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LABORATORY TESTING OF DISPERSANT EFFECTIVENESS: THE IMPORTANCE OF OIL-TO-WATER RATIO AND SETTLING TIME

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Abstract

Laboratory tests and apparatus for oil spill dispersant effectiveness are studied. A review of previous work shows that test results from different apparatus are not highly correlated and often the rank of effectiveness is also not correlated. The effect of two experimental parameters, the settling time and the oil-to-water ratio, are examined in this study and found to be very important to the final effectiveness value. Four apparatus, the swirling flask, the flowing column, the Labofina and the Mackay, are used with 3 dispersants and 16 oils to examine effectiveness values when the oil-to-water ratio is the same (1:1200) and when the settling time is maintained at the same value (10 minutes) in all apparatus. The effectiveness values resulting from the four devices are nearly identical after values from the more energetic devices are corrected for natural dispersion. The conclusions are that the most important parameters of laboratory dispersant testing are the settling time and the oil-to-water ratio. Energy is less important than previously thought and is important only to the extent that when

high energy is applied to an oil/dispersant system, dispersion is increased by an amount related to the oil's natural dispersability.

Introduction

Thirty-five laboratory dispersant effectiveness tests have been employed around the world in the past.[1-4] The primary function of these tests is to provide a numeric value of dispersant effectiveness, although tests and apparatus have also been employed for studies of dispersion phenomena. The most common apparatus employed for these tests are the Labofina, alternatively known as the rolling flask or Warren Springs apparatus, and the Mackay apparatus, alternatively known as the MNS or Mackay-Nadeau-Steelman apparatus. This study focusses on comparing results from these apparatus to two newer apparatus developed in Environment Canada's laboratories, the swirling flask apparatus and the flowing cylinder apparatus.

Previous comparisons of the different apparatus have been limited. Byford and Green compared the Labofina and Mackay tests on a series of 2 oils and 5 dispersant combinations.[5] They concluded that the ranking of effectiveness between the two tests correlated well, although the numerical values had significant variation. Meeks compared EPA, Russian, Warren Springs, and French dispersant effectiveness results for two oils and three dispersants.[6] He concluded that the results of the tests are sufficiently different that even the rank of effectiveness is not preserved. Daling and Ness compared the Mackay and Labofina Apparatus using 2 oils and 7 dispersants.[7] They concluded that numerical correlation among results is poor, but that the rank of effectiveness is consistent between the results generated using the two apparatus. Daling compared the Mackay , Labofina and IFP devices for three different oils, with three different water contents and one dispersant.[8] This comparison showed that the numerical results were not correlatable, and the ranking of effectivness also varied significantly. The present author and co-workers compared the Labofina, Mackay, oscillating hoop and swirling flask apparatus for 10 oils and three dispersants.[9] We concluded that the correlation among the numerical results was poor and that rank of effectiveness correlated only weakly. The oscillating hoop test results, in particular, correlated poorly with other results.

Little work has been done on determining the reason for the poor correlation between test results. All of the above investigators cite energy as being the most significant factor. The general conclusion has been that the differences in energy levels and the way these have been applied to the oil/water mixture result in effectiveness values that are unique. The investigators followed the specified test procedure when using an apparatus and did not vary any of the conditions. The only exception to this was the study by Daling and Ness, in which the dynamic sampling normally specified for the Labofina and Mackay apparatus was varied up to 10 minutes.[7] This factor was found to be very important in improving correlation between the effectivness values yielded by the two apparatus.

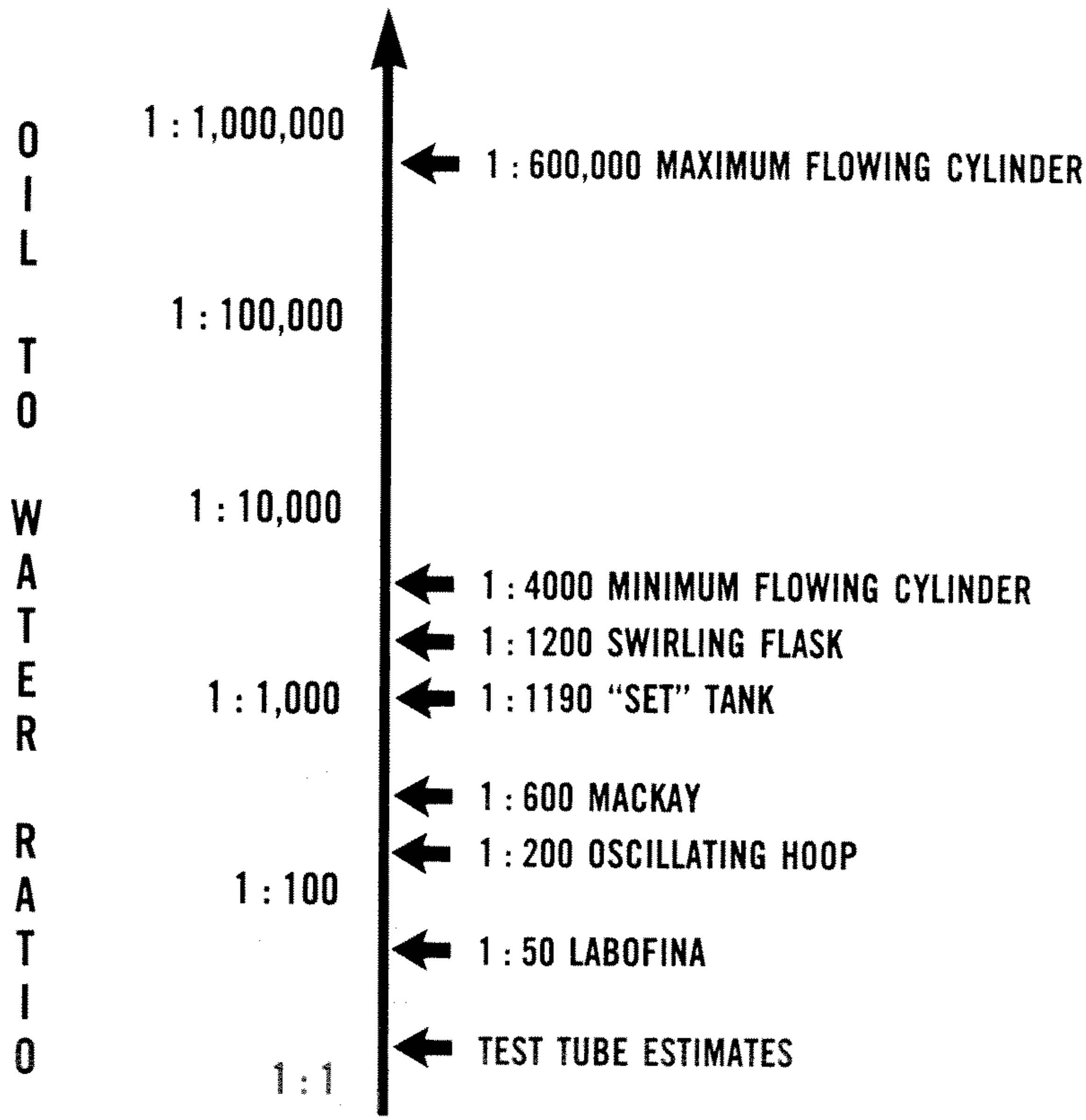
We have examined a number of variables in a number of test procedures. This paper will focus on two of these, the oil-to-water ratio and the settling time, that time between the taking of the sample for analysis and the time that the energy is no longer applied to the apparatus. Increased settling time allows large, unstable oil droplets to rise to the surface before the sample is taken and thus reduces the effectiveness values to represent only the more stable dispersions. The oil-to-water ratio varies dramatically in the various test protocol. This is illustrated in Figure 1.

