Study on Modification of Phase Change Energy Storage Materials Suitable for Biogas Fermentation

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Abstract. In this study, the problems of supercooling and phase separation of inorganic hydrated salts as phase change energy storage materials when applied to biogas generating devices were investigated. In the experiment, two common hydrated salts of zinc nitrate hexahydrate and disodium hydrogen phosphate dodecahydrate were selected as phase change materials, and tested at room temperature. Recording temperature and drawing the step cooling curve method, by adding different proportions of nucleating agent and dye to improve the supercooling and phase separation of the phase change materials, so that the reaction temperature of the biogas plant was always maintained at a suitable temperature (20-30 °C) to ensure the activity of microorganisms. The experimental results showed that sodium tetraborate decahydrate can effectively reduce the subcooling degree of zinc nitrate hexahydrate, and the azo (-N=N-) dye not only improved the solar absorption rate but also weakened the phase separation of phase change materials to some extent. This study proposed a possible reaction mechanism and provided reference for the development and application of other solar energy storage materials for bioreactors.

1. Introduction
Phase Change Materials (PCMs) are characterized by their ability to absorb or release heat during storage changes [1], [2]. In recent years, PCMs have been widely used in the field of solar energy storage, industrial waste heat recovery and agricultural greenhouse insulation, etc. In order to solve the energy shortage in rural areas and reduce the pollution of burning straw to the atmosphere, Chinese government has widely promoted waste fermentation biogas projects [3].

As a common energy storage inorganic PCMs, crystalline hydrated salt has the advantages of low cost, large thermal conductivity, high latent heat of fusion and large unit heat storage density, but the supercooling of crystalline hydrated salt during phase transformation is an unavoidable problem [4]-[7]. That is, PCMs do not crystallize when they are cooled to the freezing point, and they need to be cooled to a temperature lower than the freezing point to cause crystallization. Furthermore, biogas fermentation requires the temperature of the reaction device to be strictly maintained within a certain interval (20-30 °C) to maintain the activity of microorganisms. The problem of supercooling seriously restricts the popularization and application of phase change energy storage materials in a series of
bioreactors such as biogas fermentation plants. In northern China, biogas fermentation plants often cannot produce biogas due to large temperature difference between day and night, which seriously affects the production and life of villagers. Therefore, how to improve or eliminate the problem of supercooling of crystalline hydrated salt has become an urgent practical application problem. At present, experimental studies at home and abroad have shown that the addition of nucleating agents to PCMs can effectively suppress the problem of supercooling. However, there are few relatively studies on the application of composite PCMs in the field of bioreactors. Therefore, this paper selected the zinc nitrate hexahydrate and disodium hydrogen phosphate dodecahydrate to study the effect of the type and amount of nucleating agent on maintaining the temperature range and improved the problem of absorbing solar energy inefficiency and phase separation by adding dyes [8], [9].

2. Experimental

2.1 laboratory apparatus
In the experiment, the temperature of the PCMs were measured using a JM624 thermometer with an accuracy of ±0.1 °C, and the time was recorded using a stopwatch. The tube containing the PCMs were heated by using a six-hole digital thermostat water bath. The absorption spectrum of the phase change material mixed with the dye was measured using a Shimadzu UV-2550 UV-Vis spectrophotometer. The experimental condensing unit is shown in figure 1.

![Experimental condensing device](image)

**Figure 1.** Experimental condensing device

2.2 Preparation of materials
According to the actual conditions required for the biogas plant, hydrated salt materials which are easy to chemical produce and are cheap are selected. Depending on the conditions in which the device is actually applied, hydrated salt materials with a phase transition temperature between 20 and 30 °C or slightly above this temperature range should be selected as much as possible. Therefore, the initially selected hydrated salt materials are disodium hydrogen phosphate dodecahydrate, zinc nitrate hexahydrate, and calcium chloride hexahydrate. At the same time, according to the reference, strontium chloride hexahydrate and borax (i.e. sodium tetraborate decahydrate Na₂B₄O₇·10H₂O) were selected as nucleating agents, and the crystal parameters are shown in table 1. Considering that the simple PCMs absorb light energy inefficiently, it is proposed to add an azo (-N=N-) dye to the phase change material to enhance the light absorption performance.
Table 1. A slightly more complex table with a narrow caption.

