Experimental investigation into the influences of water loss on the exothermic process of alum-based phase change materials

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Abstract. Zero-emission solar heating is one of the most promising paths to solve the energy crisis. Increasing conversion efficiency of thermal energy is the kernel of the problem. Herein, to this day, efficiency of solar heating system is seriously restricted by the randomness, dispersion and intermittency of solar energy. In modern energy science, efficient storage and release of thermal energy is the major way to overcome the fluctuation of energy source. Alum-based phase change materials (AHS) have large phase change enthalpy and material density, especially for aluminum ammonium sulfate dodecahydrate (NAS), but its application is restricted by instability in thermal storage and release cycles. However the key factors affecting their stability are still unclear. In this paper, by studying and comparing the effect of heating duration near the boiling point of water on the crystallization process of NAS/ aluminum potassium sulfate dodecahydrate (KAS), we consider that water loss is the main reason for their poor reproducibility, which determines the concentration of nucleation basic units. With detailed analysis, it’s suggested that difference between K+ and NH4+ in polarization is primarily accounted for obvious distinction between NAS and KAS on crystallization with water loss. This work may provide a powerful guidance to the thermal performance of AHS in solar thermal conversion and promote its application in future.

Keywords: Solar heating system; Alum-based phase change materials; Water loss; Nucleation basic units

1. Introduction
Raising the penetration rate of solar energy is one of the best solutions for reduction of fossil energy consumption and environmental pollution[1]. While, the temporal and spatial mismatch between heat supply and demand set a limit for large scale solar thermal utilization. As a significant and attractive technology, thermal energy storage(TES) is well compatible with the clean energy exploit subject to intensive fluctuation[2]. Thus, more and more efforts have been devoted to establishing smart TES systems to minimum conventional energy consumption and environmental disruption[3].

In principle, thermal energy storage may be classified in the form of sensible heat during temperature change in a liquid or solid medium, enthalpy of phase change(fusion or solid-solid), or reversible thermal chemical process[4]. Among the above, latent heat storage(LHS) has been a particularly attractive technique since it gathers high energy density, quality, controllability and safety
in one[5] and it’s well compatible to current heat exchange and architectural technologies[6]. In recent works, latent heat storage plays a key role in the low-to-middle temperature solar-thermal utilization[1]. Under common ambient conditions, solar radiation can create an elevated temperature of heat transfer media from 50°C to 150°C, in this range the storage ratio of latent heat to sensible heat in heating process for phase change materials (PCM) is relatively high according to energy equation for LHS[2, 3], upon which it tends to storage more energy of high quality. So dedicated selection proper PCMs for different scenarios can effectively promote solar-thermal energy storage at the low-to-middle temperature.

Generally, basic PCMs can be classified into two types: organic and inorganic. Small supercooling, no phase separation and non-corrosiveness are common advantages of organic PCMs like paraffin, Fatty acids and alcohols[1, 2]. Nevertheless, extensive use of organic PCMs is limited by low thermal conductivity, relatively low fusion enthalpy, large volume change during phase transition and unsatisfactory price[7]. On the contrary, inorganic PCMs possess several merits such as large latent heat, high thermal conductivity, etc. that organics doesn’t. Among various inorganic PCMs including molten salts and metals and so on, hydrated salts perform best in low and medium temperature applications such as solar water heating(SWH)[8], exhaust heat recovery and HVAC energy-saving[9], and thereby, applied researches on PCMs start to march(step) toward low cost era[1].

Although, numerous achievements have been made on improving supercooling and phase separation that hydrated salts severely suffer from in practical applications[10, 11], thermal stability or reliability problem remains a barrier for its widespread, especially some hydrated salts with melting points(m.p) near boiling points(b.p) of water. In this respect, alum-based hydrated salts (AHS) phase change materials, aluminum ammonium sulfate dodecahydrate (NH4Al(SO4)2·12H2O) is typical examples with relatively high phase transition points around 94°C, which is benefit for elevating energy quality[12].

As cheap industrial raw materials with 260-280kJ/kg latent heat in addition, much larger than its analogue, KAS, NAS have amazing potential for commercial applications[13]. Unsatisfactorily, except for the large supercooling(10-20°C), but another trouble, the thermal instability affects its performance more severely[12]. Not only does the thermal instability decrease NAS’s cycling life, but also increase the fluctuation and uncertainty of freezing-points in a single cycle[14]. Worse than the supercooling, studies on thermal instability, especially for its mechanism, is more scarce so that highly targeted solutions are hardly proposed[15].

