

### Using V $\diamond$ SEP to Treat Desalter Effluent

An effective and economical solution

New Logic Research has developed an innovative and rugged Ultrafiltration Membrane System for the treatment of desalter effluent. In the past, desalter effluent has been something that a refinery has just put up with and tried to manage as best it can. Now by utilizing the proprietary VSEP Filtration System, desalter effluent can be treated and mitigated at the source.

#### Crude Oil Basics

Crude oils are complex mixtures containing many different hydrocarbon compounds that vary in appearance and composition from one oil field to another. Crude oils range in consistency from water to tar-like solids, and in color from clear to black. An “average” crude oil contains about 84% carbon, 14% hydrogen, 1%-3% sulfur, and less than 1% each of nitrogen, oxygen, metals, and salts. Refinery crude base stocks usually consist of mixtures of two or more different crude oils.

Crude oils are also defined in terms of API (American Petroleum Institute) gravity. A crude with a high API gravity are usually rich in paraffins and tend to yield greater proportions of gasoline and light petroleum products. Crude oils that contain appreciable quantities of hydrogen sulfide or other reactive sulfur compounds are called “sour.” Those with less sulfur are called “sweet.”

All crude oils are assayed and valued depending on their potential yield. Crude Oil with low assay numbers is referred to as “Opportunity Crude”. This type of oil will be more difficult to process due to higher levels of contaminants and water. This type of crude will typically give desalter equipment the most trouble and require the greatest skill of the operator.



#### Desalting - The First Step in Crude Oil Refining

Desalting and dewatering of crude oil upstream of the crude distillation unit is a key process operation for the removal of undesirable components from crude oil before it reaches any of the major unit operations. The operation of a desalting system can be very challenging due to changing process variables. At best, it is a process of measuring trade-offs and compromises.

A delicate balance must be maintained while controlling mixing intensity, wash water quality, chemical demulsifier feed and other parameters that can provide optimal salt removal. On one hand the quality of the crude overflow must be within specific standards and on the other hand the under-carry must not be so potent that it compromises the system’s dehydration abilities or fouls up downstream wastewater treatment. New legislative demands placed on effluent water quality present the operator with a difficult challenge. Optimizing the desalting process under

constantly varying conditions is a key ingredient to success of the entire refinery operation. The main function of the Desalter is to remove salt and water from the crude oil. However, many other contaminants such as clay, silt, rust, and other debris also need to be removed. These can cause corrosion and fouling of downstream equipment. Also, there are metals that can deactivate catalysts used in the process of refining.

#### Desalter Theory

The Desalter removes contaminants from crude oil by first emulsifying the crude oil with chemicals and wash water to promote thorough contact of the water and oil. The salts containing some of the metals that can poison catalysts are dissolved in the water phase. After the oil has been washed and mixed as an emulsion of oil and water, demulsifying chemicals are then added and electrostatic fields are used to break the emulsion. Desalters are sized to allow the water and oil to settle and separate according to Stoke’s Law.

In addition, solids present in the crude will accumulate in the bottom of the desalter vessel. The desalter must be periodically washed to remove the accumulated solids.

A "mud washing" system is installed in the bottom of the vessel to periodically remove the solids. Mud washing consists of recycling a portion of the desalter effluent water to agitate the accumulated solids so that they are washed out into the effluent water. These solids are then routed to the wastewater system.

Desalter effluent or undercarry is a combination of many things including the mud wash done at periodic intervals, produced water that came with the crude, and the brine wash water resulting from the dilution and removal of salts and other contaminants.

**Desalter Process**

To accomplish desalting, the crude is first preheated to 120°-150° with heat exchangers in order to reach the required viscosity level normally in the range of 5-15 centi-stoke.

The temperature is limited by the vapor pressure of the crude-oil feedstock. About 2-6% wash water is metered in ahead of the desalter as an extraction agent in addition to emulsifying agents to help dissolve salts and sediments. Intense mixing of the crude, wash water, and chemicals then takes place over a mixing valve.

Once in the pressurized desalter vessel, the salts and sediment settle with wash water and tend to form emulsions. The wash water is separated by electrostatic precipitation using high voltage and de-emulsifiers and acid. The salts that are removed are mainly chlorides and carbonates. They can cause corrosion

and fouling downstream in the heat exchangers, furnaces, and distillation units, if not removed. Electrical desalting is the application of high-voltage electrostatic charges to concentrate suspended water globules in the bottom of the settling tank. Surfactants are added only when the crude has a large amount of suspended solids.

