



## Separations Technologies to Improve Amine System Reliability: A Case Study

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Today, many refineries are finding their amine systems are struggling to handle the increased acid gas loads resulting from low sulphur gasoline and diesel production. As initiatives to increase amine and sulphur plant reliability are undertaken, it is critical that suitable filtration and separation technology is employed to remove particulate and liquid contaminants from entering the amine circuits. Marsulex Montréal Inc. operates a sulphur handling facility located adjacent to two refineries in Montréal. Hydrogen sulphide-rich amine is sent by pipeline to the Marsulex plant

where the amine is regenerated and returned to the two refineries. As part of a 50% expansion project that was completed in 2006, Marsulex Montréal Inc. chose to install the latest separations technology to reach the maximum design capacity by eliminating the particulate and hydrocarbon ingress/contamination issues that were previously reducing plant reliability due to fouling. The deployment of rich-side filtration and high-performance liquid/liquid coalescers mitigated expensive equipment replacement and saved a significant capital expense.

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## Introduction:

Today, many refineries are finding their amine systems are struggling to handle the increased acid gas loads resulting from low sulphur gasoline and diesel production. As initiatives to increase amine and sulphur plant reliability are undertaken, it is critical that suitable filtration and separation technology is employed to remove particulate and liquid contaminants from entering the amine circuits. Marsulex Montréal Inc. operates a sulphur handling facility located adjacent to two refineries in Montréal. The hydrogen sulphide laden (rich) amine solution from the various refinery contactors is gathered and transported by pipeline to the Marsulex plant for regeneration. Once regenerated, the lean amine

is returned to the two refineries' mix of contactors. The sulphur is extracted and recovered by Marsulex. Marsulex's sulphur processing facility in Montréal is one of the largest of its kind in the conventional crude oil refining industry in Canada. This facility has provided sulphur removal and compliance services to refineries in the area for more than 40 years, and has never experienced an unscheduled outage.

As part of a 50% expansion project that was completed in 2006, Marsulex Montréal Inc. chose to install the latest technology available to meet stringent requirements for plant reliability and performance.

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## Amine Contamination:

With expansions to existing refineries, the shift in crude diets to heavier and more sour "opportunity crudes" refinery amine circuits and sulphur plants are under more stress than ever before. With these increased sulphur loads, corrosion products, liquid hydrocarbons and organic acids are making their way into the amine units.

That amine cleanliness plays a crucial role in overall amine and sulphur plant performance and reliability is well known and documented. Contaminants must be reduced or eliminated to ensure reliable plant operation and environmental compliance. Refiners (and gas plants) have used different filtration and separation methods to combat the most common contaminants found in amine circuits with mixed results. What is generally accepted as good practice is that total suspended solids in an amine circuit should be kept below 1 ppmw,<sup>1</sup> and liquid hydrocarbons and organic acids must be reduced to levels as close to zero

as possible.

\* Particulate matter found in amine solutions are, generally speaking, corrosion by-products. Solid contaminants are known to stabilise foams when foaming occurs. A review of field test data from Pall's databases going back many years has shown a consistent trend – that the particle size distribution (PSD) of suspended solids is generally finer than 20 µm, with the majority of particles being found in the sub-10 µm category. This observation has been generally consistent even when total suspended solids have varied from site to site.

On the next page is a summary of amine circuit filtration data compiled from Pall's Scientific and Laboratory Services (SLS) field tests. The data is a composite of results obtained in 10 countries, from 17 refineries owned by 10 oil companies.

<sup>1</sup> Verma, Narendra; Verma, Anil; 2009, "Amine System Problems Arising from Heat Stable Salts and Solutions to Improve Performance," Fuel Processing Technology, Vol. 90, Issue 4.  
Brown, Jr, Robert L., Hashemi, Reza; 1993, "Predicting Contamination Levels of Upset Conditions in Amine

