

Surface Modification of Silica Nanoparticles by Dichlorodimethylsilane for Foam Stability and Decontamination

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Abstract: Foams stability was investigated by varying the amount of dichlorodimethylsilane (DCDMS) for the surface modification of silica nanoparticles in decontamination foam containing a surfactant and chemical reagents. In addition, a study on the oxide dissolution of a corroded specimen using decontamination foam was performed to evaluate the decontamination efficiency of the foam. The foam performance index (FPI) as an indicator of the foam stability had a higher value with surface-modified silica nanoparticles in DCDMS/Si at a mole ratio of 0.5% compared with other silica nanoparticles. The contact angle was 51, 84, and 90° with surface-modified silica nanoparticles in DCDMS/Si with a mole ratio of 0, 0.5 and 5%, indicating that a contact angle of 80-85° had a positive effect on the foam stability owing to the partially hydrophobic of silica nanoparticles. The decontamination efficiency toward dissolving iron and nickel was improved up to 10% and 20%, respectively, when using decontamination foam with surface-modified silica nanoparticles in DCDMS/Si at a mole ratio of 0.5%, compared with that containing unmodified silica nanoparticles.

Key words: Decontamination, Foam, Silica nanoparticles, Surface modification, Foams stability, Nitric acid, Contact angle

1. Introduction

Decontamination foam comprises a surfactant to generate the foam, a co-surfactant in the form of a long-chain alcohol to reduce the total number of surfactants, and chemical reactants to dissolve the contaminants on a solid surface. To increase the decontamination efficiency of this process, the contact time of the chemical reactants to the contaminated surface should be increased. Therefore, the present research is focused on increasing the contact time by adding a viscosifier, which is a biopolymer, or inorganic materials such as silica nanoparticles to the decontamination foam solution [1-3].

Silica nanoparticles increase the foam stability in the foam formulation. These particles can be specifically hydrophobized for optimal adsorption at the liquid/gas interface, which

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creates armor for the bubbles and prevents coalescence by reducing the internal gas transfer [4-6]. Conversely, hydrophilic particles remain confined in the liquid phase, and to enhance the foam stability. Kruglyakov and Taube [7] studied the drainage of foams generated from a non-ionic surfactant suspension of pyrogenic silica. Their results showed that the loss of liquid is slightly slowed when particles are present because of the steric hindrance to the liquid flow.

Recent investigations revealed a strong correlation between the hydrophobicity of the particles and foam stability. If θ contact angle is $< 90^\circ$, particles usually termed hydrophilic are held at the interface and stabilize water phase, whereas if $\theta > 90^\circ$, particles termed hydrophobic are still held at the interface but stabilize air phase. If the particles are completely wetted by air, they remain dispersed in air phase and no stable foams are formed. Partially hydrophobic particles are remained in the surface between air and water, and foams were generated (Fig. 1).

In this study, we aimed at modifying the surface of silica nanoparticles with dichlorodimethylsilane (DCDMS) reagents using methods proposed in previous studies. We also investigated the foam stability and decontamination efficiency with surface-modified silica nanoparticles to develop a new formulation of decontamination foam.

2. Experimental

Fumed silica (M-5) was purchased from Cabosil, and selected owing to its stability and in an acid medium and low cost. Various degrees of hydrophobicity were obtained through silanization of the silica particle surface with DCDMS (+99.5%, Sigma-aldrich). Hydrophilic

