Oil Removal From Acid Flow Back Operations

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Summary:
A study to evaluate the performance of Clerify™ and Crudesorb™ filtration media was performed under identical laboratory and field conditions in order to compare the effectiveness of each filtration media for removing oil from acid flow back operations. The goal of the laboratory simulations and field tests was to isolate the acid flow back stream, filter the acid flow back stream through the designated filter, and achieve water quality standards for over board water discharge. Extensive sampling was conducted on the filter influent and effluent to quantitatively demonstrate results. Based on the test results, the Crudesorb™ media 's performance is significantly higher at removing oil and grease than the Clerify™ media in all methods tested. Conducting laboratory studies the Crudesorb™ media broke a 500 ppm oil/water emulsion and removed the oil to less than 20 ppm in the effluent, whereas the 500 ppm oil/water emulsion flowed virtually unaltered through the Clerify™ media. Field tests in the Gulf of Mexico and North Sea showed that the Crudesorb™ media was able to break the oil and water emulsions and maintain water quality suitable for discharge whereas the Clerify filter had trouble with the oil-in-water emulsions typical of an acid flow back stream.

Introduction

Acidizing the sandstone formation to remove the skin and other flow inhibitors significantly improves the fluid flow near the well bore, however, frequent surface water treatment upsets occur because of commingling the very low pH acid flowback with the neutral pH main production aqueous stream. These upsets can result in increased oil and grease content in the discharged water and increased bs&w content in dehydrated crude. Khatib, et al., presented several options for handling return fluids that included barging the fluids to shore, injecting into a disposal well, neutralizing and demulsifying the acid flow back, or pumping the fluids directly to a treatment facility. Many of these options require separate holding vessels and may require several days to weeks to process the fluids. The work detailed in this paper discusses field trials and analytical results that compare the effectiveness of two commercial systems for unloading a well in a few hours without incurring main water treatment system upsets.

Composition of Filtration Media:

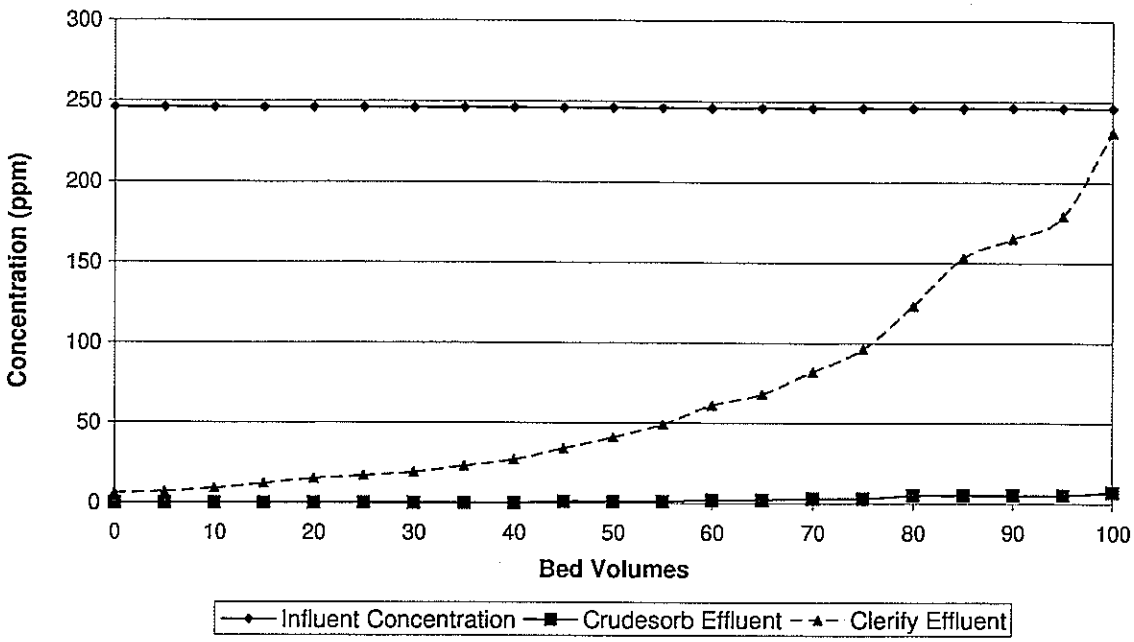
Media 1:
Clerify™ is manufactured by Axholme Resources Limited in the United Kingdom and sold by distributors throughout the world. The Clerify™ filter is composed of carboxylic acid (steric and palmitic acids) coated cellulose granular material that has been dispersed in a matrix of non-woven or gauze like fibers. The composition of the Clerify™ filter is covered by at least one PCT patent.