Experimental

Apparatus were operated according to standard procedures except as noted in this paper. The oil-to-water ratio was changed by varying the amount of oil added to the system and the water amount was kept constant at the normal specified level. The settling time was varied by sampling water from the apparatus after the specified time. In the flowing cylinder, analysis of dispersion is performed by trapping oil in a filter and analyzing oil in this filter. Settling time can not be varied in this apparatus.

The oscillating hoop apparatus employs a hoop which is moved up and down at the surface of 35 litres water. Detailed protocols for operating this apparatus have been described previously.[10] The swirling flask apparatus uses a 125 mL Erlenmeyer flask with a standard laboratory shaker to induce a swirling motion to the contents. Procedures for this device are also detailed in the literature.[10] The Mackay apparatus uses a

FIGURE 1 ILLUSTRATION OF OIL-WATER RATIO IN VARIOUS APPARATUS



high-velocity stream of air to energize 6 L water and both operating procedures and construction details are documented.[11] The labofina test employs a 250 mL separatory funnel which is rotated at 33 rpm.[12] Analysis for all four apparatus is performed by taking a sample of water from the test vessel after the run is complete, extracting the water with a solvent and measuring the absorbance at three visible wavelengths, and then assigning effectiveness on the basis of a calibration curve. All runs were performed with dispersant already mixed in the oil at a ratio of 1 to 25 by volume. This practice was adopted to achieve more repeatable results as determined in earlier experiments where both premixed and drop-wise addition were used.[13]

Physical properties of the oils used in these tests are given in Table 1. The dispersants used include the Exxon products Corexit 9527 (abbreviated C9527 in this paper) and Corexit CRX-8 (abbreviated CRX-8), and the British Petroleum product, Enersperse 700 (abbreviated EN 700). In two tests, experimental dispersants were used and were designated "test product" and "experimental dispersant".

The flowing cylinder test has been recently developed at Environment Canada's laboratory in Ottawa and no operating procedures have been previously published. The basic operating principal is that water is continuously removed from the bottom of a cylinder and replaced at the top of the cylinder. This circulation draws dispersed oil into the water column and ultimately into a filter which removes the oil and the clean

TABLE 1 TEST OIL PROPERTIES

OIL	DESCRIPTION	KINEMATIC VISCOSITY (mm^2/s AT 15°C)	DENSITY (g/mL At 15°C)
ADGO	BEAUFORT SEA CRUDE	68	0.95
AMAULIGAK	BEAUFORT SEA CRUDE	16	0.89
ASMB	ALBERTA SWEET MIXED BLEND CRUDE	8	0.84
ATKINSON	BEAUFORT SEA CRUDE	52	0.91
AVALON	NORTH ATLANTIC CRUDE	14	0.84
BENT HORN	HIGH ARCTIC CRUDE	15	0.82
FEDERATED	ALBERTA MIXED CRUDE	5	0.83
GEAR OIL	AUTOMOTIVE GEAR OIL	1700	0.88
HIBERNIA	NORTH ATLANTIC CRUDE	91	0.88
ISSUNGNAK	BEAUFORT SEA CRUDE	4	0.83
LAGO MEDIO	VENEZUELAN CRUDE	47	0.87
LUBE OIL	AUTOMOTIVE CRANKCASE OIL	255	0.88
MOUSSE MIX	BUNKER C AND ASMB MIXED	140	0.91
NORMAN WELLS	NORTHERN CANADIAN CRUDE	7	0.83
PANUK	EAST COAST LIGHT CRUDE	1	0.78
PRUDHOE BAY	ALASKAN BEAUFORT CRUDE	55	0.88
SYNTHETIC CRUDE	PROCESSED HEAVY OIL	5	0.86
TRANSMOUNTAIN	MIXED ALBERTA CRUDE	12	0.86
UVILUK	BEAUFORT SEA CRUDE	16	0.88

