EMULSIONS BREAKING WITH MAGNETIC FIELDS

R. R. Oder
EXPORTech Company, Inc.
Bldg. 242, Schreiber Industrial District
12th Street, P.O. Box 588
New Kensington, PA 15068-0588
roder@magneticseparation.com

ABSTRACT

This paper presents results obtained in bench-top testing of a novel magnetic method for breaking either water-in-oil or oil-in-water emulsions. The method employs a magnetic additive implanted in the internal phase of the emulsion and either permanent or electromagnets to coalesce the internal phase and break the emulsion. In the case of water-in-oil emulsions, iron lignosulfonate was employed as the additive. Iron naphthenate was used for oil-in-water emulsions. Laboratory measurements are presented here to illustrate application of the method to dewatering and desalting of California crude oil.

INTRODUCTION

We report development of a new approach to breaking emulsions – magnetostatic coalescence. The method implants a magnetic additive into the internal phase of the emulsion and employs magnetic fields to coalesce the magnetic phase and break the emulsion. The method is continuous in operation, capable of separating internal phase droplets in the micron size range in high throughput operation, does not plug even when processing high internal phase emulsions, and achieves high levels of recovery of the continuous phase of the emulsion. The method can be used in processing systems of a high electrical conductivity such as organic-liquid-in-water emulsions. There are no induced electric currents or electric power consumption in the emulsion and no electrodes are employed. The magnetostatic coalescence method is also safe for use around flammable materials, such as crude oil and gasoline feedstocks. While heat is not developed in the emulsion during breaking, the method can be operated over any temperature range applicable to the emulsion.

Success of the new method is largely associated with the use of surfactants which lower interfacial tension and interfacial film stability in the presence of a magnetic field. Without the proper interplay between film stability, surface tension, and magnetic field strength, the magnetized particles chain and flocculate and do not coalesce.

MAGNETOSTATIC COALESCENCE CONCEPT

Magnetostatic coalescence[1] employs additives to impart magnetic characteristics to selected liquids such as the internal phase of an emulsion and surfactants to control interfacial tension and film stability in a magnetic field. Magnetic fields are applied to coalesce the emulsion.

Figure 1 is a schematic illustration of a coalescer which employs permanent magnets to break a water-in-hydrocarbon liquid emulsion. The emulsion is pumped through the coalescer on a continuous basis. The fringing fields produced by the permanent magnets polarize the emulsion droplets which in turn produce intense attractive intra-particle magnetic forces which cause rapid coalescence of the droplets up to the 100 micron size range. This occurs throughout the volume of the coalescer. The fringing fields then attract these enlarged and magnetized droplets to the wire surfaces where coalescence is completed under very intense magnetic compressive forces. The fluid and its magnetic additive then flow down the rods and form a plug at the bottom of the coalescer where the magnetic fluid is held by vertical components of the fringing fields at the ends of the rods. Once the weight of the plug becomes too great to be supported by the fringing fields, some of the fluid will break through and exit the bottom of the coalescer. The plug forms an effective barrier which prevents loss of the continuous phase of the emulsion. Once freed from the water, the hydrocarbon phase of the emulsion flows upward and exits the coalescer at the top.

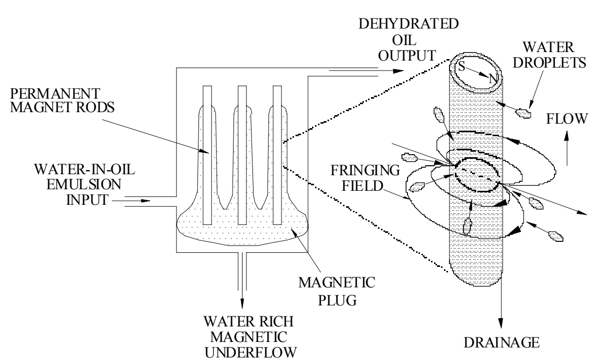


Fig. 1. Schematic Diagram of a continuously operating – high gradient magnetic coalescer

EXPERIMENTAL

A series of experiments were carried out to illustrate the effect of the magnetic field, the magnetic additive, and of the destabilizing surfactant on coalescence in a magnetic field. Additionally, two other configurations of magnetic coalescers, a magnetic settler and a high gradient magnetic separator, were investigated. Experiments were carried out to show results of separation using all three of the separators working in tandem. Lastly, the utility of the method is illustrated by showing results obtained in magnetic dehydration and desalting of a California crude oil.

Laboratory Coalescer

The laboratory scale continuously operating magnetic coalescer, shown in Figure 2, has an internal rectangular cross-section of 1.9 cm × 3.4 cm and 22.4 cm length. This coalescer employs wires which are magnetized by an externally applied magnetic field. A typical wire packing is also shown in Figure 2. The coalescer is placed within the gap of a laboratory scale electromagnet shown in Figure 3. For some tests, stainless steel wool and wire mesh were used as packing. The magnetic field in the volume of the coalescer cell could be varied from zero up to 6000 gauss. A peristaltic pump, not shown, was employed to pump the emulsion through the cell at rates up to nominally 60 cm^3/min. Experiments were carried out at room temperature.

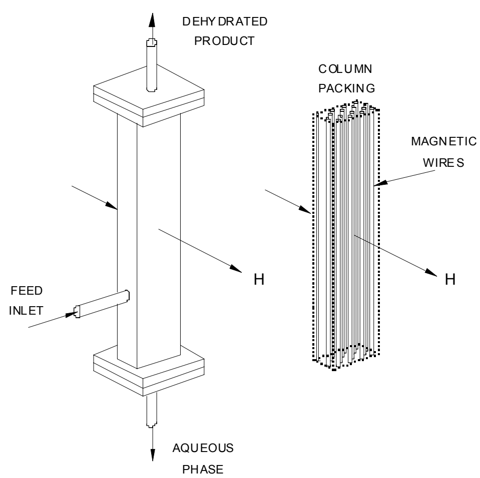


Fig.2. Magnetostatic coalescence column and packing

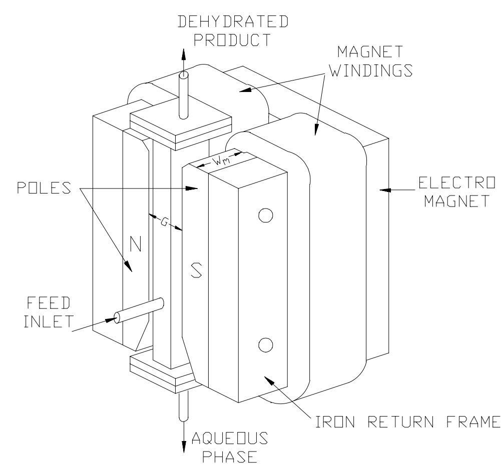


Fig. 3 Coalescer in laboratory scale electromagnet

The induced fringing fields in the volume of flow shown in Figure 4 initiate coalescence by magnetizing internal phase droplets which coalesce out in the volume of the emulsion. Once the droplets are large enough to be affected by the fringing fields, they are attracted to the polar regions on the surfaces of the wires. Use of the electromagnet to apply the magnetic field results in the induced North and South poles' being on the leading and trailing edges of the wires along the direction of the applied magnetic field as shown in Figure 4.

