The effect of artificial humic-clay complexes on oil-mineral aggregate formation: visualization using epi-fluorescent confocal microscopy

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Up to 10% of spilled oil can be dispersed under natural conditions due to mechanical energy of waves and effect of suspended particulate matter (SPM) in the sea. As a result of interaction between oil and SPM, oil-mineral aggregates (OMA) are formed. This prevents oil drops coalescence and accelerates biodegradation of oil. This mechanism can be used for development of nontoxic, environmentally friendly oil spill dispersants based on organically-modified clay particles (<1 μm). According to the reported data, the most effective clay mineral for promoting formation of OMA is montmorillonite.

In this work, we proposed to increase efficiency of oil dispersion by montmorillonite using its modification with natural amphiphylic polyelectrolytes - humic substances (HS). HS sorprion on clay minerals increase their hydrophobicity significantly changing their surface properties.

To reach this goal, we prepared two types of montmorillonite - HS complexes using HS of different origin and studied their effect on OMA formation. Clay-humic complexes were prepared using HS from soil and coal. They were sorbed onto montmorillonite with a median grain size <0,55 μm. The complexes were assigned the ciphers MPd and MPow, respectively. Grain sizes were measured using Zetatrac size analyzer. The obtained clay-humic complexes were used as oil spill dispersants. Oil-in-water emulsions were generated using a standard shaker. Then the flasks were maintained in a stationary position for 20 minutes, 1 day, 3 day and 1 week. To visualize the oil emulsions formed, an aliquotic part (20 μl) of sample was transferred onto a glass slide and covered with a glass slip. The photomicrographs were taken using Nikon A1 confocal scanning laser microscope equipped with an Ar laser source, and Nikon epifluorescence microscope (60x/1,4 oil immersion objective lens). The results are shown in Figure 1.

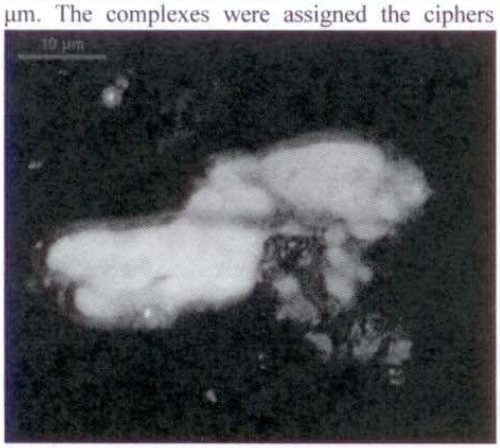

Fig.1. Confocal scanning laser microscopy optical slice through the center of a solid OMA. The signal emitted in the green channel represents the fluorescent oil. The signal in the red channel is the reflectance from mineral particles.

It was observed that oil is associated with humic-clay particles (OMA) and both MPow and MPd generated OMA with similar structure: solid and droplet.The microscopy analyses are used to confirm whether the clay-oil-water suspension contained dispersed free oil droplets, OMA or both. At complex:oil ratios of 1:3 or 1:10, more then one half volume of oil seemed to be bound into OMA.

The obtained results show an opportunity to use artificial humic-clay complexes consisting of soil and coal humic substances sorbed onto 550 nm montmorillonite particles as effective and potentially environmentally friendly oil spill dispersants. These results support the application of shoreline oil spill clean-up techniques based on the acceleration of oil-mineral fine interactions.