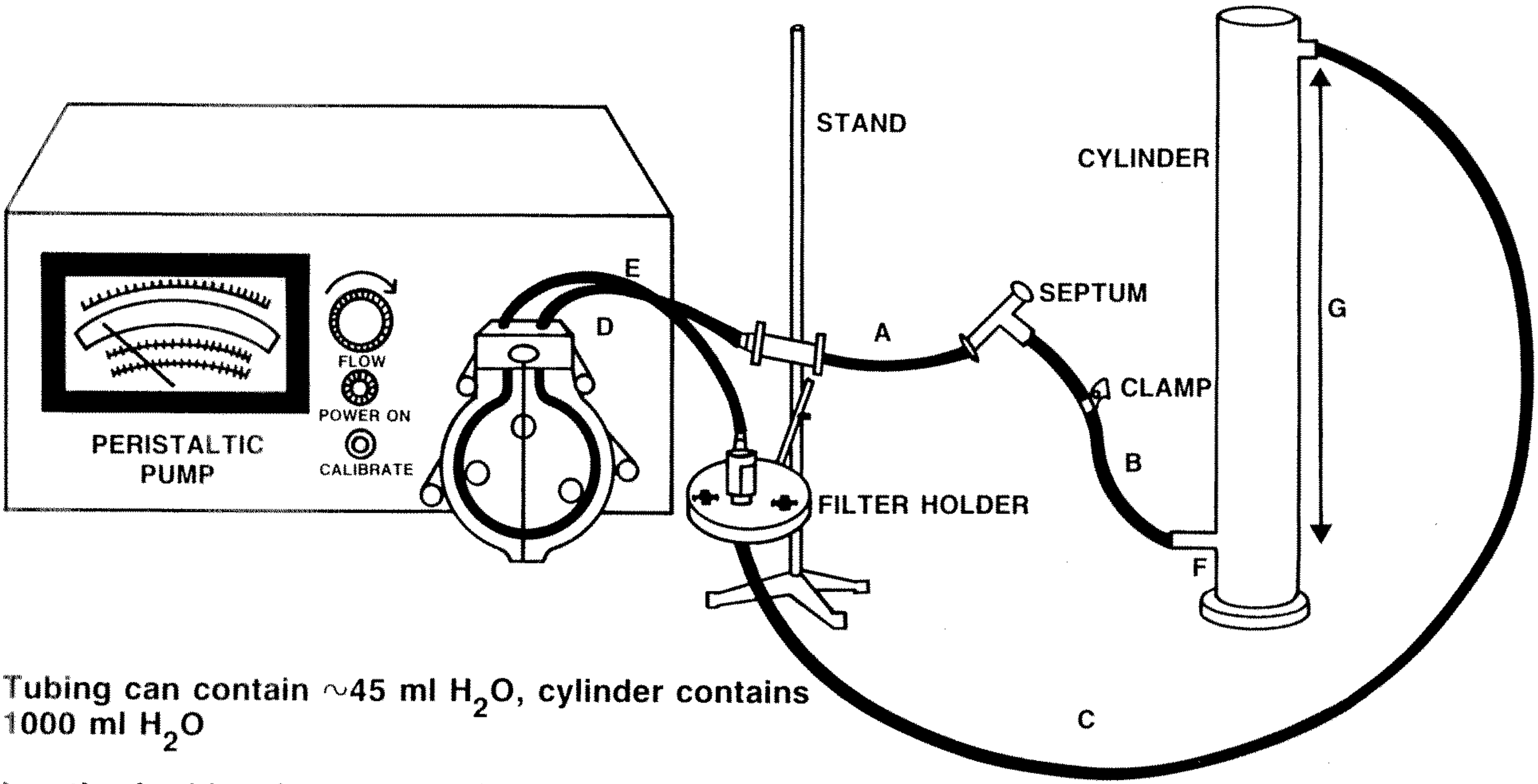
water returns to the top of the cylinder where its drop down the cylinder wall provides energy for dispersion. The apparatus is illustrated in Figure 2. The length of the cylinder is sufficiently long that only small (1 to 30 micron diameter) particles enter the hose. Any larger particles formed resurface, as confirmed by particle size analysis and visual inspection.

The procedures for operating the apparatus are summarized below. The system is assembled as shown in Figure 1 and three-stage filter loaded. The lower stage (last to encounter flow) is a standard back-up pad, the next is a 0.22 micron filter and the first or uppermost is 5 microns. The filter holder is reassembled. The vessel is filled with 1000 mL salt water (33 ppt). The peristaltic pump which has previously been calibrated to pump at 100 mL/min, is started and the hoses filled. Once equilibrium flow is achieved the specified volume of oil with dispersant premixed, is carefully placed on the centre of the water surface. The apparatus is allowed to operate for the specified period of time; 10 circulations lasting 100 minutes was the standard for the data presented here.

At the end of the run, the 0.22 and 5.0 micron filters are removed and placed into a separatory funnel, 30 mL of methylene chloride are added and the separatory funnel is shaken for 30 minutes in a wrist action shaker set for a 1.5 degree deflection. A portion of the methylene chloride is taken and its absorbance measured at 340, 370 and 400 nanometers. The percentage dispersion is taken from calibration curves prepared at each wavelength and the value reported is the average percentage at

FIGURE 2

Diagram of the Flowing Cylinder Apparatus



Tubing can contain ~45 ml H_2O, cylinder contains 1000 ml H_2O

length of tubing	A ~ 7.0 cm	Dimensions F = 3.5 cm
	B ~ 6.0 cm	G = 32.5 cm
	C ~ 50 cm	
	D ~ 18 cm	
	E ~ 13 cm	

the three wavelengths. The standard curves are prepared in similar manner as the normal runs, except that the prescribed amount of oil to represent a given percentage is injected at the septum placed in the hose line before the particulate filters. The filters are processed as before and the resulting values are used to prepare the calibration curve. This method of calibration is used to compensate for oil loss in the hoses, pump and filter assemblies.