Other less-common processes involve filtering heated crude using diatomaceous earth and chemical treatment and settling. Ammonia is often used to reduce corrosion. Caustic or acid may be added to adjust the pH of the water wash.

Wastewater and contaminants are discharged from the bottom of the settling tank to the wastewater treatment facility. The desalted crude is continuously drawn from the top of the settling tank and sent to the crude distillation tower. A properly performing desalter can remove about 90% of the salt in raw crude.

**Refinery Wastewater**

The desalter effluent is a major source of contaminated wastewater and a source of hydrocarbons as oil under carry to the extent that emulsions are not completely broken. Oil under carry can be the single largest source of oil losses to the wastewater treatment system. Reduction in the amount of Oil in the undercarry not only reduces sewer loadings but also recovers valuable raw material that would otherwise be lost. Rates vary with the water content of the crude oil and the degree of difficulty in desalting the crude, but a representative rate would be around 2-2.5 gallons of wastewater per barrel of crude oil feed to the unit. Desalter water contains salt, sludge, rust, clay, and varying amounts of emulsified oil (oil under carry). Depending on the crude oil source, it may or may not contain significant levels of hydrogen sulfide (H<sub>2</sub>S), ammonia, and phenolic compounds. Relatively high levels of suspended and dissolved solids are usually observed.

Refinery Process	Wastewater Description	Waste Byproducts
Storage Tanks	Crude Oil comes with a considerable amount of water. During storage of the crude, this water settles in the storage tanks and is periodically drained off.	Sulfides, Salts, TDS, and Oil
Desalting Unit	The Desalting process produces salt water from the washing of the crude oil. The undercarry from the desalter contains the produced water that came with the crude as well as wash water which is added prior to dealing to dilute and remove contaminants	Chlorides, Carbonates, Sulfides, and Oil
Distillation	Oily sour water is drained from the "knock-down" sump vessels of the fractionators.	Sulfur and Ammonia
LPG Caustic Washing	In the liquid petroleum gas caustic wash unit, caustic caustic is added to convert Sulfur (H <sub>2</sub> S) to Sodium Di-Sulfide (Na <sub>2</sub> S)	High Sulfides
Cooling Tower Blowdown	Water used for cooling is recirculated in a closed loop. Water drained as "blow-down" to maintain acceptable temperature and dissolved solids levels.	Corrosion Inhibitors, TDS
Miscellaneous	Other wastewaters are produced from wash down of operations, boiler blowdown, MEK de-waxing, and Propane De-asphalting	Propane, Methyl Ethyl Ketone, TDS, Oil and others

Sources of wastewater during the refinery process

### Process Variables

#### Affecting Desalter Performance

Crude Oil Quality
Crude Oil Feed Rate
Temperature, Viscosity, and Density
Electrical Field Intensity
Wash Water Quality
Wash Water Feed Rate
Emulsifiers Rate
Water Level Control
Emulsion Layer Thickness
Demulsifier Rate
Mud Washing Technique
Brine Recycling Process

#### VSEP Membrane Filtration - Enabling Technology for Desalter Effluent

The most fundamental process in a refinery operation that of separation. Since the desalter is the first step in refining of crude oil, a bottleneck at the desalter is a bottleneck for a billion-dollar refinery asset. In addition, the desalter will be the predominant source of wastewater in a refinery and an upset in the desalter can cause upsets in the wastewater treatment plant and put that system at risk of not meeting discharge requirements. The current methods of desalter operation are focused on coping and adjusting with the variations in process variables that are inevitable. The treatment method involves a crude gravity separator combined with chemical manipulation and operator expertise. This process is antiquated and less than desirable from a redundancy and processing point of view.

The VSEP polymeric membrane filtration process offers an innovative, precise, and utterly redundant separation technique for crude oil refining and processing. In addition to enabling a range of very fine selective separations,

use of membrane filtration results in reduced capital, chemical, operating, and energy-consumption costs. The potential for economic benefit to the user industry is revolutionary.

Crude oil refiners facing global competition are looking for new technologies for product manufacturing that can improve operations performance, reduce operating costs, and stem pollution problems before they occur. Conventional separation processes have been around for many years and have been optimized to the greatest extent possible. With new regulations on emissions, demand for high product quality, and burgeoning energy costs, traditional separation methods cannot achieve the purity or efficiency levels required for today's market. Innovative separation technologies are needed for this changing environment.

