High Temperature Latent Heat Transportation by Use of Hydrate Slurry Treated with Surfactants

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Abstract

The fluidity improvement of inorganic hydrate slurry that has high density of heat but have high solubility and high viscosity has been investigated. To reduce the solubility of ammonium alum into water, this paper suggests the mixture of water and ethylene glycol is used as a solvent. The mass ratio of ethylene glycol to water was changed in five steps for solubility measurements. Additionally, a cationic surfactant was tested to prevent the agglomeration of hydrate particles and to cause a drag reduction effect of the mixture. The effects of the additives on the particle size of hydrates, on the drag reduction and on latent heat characteristics in the mixture were investigated. From the results, it was found that the mixture of water and ethylene glycol effectively reduces the solubility of ammonium alum. However, the latent heat is seriously reduced at the high mass ratio of 0.8. It was also found that the present surfactant additive is not effective over the mixture mass ratio of 0.5. On the other hand, the size of hydrate particles treated with surfactants becomes smaller even at the mixture mass ratio of 0.5. From this, the present surfactant additives were concluded effectively to prevent the agglomeration of hydrate particles and to improve the fluidity of the ammonium alum hydrate slurry.

Key words : Hydrate Slurry, Ammonium Alum, Solubility, Drag Reduction

Introduction

Latent heat transportation slurries, i.e. ice/water slurry have become important more and more for process intensification.

For example, ice/water slurry including 20wt% of ice particles has three times higher than that of water. So, flow rate of ice/water slurry can be reduced to one third compared with water sensitive heat transportation system. Friction drag of a pipe flow is roughly proportional to a square value of flow rate and pumping power to a cube value. This means pumping power becomes one twenty seventh. This has a lot of merits for miniaturization of heating/cooling system.

For the purpose of high temperature latent heat transportation, inorganic hydrate slurry is one of suitable candidates. Some inorganic materials forms hydrates having high latent heat and suitable phase change temperature. In this study, ammonium alum($NH_4Al(SO_4)_2 \cdot 12H_2O$) is used as an inorganic system. Its hydrate has latent heat of 269kJ/kg and phase change temperature of 93.5°C, and ammonium alum has low toxicity. So, it is one of most suitable candidates for latent heat transportation system in high temperature. However, it has high solubility in water around 200 at 80°C and low solubility around 20 at 20°C. To obtain the effective hydrates in the transportation system, more than 66wt% of ammonium alum concentration is needed. This causes 60wt% of hydrate fraction is obtained in water at 20°C. This means the heat devices cannot be restarted again any more.

In order to improve this, we will suggest a method to reduce the solubility. Ammonium alum has very low solubility in ethylene glycol. So, as a solvent of ammonium alum, a mixture of water and ethylene glycol can be applied to reduce the solubility. First of all, the effect of the mass ratio of ethylene glycol on the solubility and on latent heat will be discussed.

Particle transportation system also has another problem. Hydrate particles easily agglomerate with each other and this causes high viscosity. To improve this low fluidity, a method using surfactant dispersants will be discussed. Modak et al.(2002) reported a small amount of some surfactants effectively prevents the agglomeration of ice particles in water. A cationic surfactant, which can be effective in high temperature, will be tested for this purpose. The present surfactants have the same structures as a drag reducing surfactants reported by many researchers (Zakin et al., 1998). Suzuki et al. (2006) reported that this kind of cationic surfactants causes effective drag reduction for trimethylolethane hydrate slurry. The present surfactants can be also expected to cause drag reduction effect on hydrate slurries.

In this paper, the friction measurements of the water/ethylene glycol mixture solvent in a pipe flow and the particle size measurement of hydrates treated with surfactants were performed to investigate whether the present surfactant effectively reduce the drag of inorganic hydrate slurry and effectively prevents the agglomeration of hydrate particles.

2. Experimental Methods

2.1 Materials

Ammonium alum($NH_4Al(SO_4)_2 \cdot 12H_2O$) was used as an inorganic system. In order to reduce the solubility of ammonium alum, ethylene glycol was mixed to deionized water. In this study, ethyleneglycol-to-water mass ratio, ξ[-], was changed from 0 to 0.7.