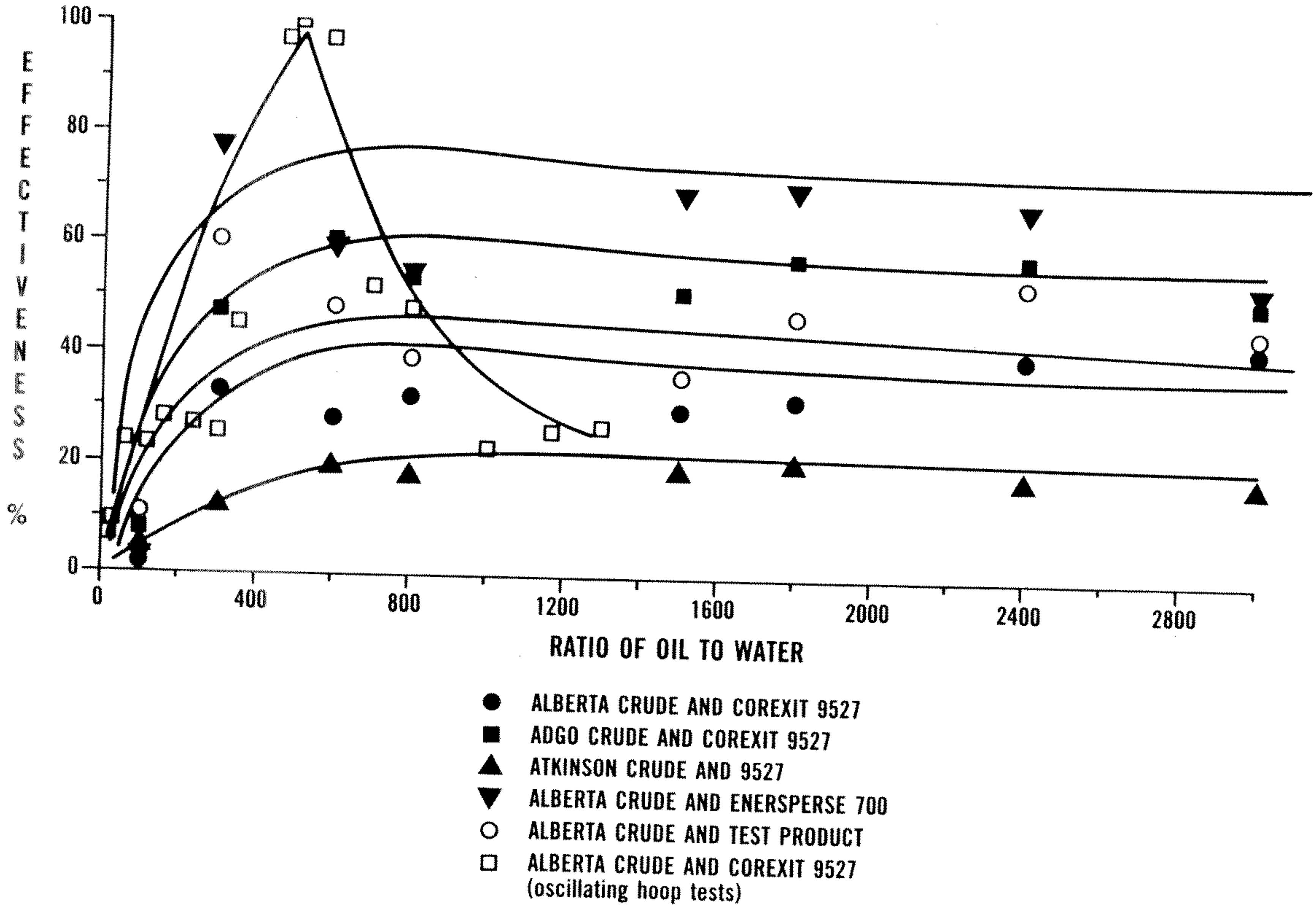
For every value presented here, at least two independent experiments were run. If values did not agree within the normal repeatability values for a particular device, repeat runs were performed until at least three values were within the repeatability percentage. The repeatability of results for each device was taken as the mean difference between duplicate runs before performing repeat runs. It can also represent the standard error or the plus and minus value noted behind many measurements. The standard error for each device is as follows: swirling flask - 3%, flowing cylinder - 5%, Mackay - 9%, Labofina - 7%, and oscillating hoop - 9%. Maximum errors can be as much as 40% for the Mackay and Labofina tests and as much as 20% for the other tests.

The Role of Oil-To-Water Ratio and Settling Time

The effects of oil-to-water ratio were first evaluated by changing the ratios in experiments using the oscillating hoop and swirling flask apparatus. These results are shown in Figure 3. The effect of changing the oil-to-water ratio in the oscillating hoop is surprisingly large and results in a sharp peak at an oil-

FIGURE 3

EFFECT OF OIL TO WATER RATIO ON EFFECTIVENESS



to-water ratio of 1:500. For two apparatus and for the different oil-dispersant combinations, the overall effect is the same. The effectiveness drops down at ratios below 1:200 and dramatically so at ratios as low as 1:20. The maximum effectiveness is seen at ratios around 1:500 and from 1:1000 becomes relatively stable up to 1:3000. It is suggested that this variation is the result of different mechanisms of dispersant action. At low oil-to-water ratios, there is a large amount of surfactant present and this surfactant interacts forming micelles rather than interacting with the oil. At low ratios, there are sufficient numbers of micelles to solubolize portions of the oil. At high oil-to-water ratios the primary interaction between oil and surfactant is the formation of dispersed particles. At ratios close to 1:500, both mechanisms come into play and apparent dispersion is increased.

The flowing cylinder was used to test the effect of increasing the oil-to-water ratio from 1:4000 up to 1:120,000. This was achieved by placing incrementally smaller amounts of oil and dispersant mixture into the apparatus. The oil-to-water ratio noted here does not take into account the recirculated water. Ten recirculations were performed per run increasing the oil-to-water ratio from a nominal 1:40,000 up to 1:1,200,000 (This form of calculation will not be used again in this paper.) To ensure that recirculation had no effect on the results, a series of experiments were performed in which clean water was pumped into the system rather than water from the filter. This series of experiments resulted in the same values as the experiments where the water was recirculated.

Figure 4 shows the results of these experiments graphically. The effectiveness values are relatively constant over the oil-to-water ratio measured. In summary, the oil-to-water ratio shows little or no effect on dispersion results when the ratio is 1:1000 or higher, but shows large effects when the ratio is at 1:500 or smaller. At 1:500 effectiveness results are the highest measured and below 1:200 effectivness values decrease significantly.

The effect of settling time has been investigated with 3 apparatus. The results for these experiments with the oscillating hoop are shown in Table 2, with the Mackay apparatus in Table 3 and with the swirling flask in Table 4. In all cases, the effect of settling time is highly dependent on the oil-dispersant combination but the effect is the same with each apparatus. An oil-dispersant combination which shows a rapid fall-off in effectiveness with time does so in all three tests. The opposite case is also true. The fact that a number of oils (for example Atkinson, Hibernia and Lago Medio) do show this decrease in effectiveness with increasing settling time indicates that they produce dispersions with larger droplets and are thus unstable. The increase in settling time beyond 10 minutes does not yield significantly different results, as can been seen in Table 4. It is suggested that the 10-minute settling time is optimal for the apparatus tested here.