Media 2:
Crudesorb™ is a proprietary, patented granular, filtration media manufactured by CETCO technology in Aberdeen, Mississippi. It is designed for removing oil & grease from aqueous streams and is formulated to withstand several common solvents used in acid flow back and completion fluids. CETCO currently has eight United States patents and four applications with many corresponding foreign filings.

Testing Method:
Laboratory: The stock solution of oil in water or oil/water emulsion was prepared and stored in a five gallon carboy. The solution was pumped with a closed system pump through a small radial flow canister at a 2-minute retention time. The influent and effluent samples were obtained periodically by detaching the appropriate sampling hose. Analysis included oil & grease analysis and total organic carbon analysis.

Experiments and Results:
Removal of Oil from Water in Laboratory: A 250 ppm mixture of field oil obtained from the Shell Mars platform in a 3.5% synthetic seawater solution was prepared and pumped through canisters of Clerify™ and Crudesorb™. One hundred bed volumes of influent were pumped through each canister and the effluent concentration was measured and charted for comparison. The results showed that the Crudesorb™ removed significantly more oil from the aqueous phase than the Clerify™ media. The Crudesorb™ effluent was below 5 ppm for the entire 100 bed volumes pumped. Oil was present in the Clerify™ media effluent immediately and resulted in poor water quality within 40 bed volumes. This data is shown in Graph 1. On a volume basis, at the point of test termination, the Crudesorb™ media lasted at least 2.5 times longer than the Clerify™ did, but the projected volume difference would be much greater if testing had continued to total break through. On an oil removed basis, the Crudesorb™ removed 3.7 times as much oil as Clerify™ did. This large difference in oil removed is due to the Crudesorb™ ability to continue to assimilate the oil much longer than Clerify™ and the intermediate values for Crudesorb™ were much lower than Clerify's™.

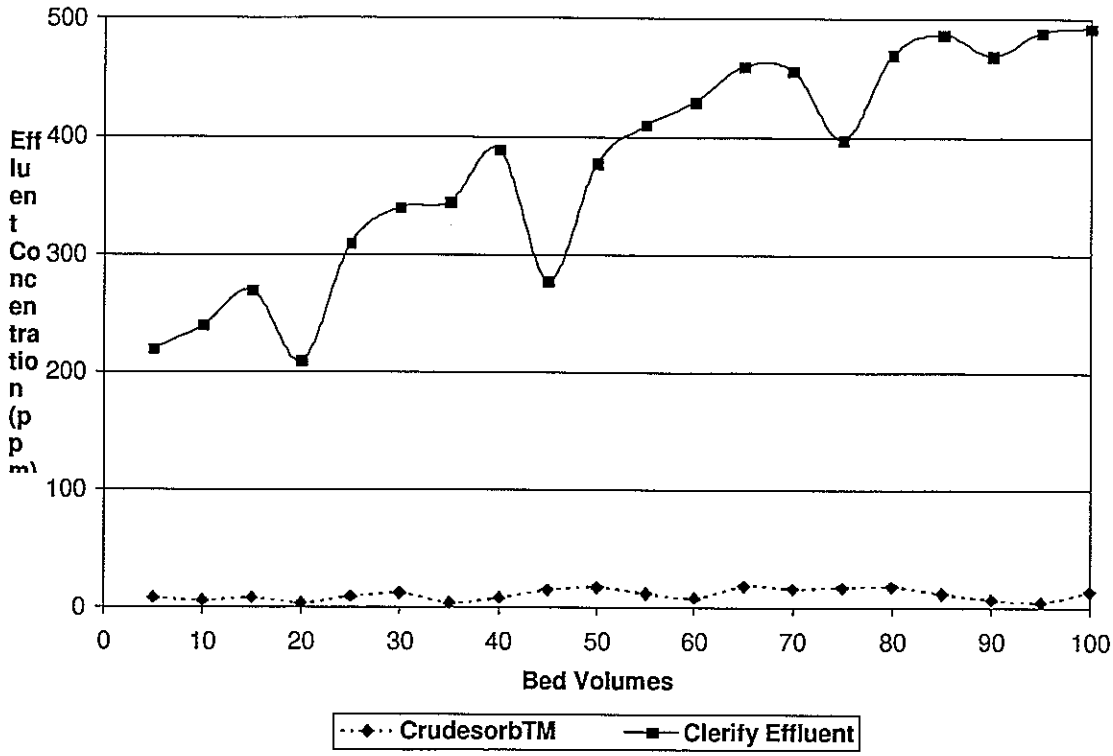
Graph 1. Comparison of Crudesorb and Clerify For Removing 250 ppm Oil From Synthetic Seawater