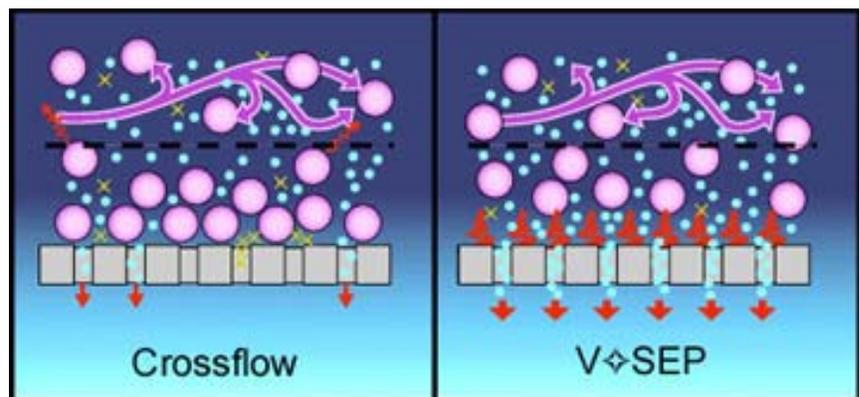
Polymeric membranes have continually evolved from their initial use as water purification and laboratory devices. Thousands of patents have been filed in recent years having to do with the polymer chemistry of membranes or the method of delivering the membrane filtration process. Approximately 50 U.S. companies are involved in the \$2.5 billion worldwide market for membrane

materials and modules. Through the innovations in membrane chemistry and design, membrane filtration technologies will establish a leadership role in the chemical processing market. Recent advancements including the invention of Teflon, Kynar, and inorganic membranes have made their use practical even for the most aggressive chemical environment.

#### The VSEP Technology

Historically, membrane manufacturers have utilized tangential or crossflow filtration to reduce solids loading of the membrane. In this method, the feed material is pumped at high velocity into the system. This creates shear forces at the surface of the membrane. However, these forces were economically limited. This has restricted crossflow type filtration to low viscosity, watery materials.

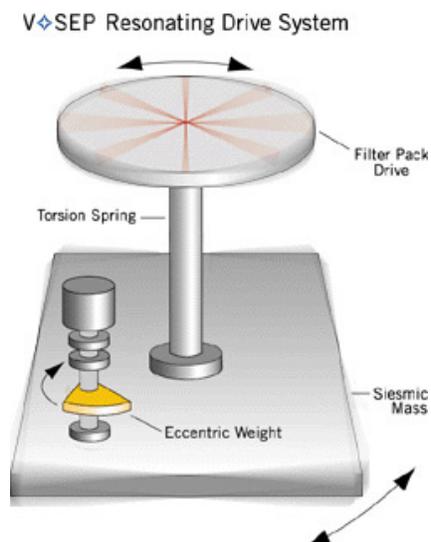
In order to overcome these limitations, a vibrating membrane system called VSEP was created by New Logic of Emeryville, California. Rather than simply preventing solids loading by pumping at high velocity, VSEP eliminates membrane blinding by vibrating the membrane surface at extremely high frequency. This vibration produces shear waves that



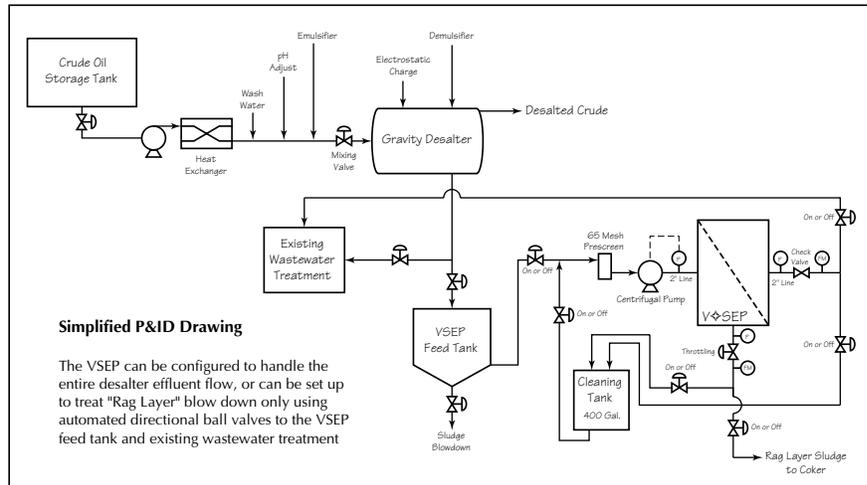
Vibration of the membrane surface prevents colloidal fouling

propagate sinusoidally from the surface of the membrane. This increase in the shear energy produces 5-15 times higher rates of filtration and also, makes membrane separations possible for very concentrated or viscous materials, like desalter effluent.