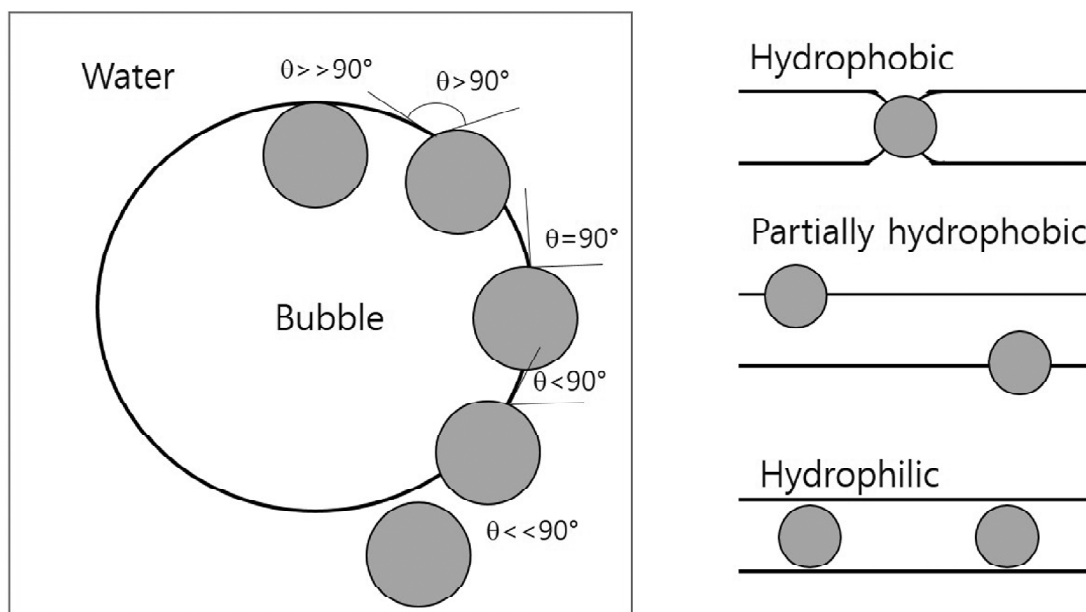


Figure 1: Schematic diagram on the stability of foam by silica nanoparticles.

silica (M-5) was silylated through a reaction with DCDMS (Fig.2). The silylation was performed with variable amounts of silane in order to control the DCDMS group. In the surface modification, 1.0 g fumed silica nanoparticles were modified using DCDMS/Si with a mole ratio of 0, 0.5 and 5% in toluene for 20 h and continuously injected by nitrogen gas. The samples were then dried in a furnace at 110 °C for 3 hrs. The content of silanol groups was determined through titration with aqueous sodium hydroxide [8]. 1 g silica NPs modified with DCDMS/Si at a mole ratio of 0, 0.5 and 5% were added to a 1% v/v Elotant™ Milcoside 100 (EM 100, LG Household & Health Care, Korea) surfactant solution in 2M HNO₃ to investigate the foam stability.

In all tests on the foam stability and structure, the foam height and liquid volume in the foam were measured using a Dynamic Foam Analyzer (DFA-100, KRÜSS, Germany). During foaming, compressed air was passed through a sintered glass frit at the bottom of a cylindrical glass vessel (40 mm inner diameter) containing the solutions and the decontamination foam. The initial liquid volume was 60 ml; the gas flow was 0.2 l/min, and was stopped after 60 s of foaming [3].

Decontamination foams were prepared using 100 ml of 2 M HNO₃ in a 1.0% v/v EM100 surfactant solution containing varying amounts of added 1 g silica NPs modified with DCDMS/Si at a mole ratio of 0, 0.5 and 5%. Approximately 250 ml of each decontamination foam formulation was generated from a 50 ml solution by shaking for 10 s in a 250 ml container, with a gas to liquid ratio of 4:1. An oxide film of nickel ferrite, prepared using electrodeposition, was placed in the middle of the bottles and left to react with the decontamination foam for 3 h at room temperature. The dissolved Fe and Ni were analyzed using atomic absorption spectroscopy after the foam decontamination test [2].