In the current work, thermal instability of NAS coupled with different additives were tested. The thermal instability was confirmed in a larger range. By comparison between pure NAS and its analogue, KAS, it was found that water loss was the most critical factor that caused the thermal instability. Influences on melting-solidification process of NAS and KAS by different amount of water loss were qualitatively explored and compared. Finally, the intrinsic mechanism for NAS and KAS’s thermal instability as well as their phenomenal differences was proposed in an attempt.

2. Experimental Section

2.1 The preparation of NH4Al(SO4)2·12H2O and KAl(SO4)2·12H2O composites

The phase change composite materials were prepared using a physical mixing method. Firstly, the samples were weighed with electronic balance, containing 20g, NH4Al-(SO4)2·12H2O or KAl(SO4)2·12H2O composites and a certain quality (0 wt%, 0.5wt%, 2.5wt%, 5wt%) of nucleating agents(FeO, Fe2O3, Fe3O4, MgCl2·6H2O, Na2B4O7·10H2O). Secondly, the samples were finely milling for performance tests.

2.2 Melting-solidification heating cycle experiments of NH4Al(SO4)2·12H2O and KAl(SO4)2·12H2O composites

The composite phase change materials were adding in test polypropylene tubes and the temperature measurement was realized using a PT100 thermal resistance. The NAS and KAS composites were
heating in a high temperature water bath (100-105 °C). When the samples melt completely and reach 100-105 °C, the samples were put in another low temperature constant water bath (10°C, 25°C, 40°C). The whole temperature variations of the samples were recorded using computer.

3. Thermal performance analysis

Thermal instability had been verified in so many conditions that pure NAS must be tested to make sure whether their thermal instability were on the same level. As was expected, there were as the scale of instability on NAS with or without additives. However, in the experiment, double peaks on exothermic curves of NAS were observed (Fig.1), either with or with nucleating additives and the two peaks might be connected together or separated, which was a phenomenon never discussed in the literatures.

Combined with the instability and double peaks phenomenon (Fig.1), we believed that some systematic factors mentioned above might not be well controlled during the experiment. To further confirm it, melting-solidification curves were measured on pure KAS, most important analogue of NAS and it was no surprise that double peaks were detected, even more frequently. Compared with common inorganic salt hydrates, phase change temperature of AHS is relatively high, close to the boiling point of water, they will lose a certain amount of water when heated, according to the duration of heating or temperature-rise rate. Rapid water vaporization was caused at temperature closed to 100°C right after melting and so the water loss was hardly controllable and inevitable. While, either in previous literatures or our early works, heating duration has never been carefully discussed and controlled. It was evident that water loss was a drawback to crystallization of AHS, but the influence has never been investigated in details and whether water loss was the dominant factor for the thermal instability was not determined. Therefore, we would systematically study the effect of water loss on the heat storage and exothermic properties of AHS, and propose the crystallization mechanism of NAS and KAS with water loss and compare their differences.

**Figure 1** Comparison of double peaks phenomenon melting-solidification curves of KAS and NAS phase change materials (a,b) KAS (c,d) NAS
We tested the melting-solidification curves of pure NAS and KAS with different heating times, where the upper limit of temperature remained near the boiling point of water (Fig.2). From figure 2, we found that the initial phase transition points of NAS and KAS both showed a tendency of gradual decline with the extension of heating time or the rise of temperature, or the transition points were close to each other but the exothermic time decreased. According to this phenomenon, we could infer that the effect of water loss on the exothermic properties of AHS was very large and would be dominant factor for thermal instability. Due to water molecules ratio in crystal NAS and KAS were the same as the original water molecule ratio in liquid, water loss would cause lower the nucleation basic units concentration. The above phenomenon showed that the initial solidification temperature of these two materials was positively relative to the basic units concentration, and under the reduced units concentration, crystallization activation energy was difficult to overcome, so lower temperature was necessary to reduce the dynamic radius of the basic units and the activation energy for crystallization. Concentration decline of the elementary units caused by water loss would not be completely homogeneous with some local ununiformity, so in each test, the decline on initial phase change point and exothermic duration would have certain differences with various heating time.