Ability to Break Oil in Water Emulsion:
In the laboratory, an oil in water emulsion was formed by adding 500 ppm oil obtained from the Mars TLP to 3.5 % synthetic seawater containing 1% Alpha 317 oil emulsifier. The Alpha 317 emulsifier was the common oil emulsifier used. This experiment was run until 100 bed volumes had passed through each filter. This comparative data can be found in Graph 2.

The laboratory results show that the Clerify™ did not break the oil in water emulsion. In fact, the Clerify™ effluent visually appeared to be unaffected by the filtration media as it was dark brown in color with a hydrocarbon smell. In contrast, the Crudesorb™ media broke the emulsion immediately and maintained good water quality throughout the test. The Crudesorb™ effluent was colorless and odorless the entire test.

Graph 2. Ability of Crudesorb™ and Clerify™ Filtration Media to Break 500 ppm Oil in Water Emulsion in Laboratory



Gulf of Mexico Field Tests

The Mars TLP was chosen as the initial site to evaluate the commercial filters for removing oil from the returned acid flowback fluid. Although, the Mars platform has a very good history of handling the fluids and maintaining good water quality, the Mars operations personnel were interested in improving their effectiveness of the acid flowback process handling. Figures 1 shows the equipment layout used for the evaluation of the filtration media.

The Crudesorb™ and Clerify™ filters were used in parallel flows initially on the A-14 well flow back. As shown in Table 1, the pressure drop across the filters was nominal. The infrared oil & grease of the influent ranged from 490 ppm to 173 ppm with an average of approximately 309 ppm. The Clerify™ filter effluent infrared analysis ranged from 310 ppm to 49 ppm with an average of approximately 181 ppm. The Clerif™ filter influent color was dark brown to black with some oil droplets on top of the sample and the effluent color was dark brown and oil was present.

The Crudesorb™ filter effluent infrared analysis ranged from 101 ppm to 19 ppm with an average of approximately 43 ppm. The Crudesorb™ filter influent color was dark brown to black with a large layer of oil on top of the sample and the effluent color was yellow with no oil present. The Crudesorb™ effluent passed all static sheen tests.

Additional tests were conducted in the Gulf of Mexico. In these tests, the Crudesorb™ and Clerify™ filters were also used in parallel flows on the MC 311 and 194 platforms. As shown in Table 2a and 2b, the pressure drop across the filters was nominal. For the MC 311 platform as shown in Table 2a, the infrared oil & grease of the influent ranged from 444 ppm to 160 ppm with an average of approximately 280 ppm. The Clerify™ filter effluent infrared analysis ranged from 310 ppm to 95 ppm with an average of approximately 210 ppm. The Crudesorb™ filter effluent infrared analysis ranged from 47 ppm to 18 ppm with an average of approximately 30 ppm.

For the MC 194 platform as shown in Table 2b, the infrared oil & grease of the influent ranged from 343 ppm to 95 ppm with an average of approximately 170 ppm. The Clerify™ filter effluent infrared analysis ranged from 265 ppm to 15 ppm with an average of approximately 79 ppm. The Crudesorb™ filter effluent infrared analysis ranged from 31 ppm to 10 ppm with an average of approximately 18 ppm.

Figure 1 Acid Flow-back Equipment Arrangement.