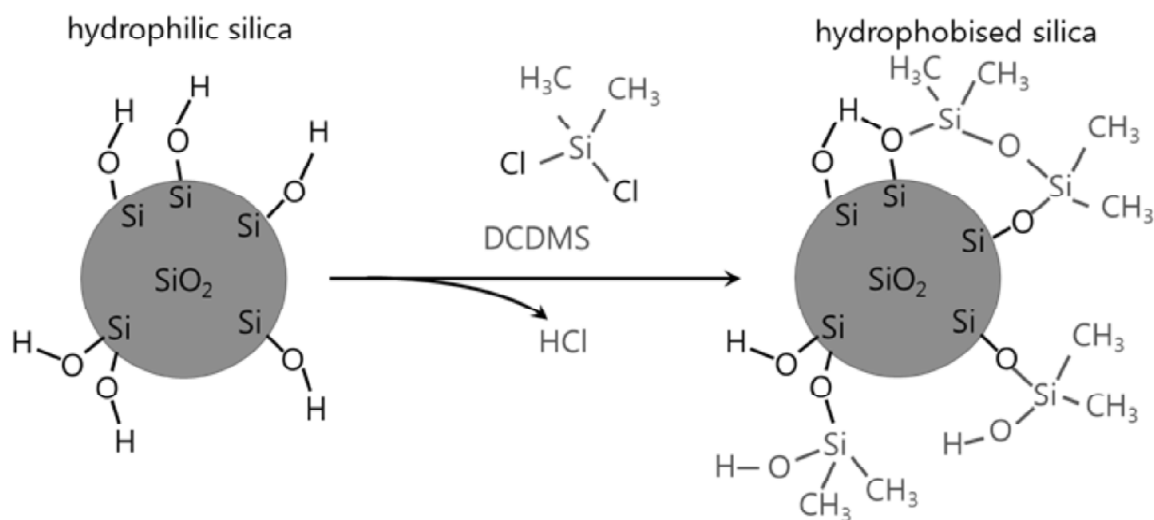


Figure 2: Schematic diagram for surface modification of silica nanoparticles (M-5, Cabosil) using DCDMS reagent.

3. Results and Discussion

In Figure 3, the foam volume remained at over 125 ml for 3 hours with surface-modified silica nanoparticles in DCDMS/Si with a mole ratio of 0.5%. However, foam decreased and remained at 40 ml after 3 h with unmodified silica nanoparticles. In surface-modified silica nanoparticles in DCDMS/Si with a mole ratio of 0.5%, the foam volume was higher than that with unmodified silica nanoparticles. However, the foam volume in DCDMS/Si with a mole ratio of 5% was continuously decreased and remained at 10 mL. This results showed that optimum foam stability was achieved in DCDMS/Si with a mole ratio of 0.5%.