The industrial VSEP unit contains hundreds of sheets of membranes, which are arrayed as parallel disks separated by gaskets. The disk stack is contained within a fiberglass reinforced plastic cylinder (FRP). This entire assembly is vibrated in torsional oscillation, similar in principle to the agitation of a washing machine. VSEP can produce extremely high shear energy at the surface of the membrane. The membrane module is attached to a spring assembly and moves at an amplitude of 7/8" peak-to-peak displacement. The membrane module oscillates at between 50 and 55 Hz. The fluid is gently pumped through the module while a highly focused shear zone at the surface of the membrane is created by the resonating oscillation. Rejected solids at the membrane surface are repelled by the shear waves and are washed away becoming more and more concentrated until the reject exits the



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### Typical VSEP Process Diagram for Desalter Effluent

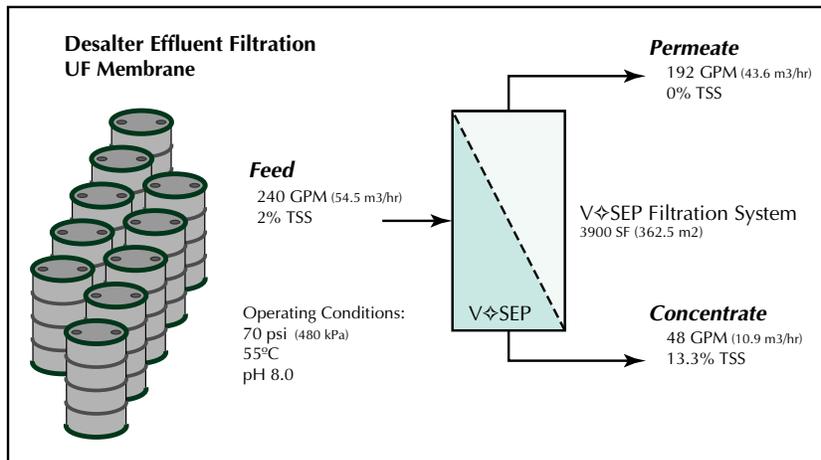
An AC motor controlled by a variable frequency speed controller provides the resonant excitation that produces the vibration. The motor spins and eccentric weight coupled to the seismic mass. Since the eccentricity of the weight (i.e., its center of mass lies heavily on one geometric side) induces a wobble, the Seismic Mass begins to move as the motor speed increases. This energy is transmitted up the torsion spring inducing the same wobble in the filter pack, however 180° out of phase. As the motor speed approaches the resonance frequency, the amplitude of the moving filter pack reaches a maximum. The resonant frequency vibration employed by VSEP is extremely energy efficient.

### VSEP Desalter Treatment Process Options

A process schematic for treatment of a typical desalter effluent process using a VSEP system is presented in the figure above. There are a number of possible scenarios for filtration. During the evacuation of the desalter undercarry, the settled solids will be washed out of the system to prevent build up. When

this happens some of the rag layer emulsion comes with it. This blow down is what can give conventional chemical wastewater treatment plants trouble. The VSEP can be set up to handle the entire flow of the desalter effluent including both the briny salt water as well as the modulating rag layer blowdown. Or, by using automated valves, the VSEP can be configured to handle only the rag layer blow down.

If the VSEP will handle the entire desalter effluent flow, the desalter is set to a continuous mud wash process to even out the solids loading in the feed to the VSEP. Then the VSEP will dewater this effluent and send a concentrated sludge to the Coker. If the VSEP will only handle the rag layer blowdown, the mud wash operator controls destination valves accordingly. While the desalter is just draining salt-water effluent, the waste will be sent to the existing treatment plant. Then just prior to a mud wash, destination valves will configure to feed the desalter effluent to the VSEP. After the mud wash, the valves revert back to the original position feeding the wastewater treatment plant.



