THE USE OF AN INORGANIC SOLIDIFIER FOR CLEAN UP OF SHORELINE OIL SPILL

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ABSTRACT

Oil spills can have a serious economic impact on coastal activities and on those who exploit the resources of the sea. The impact on marine life is compounded by toxicity and tainting effects resulting from the chemical composition of oil, as well as by the diversity and variability of biological systems and their sensitivity to oil pollution. In 2006, 11 August, an oil spill accident happened offshore of Negros and Guimaras Island in the Philippines.
Generally, it is difficult to remove the wreck oil and typically requires hard labor to scour off manually. Working with the University of the Philippines, we undertook treatments at a site off Guimeras Island. In order to easily remove the oil from the surface of rock, wood and sand, an inorganic coagulant and biostimulation was introduced to reduce oil concentration and toxicity. After treatment, we evaluated the impact of the two types of treatments. We found that using inorganic coagulant, 96% of wreck oil was easily removed; a major improvement over labor intensive methods. We also found that the solidification process enhanced the effect of biostimulation, reducing by half the amount of time needed to reduce TPH levels.

INTRODUCTION

Heavy oil spilled into the sea is usually collected by oil recovery vessels, nets or ladles. It is also possible to spread surfactants to emulsify and disperse oil for microbial decomposition, but the use of surfactants is restricted because their major component, polyoxyethylene, is toxic. Thus there is a risk of secondary contamination. Currently there are several methods of oil recovery using solidifiers.
Heavy oil that drifts ashore is recovered by a number of different methods, depending on its final resting place. On the shoreline, the oil is recovered with sand and subjected to heat and cleanup treatments at industrial waste disposal facilities. When the oil is attached to seaside rocks, it is cleaned with high-pressure hot water, but this operation is often limited because diffusing heavy oil can result in secondary contamination and because high-pressure hot water itself affects the ecosystem. This study examines the removal

effects of our developed inorganic solidifier on attached oil, as well as a biostimulation method.

MATERIALS

Solidifiers are used to control the viscosity of oil, perfume and other liquids for flowability adjustment or evaporation prevention as well as to improve soft ground. As can be seen in Figure 1, they generally solidify their target by hydration and pozzolanic reactions. Solidifiers are also used to insolubilize soil contaminants and thus stably prevent their elution. Our solidifier is an inorganic powder made from special charcoal, iron oxide, magnesium oxide, calcium oxide, and other materials. When our solidifier is applied directly on the surface of a rock stained with heavy oil, the oil solidifies and becomes easy to remove. The solidified oil, stably sealed inside, is not eluted. In addition, heavy oil solidification may eliminate physical obstructions caused by oil accumulation.