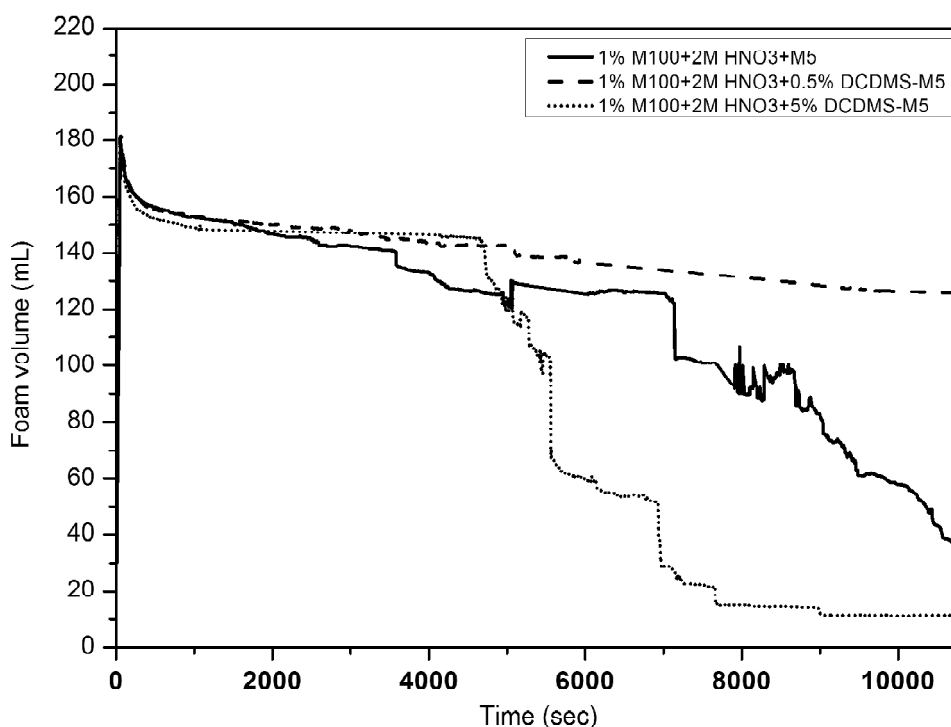


Figure 3: Time dependence of the foam volume with surface-modified silica nanoparticles in DCDMS/Si with a mole ratio of 0, 0.5 and 5% in 2 M HNO₃ for 3 h.

Figure 4 shows the foam performance index (FPI) as the foam stability had a higher value with surface-modified silica nanoparticles in DCDMS/Si at a mole ratio of 0.5% than that with other silica nanoparticles. However, FPI had the lowest value with surface-modified silica nanoparticles in DCDMS/Si with a mole ratio of 5% compared with the other silica nanoparticles, indicating that a high concentration of DCDMS can hamper the foam stability. This result showed that the optimum mole ratio of DCDMS/Si with 0.025. The contact angle was 51, 84, and 90° with surface-modified silica nanoparticles in DCDMS/Si with a mole ratio of 0, 0.5 and 5% (Table 1). This result suggests a contact

angle of 80-85° had a positive effect on the foam stability; however, a contact angle of over 90° was hydrophobic and decreased the foam stability.

When partially hydrophobic silica nanoparticles and suitable surfactants are combined, synergistic effects can be found in terms of the foamability and foam stability of the corresponding dispersions [9,10]. Previous studies reviewed the different concepts of foam stabilization mechanisms involving silica nanoparticles [11]. It has been found that silica particle layers can stabilize a fluid interface by forming a protective layer. These layers of silica nanoparticles decelerate the foam destruction.

Table 1
Foam performance index (FPI) and contact angle with surface-modified silica nanoparticles in DCDMS/Si with a mole ratio of 0, 0.5 and 5%

M-5	FPI (h=3hr)	Contact angle
0 %	1,267,757	51°
0.5 %	1,572,628	84°
5.0 %	976,815	90°

To evaluate the decontamination performance of different foams with varying amounts of DCDMS, the dissolved Fe and Ni concentrations were measured in the solution. The dissolved Fe and Ni concentration was highest using decontamination foam with surface-modified silica nanoparticles in DCDMS/Si with a mole ratio of 0.5% as compared with decontamination foam with other silica nanoparticles (Fig. 5). The decontamination efficiency toward dissolving iron and nickel was improved by up to 10% and 20%,