| Crystal system | pH | Classification  |
|----------------|----|----------------|
| Na₂HPO₄·12H₂O | 9.0| PCMs           |
| Zn(NO₃)₂·6H₂O | 4.0| PCMs           |
| CaCl₂·6H₂O   | 7.0| PCMs           |
| Na₂B₂O₇·10H₂O| 9.6| Nucleating agent|
| SrCl₂·6H₂O   | 6.8| Nucleating agent|

2.3 Experimental procedure
The phase change temperature was measured by the step-cooling curve method. The temperature value of the medium time interval was measured and the curve was drawn, and the phase transition temperature was determined according to the turning point on the curve and the parallel line segment (smooth or approximately parallel segment). In addition, physical blending was used to mix some materials, such as nucleating agents, light absorbing dyes, etc., to improve the properties of the phase change material.

Each PCM was separately mixed with the nucleating agent selected above according to different ratios, and the temperature was measured and the step cooling curve was drawn. The nucleating agent capable of reducing the supercooling phenomenon and the mixing ratio thereof can be selected by analysing the step cooling curve and observing the phase change effect. In addition, the phase change system with dye added was compared with the original system, and the step cooling curve was measured and plotted to analyse whether the dye would affect the crystallization and heat release effect of the PCMs.

3. Results and Discussions

3.1 Effect of Borax as a Nucleating Agent on PCMs
It can be seen from the Phase Rule that at normal pressure, during the solidification of pure crystals, the liquid-solid two phases coexist, and the degree of freedom is equal to zero, so the solidification temperature does not change. According to the second law of thermodynamics, under natural conditions, the direction in which the system spontaneously proceeds is the direction in which the free energy of the system decreases.

\[
\Delta G_i = \frac{Q \Delta T}{T_m}
\]  

In the formula, \( \Delta G_i \) is the unit molar free energy change from liquid phase to solid phase transition, \( kJ \cdot \text{kmol}^{-1} \), \( Q \) is the heat of fusion. The heat absorption to the environment is defined as positive, \( kJ \cdot \text{kmol}^{-1} \). \( \Delta T = T_m - T \) is the difference between the melting point \( T_m \) and the actual solidification temperature \( T \), defined as subcooling. During solidification, PCM radiates heat to the environment, \( Q \) is negative. In order to make \( \Delta G_i < 0 \), we have to make \( \Delta T > 0 \), ie \( T < T_m \). Therefore, the freezing point of the crystal should be lower than the melting point \( T_m \). The supercooling phenomenon for crystal solidification can be solved by adding a crystal nucleus, which is a nucleating agent to the material.

Figure 2, 3 are graphs of the step cooling curves of different proportions of sodium tetraborate decahydrate mixed with zinc nitrate hexahydrate and disodium hydrogen phosphate dodecahydrate. It can be seen from Fig. 2 that when 0.5 g of sodium tetraborate decahydrate is added, the degree of subcooling was reduced by about 4 °C compared with when no nucleating agent was added, and the phase transition temperature at this time was more suitable for the bioreactor and the heat preservation was more effective. The degree of subcooling when adding 1g of sodium tetraborate decahydrate was very close to the degree of subcooling when it was not added. Therefore, it can be considered that, within a certain ratio range, as the amount of nucleating agent increased, the degree of subcooling...
gradually decreased. When the ratio exceeded a certain degree, the amount of nucleating agent continued to increase, which in turn caused the degree of subcooling to start to rise again. From the step cooling curve of the mixed sample in figure 3, it can be seen that the phase transition temperature of each group of disodium hydrogen phosphate dodecahydrate and sodium tetraborate decahydrate was below 25 °C, that is to say, the degree of subcooling was above 10 °C. The increase in the amount of sodium tetraborate decahydrate added has substantially no effect on the degree of subcooling of disodium hydrogen phosphate dodecahydrate. The possible reason may be that the crystal structure is too similar and the lattice parameters are proximity, and there is a similar compatibility, that is, the two materials dissolve each other so that sodium tetraborate decahydrate cannot perform nucleation.