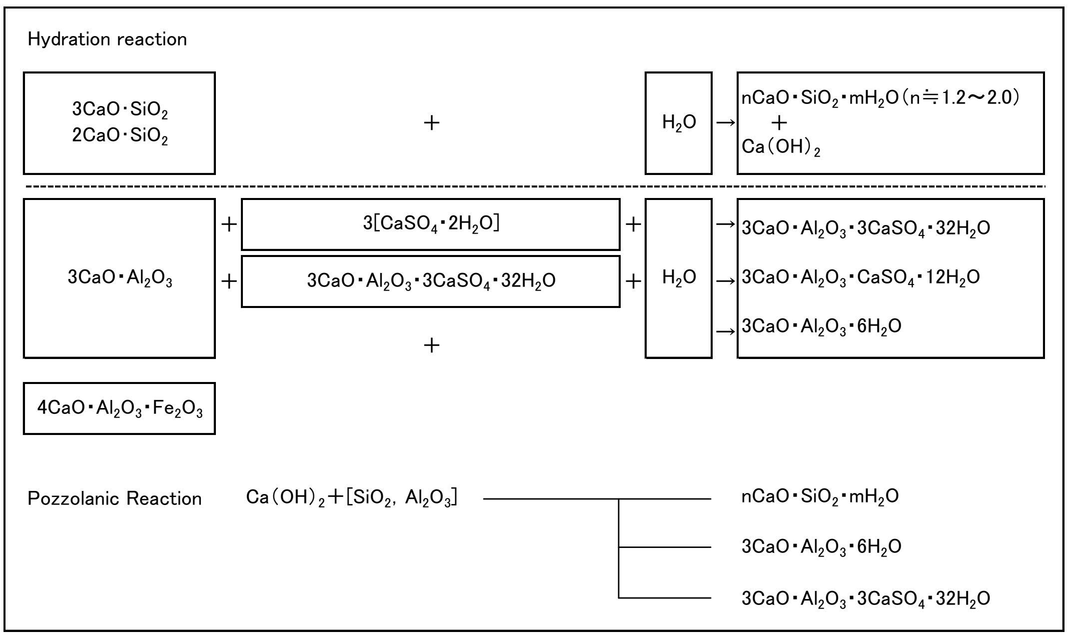

Figure 1. Hydration reaction on the hardening and Pozzolanic reaction

METHODS

Our experiment was divided into two parts: experiment I for the removal effects of our inorganic solidifier on heavy oil, and experiment II for the cleanup effects of biostimulation on heavy oil after solidification. The measured oil components were total petroleum hydrocarbon (TPH) and benzene, an oil-derived contaminant, which is designated as a toxic substance by the Soil Contamination Countermeasures Act. The oil component measurement was performed for four weeks. In addition, soil pH was measured every week, and the number of oil-degrading bacteria in the soil was measured before and after the experiment to observe the microbial community behavior induced by heavy oil.

Experiment I (removal effect experiment)
The removal effects of our solidifier on heavy oil were examined by pouring 10g of heavy oil on a flat stone and then removing the oil with a brush and the gradual application of the solidifier. This permitted the determination of the appropriate amount of solidifier necessary for complete heavy oil removal, as well as the calculation of the removal rates based on the weight of heavy oil removed. The experiment was performed three times for precise measurements of the removal effects.
Heavy oil is viscous, and if left on a surface, the oil sticks firmly to the surface. Changes in removability over time were studied by examining the removal effects of our solidifier on heavy oil left for a week on smooth-faced stone, rough-faced stone and driftwood.

Experiment II (biostimulation experiment)
Samples of heavy oil taken from the site to Japan were mixed with local gravel and treated with the solidifier. Then the samples were left standing for four hours to see how bacteria contained in the gravel would decompose oil components (TPH, benzene, pH) (Fig. 2). The tested mixtures were as follows:

- Case 1 - 10 g of heavy oil solidified with 20 g of the solidifier was mixed with 3 kg of gravel, seawater and microbial active agent (for TPH test)
- Case 2 - Heavy oil not treated with the solidifier was mixed with 3 kg of gravel, seawater and microbial active agent (for comparison)
- Case 3 - 10 g of heavy oil was mixed with 20 g of the solidifier for the benzene elution test. The experiment was performed at 20°C in a sunny room.
  Figure 2. Cases 1, 3 and 2 photos

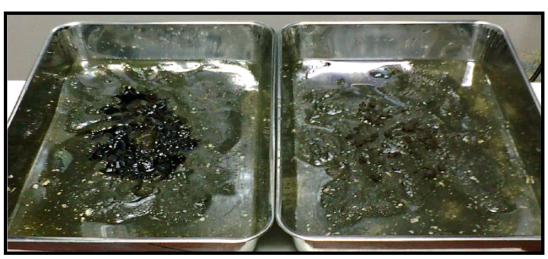

Figure 2. Sample mixture of Case 1, 3 and 2

RESULTS AND DISCUSSION

Experiment I

Removal effects of the solidifier on heavy oil
The heavy oil was almost completely removed after applying the experimental quantity (weight in grams) of our solidifier two times. Table 1 shows the removal rates of heavy oil

in the experiment performed three times. The average removal rate was 96.1%. The remaining quantity (approximately 4%) probably seeped into the stone or attached to the brush. Generally, when the solidifier is applied to soil that contains oil, the weight ratio of the solidifier to soil is only 0.03- 0.05. We removed heavy oil by applying twice the weight of our solidifier, but this amount may be reduced depending on the application method. Removal effects of the solidifier on heavy oil left attached for a certain period Heavy oil left on the stones for a week had a partly solidified surface, but the internal state was still liquid. The smooth-faced stone was almost completely cleaned of heavy oil using our solidifier (Fig. 3).

Table 1. Removal rates of heavy oil

	1	2	3	Ave.
Heavy Oil	10.0 g	10.0 g	10.0g	10.0g
Amount of removal	9.57 g	9.58 g	9.68 g	9.61 g
% of removal	95.70%	95.80%	96.80%	96.10%

Figure 3. Photo of before and after sate of removal effects

The rough-faced stone was more difficult to clean because oil was caught in grooves and hollows unreachable with the brush. The driftwood was penetrated by heavy oil, allowing only a superficial removal.