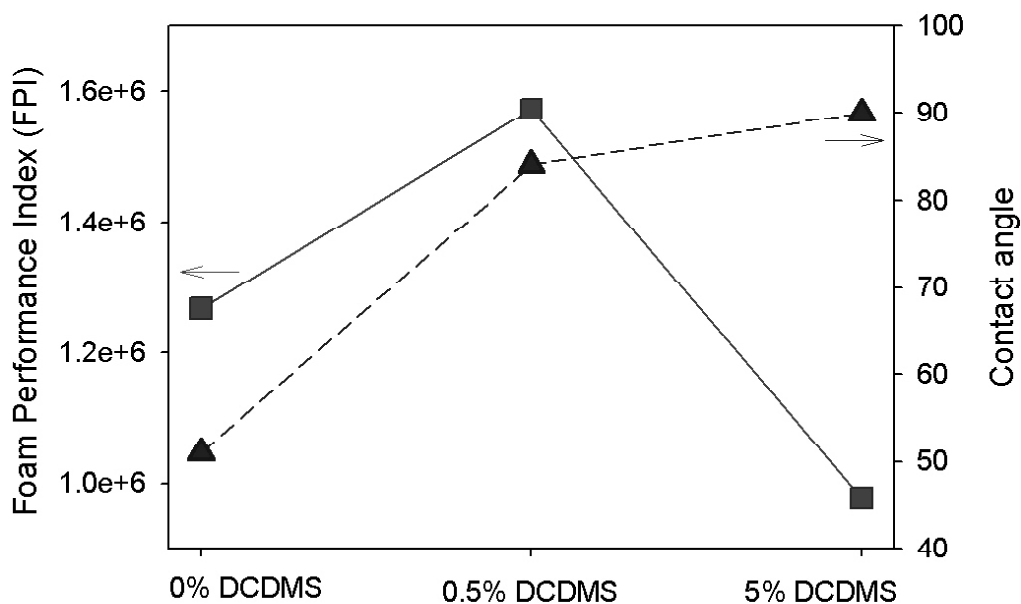


Figure 4: Relationship between foam performances index (FPI) and contact angle with surface-modified silica nanoparticles in DCDMS/Si with a mole ratio of 0, 0.5 and 5% in 2 M HNO₃ for 3 h.

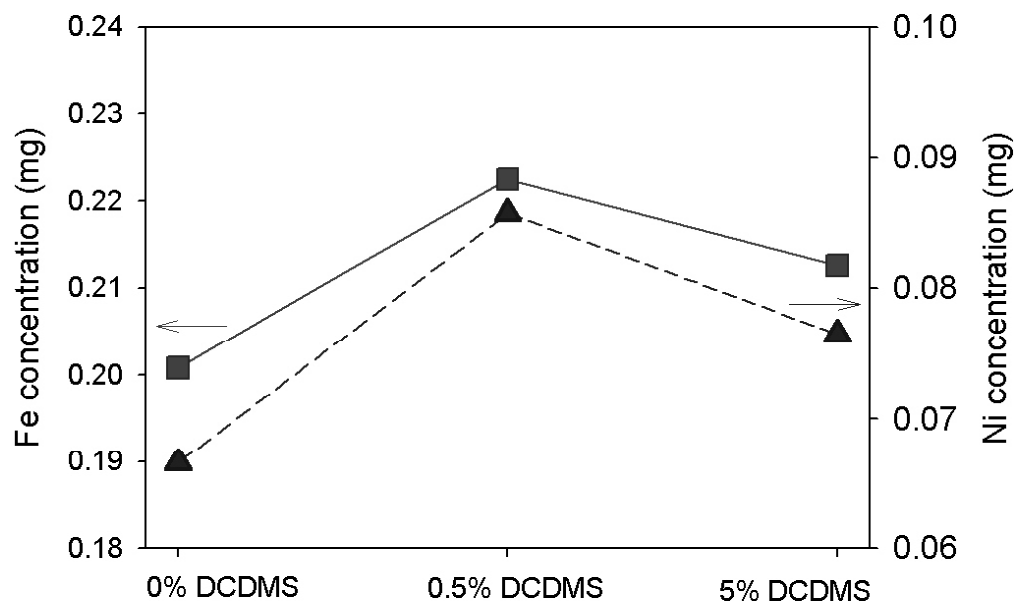


Figure 5: Decontamination performance test of decontamination foam with surface-modified silica nanoparticles in DCDMS/Si with a mole ratio of 0, 0.5 and 5% in 2 M HNO_3 for 3 hrs.

respectively. These results indicate that surface-modified silica nanoparticles have a significant effect on the dissolution of nickel ferrite oxide when combined with a chemical reagent and surfactant due to the increase of the foam stability and drainage prevention. Faure's study [12] indicates that the rate of oxide dissolution is directly proportional to the foam stability. These results suggest that the use of surface-modified silica nanoparticles in decontamination foam increases the decontamination efficiency owing to the increased foam stability.

4. Conclusions

Modified silica nanoparticles are an effective stabilizer of decontamination foam by controlling their hydrophobicity, resulting in a foam stable against collapse. In future studies, decontamination tests will be conducted on a surface contaminated with radionuclides such as cesium and cobalt.

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