Once the dispersed phase begins to coalesce on the surface of the wires, it is acted upon by gravity, which causes settling of the aqueous phase for a W/OL (water in organic liquid) emulsion. Likewise, the lighter oil phase moves upward with the flow to the top of the chamber where it flows out as the dehydrated product. Movements of the two phases along the length of the wires are not impeded by the magnetic field which, due to its horizontal orientation, produces substantially no vertical component of the magnetic force – except at the upper and lower ends of the wires.

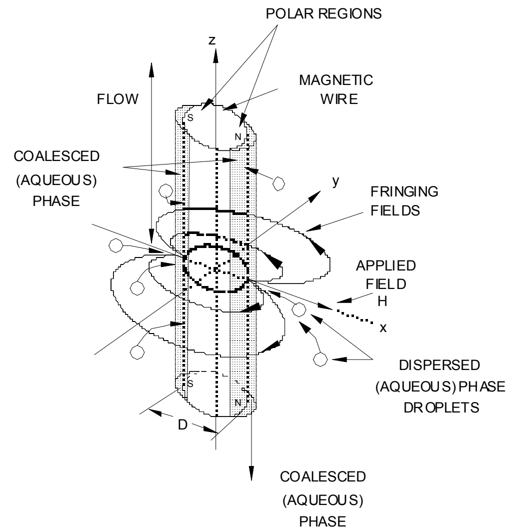


Fig 4. Fringing fields

The magnetic forces at the ends of the rods are directed back into the volume of the coalescer. At the upper end this prevents loss of magnetized particles which were not captured and remain in flow. This works to the extent that the downward directed magnetic and gravitational forces are greater than viscous drag tending to carry the particles out the top of the coalescer. This is particle size and slurry viscosity dependent. At the lower end of the coalescer the vertically directed magnetic force along with flow restriction at the lower exit tend to keep the magnetized phase inside the cell. This is advantageous. It leads to the formation of a "magnetic plug" which prevents loss of the organic or hydrophobic phase. When the weight of the supported phase containing the magnetic additive becomes too great to be held by the vertical component of the magnetic force, gravity ruptures the lower surface of the plug and pulls a portion of the material in the plug out the bottom of the coalescer.

Surfactants

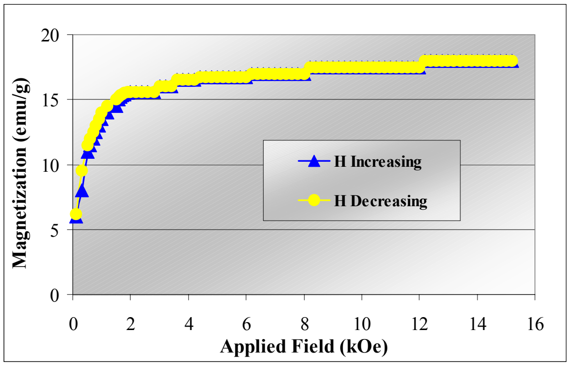
The surfactants, demulsifiers and additives tested during the experimental program described below are listed by identifier in Table I.

Table I
Surfactants, Demulsifiers and Additives Tested

Trade Name	Chemical Composition
Merpol® A	Alkyl Phosphate Ethoxylate (1,4 Dioxane)
Hypermer®-B—246	Polyoxyalkylene modified block copolymer
T-DET® N1.5	Polyoxyethylene nonylphenol
T-DET®-N40	Polyoxyethylene nonylphenol
Silwet® L7602	Polyalkylene Oxide-Modified Dimethylpolysiloxanes
Span® 80	Sorbitan monooleate
Tween® 80	Polyoxyethylene Sorbitan Monooleate
Lignosite® FML	Iron lignosulfonate
Nuodex®	6% iron naphthenate solution
Pluronic® L62	Difunctional block copolymer surfactant terminating in primary hydroxyl groups H_2C — CH — CH_3, CH_2 — CH_2 O O

Iron-Lignosulfonate Magnetization

The magnetization of dry powder iron lignosulfonate measured at room temperature with a vibrating sample magnetometer is shown in Figure 5. It can be represented by a ferromagnetic component with spontaneous magnetization of 16.4 emu/gm and a paramagnetic component with magnetic susceptibility of 49.7×10^{-6} emu/gm-oer. The low field magnetization measured in fields up to 2000 oer is shown in Figure 6. The static magnetic susceptibility measured at 3400 oer is 4800×10^{-6} emu/gm-oer which is within the range of susceptibilities determined using a Johnson & Matthey, Inc., Model MSB-1 magnetic susceptibility balance which was employed to measure the magnetic susceptibility of magnetic emulsions. The Johnson & Matthey balance employs the Gouy method.



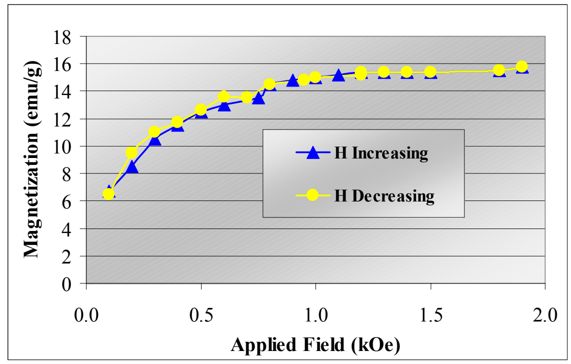


Fig. 5. Saturation magnetization of dry iron lignosulfonate. Room temperature.

Fig. 6. Low field magnetization of dry iron lignosulfonate. Room temperature.

Emulsions Preparation

Stable emulsions containing various amounts of connate water were prepared using high shear mixing and stabilizing surfactants. The organic liquids used in the emulsions were light paraffin mineral oil or crude oil. Water was the second phase. Water content in the emulsion was determined using Karl Fischer titration. Surfactants were employed to impart stability to the emulsions.

The emulsions employed in the testing consisted of the following components listed in order: hydrophobic, hydrophilic, magnetic additive, emulsifier, and destabilizer reported as percent by weight based on the emulsion, unless otherwise reported.

Magnetic Emulsions

When the water was in the dispersed phase, hydrophilic iron lignosulfonate, approximately 71-73% water, was used. Lignosite® FML is a product of Georgia Pacific Corporation. When an organic liquid was in the dispersed phase, an oleophilic paramagnetic Nuodex® iron naphthenate 6% supplied by Nuodex, Inc., was used.