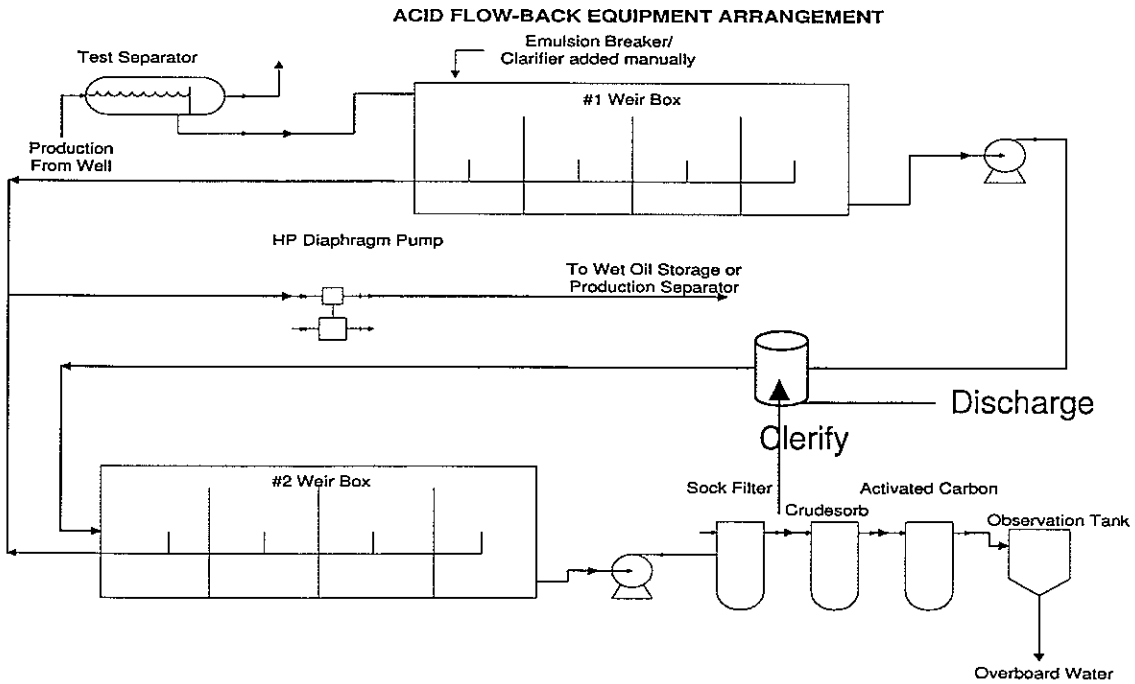


Table 1. Comparison of Clerify™ and CrudesorbTM Filters for Treating MARS TLP Acid Flowback from A-14

Date	Pressure Readings (pisg) #1	#2	#3	Flow rate GPM	Temp. C	pH	Influent Oil	Effluent Oil ppm for	
	IN	MID	OUT				ppm	Clerify Filter	CETCO Filter
11/13/1996	40	10	9	1	25	4	231	59	25
	41	10	9	1	25	4	264	64	26
	50	10	8	1.5	25	4.5	472	280	93
	45	12	8	1.5	25	5	490	301	92
	60	20	10	2	26	6.1	389	288	49
	60	20	10	2	26	6.2	347	284	42
11/13/1996	60	20	12	2	25	6	472	289	101
	60	20	12	2	25	6	422	290	74
	60	20	13	2	25	6.2	387	310	44
	60	20	12	2	25	5.9	365	308	42
	70	25	20	2	25	6.6	315	279	37
	70	25	19	2	25	6.5	318	280	38
6/12/1996	43	9	7	1	24	7	154	49	22
	42	9	7	1	24	7	270	68	29
	50	11	9	2	24	7	279	65	28
	50	12	8	2	24	6.8	315	78	30
	60	18	10	2	25	7	173	72	26
	60	18	11	2	24	6.5	192	81	29
	65	20	12	2	24	6.7	116	76	19
	70	25	21	2	25	7	222	101	23

Table 2a. Comparison of Clerify™ and CrudesorbTM Filters Mississippi Canyon 311 Acid Flowback