Experiment II

The added heavy oil formed a film on the water surface and gave off a strong odor of oil in Case 2, but there was no film or odor in Case 1 where the heavy oil was solidified beforehand. The film and odor in Case 2 disappeared four weeks later.

TPH quantitation

Table 2 and Figure 4 show the results of the experiment. Case 1 and 2 have different initial values depending on whether or not the heavy oil was solidified. Japan has not set a limit to

TPH in its environmental standards, whereas Holland has established a limit of 1000 mg/kg. Case 1 (treated with the solidifier) required 11.5 days, and Case 2 (not treated with the solidifier) required 18.3 days to go below the Dutch TPH limit, demonstrating that solidified heavy oil decomposes as much as ordinary heavy oil.

Table 2. Results of TPH measurement

TPH(mg/kg)	Control	1 week	2 week	3 week	4 week
Case 1	2000	*	*	460	230
Case 2	4000	*	*	720	280

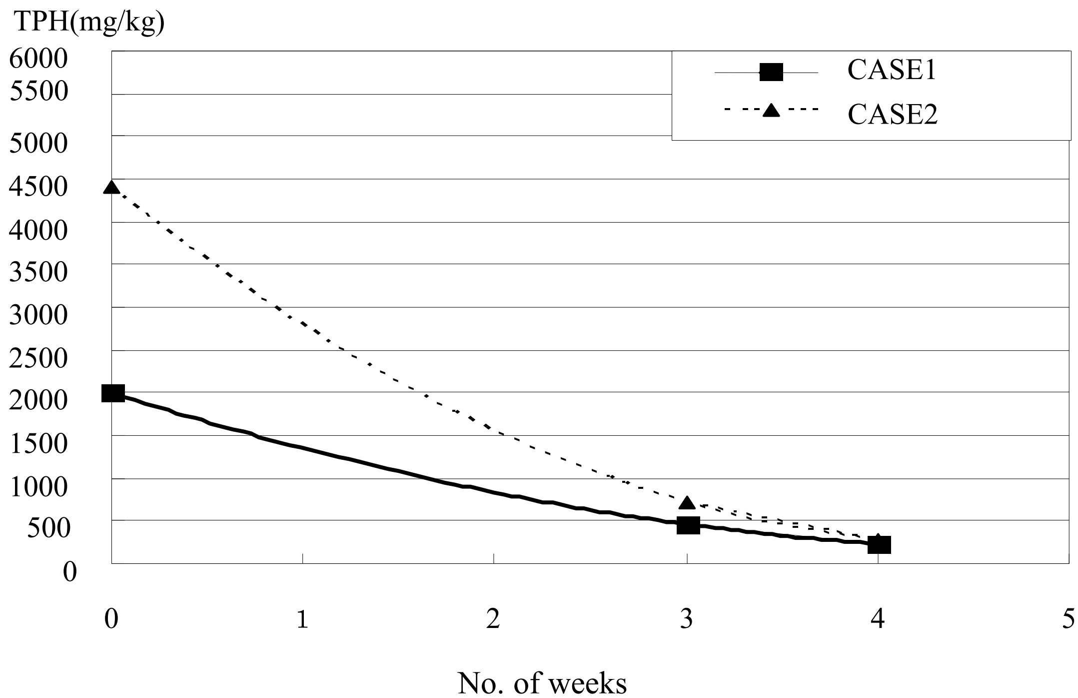

Figure 4. Decreases of TPH

Benzene elution test

Table 3 shows the results of the benzene measurement. In Cases 1 and 2, the benzene level was already below the detection limit of 0.0005 mg/l in the first stage, probably because the benzene was volatilized or mixed with soil and thus diluted. In case 3, the benzene level reached 0.39 mg/l, well above the limit of 0.01 mg/l according to the Soil Contamination Countermeasures Act, probably because the benzene was sealed by the solidifier and retained its level of concentration. However, four weeks later, the benzene level was below the detection limit, suggesting that microorganisms contained in the heavy oil decomposed the benzene using minor components, which were volatilized or contained in the solidifier as nutrients (Itagaki, 2000).