Magnetic Susceptibility

Magnetic susceptibility, χ, is a convenient measure of the concentration of the magnetic additives in the emulsion. The concentration of magnetic additive, W_F, (weight fraction) was determined by the relationship of Eq. (1).

$$W_F = \frac{\chi_E - \chi_O + (\chi_O - \chi_W)W_W + (\chi_O - \chi_S)W_S}{\chi_F - \chi_O} \qquad \text{Eq. (1)}$$

where,

$$1 = W_O + W_W + W_S + W_F. \qquad \text{Eq. (2)}$$

In Eq.(1), χ_E is the measured magnetic susceptibility of the emulsion. W_0 and χ_O are the weight fraction and the magnetic susceptibility of the oil phase, W_W and χ_W are similar for the water phase, W_S and χ_S are similar for the surfactant phase, and W_F and χ_F are the weight fraction and magnetic susceptibility of the additive. Measured values of the susceptibility of liquids, surfactants, and additives used in this work are given in Table II.

Table II
Measured Values of Magnetic Susceptibility

Material	**Magnetic Susceptibility (10^{-6} emu/g-Oer)**
Crude Oil	-0.89
Mineral Oil	-0.83
Heptane	-0.85
Gasoline	-0.80
Distilled Water	-0.72
Emulsifier K	-0.75
Tween® 80	-0.60
T-Det®N40	-0.65
Span® 80	-0.63
Pluronic® L62	-0.69
Merpol® A	-0.66
Nuodex® iron naphthenate 6%	+4.7
Iron lignosulfonate	1,000 – 4,200
Iron lignosulfonate (Dry)	4,000 – 15,000

When the additive is strongly magnetic, such as iron lignosulfonate, its concentration can be obtained approximately using the relationship,

$W_{FP} \approx (\chi_P - \chi_o)/\chi_F$,

when $(\chi_o - \chi_W)W_W << \chi_P - \chi_o$

and $(\chi_o - \chi_S)WS_S << \chi_P - \chi_o$

and $\chi_F >> \chi_o$.

The measurements of the additive concentration are of a qualitative nature. They are useful in making a quick assessment of the amount of additive remaining after coalescence. It is to be noted that the unit emu/g-Oer is equivalent to cm^3/g. In the following the value 10^{-6} emu/g-Oer may be reported as micro emu/g-Oer or micro cm^3/g or $\mu cm^3/g$.

TEST RESULTS

The versatility of the magnetostatic coalescence method has been demonstrated by breaking two exemplary types of emulsions, water-in-organic-liquid (W/OL and organic- liquid-in-water (OL/W). An application of the former type emulsion, W/OL, is illustrated in dehydration of crude oil.

Effects of Magnetic Field Strength, Retention Time, Magnetic Additive Concentration, and Destabilizing Surfactant

Wire mesh collection surfaces were used in place of rods or vertical wires. This illustrates effects of collection surface choice on both dehydration and on recovery of the continuous phase of the emulsion. This type of collection surface is more effective in separation of internal phase droplets than the vertical rods but is also prone to plugging and can exhibit loss of the continuous phase to the underflow.

Effect of Field Strength and Retention Time on Water Reduction

A stable emulsion containing 79.85% mineral oil, 16.15% water, 3.19% iron-lignosulfonate, 0.16% emulsifier K, a non-ionic demulsifier consisting of 0.32% Pluronic® L62 and 0.33% Merpol® A was prepared for use in testing. The susceptibility of the emulsion was 306 μcc/gm.

Approximately 12.75 grams of a magnetic open mesh wire insert was employed in the first stage volume to produce gradient magnetic fields for capturing dispersed phase droplets. No rods were employed. The emulsion was pumped through the coalescence cell at rates of 60, 33, and 18.5 cm^3/min resulting in retention times of 2.5, 4.5, and 8 minutes respectively. The test was continued until a 200 cc volume product was collected. Magnetic field strengths between 0 and 6000 gauss were employed.

Effects of magnetic field strength and of retention time on separation of water from the emulsion are shown in Figure 7 and Table III for several flow rates, V(cm^3/min). The magnetic susceptibility and the water content of the dehydrated emulsion are directly measured. The iron lignosulfonate concentration has been calculated from the measured susceptibility.

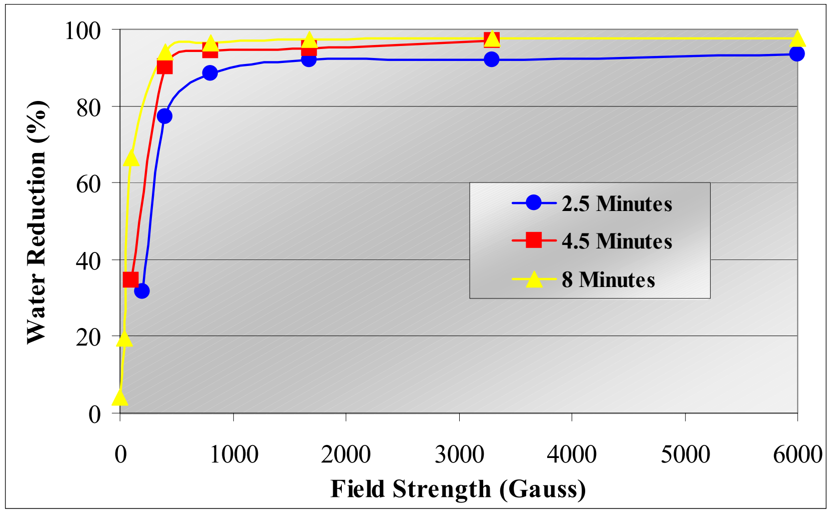


Fig. 7. Water reduction vs. field strength, wire mesh capture surface

Table III
Effects of Magnetic Field Strength and Retention Time
on Water Reduction in the First Stage with Open Mesh Wire Insert

Magnetic Field (Gauss)	Flow Velocity (cm^3/min)	Retention Time (min)	Magnetic Susceptibility (10^{-6} cc/g)	Water (wt.%)	Iron Lignosulfonate (wt.%)	Iron Lignosulfonate Reduction (%)	Water Reduction (%)
200	60	2.25	173.70	10.98	1.847	41.85	31.71*
400	60	2.25	49.80	3.65	0 .526	83.34	77.21*
800	60	2.25	24.88	1.87	0.264	91.74	88.50*
1680	60	2.25	12.19	1.27	0.134	95.75	92.09*
3300	60	2.25	13.37	1.27	0.149	95.31	92.11*
6000	60	2.25	9.57	1.05	0.107	96.63	93.48*
100	33	4.5	164.21	10.50	1.752	44.77	34.59*
400	33	4.5	13.50	1.54	0.150	95.25	90.35
800	33	4.5	13.30	0.91	0.149	95.29	94.40
1680	33	4.5	7.08	0.81	0.083	97.45	95.05
3300	33	4.5	6.33	0.49	0.076	97.58	96.96*
0	18.5	8	286.09	15.45	3.045	4.59	4.14*
36	18.5	8	161.79	12.80	1.676	46.69	19.64*
100	18.5	8	74.01	5.46	0.787	75.38	66.64
400	18.5	8	14.97	0.97	0.160	95.06	94.17
800	18.5	8	6.50	0.58	0.079	97.51	96.41
1680	18.5	8	4.94	0.43	0.058	98.23	97.33
3300	18.5	8	4.52	0.40	0.053	98.34	97.53
6000	18.5	8	2.95	0.39	0.038	98.83	97.62*

