Changes in the Properties of Spilt Oil over Time

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Introduction

Crude oil spilled in the sea by any reasons, including collision, wreckage of crude oil tanker,etc.,will transform various state, such as forming emulsion, moose by wind and waves or dispersing into the sea as small particles or precipitating its heavy portion. For smooth and appropriate response activities on spilt oil, it is required that proper selection of equipment and materials corresponding to properties(especially viscosity) of transformed oil is essential. Therefore, we have to precisely review and examine properties of transformed crude oils before hand. In this context, PAJ installed a circulating water channel simulator at Marifu Refinery, KOA OIL Co.,Ltd., in order to obtain such properties of various kind of transformed crude oil, and commenced tests since 1993FY. In this paper, we would present results obtained on twenty six (26) crude oils and one (1) heavy fuel oil(JIS.fuel oil C) as the continued efforts of “Fate of the spilt oil” Project for FY1997.

Figure 1 Circulating Water Channel

Test Oils

As indicated in the Table 1, 26 crude oils categorized into, “light”, ”Medium” and “Heavy”, from some 80 kinds of currently imported into Japan and one heavy fuel oil(Fuel Oil C,JIS spec.) in view of potential spillage, were selected.

Table 1 Test oils

Production area	Quality	Oil
Middle East	Low pour point Light-gravity	Berri Crude
		Mubarras Blend Crude
		Murban Crude
		Qatar Marine Crude
		Umm Shaif Crude
	Low pour point Medium-gravity	Arabian Light Crude
		Arabian Medium Crude
		Dubai Crude
		Forozan Blend Crude
		Hout Crude
		Iranian Light Crude
		Iranian Heavy Crude
		Kuwait Crude
		Oman Crude
		Upper Zakum Crude
	Low pour point Heavy-gravity	Arabian Heavy Crude
		Khafji Crude
		Wafra(contains Ratawi)crude
Southeast Asia	Low p. pt, Light-gravity	Attaka Crude
	Medium p. pt, Light-gravity	Light Seria Crude
	High p. pt, Light-gravity	Sumatra Light Crude
	High p. pt, Medium-gravity	Labuan Crude
	High p.pt, Heavy-gravity	Duri Crude
China	High p. pt, Heavy-gravity	Shengli Crude
Mexico	Low p. pt, Medium-gravity	Isthmus Crude
Australia	Low p. pt, Heavy-gravity	Wandoo Crude
Japan	Low p. pt, Heavy-gravity	Fuel Oil C

Test Conditions

The test conditions for these tests are shown in Table 2.

Table 2 Test conditions of experiment

Test conditions		Case1(Summer) weak waves	Case2(Summer) strong waves	Case3(Winter) weak waves	Case4(Winter) strong waves
Wave	Height (cm)	5～9	10～15	5～9	10～15
	Cycle (sec)	1	0.5	1	0.5
	wave rank	1	2	1	2
Wind	Speed (m/s)	2.6	6.4	2.6	6.4
Amount of s.water (t)		4	4	4	4
S.water depthh (cm)		60	60	60	60
S.water temp. (℃)		25	25	10	10
Amount of oil charged		10	10	10	10
Thickness of oil (mm)		1.4	1.4	1.4	1.4

Before conducting tests, we assumed typical climatic sea conditions for the experiments as follows:

“Summer” sea water temperature 25℃

“Winter” sea water temperature 10℃

Other parameters which affecting transformation of spilt oils also assumed as indicated in the Table 2.

As for the one of parameter, wave, we set 2 types of wave referred to “the wave ranks(wave height)” specified by the Japan Meteorological agency, however, waves generated for the test have larger energy than the waves specified in the “wave ranks”. Anyhow, we defined waves generated in the channel as follows:

“weak wave” represents calm sea condition.

“strong wave” represents rough sea condition.

The Figure 2 and 3 shows “weak wave” and “strong wave” respectively.

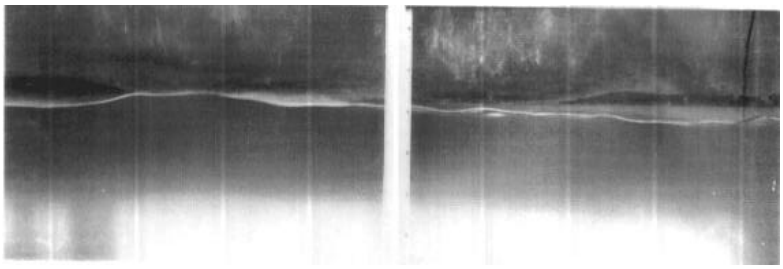


Figure 2 Weak Wave

Figure 3 Strong Wave

Test Procedure

For this test, crude oil(heavy fuel oil) was poured on the sea-water in the circulating water channel which have generated designed waves. Samples of crude oil(heavy fuel

oil) which going to be transformed were taken from the surface of sea-water in the channel at designated interval for 96 hours. Then, the samples were tested for water content, viscosity, density and evaporation rate. Further, we applied a gas chromatographic technique for measuring evaporation rate.