Date	Pressure Readings (pisg)			Flow rate	Temp.	pH	Influent Oil	Effluent Oil ppm for	
	#1	#2	#3	GPM	C		ppm	Clerify Filter	CETCO Filter
	IN	MID	OUT						
02/27/1997	40	10	7	1	25	5.5	202	98	18
	41	10	7	1	24.6	5.3	210	95	19
	38	12	8	1.5	25	5.7	256	145	28
	38	11	8	1.5	25	5.9	248	144	25
	35	10	7	2	26	6.1	276	158	31
	36	10	7	2	26	6.2	266	159	30
02/28/1997	43	12	8	2	25	7.6	400	226	46
	42	12	7	2	25	7.5	420	270	45
	43	11	7	2	25	7.2	444	310	47
	42	12	8	2	25	7.1	257	308	30
	43	12	8	2	25	7.2	220	309	24
	41	11	7	2	25	7.1	160	301	19

Table 2b. Comparison of Clerify™ and Crudesorb™ Filters Mississippi Canyon 194 Acid Flowback

Date	Pressure Readings (pisg)			Flow rate	Temp.	pH	Influent Oil	Effluent Oil ppm for	
	#1	#2	#3	GPM	C		Ppm	Clerify Filter	CETCO Filter
	IN	MID	OUT						
12/4/1997	30	7	3	1	25	7	103	15	12
	30	7	3	1	25	7	110	17	12
	27	6	3	1	25	7	95	17	10
	28	6	3	2	26	7	170	59	21
	23	6	2	2	26	7	196	102	20
	25	6	3	2	26	7	343	265	31

North Sea Field Tests

Results were obtained from a North Sea platform that had operational experience with both the Clerify™ and Crudesorb™ filters. 2,000 barrels of acid flow back fluids were contained and filtered for oil and grease removal with Clerify™ filters. Table 4 shows the results of the first 12 hours of the treatment effort. The results show that the effluent oil & grease concentration exceeded the regulatory limit the entire test and the water was not discharged.

Table 4. Analytical Results from 12 Hours of Filtering North Sea Acid Flow Back with Clerify™ Filters

Sample Time	Sample pH	Influent Infrared Oil & Grease Concentration (ppm)	Effluent Infrared Oil & Grease Concentration (ppm) **40 ppm regulatory standard**
0300	1	538	450
0400	1	653	425
0500	1	1,215	654
0600	1	1,514	870
0700	1	986	435
0800	4	687	610
0900	4	461	430
1000	4	834	612
1100	4	950	513
1200	5	1,190	413
1300	5	536	316
1400	5	810	265
1500	5	713	243

For the platform's next acid flow back, the Crudesorb™ process was used to filter the fluids to remove oil and grease. Table 5 shows the results that met the regulatory compliance the entire test and the water was discharged directly.

Table 5. Analytical Results from 12 Hours of Filtering North Sea Acid Flow Back with Crudesorb™ Filters

Sample Time	Sample pH	Influent Infrared Oil & Grease Concentration (ppm)	Effluent Infrared Oil & Grease Concentration (ppm) **40 ppm regulatory standard**
1300	1	345	23
1400	1	354	25
1500	1	2550	16
1600	1	2500	17
1700	1	1036	9
1800	1	1049	13
1900	1	1200	15
2000	1	1327	14
2100	2	1280	17
2200	2	1710	19
2300	3	847	31
2400	3	934	27
0100	3	423	23

Conclusion: Based on the test results, the Crudesorb™ media out performed the Clerify™ media in all methods tested for removal of oil and grease in acid flow backs. In the laboratory study, the Crudesorb™ media broke a 500 ppm oil/water emulsion and maintained high water quality in the effluent. The Clerify™ media did not successfully treat the emulsion; which resulted in poor water quality the entire laboratory test. In a field evaluation on the Mars TLP, the Crudesorb™ filters were used to unload two wells. The effluent oil concentration infrared analysis averaged 43 ppm and static sheen test were in compliance during the entire test. As a result, the Crudesorb™ filtered water was discharged directly overboard. During the same test, the Clerify™ filters infrared results averaged 181 ppm for the Mars TLP, or four times greater than the Crudesorb™ results. At the Mississippi Canyon, tests were run at the 311 and 194 platforms. The Clerify™ effluent averaged 210 ppm and 79 ppm respectively, whereas the Crudesorb™ effluent averaged 30 ppm and 18 ppm respectively. In a North Sea trial, the Clerify™ filters did not remove sufficient oil to meet the regulatory standard for a 12-hour test. In a separate 12-hour test, the Crudesorb™ filters did meet the regulatory standard.