The effect of settling time is the single most-important factor in the operating protocol of the various effectiveness

FIGURE 4 EFFECT OF HIGH OIL TO WATER RATIOS ON EFFECTIVENESS

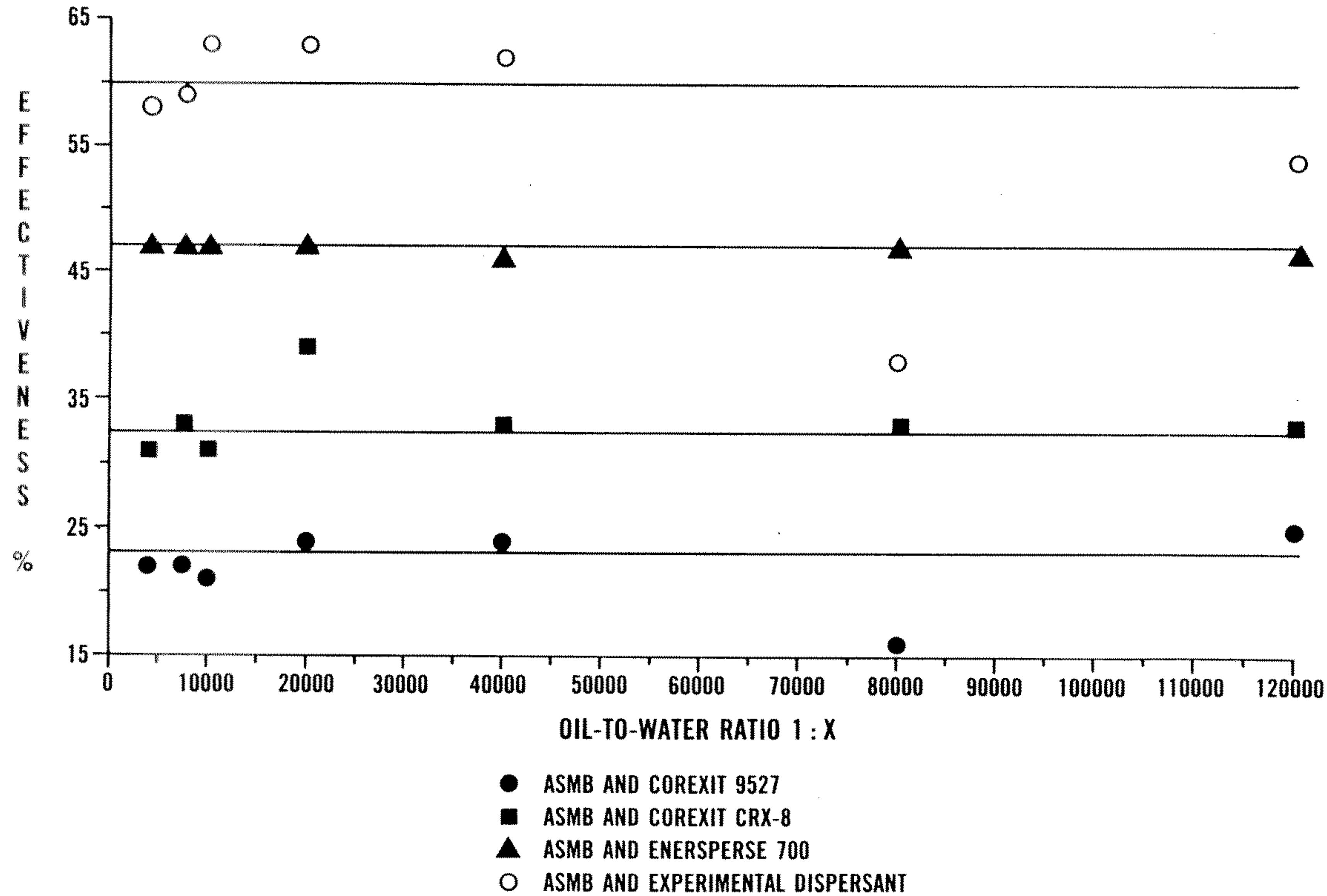


TABLE 2 EFFECT OF SETTLING TIME IN THE OSCILLATING HOOP

OIL	DISPERSANT	PERCENT DISPERSION	
		NO TIME	5-MINUTE
AMAULIGAK	C9527	100	90
	CRX-8	100	56
	EN 700	92	64
ASMB	C9527	51	26
	CRX-8	82	21
	EN 700	91	82
ATKINSON	C9527	92	52
	CRX-8	86	48
	EN 700	86	78
AVALON	C9527	84	40
	CRX-8	87	18
	EN 700	52	16
FEDERATED	C9527	93	33
	CRX-8	62	23
	EN 700	92	54
HIBERNIA	C9527	94	50
	CRX-8	76	65
	EN 700	81	54
ISSUNGNAK	C9527	100	51
	CRX-8	85	7
	EN 700	98	91
LAGO MEDIO	C9527	86	10
	CRX-8	89	64
	EN 700	86	64
NORMAN WELLS	C9527	62	29
	CRX-8	67	17
	EN 700	67	57
PRUDHOE BAY	C9527	92	65
	CRX-8	88	37
	EN 700	84	73
TRANSMOUNTAIN	C9527	84	76
	CRX-8	84	37
	EN 700	84	78
UVILUK	C9527	84	76
	CRX-8	83	45
	EN 700	78	72