A cationic surfactant, behenyltrimethylammonium chloride (trade name: Arquad 80/22) was applied as a dispersant and as a drag-reducer. The concentration of the surfactants was set to 2,000ppm. For the formation of rod-like micelles, sodium salicylate was used as a counter ion. The concentration of sodium salicylate was set at 1,200ppm as its molar ratio to surfactants became 1.5.

2.2 Experimental methods

In this study, the effect of ξ on solubility, latent heat, drag reduction characteristics of the mixture solvent and particle size were investigated.

Solubility of each solution was defined as the limitation of dissolving ammonium alum to each mixture. Temperature was increased by a step of 10°C from 20°C. As hydrates of ammonium alum begin melting in high temperature, the measurements were only performed at the lower temperature than its phase temperature measured by the DSC system explained in the following.

Latent heat of ammonium alum in the mixture was measured by use of a differential scanning calorimeter (DSC-60, Shimazu Ltd.). Each solution of 0.2g was set to DSC system with temperature increase of 2K/min.

Friction coefficients of the mixture solvent without ammonium alum were measured by use of once-through flow system as shown in Figure 1. This system consists of a pressurized tank, a magnetic flow meter and a test pipe with 5mm of diameter. After the sample was stored in the tank and pressurized, the valve located at the downstream end of test pipe was opened to let the fluid flow into the test pipe. Pressure in the tank gradually decreases and so flow rate also decreases gradually. Flow rate and pressure difference between pressure taps with 500mm (100 times of pipe diameter) distance allocated at 880mm (176 times of pipe diameter) downstream from the inlet of the test pipe were simultaneously measured by a pressure difference transducer and an electro-magnetic flow meter, respectively, under a pseudo-steady condition. With this system, Reynolds number based on water viscosity ranged from 2,000 to 30.000.

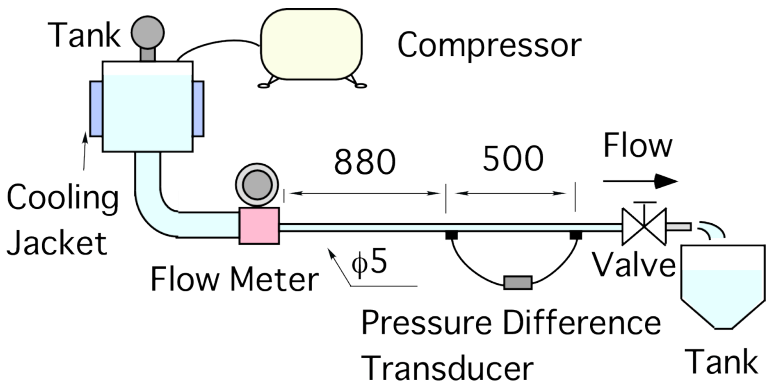


Figure 1 Once-through Flow System for Drag Reduction Effect

The particle size of ammonium alum hydrates was measured by use of a microscope controlling temperature. The temperature of each ammonium alum solution was increased to 95°C in order to melt all hydrates. After this, the temperature of each solution was kept constant at 50°C. From digital photos of the microscope, the particle size was measured by image processing method

3. Results and Discussion

3.1 Solubility improvement

Figure 2 shows the solubility of ammonia alum in water-ethyleneglycol mixture. In high temperature region, it is difficult to recognize the difference between solution and melting of hydrates. So, the results were shown in enough low temperature.

From this figure, it is found that the solubility of ammonia alum can be reduced in the mixture of water and ethylene glycol. The solubility decreases as increase of the mixture ratio of ethylene glycol, ξ. It can be concluded that the solubility becomes enough low when ξ is more than 0.7. From this, it is found that this hydrate slurry has enough fluidity at a room temperature.