**Figure 1:**  
Composite of TSS  
Results for Various  
Amines

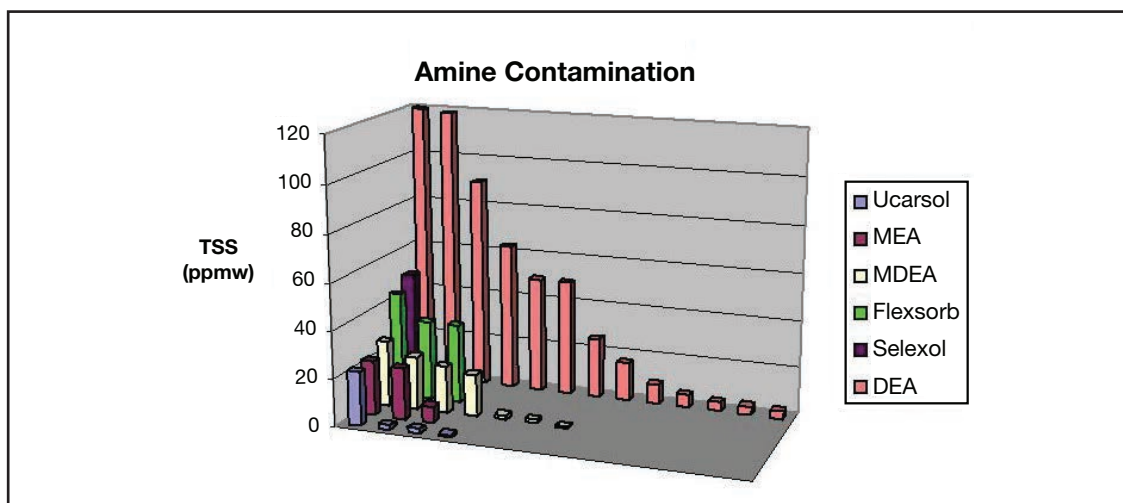


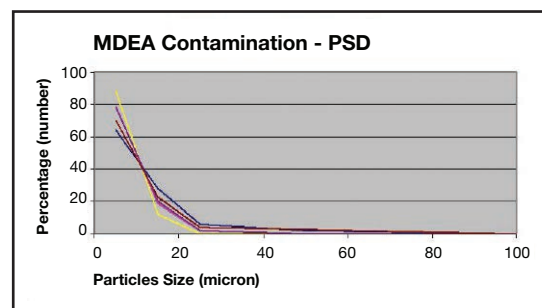
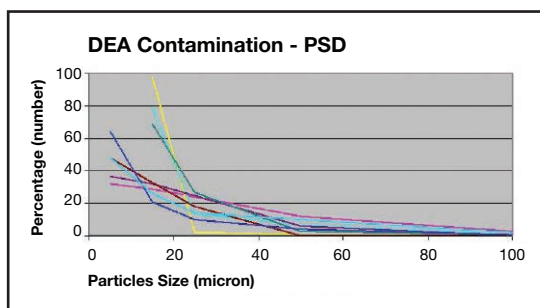
Figure 1 above shows DEA as the most sampled amine, and exhibiting the widest band of contamination – ranging from a few ppmw to nearly 120 ppmw. What is telling is that in nearly all cases, the TSS levels exceed the recommended best practice of no more than 1 ppmw suspended solids as advised in the

expert literature.

In the figures below, we see the PSD for several samplings of DEA and MDEA (Figures 2 & 3) showing that the majority of particles are sub-20  $\mu\text{m}$  in size.

**Figure 2 (left):**  
PSD for DEA  
Samples

**Figure 3 (right):**  
PSD for MDEA  
Samples



In complex refineries, ingressing liquid hydrocarbons can come from amine/LPG contactors or as condensibles in the refinery fuel gas. Typically, poor liquid/liquid contactor outlet disengagement between LPG and amine or inadequate inlet separation of free liquids in refinery fuel gas entering vapour/liquid contactors is the root cause. In complex refineries where there are multiple contactors, and when it is difficult to pin-point culprit streams, the best option is to deploy central filtration and separation as a means to eliminate free liquid hydrocarbons from the amine. High-performance liquid/liquid coalescers (Pall's PhaseSep® technology) can break the stable, rich-amine/hydrocarbon emulsion that can have adverse effects on the amine unit and sulphur plant operations, which can in turn impact overall refinery  $\text{SO}_2$  emissions.