*Oil in Iron Lignosulfonate/Water Product

The data points marked by an asterisk (*) in Table III correspond to runs where small amounts of oil was observed in the underflow taken from the first stage coalescer. Measurements shown in Table III were made using a wire mesh surface which had both horizontal and vertical elements. The water reduction is better with this type collector than for rods but has problems associated with oil breakthrough. Even though water reduction may have been good, loss of oil in the underflow where water and iron lignosulfonate are separated from the coalescer is undesirable because it indicates a loss of organic liquid by the process. There is a tradeoff possible between water reduction and oil recovery which will be affected by the choice of collection surface.

Values of the iron lignosulfonate content in the dehydrated product shown in Table III are characteristic of the results observed in this work. Reductions in iron lignosulfonate concentration greater than 90% are easily achieved using magnetic fields from 400 to 800 gauss for retention times as low as 2.25 minutes. The use of field strength above 800 Gauss does not bring significant improvement in water reduction. This is to be compared with typical retention times of hours for electrostatic coalescers used in petroleum desalting and dehydration.

Effects of Magnetic Additive Concentration on Water Reduction

Stable emulsions with three levels of connate water (4.37%, 9.08%, and 16.86%) were prepared for the test work. Varying amounts of iron lignosulfonate were added to each of these emulsions to investigate the effects of its concentration on dewatering in the first stage coalescer. A retention time of 8 minutes was used for all test work. The applied magnetic field ranged from zero to 3300 gauss. The concentration of Merpol® A was adjusted to 1% of total water. Results of the separations are given in Figure 8. 12.75 grams of open mesh wire was used to generate gradient fields inside the coalescer for these examples.

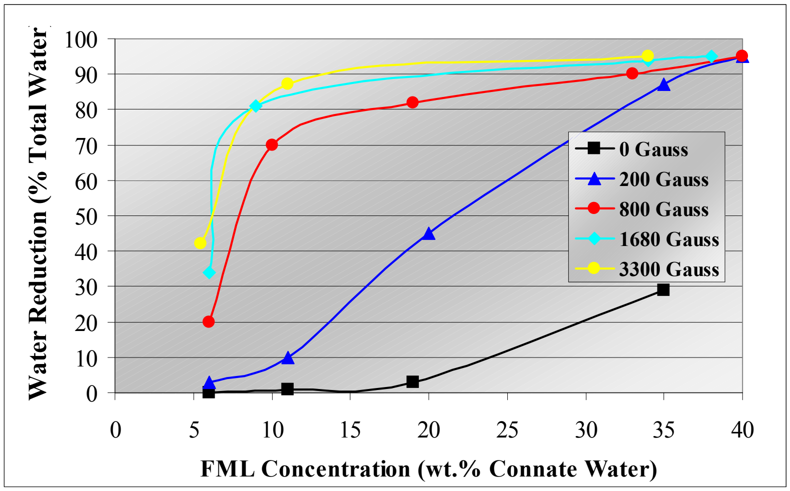


Fig. 8. Water reduction vs. iron lignosulfonate concentration for magnetic fields up to 3300 gauss

Addition of iron lignosulfonate in concentrations greater than 20% based on connate water results in partial demulsification in zero magnetic field strength.

The results for 200 Gauss show that at least 12% iron lignosulfonate based on connate water is required to show effects on water reduction. At this low field strength concentrations of iron lignosulfonate up to 40% based on connate water are required to achieve effective demulsification.

For magnetic fields greater than 800 Gauss, water reductions between 70% and 98% are achieved when concentrations of iron lignosulfonate greater than 10% are used.

Use of low levels of the magnetic additive greatly increases the practicality of the method. It permits use of low levels of the magnetic field strength and improves oil recovery by achieving virtually complete coalescence.

Effect of Surfactant on Water Reduction and Oil Recovery

The purpose of the measurements was to determine the interaction of Merpol® A and the magnetic field strength in reducing water content in the first stage coalescer output. Splits from a stable emulsion were prepared which contained no Pluronic® L62. The content of Merpol® A was varied from zero up to nominally 4% based on total water. The magnetic emulsion contained the same amount of iron lignosulfonate (3.2% based on total emulsion) as used in the previous example. It was pumped through the cell at a flow rate of 18.5 cm^3/min corresponding to a retention time of 8 minutes. Approximately 12.75 grams of wire mesh previously described were employed in the first stage coalescer. The results of the separations are given in Figure 9.

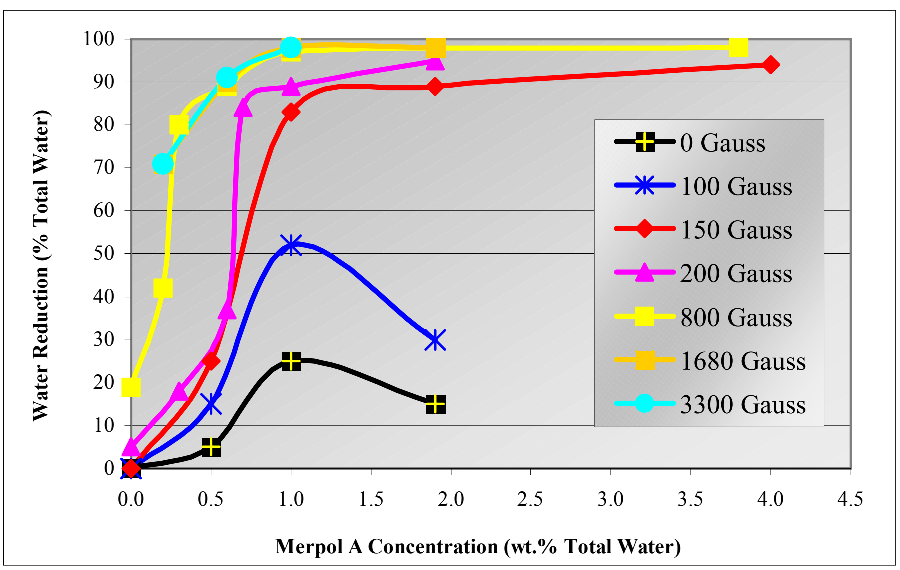


Fig 9. Effect of Merpol® A upon water reduction in different magnetic fields

A magnetic field strength of 150 Gauss is sufficient to achieve water reductions greater than 80% in the first stage coalescer containing wire mesh when the concentration of Merpol® A reaches its solubility limit which is 1% based on total water. Higher concentrations of Merpol® A are not necessary to achieve significant dewatering in the coalescer. With Merpol® A at the 1% concentration level, magnetic fields of 800 Gauss result in water reductions greater than 90% in the first stage coalescer.