**VSEP Block Diagram for Desalter Effluent**

The VSEP can be constructed using a variety of membrane types. In this case, the filtrate from the VSEP would go to an existing wastewater treatment facility and the only objective is to remove suspended oil and solids to take the load off the treatment plant and prevent upsets. New Logic has over 200 membranes to choose from and can use any membrane from reverse osmosis to microfiltration and will select a membrane that meets the specifications required. VSEP can be configured using tighter membranes that would bypass the wastewater treatment plant altogether and produce water suitable for discharge.

### Case Study Process Conditions

The oily wastewater is fed to the VSEP treatment system at a rate of 240 gpm. The VSEP system will monitor tank level and will adjust based upon demand. The VSEP feed tank acts as a primary settling tank. It is cone bottomed and heavy solids settle quickly where they are purged. The feed to the VSEP is taken out of the side of the tank to eliminate excessive maintenance cleaning of a protective 60 mesh pre-screen to the VSEP. As the system initiates, a feed pump will spin up to a pressure of 70 psig. Then a modulating

valve will throttle the flow of the reject to a rate that will produce the desired concentration of suspended solids. Three industrial scale VSEP units, using ultra-filtration membranes are used to treat the 240 gpm process effluent. The concentrated reject stream is at a concentration of about 13.3% TSS and is sent to the Coker for recovery of the oil and hydrocarbons. VSEP generates a permeate stream of about 192 gpm which is sent on to the existing wastewater treatment plant. The permeate contains less than ~ 1 mg/L

of total suspended solids (TSS). Membrane selection is based on material compatibility, flux rates (capacity) and concentration requirements. In this example, the TSS reduction is well over 99% while the oily waste is concentrated from a starting feed of 1.5-2% to a final concentrate of 13.3% by weight.

### Use of VSEP Oily Sludge as Coker Feedstock

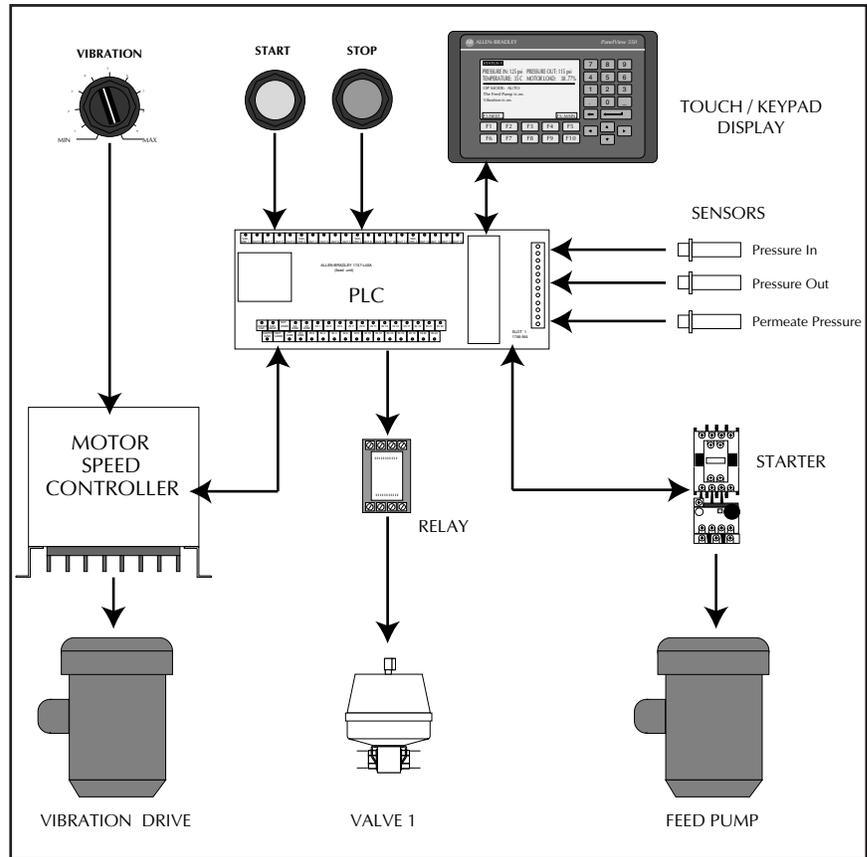
Refineries that have Coker operations can consume quantities of oil bearing waste and residual streams as Coker feedstock without affecting petroleum coke product quality. Oil-containing VSEP sludge can be used as Coker feedstock as a method to dispose hazardous waste and also to recover the oil. Other sludge sources that have been successfully fed to a Coker unit include exchanger bundle sludge, filter cake from tank cleaning, primary treatment sludge, oil emulsions, and slop oil emulsion solids. Coke product specifications are typically the limiting factor in determining how much of this material can be processed.