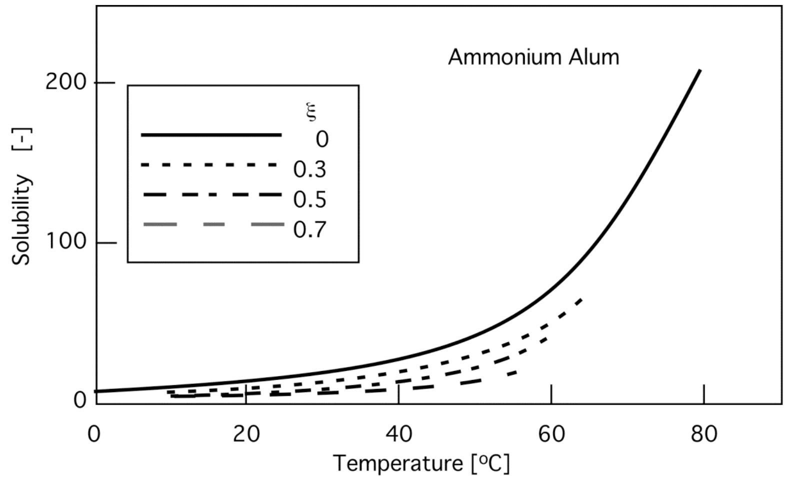


Figure 2 Solubility of Ammonium Alum in the Mixture

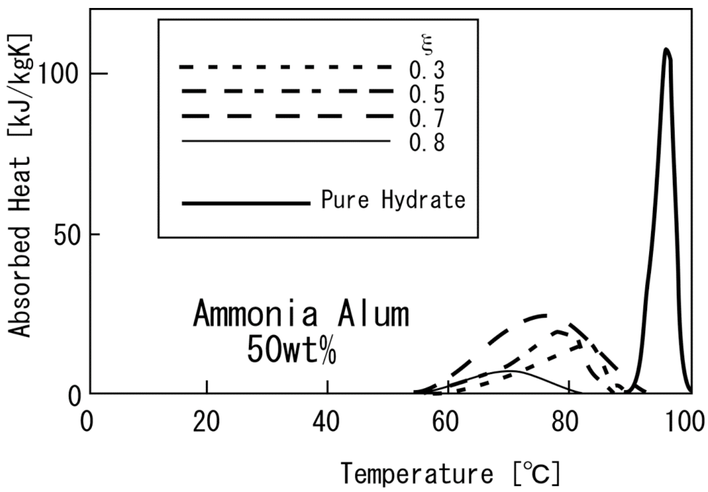


Figure 3 DSC Curves of Ammonium Alum Slurries

3.2 Latent heat

Figure 3 shows the latent heat of ammonium alum when it is dissolved in the water/ethylene glycol mixture.

As the mixture ratio of ethylene glycol increases, the latent heat increases until ξ=0.7. This is caused by the decrease of solubility as described in the previous section. The decrease of solubility leads to the increase of hydrate particles having latent heat.

On the other hand, the latent heat decreases in the case of ξ=0.8. This is because the existence probability of water molecular in the mixture becomes low for the formation of hydrates. Then, it can be concluded the optimum condition for using hydrate latent heat is the mixture ratio of 0.7.

3.3 The effect of surfactant addition for drag reduction effect

In order to study the possibility if the drag reduction occurs or not, the drag reduction effects were measured for the mixture without ammonium alum, at first. Figure 4 shows the results. In this figure, solid lines indicate the following theoretical and empirical equations.

$$f = 16/Re \quad \text{laminar flow} \tag{1}$$

$$f = 0.0791 Re^{-0.25} \quad \text{turbulent flow} \tag{2}$$

Here, f[-] is friction coefficient and Re[-] is Reynolds number based on water viscosity.