Water reduction is improved with use of Merpol® A and, while not shown, the tendency to discharge oil in the underflow was lessened with its concentration of nominally 0.33 % and higher. The advantages of the continuous magnetic coalescer are that it can achieve high throughput, it is continuous in operation, and it achieves high recoveries of the continuous phase of the emulsion. A disadvantage lies in the fact that sub-micron sized agglomerates of the internal phase of the emulsion with magnetic additive can escape through the top of the unit. This happens because there are always some internal phase droplets which do not coalesce to sizes which can be captured or held within the first stage coalescer. These droplets represent a very small amount of the internal phase of the emulsion. They can be captured in downstream separators of a variety of types and form.

Downstream Magnetic Separators for Removing Very Small Particles

The following illustrates use of other types of magnetically assisted coalescers to remove the final amount of this material These are polishing separators. They are not necessarily continuous in operation.

Magnetically Assisted Settling

Another version of the coalescer can employ permanent or electromagnets in a settling configuration as illustrated in Figure 10. This configuration is effective in separating the magnetic components of an emulsion which are not separated in the vertically oriented coalescer. Water concentrations in the nominal 0.1 wt.% range are possible. This type of coalescer is employed as the second stage of treatment in the examples to follow.

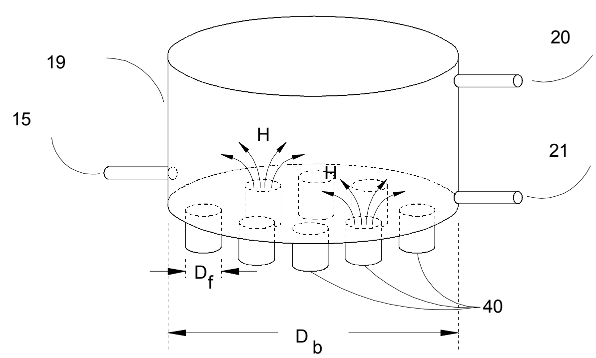


Fig. 10. Magnetic settler.

High Gradient Magnetic Separation (HGMS)

A third type of coalescer is the high gradient magnetic separator (HGMS) tried by others. It is used here to prepare organic liquids with water and magnetic additive concentrations in the 10 – 100 ppm range. HGMS was originally developed to separate sub-micron iron-stained anatase and leucoxene minerals from kaolin clay to improve its whiteness and brightness. The mineral color bodies, consisting of roughly 5 wt.% of the solids in a slurry of otherwise diamagnetic solids, could not be removed by chemical leaching.

Multi-Stage Processing

Tests were carried out to demonstrate the effects of processing in three stages, i.e., a first stage continuous coalescer of the type shown in Figures 2 and 3 followed by a field assisted settler such as shown in Figure 10, and an HGMS separator to break emulsions of water in organic liquid (W/OL). The rods used in first stage packing were carbon steel and had diameter of 0.044 inches. The rod packing of the first stage coalescer was replaced with stainless steel wool for HGMS processing.

For some of the tests, stable emulsions of water-in-organic liquid (W/OL) were prepared by first mixing mineral oil with connate water and emulsifier K. Next the magnetic additive, iron lignosulfonate, water, and destabilizing surfactants were added to the stable emulsion and these materials were used as feed to the magnetostatic coalescer. In one test, a raw crude oil which contained emulsified water was used. Only the magnetic additive and a destabilizing surfactant were added to this stable emulsion.

Effect of Surfactant on Continuous Operation

Tests were carried out to demonstrate that use of the destabilizing surfactant allows the first stage to be operated as a continuous coalescer with high levels of continuous phase recovery and to demonstrate the overall effect of treating the product of the first stage continuous coalescer with field assisted settling.

Demulsification with Surfactant

Tests were carried out using the destabilizing surfactant Merpol® A. For these tests a magnetic emulsion containing 80.08% mineral oil, 16.43% water, 3% dry iron lignosulfonate, 0.16% emulsifier K and 0.33% Merpol® A was used. The magnetic susceptibility of the emulsion was 286×10^{-6} cm^3/gm.

Emulsion was pumped through the first stage coalescer with a flow rate of 30 cm^3/min for a period of three hours. A total of seventy (70) 0.044 inch diameter vertical steel rods were employed in the coalescer for the tests. The output of the first stage coalescer was sampled every 15 minutes and analyzed for magnetic susceptibility and water content. The results are shown in Table IV. The feed, which contained 16.43% water on average, had water content ranging from 0.43 to 1.14% after treatment in the first stage.

Table IV
Results of Continuous Magnetostatic Coalescence of a
16.43% Water in Mineral Oil Emulsion Containing Merpol® A

	First Stage Coalescer Output		**Field Assisted Settler Output**	
Time (Min.)	**Magnetic Suscep. (10^{-6} cm^3/g)**	**Water (wt.%)**	**Magnetic Suscep. (10^{-6} cm^3/g)**	**Water (wt.%)**
Initial	7.31	0.58	0.30	0.12
15	4.79	0.43		
30	13.54	1.04	0.26	0.12
45	8.10	0.64		
60	7.83	0.65	0.39	0.13
75	6.61	0.69		
90	8.45	0.68	0.39	0.12
105	18.06	1.14		
120	16.12	1.14	0.32	0.10
135	13.38	0.93		
150	12.15	0.86	0.23	0.10
165	8.13	0.68		
180	15.29	1.04	0.35	0.11

Every thirty minutes, a 25 cc sampling of the first stage coalescer output was taken for treatment by gravity assisted settling. The sample was placed in a beaker standing over a permanent magnet which produced a field of 1500 Gauss and a magnetic field gradient of 1000 Gauss/cm, both measured at the face of the magnet. The contents of the beaker were left in place resting on the top of the magnet for a period of three (3) hours. After that time, the contents were carefully decanted and measured for magnetic susceptibility and water content. The results of those measurements are shown in the right two columns of Table IV.

It can be seen that the combined process of continuous magnetic demulsification in the first stage coalescer treatment followed by field assisted settling is capable of producing a consistent product with water and iron lignosulfonate reductions greater than 99%. There was no mineral oil visible in the first stage coalescer underflow which indicated no significant oil loss by the method.

Demulsification Without Surfactant

Tests were carried out using the first stage coalescer and field assisted settling as described above, but without the destabilizing surfactant. For these tests a stable emulsion was prepared which contained 80.41% mineral oil, 16.42% water, 3.01% dry iron lignosulfonate, 0.16% emulsifier K, and no Merpol® A. The magnetic susceptibility was 283×10^{-6} cm^3/gm. The results of these tests are shown in Table V.