Test Results

As indicated in the Table 3, crude oils tested are classified into 9 groups based on their dominant properties, i.e, density, kinematic viscosity and pour point.
A series of test results for each crude oil are summarized in the Table 3.
By this classification, we recognized that respective group has characteristic tendency on change in properties.

Table 3

Group	Range of properties			Crude oil
	Density @15℃(g/cm3)	Kinematic Vis. @15℃ (cSt)	Pour Point (℃)	
①Low Pour Point, Extra Light Gravity	0.79～0.84	1.1～4.2	-60～-5	Murban,UmmShaif, Q.Marin,Berri, Mubarras,Attaka
② Low Pour Point, Light Gravity	0.85～0.87	4.1～6.1	-55～-20	Arabian Lt,Dubai, Hout, Iranian Lt, Isthmus, U-Zakum
③ Low Pour Point, Medium Gravity	0.85～0.88	6～10	-45～-10	Oman,Iranian Hy, Kuwait, Forozan B,Arabian M
④ Low Pour Point, Heavy Gravity	0.89～0.92	10～36	-40～-25	Arabian Hy,Khafji,Wafra, Wandoo
⑤ Medium Pour Point, Extra Light Gravity	0.79～0.87	1.8～2.1	7.5～-12.5	Labuan,Lt Seria
⑥ High Pour Point, Extra Light Gravity	0.77～0.84	1.7～3.0	15～30	
⑦ High Pour Point, Light Gravity	0.83～0.85	6～15	22.5～40	Sumatra Lt
⑧ High Pour Point, Heavy Gravity	0.86～0.90	22～100	30～-40	Shengli
⑨ High Pour Point, Extra Heavy Gravity	0.92～0.97	150～600	5～17.5	Duri

①Group 1: Low pour point-extra light gravity

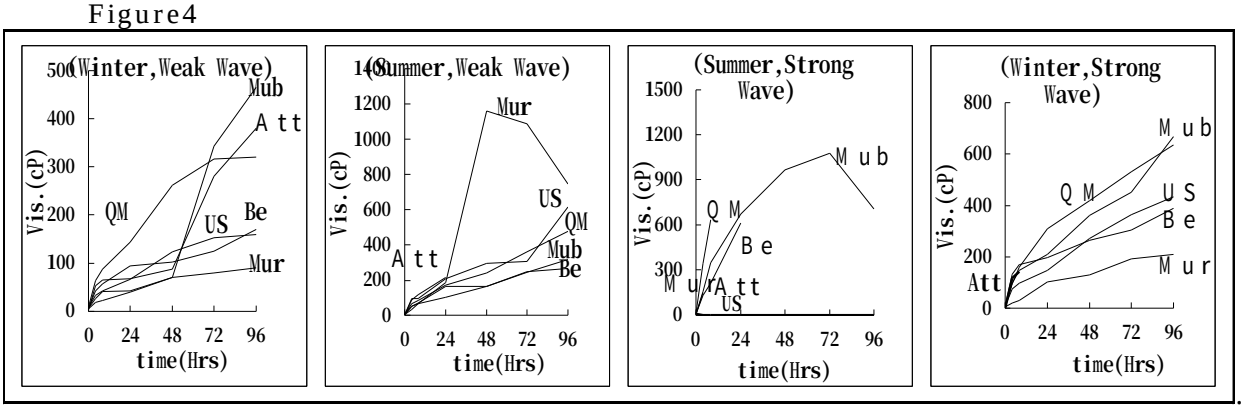
- Increase of viscosity does not exceed 1,000 cp even after 96 hours.
- Tend to disperse into sea water by “strong waves”.
- In cold climate (winter), tend to form fragile emulsion impregnated with air

bubbles.

- As for paraffin rich crude from southern region, lighter fraction is evaporated in a short time period and solidified.

The figure 4 shows the changes of viscosity on crude oil belonged to Group 1.

Figure4



② Group 2: Low pour point-light gravity.

③ Group 3: Low pour point-medium gravity.

- As for these two groups, the change in properties are quite different depending on their origins. Some are forming unstable emulsion while the others are forming stable emulsion of which tend to transform firm mousse.
- As can be seen on Dubai and Forozan Blend crude, the change in properties are extremely varied by different conditions.