**700,000 gpd VSEP Ultrafiltration Membrane System**

### VSEP - An Engineered Solution

The VSEP membrane filtration system has been designed specifically for the chemical-processing user. The systems are completely automated, compact, and reliable. With very few moving parts, maintenance is simplified. Each VSEP system built is custom designed for a particular application with special materials of construction including exotic alloys and thermoplastics to fit the job. The VSEP is a complete integrated Plug and Play process requiring only process in and process out connections during installation. The system is controlled using a sophisticated Allen Bradley Industrial Computer that monitors data and implements the program functions in a seamless and automatic process. The VSEP controls are compatible with plant Distributed Control Systems (DCS) and can be operated as stand-alone devices or as a component of a much larger process



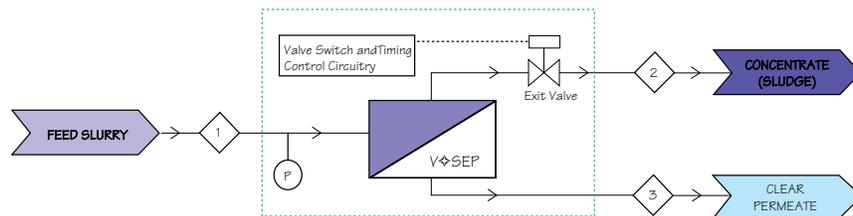
VSEP Control Scheme Block Diagram

One of the most important considerations in plant design or in considering upgrades to an existing process is the footprint of the system considered. VSEP membrane systems are inherently small in footprint and being modular can be rearranged to fit irregular shapes and areas available. Most of the time, VSEP can be installed without any modifications to the building or structure. The VSEP is able to use space very efficiently due to its intrinsic vertical design and lack of need

for pre-treatment or other ancillary equipment. A typical system will have a pumping and piping interface skid that is approximately 60 SF. Then VSEP modules are installed in parallel or in series that are 4' by 4' in footprint size. A typical VSP system can be installed in a small room. When compared to evaporators, clarifiers, or filter press units, the VSEP can result in dramatic construction cost savings for the new

facility improvements needed to house the system.

New Logic will assist in the complete process design from start to finish. A well thought out plan is key to a successful operation. New Logic's staff of chemical, mechanical, and electrical engineers participate in the project design for a comprehensive engineered solution. The typical project development occurs in the following stages:



### Precise Membrane Filtration with Automated Controls

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- Phase 1 Project Feasibility Study
- Phase 2 Project Conceptual Study
- Phase 3 Preliminary Engineering
- Phase 4 Detailed Design & Procurement
- Phase 5 Construction
- Phase 6 Start-up



New Logic has a very comprehensive Pilot Testing Program

The permeate quality from the VSEP can be controlled through laboratory selection of membrane materials available to fit the application parameters. Successful pilot tests have been conducted at New Logic for many kinds of oily wastewater treatment. Depending on process temperatures, membrane selection and the



VSEP installed at a Volkswagen Plant for Coolant Recovery

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requirement for solids concentration or BOD/COD removal for effluent streams, the permeate flux rate in the VSEP can range from 15 to over 150 gallons per day per square foot (GFD).

### Other VSEP Applications

New Logic has a great deal of experience when it comes to desalting and has installed industrial equipment for similar industrial applications including the desalting and diafiltration of Carbon Black, Iron Oxide, Chromium Blue Pigment, Methyl Cellulose, Polyvinyl Acetate, and other polymers and pigments.

