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Abstract

Water, ash, and inorganic components in the heavy fuel oil drawn from the *Nakhodka*'s cargo tanks and the drifted oils were determined in order to estimate the effects of the oils on the environment and the health of people. The oil drawn from the *Nakhodka*'s cargo tanks included 61.6% of seawater and the water contents in the drifted oils were 41.7-64.3%. Ash content in the drawn oil was 3.89% as the ignition residue. Multi-element in the ash was determined by ICP-OES and AAS. Aluminum in the drawn oil was very high concentration of 123 ppm and presumed that it was artificially added as a pour point depressant of heavy fuel oil. It was observed that the oil formed a water-in oil emulsion by the optical microscope. The pH of water phase in the oil was 6.52. The change of physical properties of heavy fuel oil with passage of time was confirmed by the simulation.

Introduction

On January 2, 1997, the Russian-registered tanker *Nakhodka* that piled the heavy fuel oil C of about 19000kL sank in offshore 106km in Oki Island in the Sea of Japan. On January 7, the ship's bow ran offshore and aground on Anto in Mikuni in Fukui

Prefecture, and the large heavy fuel oil released. The spilled oil came ashore from Echizen coast in Fukui Prefecture over sandy beach in Katano coast in Ishikawa Prefect. on January 8. In the *Nakhodka* oil spill accident, it was very important to evaluate whether the components in the fuel oil does not influence the environment and whether it does not influence the health of the people working on the recovery operation of the spilled oil. The concentrations of inorganic components and organic substances in the spilled oil that came ashore to coast had to be analyzed in order to do those evaluations. At the same time, the analysis of the oil that had remained in the *Nakhodka*'s cargo tanks was an important problem. The work that pumped the oil remained in the ship's cargo tank was very difficult for the rough weather in the winter. As the result, the remained oil was closed in the ship's cargo tanks with seawater, and it kept be shaken by raging waves. It was presumed to entrap the much seawater in the oil, since the period until it pumped the oil out was long. Therefore, the analysis values had to be corrected by the water content in the oil in order to rightly evaluate the concentration of inorganic components and organic substances in the oil. In this study, the following were measured: Inorganic components and water content in the fuel oil that was related to the spill accident. In addition, the ash content was measured, because the increase of the quantity of inorganic components in the oil was considered, since seawater was contacted in the long term. The analysis of the inorganic components in the oil was essential in order to judge whether there is no problem in the waste disposal of the oil recovered.

Method

Samples

A sample of the heavy fuel oil remained in the ship's cargo tank was pumped out of the *Nakhodka*'s bow on February 6, 1997, and the samples of the drifted oil were collected from Mikuni coast in Fukui Prefecture and the coast in Noto Peninsula jutted out a long way into the Sea of Japan. The heavy fuel oil C used as a sample for the simulation was purchased from Nippon Oil Co.

Reagents and solutions

Commercial standard solutions of 1000mg L^{-1} of various metallic elements were purchased from Wako (Kyoto, Japan). All the chemicals used were of analytical-reagent grade. All the solutions were prepared with distilled deionized water.

Instruments

Atomic absorption measurements were made with a Hitachi Z-6500 spectrophotometer. A Shimadzu, model ICPS-1000III inductively coupled plasma optical emission spectrometer with a standard ICP touch and an auto-sampler was used for all the measurements. An energy dispersion X ray fluorescence spectrometer (ED-XRF, JSX-3201 ELEMENT ANALYZER, JEOL) was used for the detection of elements in the ignition residues. Acidity was measured with a pH meter (ION METER Model IM-20E, TOA) provided with a combined glass-Ag/AgCl electrode.

Experimental Methods

The measurement of water content in the oil

The oil of 5～10g was placed in 500ml round-bottomed flask for the distillation, and 100ml of the mixed solvent of toluene-xylene (2+8) was added (by JIS 1996). Boiling tips were added to the flask, after the oil was made to disperse by mildly shaking the flask, and reflux equipment was installed in the flask, and the bottom of flask was heated with a mantle heater. The water in fuel oil formed the azeotropic mixture between toluene and xylene, and it became the fractionation of low boiling point, it was collected in the water-measuring tube. After the distillation was kept, until the volume of water collected in water-measuring tube became fixed, and the aqueous phase in water -measuring tube was transferred into a small centrifugal separation tube by a pipette. Then, it was centrifuged at 3000rpm for 10 minutes. The aqueous phase in the centrifugal separation tube was taken out in a small beaker, and the weight of the aqueous phase was measured. The amount of water in the oil was calculated from this value. On the other hand, the recovery rate of water obtained by using a known amount of distilled water instead of the oil.