Within the amine circuit itself, the impact would

be felt in the rich/lean heat exchangers, regenerator, re-boiler tubes, and tower trays and packing, if left untreated. The consequences can range from heat exchanger fouling, hydrocarbon ingression in the sour-water reflux discharge, increased corrosion, high amine losses due to foaming in contactors, formation of amine degradation products, and/or generation of heat stable salts.

The efficiency of the sulphur recovery unit and the converter catalyst life are also affected by carried-over hydrocarbons in the acid gas. In the event of a serious hydrocarbon carry-over episode, the consequences can be much more severe, including soot deposition in the converters, runaway hydrocarbon combustion in the Claus unit, and high  $\text{SO}_2$  emissions resulting in regulatory penalties and possibly expensive capacity reductions. In the worst cases, there might be the necessity to switch to sweeter crude slates as a mitigating strategy.

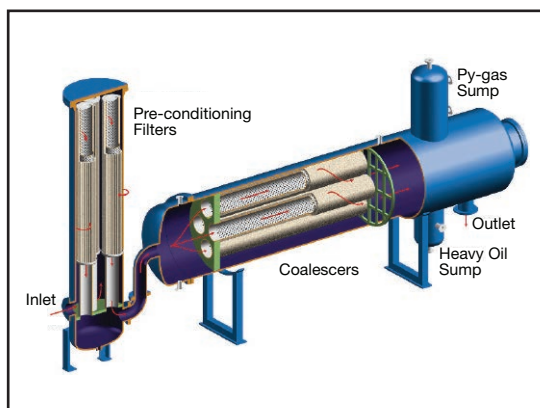
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## Rich-Side PhaseSep Liquid/Liquid Coalescer to Separate Hydrocarbons:

In the rich-amine side of the process, the proposed system will perform a dual role as follows:

- 100% Rich-Side Filtration - remove solid particles - mainly FeS corrosion products
- Eliminate the free-hydrocarbon ingress to the downstream process to near solubility levels

**Figure 4:**  
Full-Flow Rich-Side  
Filter and  
Liquid/Liquid  
Coalescer System



The PhaseSep coalescer is a multiple-stage system starting with pre-filtration (see Figure 4 below) that will remove particulate matter, provide protection, and pre-condition the feed to the coalescer. The coalescence stage that follows breaks the emulsion and allows the capture of dispersed hydrocarbon phase droplets, resulting in the separation of the two dissimilar streams. PhaseSep Liquid/Liquid coalescers operate over a wide range of conditions, including where:

- The emulsion has an IFT as low, or lower than 5 dyne/cm (PhaseSep coalescers have been applied in applications with an IFT as low as 0.5 dyne/cm)
- The dispersed phase fluid is hydrocarbon,

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There are three essential steps to achieving an efficient liquid/liquid separation:

### Stage 1: Pre-filtration

A rich-side full-flow pre-filter is essential to protect and provide maximum operating life to the liquid/liquid (L/L) coalescer. At the same time, and more importantly, 100% rich-side filtration prevents the passage of suspended solids that may deposit in downstream equipment such as rich/lean heat exchangers, column packing or trays, and re-boilers.

### Stage 2: Coalescence

The two-phase liquid emulsion enters the coalescing element and flows inside-to-outside. This is where small, suspended droplets of the dissimilar fluid come together, or coalesce, as the emulsion moves through the proprietary, specially formulated coalescer medium.

### Stage 3: Separation

The coalesced dispersed phase separates in the settling zone of the coalescer housing. Due to the density difference on the two phases, these separated liquids exit through separate drain and outlet connections at the back end of the L/L coalescer housing.

## The Marsulex Experience:

Up until 2004, the Marsulex amine unit was relatively reliable. Although the unit never had to be shut down for unplanned maintenance, its efficiency and maintenance costs were affected by amine contamination. The residence time of the flash-drum was 22 minutes on average, with a design residence time of 19 minutes. This was sufficient to handle most hydrocarbon carry-over conditions. A simple particle filter assembly was installed on a 15 - 20% kidney loop on the lean amine side. It offered partial filtration of the lean amine prior to the refiners' contactors, but no protection for the Marsulex amine unit and sulphur plant.

Following the planned 2006 expansion project, the maximum amine recirculation flow capacity would increase, and therefore, reduce the

residence time in the flash-drum. The operational residence time would be reduced to 13 minutes (at operating liquid level) or 9 minutes (at 50% liquid level). This was considered insufficient to adequately separate liquid hydrocarbon from the amine, raising serious concerns about the reliability of the plant under the new operating regime.