Table V
Results of Continuous Magnetostatic Coalescence of a
16.42 % Water in Mineral Oil Emulsion Containing No Merpol® A

	First Stage Coalescer Output		**Field Assisted Settler Output**	
Time (Min.)	**Magnetic Suscep. ($10^{-6}cm^3/g$)**	**Water (wt.%)**	**Magnetic Suscep. ($10^{-6}cm^3/g$)**	**Water (wt.%)**
Initial	22.8	2.00	1.68	0.31
15	172.5	10.83	1.25	0.21
30	221.1	13.00	1.36	0.20
45	218.7	13.58	1.37	0.20
60	208.8	12.79	1.39	0.18

The data show that the first stage coalescer does not operate well without the destabilizing surfactant. Indeed, the test was terminated after one hour because of backup of the coalesced material in the first stage coalescer. Without Merpol® A the first stage filled with partially coalesced emulsion because internal phase droplets which chain in the magnetic field bridge the gap between magnetic rod inserts. The chains have low specific gravity and are held in place between the magnetic rods and do not drain out of the cell as is the case with droplets of higher specific gravity which have completely coalesced. This results in loss of active volume in the coalescer which results in poor dewatering and in backup which requires intermittent cleaning. This requires the first stage to be operated as a batch coalescer. Further, significant amounts of mineral oil were observed in the first stage underflow, indicating oil loss.

Even with no destabilizing surfactant, the field assisted settler achieved good dewatering as shown in Table V. However, floccs of unresolved emulsions were found in the bottom of the settler when no Merpol® A was used. This defeats the objective of obtaining high recoveries of the organic liquid. The use of a destabilizing surfactant is beneficial to the process.

HGMS Polishing

A series of experiments was carried out to illustrate the use of conventional batch operated HGMS as a polishing operation in magnetic dehydration of organic liquids. Conventional batch operated HGMS is not practical as a general means for magnetostatic coalescence because the filter plugs rapidly when the feed water content is generally above 0.5%.

In the results presented here, a batch operated HGMS unit was used to achieve final dewatering of the low water content product of two stage processing. Magnetic emulsions were prepared for these tests which were typical of the output of the magnetic assisted settler. The feed emulsion contained 99.7% mineral oil, 0.13% water, 0.01% dry iron lignosulfonate, 0.16% emulsifier K, 0.002% Merpol® A and had a magnetic susceptibility of 0.25×10^{-6} cm^3/gm. The results of processing in which the field strength, the flow rate, and the processing time are varied are shown in Table VI.

Table VI
HGMS Dewatering of 0.13 % Water Emulsion

			Product Characteristics		
Magnetic Field (Gauss)	**Retention Time (Min.)**	**Processing Time (Min.)**	**Magnetic Suscep. (10^{-6} cm^3/g)**	**Water (wt.%)**	**Water Reduction (%)**
0	4.5	60	-0.47	0.033	75.55
800	4.5	1	-0.83	0.008	93.87
800	4.5	30	-0.83	0.009	93.43
800	4.5	45	-0.82	0.009	93.43
800	4.5	60	-0.83	0.008	93.80
6420	37	60	-0.88	0.008	94.09

In processing for 60 minutes, approximately 75% reduction in emulsified water content was achieved in flow through the magnetic matrix with a 4.5 minute retention time even when the magnetic field was zero. This mechanical capture is associated with coalescence on the hydrophilic surface of the ferritic stainless steel wool. Much greater water reduction was achieved, however, when a magnetic field was applied.

A magnetic field of 800 Gauss and a retention time of 4.5 minutes is sufficient to achieve more than 93% removal of water from the emulsion. Water contents in the 80 ppm range are achieved. This is less than the water that was contained in the mineral oil used to make the emulsion, which was typically 270 ppm. The diamagnetic susceptibilities of the dehydrated products are near those of the oil and oleophilic additives used for the study, indicating near complete removal of the iron lignosulfonate.

Use of field strength higher than 800 Gauss and retention time longer than 4.5 minutes does not lead to significant increase in water reduction. It is further important to note that for operating periods up to one hour, no break-through of the batch HGMS matrix is indicated when operating at 800 Gauss and 4.5 minutes retention time. With the levels of field strength and retention time the same as used in the first stage continuous coalescer, the method is practical for polishing applications in the magnetostatic coalescence process.

Figure 11 illustrates the effect of the overall process. In the figure, Beaker A shows the light paraffin oil used in the experiments. It was found to contain 274 parts per million water. Note that it is clear and transparent. Beaker B in the figure shows the emulsion used for the experiments. It contains 21.6 wt.% water and iron lignosulfonate. Beaker C shows the oil product prepared by the first stage magnetic coalescer. The product of the three stage process, Beaker D, contains 0.035 wt.% water. The amount of additive remaining in the product is negligible.

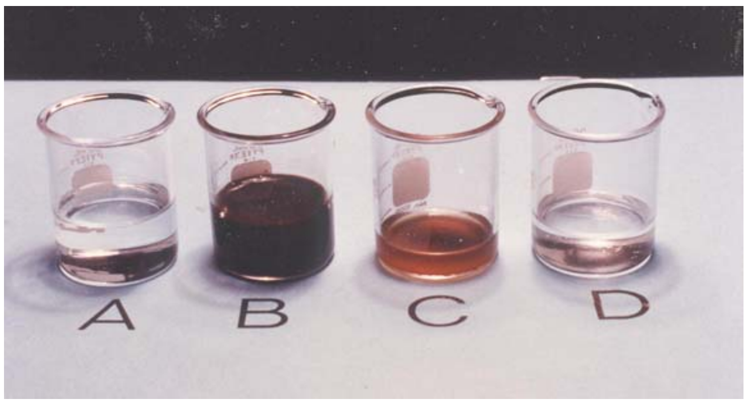


Fig. 11. Products of 3-stage magnetostatic coalescence

Examples of Multistage Processing

Tests were carried to demonstrate the applicability of the coalescer to dewatering a California light crude oil.

Demulsification of High Water Content Crude Oil

The crude oil, collected at the well head, contained 75.37% water and had a magnetic susceptibility was -0.83×10^{-6} cm^3/gm.

The crude oil was treated with 305 ppm dewatering Silwet® L7602. Water containing a small amount of impurities (particulates and a hydrocarbon fraction) was immediately separated from the oil without exposure to a magnetic field. The resulting oil contained 17.13% water and the magnetic susceptibility was -0.84×10^{-6} cm^3/gm. The water separated in this operation had a magnetic susceptibility of -0.78×10^{-6} cm^3/gm and a specific gravity of 1.03.

Iron lignosulfonate was mixed with this oil to produce an emulsion containing 73.44% dry crude oil, 23.54% water, 3.01% dry iron lignosulfonate and 0.008% Silwet® L7602. This emulsion was processed at ambient temperature of 25°C through a coalescer containing seventy (70) 0.044-inch diameter magnetic rods as shown in Figures 2 and 3. A retention time of 4.5 minutes was employed. The magnetic field strength was 800 Gauss. The water content and magnetic susceptibility of overflow samples collected at various times after initial spill over are shown in Table VII.