The measurement of ash content in the oil

The measurement of the ash content in the oil was carried out by method in JISK2272 (by JIS 1986). About 2g of the sampled oil were taken in a platinum dish, and the mass was precisely weighed. The equal mixture (10ml) of toluene and 2- propanol was added to the platinum dish. After putting the small several pieces of filter paper to the platinum dish, set fire on it and the fuel oil was burnt. All fuel oil in the platinum dish was carbonized, and the platinum dish was placed in an electric furnace, and it was heated at 780℃ for 60 minutes. The ignition residue was weighed, after the platinum dish was cooled to the room temperature in a desiccator. The ash content in fuel oil was calculated from the ignition residual quantity.

The determination of inorganic components in the oil

The inorganic components in the oil were determined by two methods (by Nippon Bunseki Kagakukai, 1991). In the first method, the test solution was prepared by dissolving the ash in 6M hydrochloric acid and by filtrating an insoluble substance. The solution was made to be a constant volume, and the inorganic components in the solution were measured by ICP-OES. In the second method (called a simplified method), 0.04g of the fuel oil was taken in a test tube with a plug, and was diluted by addition of about 5ml of petroleum ether. After 2ml of 2M nitric acid was added to the test tube, it was shaken by a shaker for about 7 minutes, and the mixture was centrifuged. The metallic elements in the fuel oil were extracted in the acid. The acidic aqueous phase was transferred a measuring flask, and it was made to be a constant volume. The concentrations of metals such as Al, Cr, Mn, Cu, and Pb in the solution were determined by the atomic absorption method.

The measurement of acid insolubles

A remained insoluble substance was collected on a filter paper by filtration, when the ash was dissolved in 6M hydrochloric acid. The insoluble substance was observed by the scanning electron microscope, and the shapes and including elements were examined.

The measurement of pH of seawater phase in the oil

The fuel oil was taken in a conical centrifugal separation tube (10ml), and it was centrifuged at 4000rpm for 60 minutes. The seawater phase in lower layer was taken out by a pipette, because it was divided into the bilayer of seawater phase and fuel oil phase. The pH of separated seawater phase was measured with a pH meter.

Results and Discussion

The oil drawn from the *Nakhodka*'s cargo tanks and the spilled oil came ashore the coast had different physical properties than the original heavy fuel oil C, most notably increased viscosity and appearance. Mixing processes of the oil and seawater were dramatically increased by waves caused by stormy weather in winter. As a result, the oil formed a water-in oil emulsion as a chocolate mousse. This emulsion state of the oil and seawater was observed with an optical microscope. A drop of the fuel oil was taken on a slide glass for microscope, and a cover glass was put in the top. Holding the cover glass in the finger thinly spread the heavy oil. The seawater separated from the oil, and the water droplet was formed. It was proven that the oil contained the seawater of considerable amount, because there was much proportion of the seawater part. The water content of the mousse was tested and found to be about 40-60%. The seawater phase in the mousse dissolves the various components in the oil, and it seems to become an equilibrium state. Therefore, pH of the seawater phase is anticipated with that it differed from pH of original seawater.

The water in the oil

There is a measuring method of water in petroleum at JISK2275. The measuring range of JIS methods using 100ml of oil is amount of water of 0.1% or less from several %. However, the water content in the fuel oil drawn from the *Nakhodka*'s cargo tanks was estimated with several decade % by the preliminary experiments. Therefore, 10ml or less of the oil was used in a series of experiments. In the determination of water in the oil, the recovery rate of the water was 96.8%. The results are shown in Table 1. The water in the oil drawn from the *Nakhodka*'s cargo tanks was 61.6%. At present, the water in the heavy fuel oil C of the marketing has been standardized with 0.5%～2.0% or less. Therefore, it is clear that how the much seawater was entrapped in the oil remained in the ship's cargo tanks, Similarly; the drifted oil had high water content. The water in the drifted and bailed oil was measured, and the results are shown in Table 1. For the comparison, the simulation was carried out in which the heavy fuel oil C of the marketing was made to contact sea water at 20-30℃ during 3 weeks. It was proven that the viscosity of the oil increased with the increase of the water content and the color of the oil changed from the dark brown to dark brown, while contact time with seawater was lengthened. However, the clear relation could not be recognized between the water content and the color of oil.