The Figure 5 and 6 shows the changes of viscosity of Group 2 and Group 3 oils respectively.

Figure5

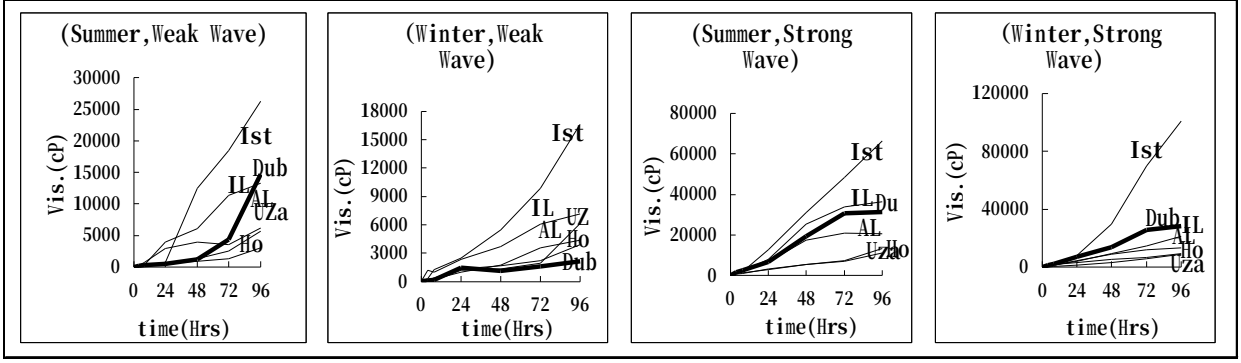
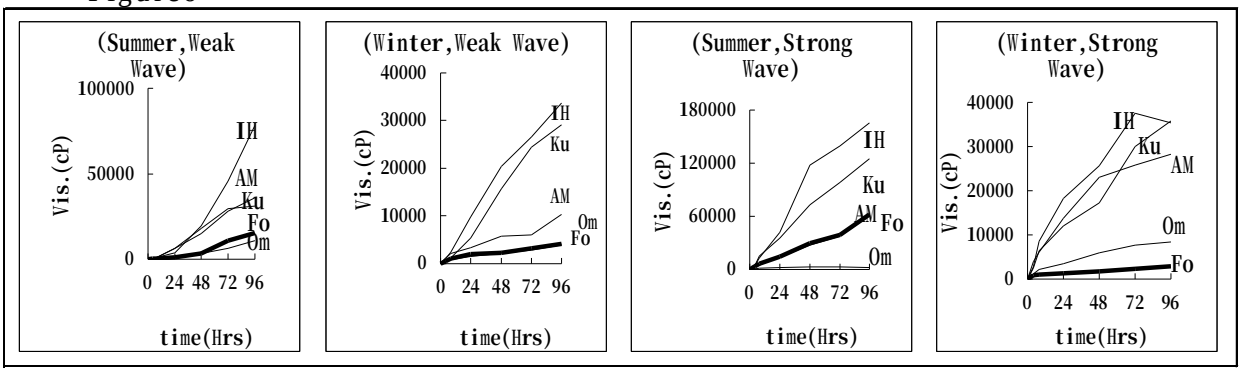


Figure6

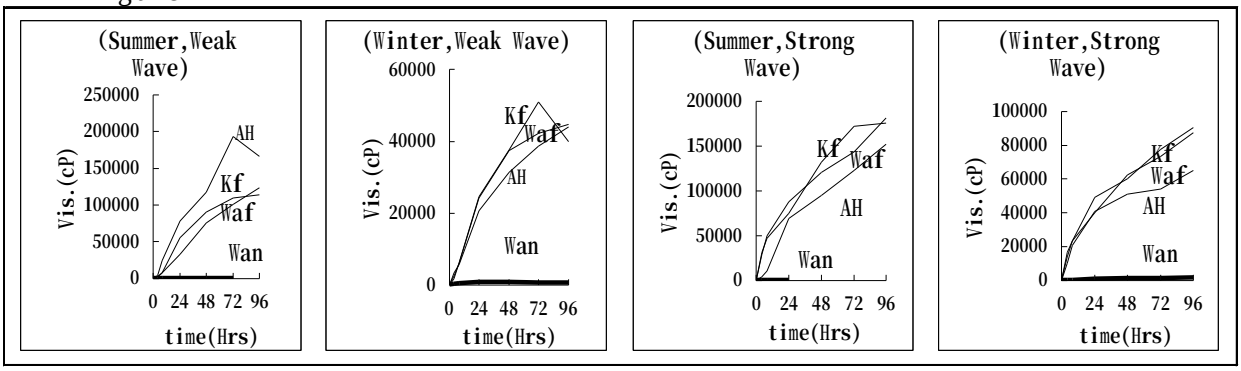


④ Group 4 : Low pour point-Heavy gravity

- Crude oils origined in the Middle East tend to form similar firm mousse, regardless of conditions.
- Wandoo crude origined in Australia does not form emulsion, but disperses into seawater with “strong waves”.