In preparation, Marsulex invited Pall to perform an on-site demonstration of rich-side full-flow pre-filtration and L/L coalescence. Testing performed during the fall of 2004 helped better define the level of contamination at the outlet of the existing flash-drum. The site trials also validated the effectiveness of rich-side filtration, and confirmed the efficiency of the liquid/liquid coalescer technology at separating hydrocarbons from rich-amine.

### During on-site testing, the following observations were made:

1. Even with adequate flash-drum residence time, hydrocarbon/amine emulsion remained stable, as evidenced by rich-amine samples remaining hazy for longer than three weeks (see Figure 5-B). Pall's high-efficiency PhaseSep liquid/liquid coalescer was capable of breaking and separating this emulsion in a single pass.
2. Rich-amine particulate concentrations vary substantially depending on the refinery's operating conditions at a given point in time. Using a 10µm absolute-rated filter (Beta10 µm = 5000) helped reduce

suspended solids to concentrations near or below 1 ppmw.

3. Hydrocarbon (C5 to C60) levels found upstream of the L/L coalescer pilot unit ranged from 86 to 193 ppmw, and included low levels of benzene, toluene, ethylbenzene, and xylene. Pall's PhaseSep L/L coalescer reduced overall hydrocarbon levels to near solubility in amine, based on a total extractable hydrocarbon analysis, utilizing a Horuba Oil Content Analyzer (extractive IR analyzer).

4. The average solids loading at the outlet of the flash tank (inlet of the rich-side filter) was 5 ppmw, with the lowest data point being 2 ppmw and the highest being 10 ppmw.

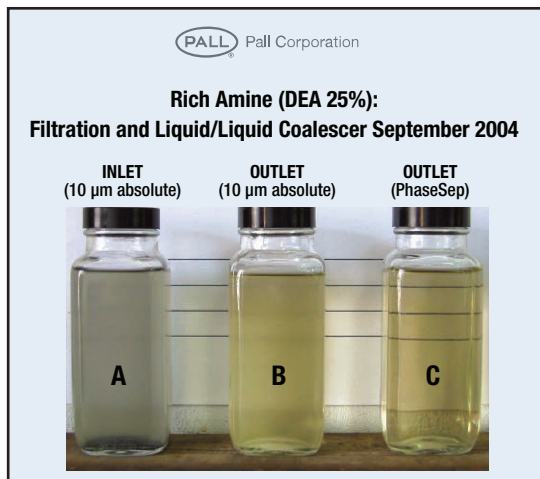
The average solids loading at the outlet of

**A:** Rich-amine sample at the outlet of the flash tank. Note the solution color, indicative of finely divided corrosion particles – FeS.

**B:** Rich-amine sample following 10 µm (Beta 5000) filtration. Note the haze – indicative of a stable emulsion. This sample remained hazy and unchanged for three weeks.

**C:** L/L coalescer outlet sample – clear and bright after a single pass through the PhaseSep L/L coalescer. Emulsion was broken and liquid hydrocarbons separated.