There was a special phenomena for NAS and KAS during crystallization after high temperature heating (near the boiling point). Heating processes would split into two steps with the extension of heating time, therein, the occurrence of second peak delayed and the starting exothermic temperature lowered consequently. The lasting time and intensity of the two peaks were similar in differences and evolution tendency (Fig.2), particularly of KAS. This was probably due to the increase of water loss with the extension of heating time. Water in the liquid could not meet the requirements for forming complete basic units for most NAS and KAS, and they could not be completely crystallized at one time. But according to the real-time macroscopic observation (Fig.3), despite with a few amount of water loss, the samples were still in a mixed solid state with crystals and gels. This case suggested that most NAS/KAS molecules, in the form of partially coordinated intermediate units would still grow along with crystal nucleus formed by basic units, with a lot of water molecules vacancies left. As the temperature decreased, the samples would absorb a lot of water again, so, these water vacancies were not stable and could be filled and rearranged significantly after water accumulation to a certain extent. This led to a burst of heat release and namely the second exothermic peak.

Figure 2 Time-dependent melting- solidification curves of KAS and NAS phase change materials (a,b) KAS (c,d) NAS
Although on the whole, NAS and KAS had the similar trend above in the phase transition of solidification, there were still many detailed differences in cooling curves between them with prolonged heating time. The initial phase change point of NAS which decreased rapidly with the extension of heating time could even get down to the sink temperature (Fig.1d), and was greatly affected by additives and solvents (Fig. 4). The initial point decreased slowly for KAS and stayed mainly between 40-70°C (Fig.5), it had a better tolerance of additives and solvents (Fig.6). For NAS, double peaks phenomena was not a matter of course with the extension of the heating time. Sometimes, despite long time heating, there would be only a strong single exothermic peak at very low initial phase change point. The double peaks phenomena with a weak first one at relatively low temperature
and the other strong one was also usually observed.

![Figure 6 Melting-solidification curves of KAS phase change materials with ethylene glycol](image)

We suggested that markedly faster decrement of basic units in NAS than in KAS with extension of heating duration was the reason for their differences in cooling process. Fundamentally, that polarization from Al\(^{3+}\) to H\(_2\)O with the existence of K\(^+\) or NH\(_4\)^+ payed for the phenomena mentioned above. Potassium ion was a hard acid ion with weak polarization ability, which would not affect coordination between aluminum ion and water molecules, while, ammonium ion was a soft acid ion with strong polarization ability, which can hydrolyze. The coordination effect between water molecules and aluminum ions would be weakened by NH\(_4\)^+ and hydrogen ions generated by hydrolysis. Therefore, the nucleation basic unit of KAS was easier to form, aggregate and grow. In fact, the crystallization of aluminum potassium sulfate was relatively uniform in liquid (Fig.3). For NAS, the formation of nucleation basic unit was strongly dependent on water content, polarization ability would be not enough with insufficient water content, difficult to form adequate basic units, so the undercooling was very large and the starting point delayed seriously. It was also found that the crystallization of NAS didn’t undergo an uniform growth, but started from a certain point adhere to the container wall or the surface between air and liquid. It could be accounted that crystallization can only start at enough local basic units concentration when the total unit was insufficient, which indeed increased the uncontrollability of NAS crystallization process.

4. Conclusions
Heat storage is the most popular technology to deal with the source fluctuation in solar thermal utilization. Practical application for alum-based phase change materials of large phase change enthalpy and material density is restricted by instability in solidification-melting tests. In this paper, by studying and comparing the effect of heating duration near the boiling point of water on the crystallization process of aluminum ammonium sulfate (NAS)/aluminum potassium sulfate (KAS), we consider that water loss is the main reason for their poor reproducibility, which determines the concentration of nucleation basic units. However, the main cause of the double peaks phenomenon is the rearrangement or filling of large number of water vacancies left by long-time heating with sufficient water supplement from environment again, and these behavior lead to intensive exothermic effect. With detailed analysis, it’s suggested that difference between K\(^+\) and NH\(_4\)^+ in polarization is primarily accounted for obvious distinction between NAS and KAS on crystallization with water loss.

This work is helpful for improving their stability and performance of alum-based phase change materials, especially aluminum ammonium sulfate, in solar thermal utilization and this is also an enhancement of potential for future application.

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