Table 3. Results of benzene measurement

Benzene	Control	1 week	2 week	3 week	4 week
Case 1	less 0.0005	less 0.0005	*	less 0.0005	less 0.0005
Case 2	less 0.0005	less 0.0005	*	less 0.0005	less 0.0005
Case 3	0.39	*	*	*	less 0.0005

Soil pH

Table 4 and Figure 5 show the results of the soil pH measurement. Throughout the experiment, the pH was in the range of 5-10 where oil-degrading bacteria can proliferate. During the first three weeks, the pH fell by approximately 0.8 in Case 1 and Case 2. The slight shift toward acidity is attributable to carbon dioxide produced as a result of the ultimate degradation by microorganisms. However, during the following week, the pH rose by 0.33 in Case 1 and 0.28 in Case 2. The structure of the soil microbial community changes significantly depending on the amount of decomposable organic compounds. In oil-containing soil, oil-degrading bacteria proliferate preferentially, reducing the diversity of the microbial community. After that, the diversity turns upward with the decrease of decomposable objects, and the composition of the microbial community finally returns to the original state. During the first three weeks, TPH was decomposed up to 77% in Case 1 and 84% in Case 2. The rise in pH in Case 1 and Case 2 can be explained by the depletion of decomposable objects for oil-degrading bacteria. Thus, presumably, the composition of the microbial community returned to the original state and the degradation of heavy oil stopped.

Table 4. Results of soil pH measurement

pH	Control	1 week	2 week	3 week	4 week
Case 1	8.85	8.68	8.4	8.04	8.37
Case 2	8.85	8.83	8.37	8.08	8.36

Number of oil-degrading bacteria

The number of oil-degrading bacteria was 1.7×10^{4} cfu/g at the start of the experiment, but bacteria were not detected at the end of the experiment (Table 5). Those bacteria seemed to have been destroyed by the original bacterial biota because TPH was almost totally decomposed during the first three weeks.

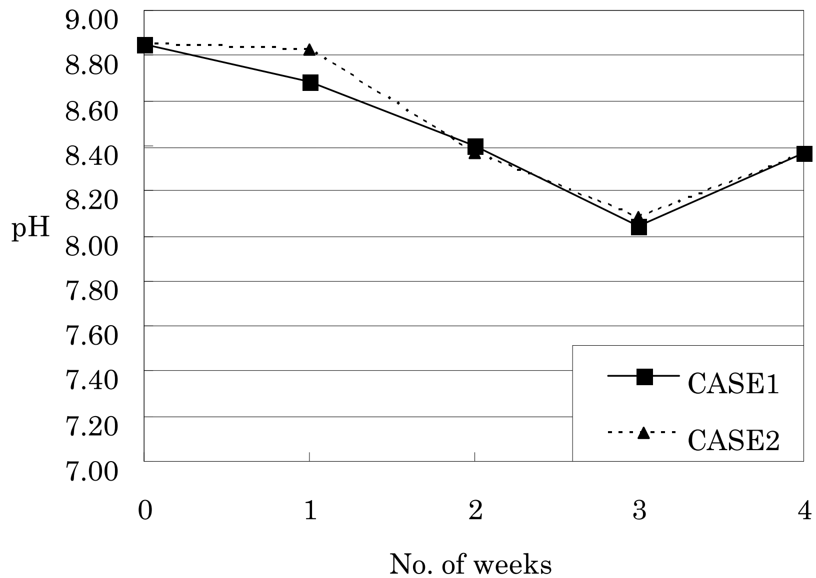

Figure 5. Variation of pH

Table 5. Results of measurement of the No. of oil-degrading bacteria

(cfu/g)

	Start of Exp	End of Exp.
Case 1	1.7×10^4	not detected
Case 2	1.7×10^4	not detected

CONCLUSION

We examined the removal effects of our inorganic solidifier on attached oil as well as a method of cleaning up beached oil using the inorganic solidifier in combination with an active microbial agent. Our findings are as follows:

• Our solidifier proved to be effective in removing attached oil, showing an average removal rate of 96.1%. Heavy oil was almost completely removed by applying solidifier to the heavy oil in a 2 to 1 weight ratio. However, the effects are minimal on oil attached to a rough surface or oil which is absorbed into the interior of objects. These situations continue to require additional removal tools such as brushes.

• Our experiment on the cleanup effects of biostimulation on heavy oil after solidification showed that TPH was decomposed by up to 80% during the first three weeks, demonstrating that solidified heavy oil decomposes as much as ordinary heavy oil. Solidification reduced the initial TPH level by more than half. In our experiment, the TPH level in solidified heavy oil fell below 1000 mg/kg a week earlier than in unsolidified heavy oil, significantly shortening cleanup periods.

REFERENCE

Itagaki, Eiji.(2000). Research on Japan Sea, No. 31 pp121-133