TABLE 3 EFFECT OF SETTLING TIME IN THE MACKAY APPARATUS

OIL	DISPERSANT	PERCENT DISPERSED AFTER SETTLING NO TIME	5-MINUTE	10-MINUTE
ASMB	C9527	99	88	83
	CRX-8	69	26	21
	EN 700	94	93	91
ATKINSON	C9527	99	31	24
	CRX-8	99	30	23
	EN 700	85	23	16
AVALON	C9527	92	28	22
	CRX-8	85	16	12
	EN 700	74	22	21
FEDERATED	C9527	73	12	7
	CRX-8	91	70	66
	EN 700	95	83	81
HIBERNIA	C9527	100	64	52
	CRX-8	94	30	25
	EN 700	92	38	31
ISSUNGNAK	C9527	100	88	81
	CRX-8	100	92	83
	EN 700	100	93	86
LAGO MEDIO	C9527	20	0	0
	CRX-8	78	22	18
	EN 700	95	28	12
NORMAN WELLS	C9527	100	65	55
	CRX-8	98	77	74
	EN 700	100	90	81
PRUDHOE BAY	C9527	95	43	30
	CRX-8	90	27	22
	EN 700	90	69	67
TRANSMOUNTAIN	C9527	99	82	81
	CRX-8	100	30	23
	EN 700	95	77	70
UVILUK	C9527	94	80	77
	CRX-8	82	45	44
	EN 700	93	91	87

TABLE 4 EFFECT OF SETTLING TIME IN THE SWIRLING FLASK

OIL	DISPERSANT	PERCENT DISPERSION AFTER SETTLING TIME IN MINUTES							
		0	2.5	5	7.5	10	12.5	15	20
ASMB	C9527	68	43	37	33	30	30	29	29
	CRX-8	76	53	44	43	34	33	33	31
	EN 700	81	74	74	71	63	61	60	58
ATKINSON	C9527	86	62	55	47	47	41	42	41
NORMAN WELLS	EN 700	98	83	85	69	71	71	70	69
		60	120	240	420				
ASMB	C9527	22	20	12	14				
	CRX-8	28	11	13	10				
	EN 700	43	24	18	16				

experiments. The effect can be as much as one order of magnitude for a particular oil-dispersant combination and is repeatable. Furthermore the effect is consistent among different apparatus.

Testing of Dispersant/Oil Combinations Using Similar Protocols

A series of tests was conducted to test the hypothesis that the settling time and oil-to water ratio is very important to the outcome of the dispersion effectiveness. Four devices were used, the swirling flask, the flowing column, the Labofina and the Mackay apparatus. Published protocols were adhered to with three exceptions. The oil-to-water ratio was set to 1:1200 in each apparatus except in the case of the flowing cylinder where because of the ability to analyze the samples, the minimum is 1:4000. The settling time was set to 10 minutes in all cases except again in the case of the flowing cylinder where this parameter is not relevant. Thirdly, the analysis was performed using the procedure of exacting with methylene chloride, analyzing at three wave lengths and averaging the results. This procedure results in greater accuracy than published procedures where only one wavelength is used.

The results of this comparison testing procedure are shown in Table 5. The tests were conducted using 16 different oils and three different dispersants, the Exxon products Corexit 9527, CRX-8, and the British Petroleum product Enersperse 700 (formerly known as BP MA-700). As Table 5 shows, the dispersant effectiveness values are nearly identical for the four tests except for higher values in the Labofina and Mackay tests, especially for the Adgo, Amauligak, Atkinson, Issungnak, lube,

TABLE 5	EFFECTIVENESS IN DIFFERENT APPARATUS				
OIL	DISPERSANT	DISPERSABILITY IN PERCENT			
		SWIRLING FLASK	FLOWING CYLINDER	LABOFINA	MNS
ADGO	9527	61	52	78	64
	CRX-8	42	40	77	87
	EN 700	67	59	76	93
AMAULIGAK	9527	48	38	86	44
	CRX-8	56	46	73	85
	EN 700	54	39	59	73
ASMB	9527	22	21	31	39
	CRX-8	28	31	34	61
	EN 700	43	43	62	76
ATKINSON	9527	7	18	57	17
	CRX-8	9	10	47	19
	EN 700	8	18	55	22
BENT HORN	9527	29	46	29	29
	CRX-8	27	37	27	51
	EN 700	44	51	19	42
FEDERATED	9527	39	35	51	35
	CRX-8	23	31	35	76
	EN 700	38	42	70	76
GEAR OIL	9527	29	18	18	12
	CRX-8	40	25	27	10
	EN 700	10	6	15	30
HIBERNIA	9527	6	12	23	6
	CRX-8	9	10	19	9
	EN 700	7	8	23	14
ISSUNGNAK	9527	24	22	61	41
	CRX-8	42	76	35	100
	EN 700	42	60	75	100
LAGO MEDIO	9527	7	8	29	16
	CRX-8	11	15	19	19
	EN 700	10	23	24	27
LUBE OIL	9527	13	19	40	44
	CRX-8	14	24	40	53
	EN 700	13	23	40	80
MOUSSE MIX	9527	9	15	27	30
	CRX-8	11	25	18	26
	EN 700	24	32	23	43
NORMAN WELLS	9527	41	55	65	47
	CRX-8	60	47	70	65
	EN 700	63	53	74	89
PANUK	9527	100	100	89	100
	CRX-8	93	100	85	100
	EN 700	100	100	87	100
PRUDHOE BAY	9527	7	13	47	27
	CRX-8	5	16	38	23
	EN 700	17	14	48	37
SYNTHETIC CRUDE	9527	57	50	78	83
	CRX-8	69	55	40	91
	EN 700	61	39	76	88

TABLE 6 NATURAL DISPERSION

OIL	DISPERSION (%) LABOFINA	MACKAY
ADGO	18	23
AMAULIGAK	30	14
ASMB	11	20
ATKINSON	37	10
BENT HORN	0	4
FEDERATED	10	2
GEAR OIL	0	0
HIBERNIA	11	0
ISSUNGNAK	40	34
LAGO MEDIO	11	2
LUBE OIL	20	24
MOUSSSE MIX	5	0
NORMAN WELLS	21	8
PANUK	NM	NM
PRUDHOE BAY	13	10
SYNTHETIC CRUDE	20	20