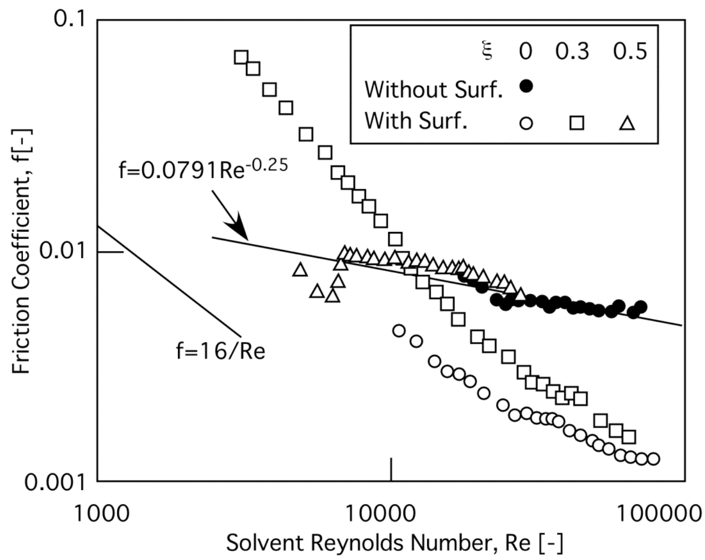


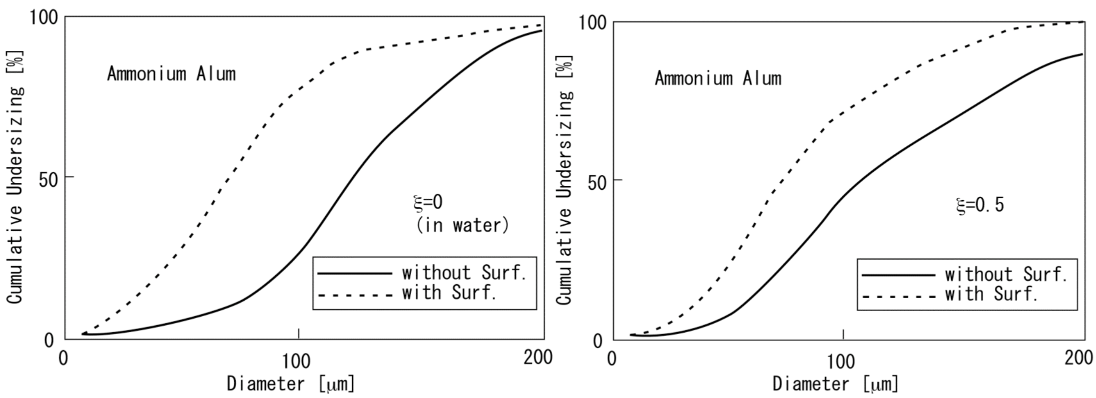
Figure 4 Friction Coefficient of the Mixture Treated with Surfactants

From this figure, it is found that friction coefficient of water and of the mixture at 0.3 with surfactants takes lower values than Newtonian turbulent flow in the region of Re>12,000. This indicates that the present surfactants cause effective drag reduction for the mixture. However, the friction coefficient at x=0.5 shows almost the same values as those of water flow. At high mixture rate of ethylene glycol, the number of water molecules surrounding surfactant molecules is reduced. Then, the formation of micelle structure causing drag reduction is disturbed. Less number of water molecules around surfactants exists in high concentration solution of ammonium alum. Thus, the present results indicate that the present surfactants cannot realize drag reduction effect for high concentration solution of ammonium alum.

3.4 Dispersion effect of surfactants

The present surfactants in Section 3.3 were not found to reduce drag of hydrate slurry of ammonium alum. In this section, particle size of ammonium alum hydrates will be discussed.

Figure 5(a) and (b) show the cumulative undersizing of ammonium alum hydrate treated with surfactants in the mixture at ξ=0 and 0.5, respectively.



(a) ξ=0 (b) ξ=0.5

Figure 5 Cumulative Undersizing of Ammomium Alum Hydrates in Slurries

From this figure, it is observed that particle size of ammonium alum hydrates is reduced by surfactant treatment, compared with results in the cases without surfactants. This indicates that the present surfactants show effective dispersion ability. Unfortunately, the present surfactants does not cause drag reduction effect, but reduces particle size of ammonium alum hydrate even at the high concentration mixture of ξ=0.5.

4. Conclusions

In this study, the fluidity improvement of inorganic hydrate slurry which have high density of heat but have high solubility and high viscosity has been investigated. To reduce the solubility of ammonium alum into water, this paper suggests the mixture of water and ethylene glycol is used as a solvent. Additionally, a cationic surfactant was tested to prevent the agglomeration of hydrate particles and to cause a drag reduction effect of the mixture.

From the results, it was found that the mixture of water and ethylene glycol effectively reduces the solubility of ammonium alum. However, the latent heat is seriously reduced at the high mass ratio of 0.8. It was also found that the present surfactant additive is not effective over the mixture mass ratio of 0.5. On the other hand, the size of hydrate particles treated with surfactants becomes smaller even at the mass ratio of 0.5. From this, the present surfactant additives were concluded effectively to prevent the agglomeration of hydrate particles and to improve the fluidity of the ammonium alum hydrate slurry.

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