The pH of the seawater phase separated by centrifuging the oil in a mousse was measured. The pH of seawater in the oil was 6.52. The pH of usual seawater is about pH 8.2, and there is buffer action on the seawater. Therefore, there should be hardly

Table 1 Water contents in various oils

Sample and Station	Collected Date	Water Content(%)**
Drawn oil *	1997.2.6	61.6
Drifted oil		
Shioya	1997.1.11	46.1
Nanatu shima	1997.1.16	43.5
Mikuni beach park	1997.1.19	49.4
Suzu nagahashi	1997.2. 3	47.2
Mikuni	1997.2. 8	41.7
Monzen shikaiso	1997.2.18	64.3
Suzu nagahashi	1997.3.20	59.7
Simulation ***		
model (1)	10°C, 23 days	51.6
model (2)	20°C, 23 days	47.1
model (3)	20°C, 20 days	59.3

* The oil drawn from the Nakhodka's cargo tanks

** Mean value from three replicates

*** Heavy fuel oil C of the marketing was used as a sample.

that pH of the seawater becomes a value of the acidity. Considerable acidic components in heavy fuel oil dissolved in seawater and seemed to be made to lower pH.

The ash content in the oil

As a result of containing the seawater over 50%, the volume of the oil drawn from the ship's cargo tanks and the drifted oil was nearly doubly, and the viscosity increased. The recovery operation of the oil became with the difficulty, because the physical property changed. In addition, the considerable amount of salts that derive from seawater will be included in the ignition residue of the oil. Then, the ash contents in the oil were examined. The ash content in the oil drawn from the ship's cargo tanks was 3.89%. This ash content is a very high value, as the ash content of heavy fuel oil C of a Japanese Industrial Standard is 0.1% or less. Main components in the ash were sodium chloride and magnesium oxide. There was considerable part of reddish brown in the white ash content. From the results of chemical analysis and scanning electron microscope measurement, it was confirmed that the part of reddish brown was an iron compound. The service life of the *Nakhodka* had expired in a past, and the corrosion of the ship hull seemed to considerably advance. Therefore, it was estimated that iron rust of ship hull was entrapped in the oil, because the ship hull kept be shaken in raging waves.

The inorganic components in the oil

The analytical results of inorganic components in the fuel oil drawn from the ship's cargo tanks are presented in Table 2. The concentration of magnesium was calculated with 794ppm, when the water in the oil was made to be seawater. In this calculation, the value of 1290ppm (by Araki et al, 1985) was used as magnesium in general seawater. It is proven that magnesium in the ash was originated from seawater, because the calculated value agreed with the analytical value of 786ppm.

Table 2 Ash, acid insolubles, and inorganic components in the oil drawn from the *Nakhodka*'s cargo tanks

	Ash	Insolubles	Elements (ppm)**											
	(%)	(%)	Mg	Al	Si	V	Cr	Mn	Fe	Ni	Cu	As	Cd	Pb
Drawn oil	1.30	0.10	786	123	254	8.2	7.8		185	5.2		20	0.74	
	(3.89)	(0.26)	(2050)	(320)	(661)	(21)	(20)		(482)	(13.5)		(52)	(1.9)	
				138*				0.24*			0.67*			0.27*
				(359)				(0.63)			(1.7)			(0.70)
Heavy fuel oil C	0.03>	n.d.	n.d.	2.1	n.d.	32	0.043		2.7	0.21		11	n.d.	
				4.3*			n.d.	0.022*			n.d.			0.24*

n.d., not detected.
* Values measured by the simplified method.
** Mean value from three replicates
The values with ( ) are corrected by water content in oil.