**Figure 5:**  
Test Samples



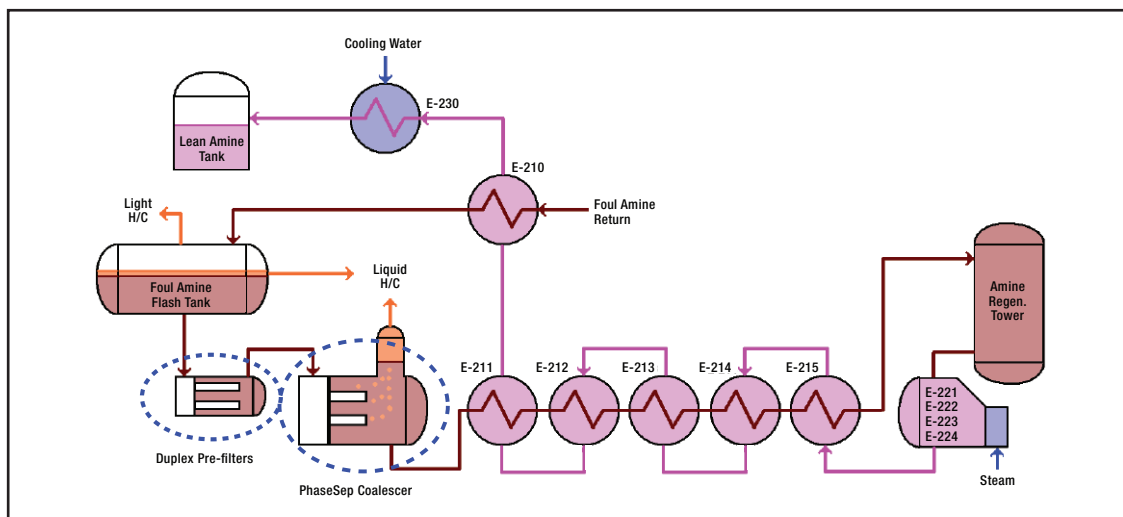


## Marsulex Solution:

Based on the field trial results, Marsulex made the decision to install a full-flow, duplex

filtration package followed by a full-flow high-performance PhaseSep liquid/liquid coalescer

**Figure 6:**  
Marsulex Amine  
Unit Flow  
Schematic



**Figure 7 (left):**  
Duplex Ultipleat®  
High Flow  
Rich-Amine Filters



**Figure 8 (right):**  
PhaseSep L/L  
Coalescer Unit



## Marsulex Operating Data:

The rich-side filter and coalescer units were installed early in 2006 and started up in June of that year. Prior to start-up of the equipment, the rich-amine was hazy and had a green/gray color at the outlet of the flash tank. Since the unit has been in operation, amine samples at the outlet of the filtration and coalescing system are clear and bright, exhibiting the characteristic light straw color of a clean amine, just as was seen in Figure 5-C.

It was observed both in amine analysis and overall process stability that the amine quality has improved. The most significant

improvement has been in the consistently low concentration of suspended solids. Prior to the rich-side filtration coming on-line, the total suspended solids in the circuit would reach 30 ppmw. Today, the solids are found to be in the 1 ppmw range on average, downstream of the rich-side filter. With the L/L coalescer in place, the continuous low-level hydrocarbon ingress is being removed everyday. More critically, when episodic hydrocarbon spikes occur, the L/L coalescer responds immediately by separating the liquid hydrocarbon slugs, preventing circuit contamination and

## Upset:

Since start-up of the rich-side filters and L/L coalescers, there has only been one major hydrocarbon carry-over to the Sulphur Recovery Unit (SRU) and one major foaming incident at the refinery contactors.

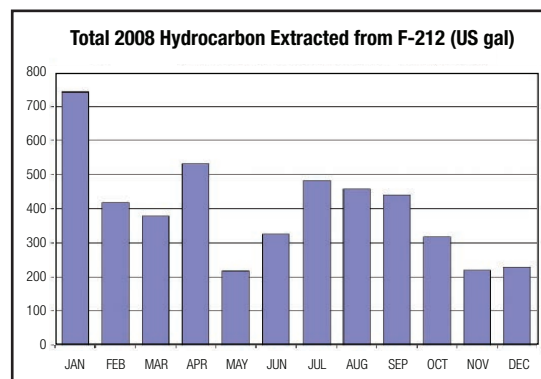
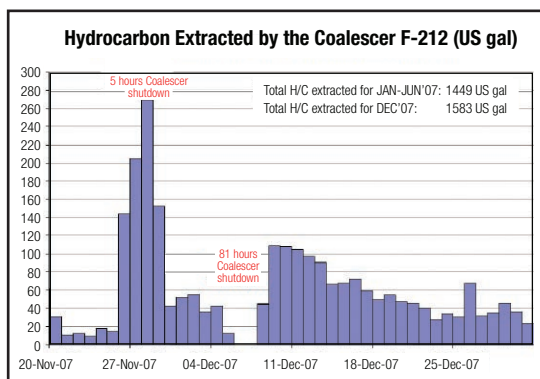
On the first occasion, an upset occurred at the time when the filters and L/L coalescer were by-passed for filter element change-out. This was during a period of very high solids, and filter life was short. The event should have been a warning for the larger hydrocarbon spike that followed. Following the five-hour shutdown to replace the filter elements, it

took three days and eight filter replacements to clean the particles and hydrocarbon out of the amine loop and restore stability.