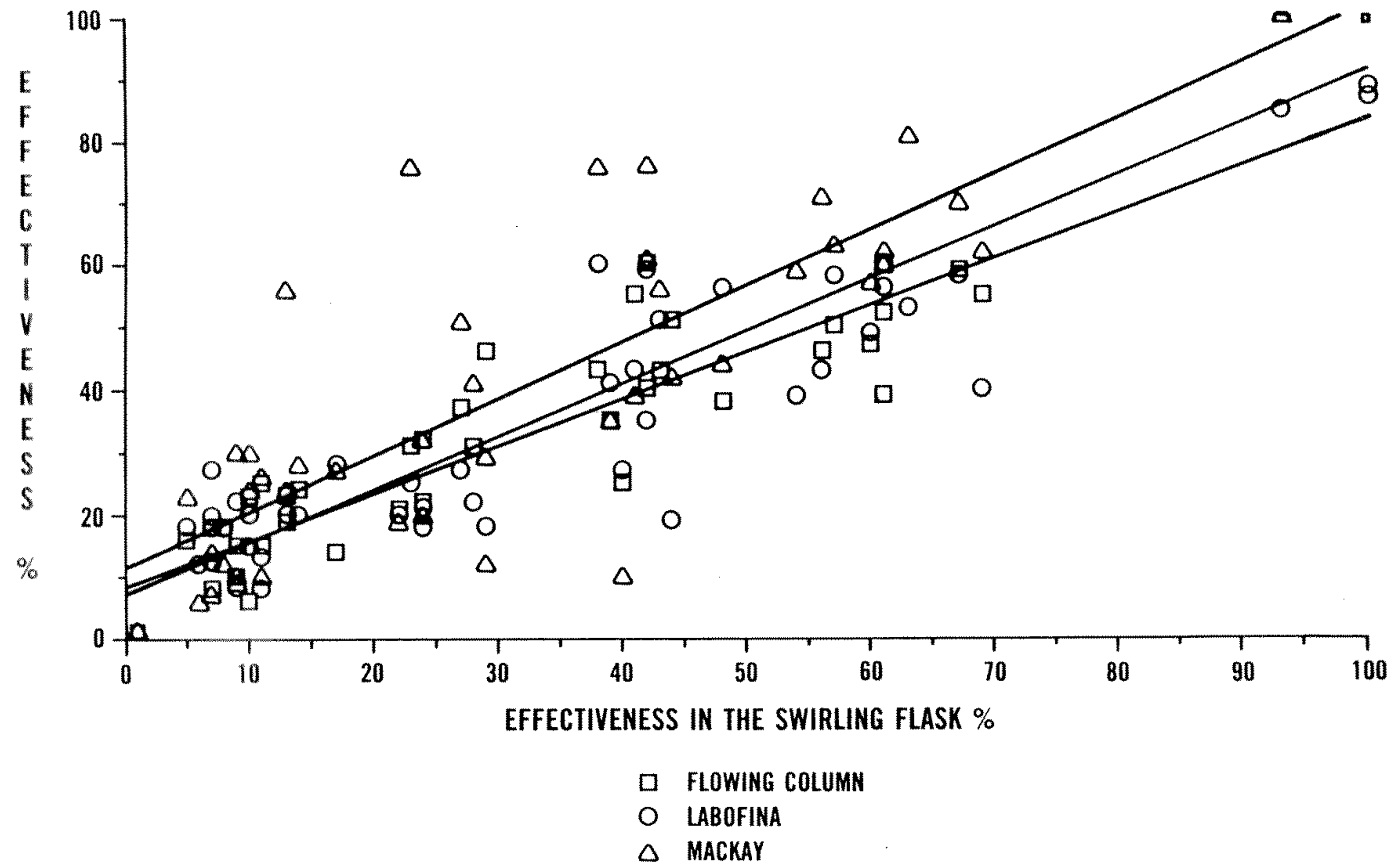
Norman Wells and Synthetic crude oils. These oils happen to be the ones that are very readily dispersed naturally, that is without the use of dispersant. To test if this was the case, the natural dispersability of all the test oils was measured using the published protocols for the Labofina and the Mackay apparatus. The results are presented in Table 6. This table shows that indeed these oils show high natural dispersabilities in the two apparatus. The values of natural dispersability were then used to correct the dispersability values. Table 6 presents the corrected effectiveness results. This table shows that virtually identical dispersant effectiveness results are produced by all four apparatus when the oil-to-water ratio is the same at 1:1200, when the settling time is 10 minutes, and when the results from the two energetic devices, the Labofina and Mackay are corrected for natural dispersion. The high correlation among test results is also illustrated in Figure 5. The lines shown in this figure were fitted by regression. The upper line represents the correlation of the Mackay and the swirling flask results. The middle line shows the correlation of the flowing column results with the swirling flask results and the lower line shows the same for the Labofina results. The correlation coefficients are 0.72 for the Mackay results and 0.84 for the other two apparatus. This indicates that correlation is best for the Labofina and flowing column apparatus.

Discussion and Conclusions

The results indicate that laboratory dispersant effectiveness results can be similar even if measured in very

TABLE 7	EFFECTIVENESS IN DIFFERENT APPARATUS				
AFTER CORRECTION FOR NATURAL DISPERSION					
OIL	DISPERSANT	DISPERSABILITY IN PERCENT			
		SWIRLING FLASK	FLOWING CYLINDER	LABOFINA MODIFIED	MNS MODIFIED
ADGO	9527	61	52	60	60
	CRX-8	42	40	59	61
	EN 700	67	59	58	70
AMAULIGAK	9527	48	38	56	44
	CRX-8	56	46	43	71
	EN 700	54	39	39	59
ASMB	9527	22	21	20	19
	CRX-8	28	31	22	41
	EN 700	43	43	51	56
ATKINSON	9527	7	18	20	7
	CRX-8	9	10	10	10
	EN 700	8	18	18	12
BENT HORN	9527	29	46	29	29
	CRX-8	27	37	27	51
	EN 700	44	51	19	42
FEDERATED	9527	39	35	41	35
	CRX-8	23	31	25	76
	EN 700	38	42	60	76
GEAR OIL	9527	29	18	18	12
	CRX-8	40	25	27	10
	EN 700	10	6	15	30
HIBERNIA	9527	6	12	12	6
	CRX-8	9	10	8	9
	EN 700	7	8	12	14
ISSUNGNAK	9527	24	22	21	20
	CRX-8	42	76	35	76
	EN 700	42	60	35	76
LAGO MEDIO	9527	7	8	18	14
	CRX-8	11	15	8	10
	EN 700	10	23	13	24
LUBE OIL	9527	13	19	20	24
	CRX-8	14	24	20	28
	EN 700	13	23	20	56
MOUSSE MIX	9527	9	15	22	30
	CRX-8	11	25	13	26
	EN 700	24	32	18	32
NORMAN WELLS	9527	41	55	43	39
	CRX-8	60	47	49	57
	EN 700	63	53	53	81
PANUK	9527	100	100	89	100
	CRX-8	93	100	85	100
	EN 700	100	100	87	100
PRUDHOE BAY	9527	7	13	27	14
	CRX-8	5	16	18	23
	EN 700	17	14	28	27
SYNTHETIC CRUDE	9527	57	50	58	63
	CRX-8	69	55	40	62
	EN 700	61	39	56	62

FIGURE 5 COMPARISON OF RESULTS FROM FOUR APPARTATUS



different apparatus. The most important factor in achieving the same results is the settling time allowed before taking the sample. The oil-to-water ratio is the next most important factor and finally correction for natural dispersion is necessary in the more energetic apparatus.