On the other hand, level of iron was abnormally higher than the concentration in seawater. seems to be a result of entrapping the rust of the *Nakhodka* ship hull, as mentioned above. The origin of the silicon seems to be a result of entrapping marine microorganism such as the plankton or sandy fine particle in the heavy oil. The concentration of silicon in the general seawater is 0.5-10ppm. The concentrations of vanadium, manganese, chromium and lead in ordinary seawater are under a few ppb, and it did not considered to entrap these elements from seawater. Therefore, it will be able to evaluate the concentration of these elements with the elemental composition in original oil. The concentration of aluminum was very high, and it was not an origin from seawater (aluminum in seawater is 2ppb). The general heavy fuel oil does not contain the aluminum of the high concentration. Therefore, aluminum in the oil was presumed that it was artificially added. That is to say, it was considered that a metallic soap was added as a pour point depressant of heavy fuel oil. Aluminum salt of higher saturated fatty acid is thought as the metallic soap (by Sangyou Haikibutu 1978). Arsenic also detected a few 10ppm, though the ash was heated at about 800℃ in several hours. Special attention is necessary, when the disposal of recovered oil is done, because the arsenic concentration is higher than heavy fuel oil C of the marketing. The heterogeneity of the sampled oil may produce the dispersion of the measured value, when the inorganic components in the oil are measured by chemical analysis. Therefore, it is very important to sampling the heavy oil homogenized by sufficiently stirring.

The acid insoluble substances in the oil

There were the substances that did not dissolve in the acid, when it dealt with the ash in hydrochloric acid in order to analyze inorganic components in the oil. Acid insoluble substances were over 0.1%, and showed the brown from pale red color. The microscope observed the following: Material that seemed to be the iron rust of various forms and sandy fine particle. Then, iron, aluminum and silicon were main components in the insoluble substances by XRF.

The simulation on the change of heavy fuel oil

Heavy fuel oil C of the marketing was made to contact the seawater at the fixed temperature, and a change with passage of time of the oil was observed. The oil floated on the seawater surface, when seawater was slowly stirred. The color of the oil slightly changed to brown from dark brown for a few days, and it began to form small lump. After the week, the color of the oil became dark brown, and the lump became a shape of the ball. After three weeks, the viscosity of the oil increased, and it became the appearance of chocolate mousse, which resembled the oil drawn from the Nakhodka's cargo tanks, and the oil drifted ashore the coast. At that time, pH of the seawater that had contacted the heavy fuel oil was lowered at 7.74-7.79. The results are present in Table 1. The difference of the agitation temperature did not cause large effect for the amount of water in the oil. On the other hand, the different mixing speed was used in order to examine the effect of the agitation. The experiments at about 20℃ produced the difference in the water content. It can therefore be presumed that the water content of the oil that has been spilled on the sea surface depends on the weather. It is considered that the water content of the oil lowers, if the weather is moderate. However, the water content in heavy oil was over 50%, since the oil spilled from the *Nakhodka* happened in the rough weather in winter season.

Conclusion

The heavy fuel oil drawn from the *Nakhodka*'s cargo tanks and the oil drifted ashore the coast contained the seawater over 50%. Therefore, the volume and viscosity of the oil abnormally increased, it is thought that the recovery operation of the oil became very difficult. As a result of analyzing the inorganic components in the ash that burnt the oil drawn from the ship's cargo tanks, the following were detected: Iron, aluminum and silicon of the high concentration. The high concentration of aluminum is presumed to derive from a metallic soap added to the heavy fuel oil. Iron is estimated with that the rust of the ship hull was entrapped. It is necessary to correct rightly the analytical values by water content to estimate the effects on the human body, marine animals and plants, and environment. In addition, it is important to homogenize the oil, before the oil for the analysis is sampled.

References

Araki, S. Numata, M. and Wada, I.(1985). Kankyo Kagaku Jiten. Kagaku Doujin, Tokyo, 113pp.

JIS K2273(1996). Crude petroleum and petroleum products; the test methods of water. Japanese Industrial Standards Committee, Tokyo.

JIS K2273(1986).The test methods of ash with sulfuric acid and ash of Crude petroleum and petroleum products. Japanese Industrial Standards Committee, Tokyo.

Nippon Bunseki Kagakukai, ed. (1991). Bunseki Kagaku Binran (4th ed). Maruzen, Tokyo, 959pp.

Sangyou Haikibutu no Shori Sairiyou HenshuIinnkai, ed. (1978). Haikibutu no Shori Sairiyou. Sangyou Gijyutu Chousakai, Tokyo, 576pp.