Table VII
Water Content and Magnetic Susceptibility of
California Light Crude Oil (17.13 % water)Treated by Coalescer
H = 800 Gauss, Retention Time = 4.5 Minutes

Sample Collection Time (Minutes)	**Water Content (wt.%)**	**Magnetic Susceptibility (10^{-6} cm^3/g)**
7	0.96	10.24
14	1.19	12.07
21	1.46	18.18
28	1.36	15.57
35	1.26	13.04

Magnetostatic coalescence of crude oil using the coalescer and Silwet® L7602 as the destabilizing surfactant can prepare dehydrated crude oil which has the same levels of water content as do emulsions prepared from light mineral oil which are processed using Merpol® as the destabilizing surfactant. It is important to note that the magnetic demulsification was carried out at ambient temperature, 25°C. No elevated temperature was employed, as is common in electrostatic demulsification.

Demulsification of Low Water Content Crude Oil Using HGMS

The product of the coalescer treatment described in the section above which contained Silwet® L7602 was further processed in a field assisted settler to prepare a low water content emulsion to be treated by HGMS. The emulsion contained nominally 99.42% California crude oil, 0.54% water, and 0.046% dry iron lignosulfonate. This emulsion was processed through an HGMS unit operating at 1680 Gauss. The retention time was 8 minutes. The water content levels and magnetic susceptibilities of samples collected at various times after the initial spill over are given in Table VIII.

Table VIII
Water Content and Magnetic Susceptibility
of 0.54 % water California Crude Oil Treated by HGMS
at 1680 Gauss with 8 Minute Retention Time

Sample Collection Time (Minutes)	Water Content (wt.%)	Magnetic Susceptibility (10^{-6} cm^3/g)
1	0.063	-0.89
9	0.059	-0.89

These tests illustrate that magnetostatic coalescence can prepare refinery quality feedstocks from high water content California crude oil.

Magnetostatic Coalescence of an Oil in Water Emulsion

Emulsions of the OL/W type (organic liquid in water) made from mineral oil and heptane were broken in a batch coalescer cell. Approximately 30 cc of emulsion was used for each study.

The OL/W emulsions used are significantly different from W/OL emulsions containing iron lignosulfonate in several ways. First, the iron naphthenate 6% is at least two orders of magnitude less magnetic than hydrophilic iron lignosulfonate. Secondly, mixtures of several emulsifiers (Tween® 95, T-Det® N40 and Span® 80) were employed to create stable magnetic emulsions. As was the case with W/OL emulsions, after an emulsion is broken, the water moves to the bottom of the cell because of its higher density. Unlike the W/OL emulsions, however, the magnetic susceptibility is observed to increase in the organic liquid phase after coalescence because the magnetic additive is organic liquid soluble.

An emulsion was prepared containing water, heptane, iron naphthenate 6%**,** and oleophilic surfactants, Tween® 95, T-Det® N40 and Span® 80. The emulsion contained 61% water and had a magnetic susceptibility of 0.19×10^{-6} cm^3/gm. The emulsion was placed in a field of 10,000 Gauss for 80 minutes.

Upon removal from the magnetic field, a water/heptane interface was observed. The top and bottom layers were removed separately and analyzed. The water content of the top layer had decreased to 53.9% and the magnetic susceptibility had increased to 0.28×10^{-6} cm^3/gm, while the water content and the magnetic susceptibility of the bottom layer were measured as 83.5% and -0.5×10^{-6} cm^3/gm, respectively.

The effect of magnetic field strength was measured for an emulsion prepared from mineral oil, water, iron naphthenate 6%**,** and oleophilic surfactants, Tween® 95, T-Det® N40 and Span® 80. The initial emulsion contained 76% water and had a magnetic susceptibility of 0.19×10^{-6} cm^3/gm.

The emulsions were exposed to magnetic fields of 3,000, 5,000, and 10,000 Gauss for 20 minutes and allowed to settle for 20 minutes, whereupon the top 1/3 of the coalescer cell was removed and analyzed. The results, given in Table IX, show an increase in the magnetic susceptibility of the top portion of the emulsion and a decrease in water content as expected. The data indicate that the emulsion is being broken by a magnetic field and show that the degree of breaking increases with the magnetic field strength.

Table IX
Effect of Magnetic Field Strength on Magnetic Susceptibility and Water Content of Mineral Oil Separated from an Emulsion Containing Iron Naphthenate 6%

Magnetic Field (Gauss)	**Final Water Content (%)**	**Magnetic Susceptibility (10^{-6} cm^3/g)**
3,000	72.9	.27
5,000	71.8	.34
10,000	72.6	.42

Conceptual Process

The operations described above can be incorporated into a comprehensive process for treatment of mixtures of immiscible liquids of a wide variety of characteristics. The resulting process consists of the unit operations of mixing, coalescence, polishing, and additive recycle as shown in Figure 12 for the case of a water-in-hydrocarbon liquid emulsion. In the mixing operation makeup surfactant and a magnetic additive are mixed with the raw feed. The emulsion is then fed to the coalescence operation employing the continuously operating coalescer, and then, if needed, to a "polishing" operation. The magnetic additive is recovered from the underflow from the continuously operating coalescer and the polishing operations. A portion of the surfactant may exit with the water, salt, and corrosives.

By adjusting flow rate, magnet field strength, and magnet configuration, the process has been shown to remove more than 99.9% of the water at hydrocarbon recoveries typically greater than 99%. The polishing stage is used when it is necessary to produce dehydrated products with water content in the ppm range or when the last vestiges of the magnetic additive are to be removed from the product. The polishing stage may consist of additional continuously operating coalescer units, field assisted settlers, high gradient magnetic separation (HGMS), or other non-magnetic means.