In addition, New logic has installed equipment for other oil/water and oil/solids separations including:

- Filtration of Used Crankcase Oil
- Dewatering of oily wastewater from haulers
- Recycling of oil based coolants
- Produced Water Filtration
- Glycol Recovery
- Tank Bottoms Treatment
- Tank Washdown Water
- Truck and Bus Washwater

### Benefits of VSEP when used for Desalter Effluent

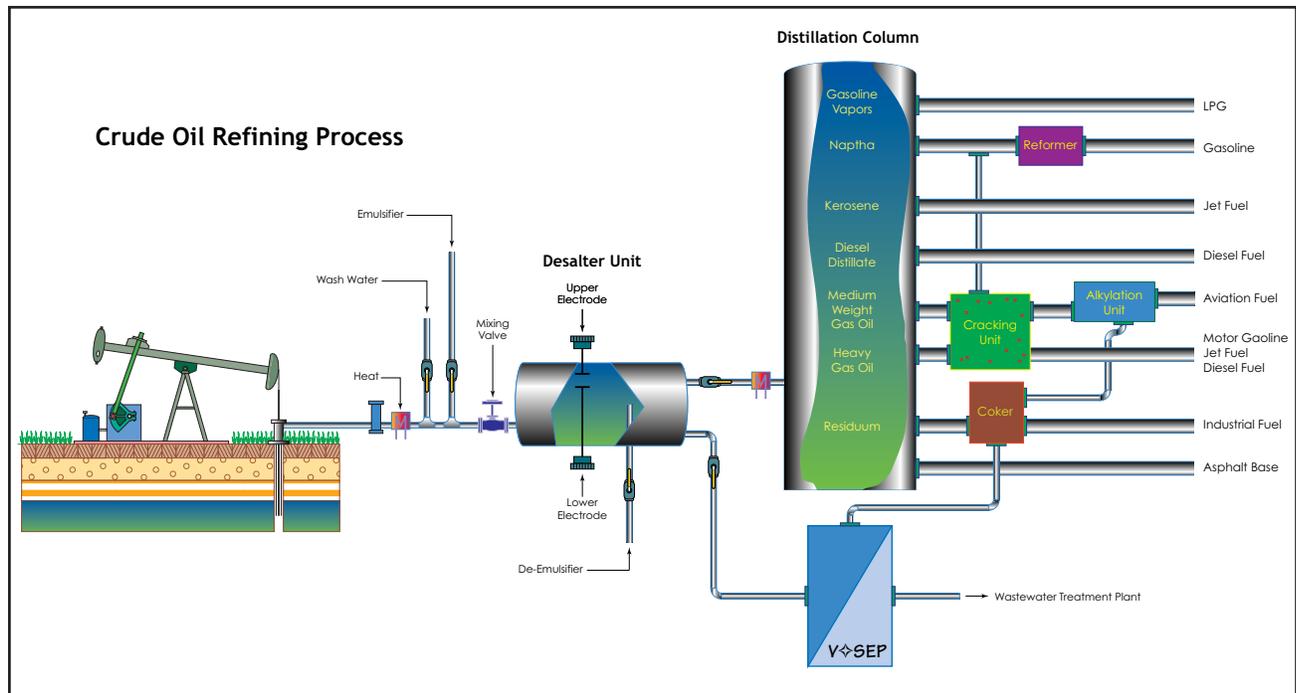
#### Redundancy

The VSEP is installed as a side stream to the desalter effluent. It is used on a demand basis and will initiate automatically based upon tank level. It offers many kinds of redundancy options in operation that are very important to refinery operations. First, the VSEP system can be bypassed completely if desired and the desalter effluent will be treated in the same manner as it is now. Or the VSEP can handle the entire desalter flow and help to take the load off of the existing wastewater treatment, thus increasing its capacity and safety margin when it comes to discharge. VSEP units are modular and easy to install in parallel for complete redundancy



VSEP installed for Used Crankcase Oil Filtration & Recycling

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### VSEP Advantages

#### Debottleneck the Entire Refinery

Since the desalter is the first step in refining of crude oil, it is critical that this piece of equipment be consistent and reliable. Because oil is superheated and pressurized during refining, it is not a process that you can just turn off with a switch. Shut downs can take hours or days to complete. In addition, the profitability of the refinery depends on getting maximum use out of the refinery asset and personnel on staff. Process upsets cannot be tolerated. The desalter has been identified as a very significant threat for bottlenecking the entire refinery operation including the refining of oil and the wastewater treatment that comes from it. Installation of VSEP can mitigate or eliminate the possibility of desalter bottleneck. VSEP is a redundant and effective tool that can be used to reduce process risk.

