in a loss-free fashion for use in winter time in some sort of "thermal battery"?

Sodium sulfide hydrate salts ($Na_2S.nH_2O$) exhibit a large energy density (2.66 GJ/m^3 going from the pentahydrate to the hemihydrate [1]) in the right temperature and pressure regime. Absorption of water vapor can take place at sufficiently high temperatures (40-60°C) to deliver heat while desorption can occur at relatively low temperatures (<83 ºC). This material attracted noticeable interest in the past [2,3], but application suffered from lack of demonstration results due to chemical, physical and mechanical stability issues. For thermal energy storage systems, the forms of instability and related concerns are:

1. Chemical instability involves chemical reactions, (a) reaction with oxygen from air (oxidation) forming sodium sulfite salt causing a loss of energy density of the material, (b) reaction with carbon dioxide from air (carbonation) forming sodium carbonate salt and release of hydrogen sulfide gas that is toxic already at low concentration. Reaction of sodium sulfide with metals forming metal sulfides weakens the system construction by corrosion while simultaneously hydrogen gas is released. Accumulation in the vapour space of the thermochemical system of inerts like hydrogen or hydrogen sulfide gas reduces the heat generating capacity of the system.
2. Physical instability involves phase transitions of the sodium sulfide hydrate salt that may lead to destabilization of the salt embedded in the system. In the phase diagram of sodium sulfide hydrate salts [3] it can be observed that (1) at a temperature of 49°C a phase transition of the nonahydrate salt to the pentahydrate salt occurs while simultaneously a solution of sodium sulfide forms, (2) at a temperature of 83°C the pentahydrate structure partially dissolves while it forms a solution of sodium sulfide.
3. Mechanical instability concerns stability of the bed of the salt hydrate crystals in the thermochemical system. The stability of the bed may decrease during absorption and desorption steps while cycling because of phase transitions of the salt hydrates, for example because the different hydrates have different densities (volume expands and shrinks).

In the p,T diagram of sodium sulfide hydrate salt [2, 3] the different phases of the sodium sulfide hydrate salt during cycling are described. Typically absorption of water vapour (hydration) takes place at a temperature of 40-60°C (depends whether the heat is delivered for heating or for warm water) while the vapour pressure is approximately 12 mbar (corresponding to a winter water temperature in the evaporator of 10°C). Desorption of water vapour (dehydration) typically occurs at a temperature of 80°C to prevent partial dissolution of the sodium sulfide hydrate salt at a vapour pressure of 24 mbar (corresponding to a summer water temperature in the condenser of 20°C).

Preferably, during operation of the thermochemical system only solid phases of the sodium sulfide salt hydrates are present. When the hydration step takes place at 40°C the dry hemihydrate form of the sodium sulfide salt will absorb water vapour while it transforms to the pentahydrate salt and if sufficient water vapour is present is will transform further to the nonahydrate. When the hydration takes place at 60°C the pentahydrate salt will form together with a solution of sodium sulfide. When this material is subsequently cooled below 49°C in the presence of more water vapour also the nonahydrate phase can form. Practically, to deal with these phase changes in previous research a stabilizing material like cellulose fibers was mixed through the sodium sulfide hydrate salt [2].

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