Structural changes of diatomaceous earth by heat treatment

*Naoya Sasaki[1,2], Akane Arasuna[1], Masayuki Okuno[1]

1. Kanazawa University, 2. Industrial Research Institute of Ishikawa

In this study, the structural changes in the diatomaceous earth from U.S.A (Grade D110, Celite Co.) by heat treatment up to 1200˚C were investigated using XRF, XRD, ATR-IR and Raman spectroscopy. These results provide important information to elucidate the structure of fossilized diatom shell that has been rarely reported and the characteristic of structural change by heat treatment comparing the previous result for diatom.
The results of chemical analysis show this sample included of 93.1 mass% SiO_2 due to diatom shells and also containing a small amount of Al_2O_3, Fe_2O_3, MgO and CaO from clay minerals. Observed TG curve of this sample shows it contains about 12 mass% of H_2O molecules and OH. The diatomaceous earth samples were heat-treated at 200, 400, 600, 800, 900, 1000, 1100 and 1200˚C.
The XRD patterns for samples up to 800˚C show broad amorphous phase peaks at around 2θ=22˚ and weak diffraction peaks at around 2θ=19˚ due to clay minerals. The XRD patterns for heat-treated samples at 900 and 1000˚C showed amorphous phases. This means clay minerals amorphized at 900˚C due to dehydration. At 1100˚C and 1200˚C, cristobalite phase were observed. The positions of broad peaks for amorphous phase show the samples have 6-membered rings of SiO_4 tetrahedra as the basic structural unit. On the other hand, previous results for thermal change of diatom show crystallization above 800˚C.
ATR-IR spectrum for non-treated sample is similar with that of diatom except sharp O-H band at around ν=3620cm^{-1}, this band could be attributed to OH of clay minerals. On the other hand, the broad band ν=2800-3700cm^{-1} could be attributed H_2O molecules in amorphous SiO_2 phase. se bands disappeared by heating at 900˚C. This result is consistent with that of XRD measurement. bands at ν=800 and 1020cm^{-1}, which are attributed to the Si-O-Si bending vibration and the Si-O stretching mode show not large thermal change up to 1000˚C. Over 1000˚C, these bands shift their position and become sharp by crystallization of cristobalite.
Raman spectrum at ν=200-800cm^{-1} of non-treated sample is also similar with that for diatom of the previous work. This mean the basic structure of diatomaceous earth composed 6-membered rings of SiO_4 tetrahedra. Because, the intensity around ν=450cm^{-1} is strong, which band could be attributed symmetric stretching band of Si-O-Si. By increasing treated temperature up to 1000˚C, the intensities around at ν=450, 490 and 600cm^{-1} increase. This means 6-membered rings of SiO_4 tetrahedra are largely increased and 4- and 3-membered rings appear and the nanostructure becomes similar to the spectrum SiO_2 glass by heat treatment. This Raman spectrum change is not similar with that of diatom. Furthermore, the structural changes of diatomaceous earth by heat treatment show a different tendency from the diatom that have been reported so far. Now, we can guess that the difference of temperature change in XRD between diatom and diatomaceous earth can be probably due to the small quantity of clay minerals and fossilization process diatom to diatomaceous earth.