**Figure 2.** The cooling curve of zinc nitrate hexahydrate and sodium tetraborate decahydrate mixing.

**Figure 3.** The cooling curve of Disodium hydrogen phosphate dodecahydrate and Sodium tetraborate decahydrate mixing.

### 3.2 Effect of Strontium Chloride Hexahydrate as a Nucleating agent on PCMs

**Figure 4.** The cooling curve of zinc nitrate hexahydrate and Strontium chloride hexahydrate mixing.

**Figure 5.** The cooling curve of Calcium chloride hexahydrate and Strontium chloride hexahydrate mixing.

Figure 4, 5 are graphs of the step cooling curves of different ratios of strontium chloride hexahydrate mixed with zinc nitrate hexahydrate and calcium chloride hexahydrate. According to the step cooling curve of the mixed sample in figure 4, the phase transition temperature of the material was below 25 °C, that is, the degree of subcooling was above 10 °C. As the amount of strontium chloride hexahydrate added increases, the degree of subcooling of zinc nitrate hexahydrate decreases slightly. It can be considered that the addition of strontium chloride hexahydrate had little effect on improving the degree of subcooling of the material; when the amount of nucleating agent was different, the phase change rate was the fastest when adding 1% strontium chloride hexahydrate, and the subsequent phase transition speed was gradually slowed down. It can be seen from the step cooling curve of the mixed sample in figures 5 that the phase transition temperature was always above 30 °C. That is to say, the addition of strontium chloride hexahydrate may increase the instability of the material, it would start to
radiate heat when it had not fallen within a given temperature range, thereby causing overheating. From the perspective of crystal structure, zinc nitrate hexahydrate belongs to the tetragonal system, calcium chloride hexahydrate belongs to the trigonal system and strontium chloride hexahydrate belongs to the hexagonal system. There is a certain difference between the two hydrated salts, which may be one of the reasons for the abnormal phase transition temperature of the material.

3.3 Effect of adding dye
UV-visible absorption spectra of dyes and phase change materials were determined using an ultraviolet-visible spectrophotometer. The results are shown in figures 6. From bottom to top are the UV-visible absorption spectra of PCM, dyes and the mixture of PCM and dye. It can be seen that PCM has a greater absorbance than a single PCM and dye due to the addition of dye. It can be considered that the heat storage property of the phase change material is combined with the light absorbing property of the dye to improve the absorbance compared to the pure dye.

![Figure 6. UV-visible absorption spectrum of phase change materials with dye.](image1)

In addition, figures 7 and 8 show the step cooling curves of disodium hydrogen phosphate dodecahydrate and zinc nitrate hexahydrate after dye addition. It can be seen that the dye has no effect on the degree of subcooling of disodium hydrogen phosphate dodecahydrate. The effect is that the zinc nitrate hexahydrate can slightly reduce the degree of subcooling, about 3-4 °C. At the same time, compared with the sample without added dye, the composite phase change material after dye addition has better crystallization condition and basically nucleation crystallization, indicating that the dye does alleviate the phase separation. Therefore, it can be concluded that the dye not only does not hinder the phase change of the phase change material, but rather helps the phase change material to crystallize better.

![Figure 7. The cooling curve of disodium hydrogen phosphate dodecahydrate with dye after solarisation.](image2)

![Figure 8. The cooling curve of zinc nitrate hexahydrate with dye after solarization](image3)
4. Conclusions
In this paper, the problem of supercooling in PCMs suitable for biogas plants was studied, a suitable nucelating agent and dye were selected to modify the system. The study explored the influence of the type and amount of nucleating agent on the degree of subcooling of phase change materials, and tried to add dyes to improve the light absorption properties of phase change materials. The main conclusions are as follows:

- With disodium hydrogen phosphate dodecahydrate as PCM, the composite phase change material with borax as nucleating agent is not very effective, and the phase transition temperature is basically below 25 °C, that is, the degree of subcooling is above 10 °C.
- Selecting zinc nitrate hexahydrate as the PCM, the phase transition temperature was 27.8 °C after adding 5% sodium tetraborate decahydrate, and the degree of subcooling was reduced by about 4 °C compared with that before the addition.
- The addition of dyes can improve the light absorption properties of phase change materials, make the materials make full use of solar energy, greatly improve the light absorption efficiency of the materials, and at the same time, the dyes have a certain viscosity, which can alleviate the phase separation to a certain extent and improve Crystallization effect.
- From the experimental results and analysis and calculation, 5% zinc nitrate hexahydrate added with sodium borate decahydrate was the best in the two materials tested; from the practical point of view, it is necessary to consider the energy source of the PCMs. Considering the efficiency of the PCMs in absorbing sunlight, zinc nitrate hexahydrate with 2% dye is more suitable.

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