#### Skill of the Operator

The rag layer blow down is the primary cause of process upsets and the manipulation of this process requires a very skilled operator or group of operators who cannot afford to make mistakes. The normal salty water discharge from the desalter is relatively benign and can be handled easily by existing processes. The fact that the quality of the crude changes and that the blow downs are done at specified intervals means that this process is a constant game of tweaking and cajoling. Installation of the VSEP with the set purpose of processing the problematic rag layer blowdown removes this process headache from the effluent operator's daily chores. When VSEP is installed, the frequency of blowdown, the effectiveness of the demulsifiers, and the variations in the crude are unimportant and no longer pose a process upset threat.

#### Reduce the Load on the Existing Wastewater Treatment Plant

The desalter can be the primary source of wastewater to the wastewater treatment plant. The desalter operator must constantly be careful about the discharge of the desalter so that the treatment plant is not overloaded or unable to handle the hazardous materials that come from the desalter. Sometimes this can mean lesser quality desalted crude is produced as a trade off to not swamping the treatment plant. Desalter effluent is the primary source of oil to the treatment plant. Many times the existing wastewater treatment plant is at capacity and the amount of oversize and safety factor is marginal. VSEP is a very effective tool that can be used to control the load on the treatment plant. Since the VSEP can take the rag layer blow down out of the wastewater loop and send it to the Coker, this alone reduces the load significantly. The VSEP can also be



configured to handle the entire desalter effluent further reducing the load on the treatment plant. The VSEP can also be configured to handle the desalter effluent completely and bypass the existing treatment plant. These options give process engineers ultimate ability to maximize the use and capacity of the existing wastewater treatment facility.

### Improve Desalted Crude Quality

During the desalting operation, the operator will attempt to perform a separation of contaminants in the oil including water, salts, and suspended solids. While doing this he will attempt to maximize the yield of crude oil from each barrel. Unfortunately, this cannot be a perfect separation and some amount of contaminants will move forward with the crude oil. Also, some oil will go out with the wastewater. This is a balancing act done everyday and adjustments are made constantly to the operation of the desalter. The compromise that the operator makes is to not send too much oil out as wastewater. By doing this, more contaminants are left behind instead of being purged. When a VSEP is installed, the amount of oil in the discharge and the frequency and veracity of blow downs is not important and any oil that is sent out as wastewater is recovered by the VSEP and sent to the Coker. By doing this, the operator has more flexibility to increase the

quality of the desalted crude and reduce the amount of contaminants that move forward in the process.

### Allow for use of Opportunity Crude

Opportunity crude is a curious name for lesser quality oil that is more difficult to treat. Assays are done on oil to measure its potential value. Opportunity crude typically is purchased accordingly. Since it will cost more to process, it is priced lower on the market than higher quality crude that would have a higher yield and put less demand on the processing equipment. The decision to buy opportunity crude is basically made on whether the desalter can handle it or not. The desalter can be a rate limiting process and may dictate the types of crude that a refinery can process. By undoing the bottleneck at the desalter, installation of a VSEP system can mean that lesser grades of crude can be processed without the normal associated risk of process upsets in the desalter.

### Company Profile

New Logic is a privately held corporation located in Emeryville, CA approximately 10 miles from San Francisco. New Logic markets, engineers, and manufactures a membrane dewatering and filtration

systems used for chemical processing, waste streams, pulp & paper processing, mining operations, and drinking water applications. The VSEP technology was invented by Dr. Brad Culkin in 1985. Dr. Culkin holds a Ph. D. in Chemical Engineering and was formerly a senior scientist with Dorr-Oliver Corporation. VSEP was originally developed as an economic system that would efficiently separate plasma from whole blood. The company received a contract to produce a membrane filtration prototype, which would later be incorporated into a blood analyzer system.

Today's **Series i** (Industrial) VSEP is a full scale model and comes in sizes ranging from 100 Square Feet to 2000 Square Feet. Successful industrial VSEP systems are in place world wide including Europe, Central Asia, Southeast Asia, Australia, South America, Canada, Mexico, and of course here in the United States. After outgrowing two previous locations in the last ten years, New Logic is now located in a 40,000 square foot manufacturing building in Emeryville. The plant has extensive equipment and machinery for manufacturing nearly all the VSEP parts. Manufacturing, assembly, and testing of all equipment takes place at this site. Systems and procedures are in place and geared towards high standards of quality control and have met the acceptance criteria of stringent applications such as nuclear waste processing.

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