The Figure 7 shows the changes of viscosity on Group 4 oils.

Figure7

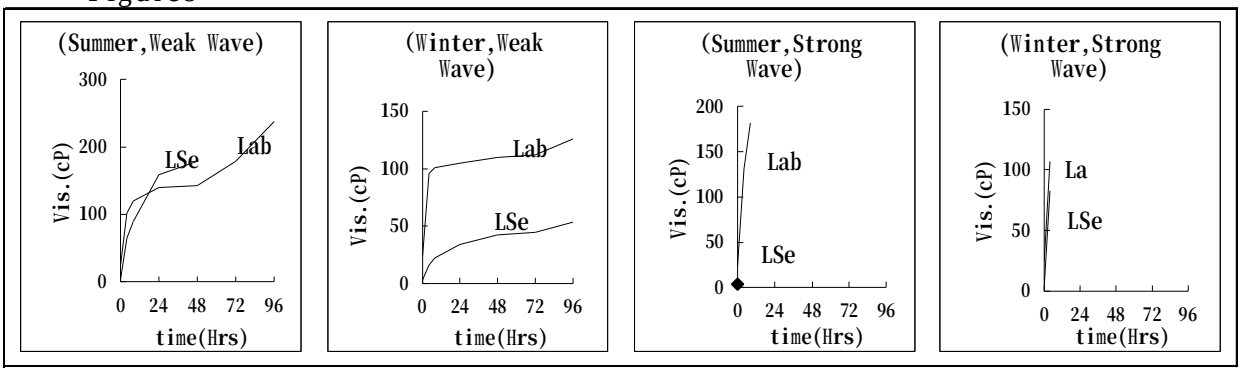


⑤ Group 5: Medium pour point-extra light gravity

- Only unstable emulsion is formed.
- In cold climate (winter), the oil solidifies.
- The oil disperses into seawater with “strong waves”.

The Figure 8 shows the change of viscosity on Group 5 oils.

Figure8



⑥ Group 6: High pour point-extra light gravity.

Group 7: High pour point-light gravity.

Group 8: High pour point-Heavy gravity

Group 9: High pour point-Extra Heavy gravity.

As to the high pour point groups (Group 6 to 9), they tend to form a range of semi-solidified to solidified lump or patch contacting with seawater which has relatively cold temperature compared to their own high pour points. Also, since it appears no remarkable changes in properties, we do not touch them further in this paper.

Conclusion

- Emulsion forming tendency of spilt oils seem to be depending on their origin which closely related to its composition. (Refer to the Attachment Table 1)
- In general, crude oil having high asphaltene content tends to form emulsion easily. There is a positive correlation between asphaltene content and emulsification tendency.(Refer to the Attachment Figure 1)
- Crude oils classified to Group 1 (low pour point-extra light gravity) form only unstable emulsion, and tend to disperse into seawater.
- Crude oils classified to Group 3 (low pour point-medium gravity) tend to form various type of emulsion.
- Crude oils classified to Group 4 (low pour point-heavy gravity) which usually have high asphalten content tend to form firm mousse.

A prospect for further study

It is beneficial and important for us that grasping change in properties of all crude oils being imported to Japan, they are more than 80 kinds, for preventing or responding potential hazard caused by those crude oils.
At this time of period, we have gathered 27 sets of data for “change in properties” of spilt oils, however, we are going to accumulate another same sets of data for establishing a comprehensive data-base and simulation software to predict any kind of ”Fate of spilt oil” in the near future.
Now we are making efforts to develop the said simulation software effective even for unknown sources.

Attachment

Attachment Table 1　Emulsions forming tendency by origin and gravity

Production area	Tendency to form emulsions			Characteristics
	Light-gravity	Medium-gravity	Heavy-gravity	
Middle East	★	★★	★★	High aroma, resin and asphaltene contents.
Mexico	★	★★	★★	High aroma, resin and asphaltene contents.
Southern regions	✓	★	★★	Saturated HC rich, high wax content.
China	✓	★	★	Saturated HC rich, high wax content.
Australia	✓	✓	✓	Saturated HC rich, low wax and low asphaltene content.

Note: The number of ★ shows, emulsion forming tendency.

Attachment Figure 1　Relationship between the asphaltene content and the emulsion forming tendency.