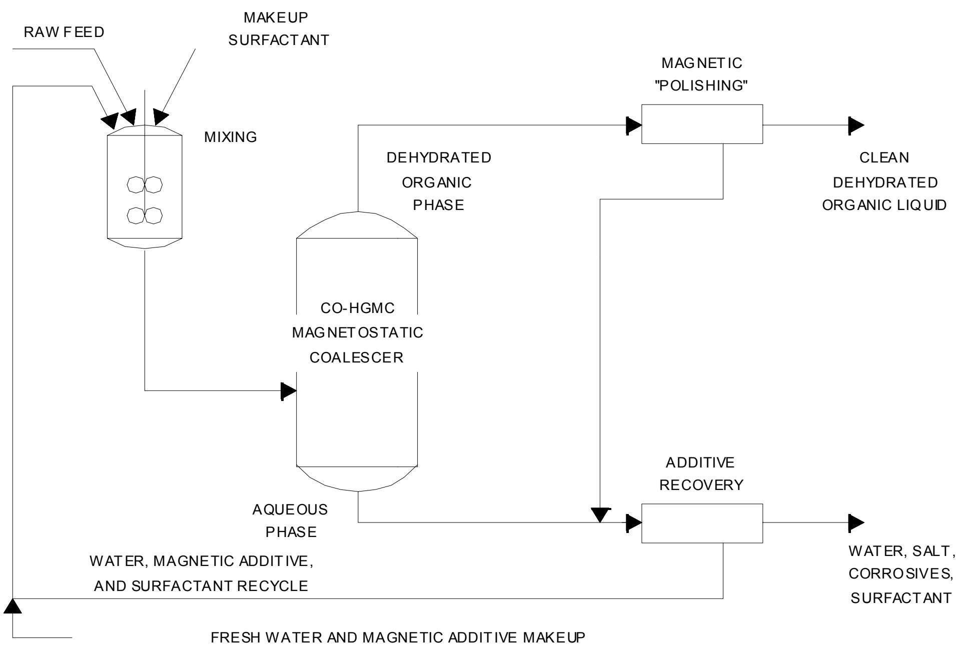


Fig. 12. The MagneCoal process for treating immiscible liquids of water in organic carrier fluids

Magnetostatic coalescers can be used to break emulsions of the water-in-oil or the oil-in-water type. When water miscible liquids form the internal phase, iron based lignosulfonate has been used to impart magnetism to the hydrophilic component. Various hydrophobic ferrofluids can be employed in processing oil-in-water emulsions. A surfactant may also be used to prevent flocculation and to promote rapid coalescence of the internal phase droplets in a magnetic field. The magnetic additive is recovered for reuse

Magnetic Additive Recovery For Recycle

In the laboratory work the iron lignosulfonate was recovered by thermal drying. In an attempt to develop an alternative approach, a magnetic method was employed to shear the water off the lignosulfonate.

Magnetic Fractionation of Iron Lignosulfonate. In a test of magnetic recovery of iron lignosulfonate, 1.459 grams of dry iron lignosulfonate were mixed with 92.573 grams water to make a mixture of 1.55 wt.% iron lignosulfonate and 98.45 wt.% water, simulating a dilute underflow from the coalescers from which iron lignosulfonate is to be recovered. The magnetic susceptibility of the dry additive was 9463×10^{-6} cm^3/gm.

This mixture was pumped through a matrix of fine grade ferritic stainless steel wool magnetized at 20,000 Gauss. The flow rate through the matrix was 6 cm^3/min. The "non-magnetic" product contained 0.755 grams dry iron lignosulfonate and 85.045 grams water. The magnetic susceptibility of the "non-magnetic" product was 1217×10^{-6} cm^3/gm. This represented 50.64 wt.% of the dry iron lignosulfonate in the feed and 91.85% of the water in the feed. Thus 49.36% of the dry iron lignosulfonate in the feed remained in the "magnetic" fraction contained in the separation matrix. This fraction contained 8.15% of the water in the feed. The magnetic susceptibility of the dry iron lignosulfonate in the "magnetic fraction" was 17380×10^{-6} cm^3/gm.

The iron lignosulfonate employed consists of a distribution of molecular moieties with differing magnetic susceptibilities. HGMS has been used to separate strongly magnetic iron lignosulfonate from large amounts of water. Various methods are available for its removal from the unmagnetized HGMS filter bed which do not add water to the recycle iron lignosulfonate. These include rinsing with gases such as compressed air or with an organic liquids.

POTENTIAL APPLICATIONS

Magnetostatic coalescence has the potential to be applied to many novel applications as shown in Table X. It may be used to replace or augment electrostatic coalescence now used in petroleum refining; it may be used in the recovery of the oil phase of OL/W emulsions produced in enhanced recovery operations in oil fields; it is especially useful in processing high water and salt content crudes; and it may be developed as a new approach to emulsion contactors for use in several innovative applications. Noteworthy among these applications is caustic washing to desulfurize and remove organic acids from gasoline feedstocks; alkylation in petroleum refining; removal of impurities from the products of chemical reactions; and selective protein recovery from fermenter broth in bioprocessing applications.

The method is applicable to breaking emulsions of high solids content and may handle thermally unstable and complex organic materials which now pose problems for solvent extraction in the biotechnology area. The magnetostatic coalescence method may also allow the use of more stable emulsions in liquid membrane technology.

Table X
Potential Applications of Magnetostatic Coalescence

Industry	Application
Petrochemicals	Dehydration & desalting of crudes
	Mixed liquid processing
	Purification
	Waste minimization
	Solids stabilized emulsions
Pharmaceutical & Bioengineering	Fermenter broth extraction
Chemicals & Minerals	Chemical & heavy metal separation
	Liquid membrane
Environmental	Solids stabilized emulsions
	Removal of hydrocarbon solvents
Fuels	Fischer-Tropsch
	Demisting

Especially noteworthy is an adaptation of the technology for recovery of sub-micron sized iron catalyst particles employed in Fischer-Tropsch treatment of syngas, CO and H_2, produced in coal gasification. The magnetostatic technology has been tested in this application[2] and extended to a high throughput method for separation of ultra fine particles from viscous flows (patent pending).[3] Figure 13 is a photograph of a nominal 50 BBL per day test unit for separation of submicron sized iron catalysts from Fischer-Tropsch wax.

Fig. 13. 50 BBL Test unit for recovery of sub-micron iron catalysts from Fischer-Tropsch wax

CONCLUSIONS

- Emulsions can be broken using magnetic additives and magnetic fields.
- Surfactants play an important role in lowering interfacial tension and destabilizing the interfacial film. Practical concentration of ferrofluids such as iron lignosulfonate are adequate for most applications.

- Destabilizing surfactants for use in a magnetic field are available.

- Magnetic fields of the order of a few hundred gauss are sufficient to achieve $90^{+}\%$ separation of water from W/OL emulsions of interest. Practical levels of the magnetic field are adequate.

- Retention times required in the magnetic method are very low compared to those in conventional electrostatic coalescers.

- A microcell method has been demonstrated to guide choice of surfactants for the application. A description of this method will be published elsewhere at a later date.

- Magnetostatic demulsification can be applied to a wide range of applications.

Results achieved to date are summarized in Table XI.

Table XI
Coalescence Data
Feed: 80.08% Mineral Oil, 16.43% Water
3% Dry Iron Lignosulfonate, 0.16% Emulsifier K, 0.33% Merpol® A

	Magnetic Susceptibility (10^{-6} cm^3/g)	**Water (wt.%)**	**Oil Recovery wt.%**
First Stage Coalescer Output	+10.8	0.81	99.993
Field Assisted Settler Output	+.32	0.11	99.9996
HGMS Output	-0.88	0.008	99.998
Overall		**0.008**	**99.99**

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