The second incident was most likely due to hydrocarbon contamination of the amine during a coalescer shutdown. However, given the system is a closed loop, it cleaned up and recovered once the coalescer was returned to service. Employing the best practice of rich-side filtration and hydrocarbon coalescence proved the system can, and will, recover quickly. The alternative is unchecked contamination of the circuit that conventional separations techniques are inadequate at

**Figure 9 (left):**  
Coalescer  
Performance, 2007

**Figure 10 (right):**  
Coalescer  
Performance, 2008



Since December 2007, the system has been operating without any required coalescer shutdown. In February 2009, there was another major hydrocarbon carry-over from one of the refineries. This time the coalescer extracted 840 US gallons (20 bbl) of hydrocarbon liquid over a two-day period. High solids did not accompany this event, and the filter did not plug prematurely. With the separation train remaining on-line, there was no impact on the amine loop and the situation returned to normal as soon as the hydrocarbon contamination source was located and addressed.

To date, the amine heat exchanger train, re-boilers, and regenerator tower have been performing without any need for shutdown. Unfortunately, we cannot compare performance before and after the installation of the rich-side equipment because the entire circuit was significantly modified during the 2006 project. However, directionally, Marsulex can confirm the general fouling tendency is greatly reduced vs. prior to the filtration unit start-up.

Today, Marsulex is projecting a three-year or better turn-around schedule for the entire heat exchanger train. The re-boiler cleaning schedule will be based on the trends revealed from Marsulex's monitoring program.



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## Process Benefits:

The most important benefit that the system provides is an increase in overall reliability of the amine system and sulphur plant. While the system's ability to allow for quick recovery after a particulate and/or hydrocarbon contamination event – which keeps the system performing at capacity – is the primary benefit, the operating costs are also greatly improved due to longer time between cleaning, and better hydrocarbon recovery.

The lean/rich exchangers cleaning frequency has returned to a PM (preventative maintenance) schedule, five in three years vs. a required eight in three years due to significant fouling of the heat exchanger train. Over time, Marsulex will re-assess the schedule based on inspections. The frequency reduction

is expected to save a minimum of \$100,000 on maintenance costs. This is in addition to the energy savings realized with reduced steam consumption in the regenerator re-boiler (not calculated here).

The liquid/liquid coalescer allowed greater liquid hydrocarbon recovery when compared to the flash-drum alone. On average, the amount of liquid hydrocarbon recovered is increased by 25%. For example, in 2008, this resulted in the recovery of an additional 4,830 US gallons (115 bbl) of liquid hydrocarbon. This offsets fuel costs since the recovered oil is now being fed to a boiler. Most importantly, the removal of this volume of hydrocarbon ensures amine circuit stability, and protection of the

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## Conclusion:

Rich-amine filtration and liquid/liquid coalescence is crucial for the removal of particulate matter such as corrosion products and liquid hydrocarbons circulating in the amine loop immediately downstream of the flash-drum. As demonstrated at Marsulex, the best practice targets of ~1 ppmw (avg.) suspended solids, and free liquid hydrocarbon levels at near solubility, are achievable.

High performance liquid/liquid coalescers provide a more efficient and economical means for the removal of liquid hydrocarbons from an amine stream when compared to carbon beds or centrifugal devices. Liquid/liquid coalescers are also a highly efficient means to control incoming hydrocarbon slugs and maintain amine loop stability after an event.

The filtration and separation train provides protection of the lean/rich heat exchangers, regenerator tower, and reboilers and lean amine coolers. The benefits are: reduction in overall energy consumption, acid gas mass transfer maximisation, prevention of foaming episodes and loss of amine, maintaining the re-boiler tubes in good condition, which prevents fouling and formation of local 'hot-spots' responsible for amine degradation, and the initiation of the problematic corrosion cycles.

Refineries have to assure amine and sulphur plant performance and reliability in parallel with production of low sulphur gasoline and diesel. The Marsulex case study emphasizes that there exists a robust and reliable means to control particulate and liquid hydrocarbon contamination.



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