These findings have far-reaching implications; first, energy is not as important to laboratory testing as was traditionally thought, secondly the fact that effectiveness values tend to one value for a given oil/dispersant combination suggests that this value may have physical implications or meaning, and thirdly there will be impact on the selection of testing apparatus.

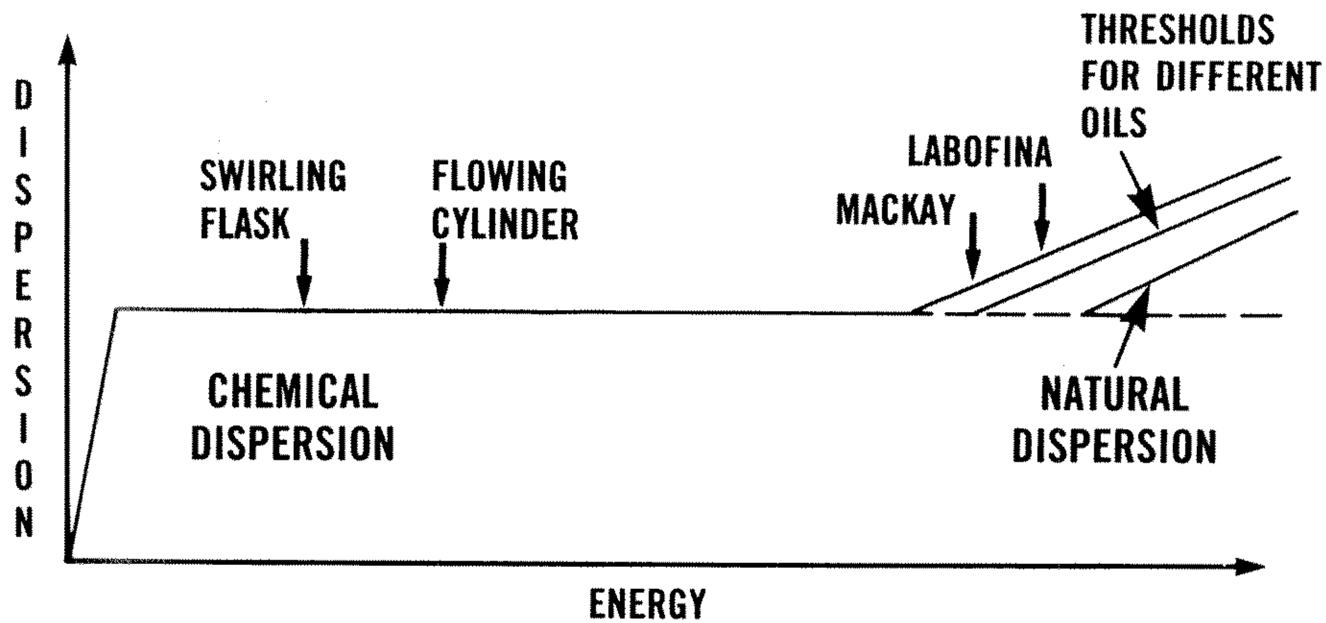
Energy has long been thought to be the most important factor in laboratory dispersant effectiveness testing.[14,15] It was felt that results could only be correlated with the energy level and that this would have to be measured at sea to give true indication of dispersant effectiveness there. For example, one thought that if one could have an energy measuring device appropriate to oil spill dispersion, one could measure the energy at sea and subsequently in a laboratory device and assign a sea-state equivalent value to this laboratory device, Beaufort 3 as an example. The laboratory measure would then represent dispersion only at that energy level. The four devices used in this study have, by visual examination, widely varying energy levels. The energy level of the Labofina and Mackay are much higher than that of the swirling flask and the flowing cylinder devices. This is borne out by the fact the one cannot measure natural dispersabilities in either of the latter two devices, irrespective of operating conditions. The observation in this study that the apparent energy differences in the apparatus, did not lead to major differences, leads one to conclude that energy does not have a major role in determining effectiveness other than a contribution which correlates with natural dispersability.

The hypothesis to explain these results is illustrated in Figure 6. The energy to initiate chemical dispersion is low and stays relatively constant until thresholds for the natural dispersion are reached. The threshold at which an oil is naturally dispersed is a function of oil composition and is relatively unique to an oil.

The second impact of the finding that all effectiveness values tend to one value, implies that the values may have some meaning in physical or chemical terms. Perhaps these values represent the maximum dispersion under normal conditions in the laboratory or at sea. Recent work has shown that the major losses associated with effectiveness at sea are physical losses of dispersant and because these tests were performed with dispersants pre-mixed with the oil, they may indeed reflect a maximum value.[13,15]

Finally, because laboratory effectiveness values tend to one value, selection of apparatus can be made on the basis of simplicity, ease of use, and best repeatability. The swirling flask test is the most repeatable, easiest to use, simplest and permits the most tests to be performed in one day. The Labofina is the second apparatus in terms of ease of use and speed, but is the third in terms of repeatability. The flowing cylinder is

FIGURE 6 CONCEPTUAL RELATIONSHIP BETWEEN AMOUNT OF DISPERSION AND ENERGY IN LABORATORY APPARATUS



third in terms of complexity, is the fourth in terms of numbers of runs performed per day , but is second in terms of repeatability. The Mackay test is rated last; it is poor in all categories noted.

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