

# Exploiting opportunities with challenging crudes

## Chemical treatment techniques solve many of the processing problems encountered in refining opportunity crudes

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**T**he refining industry has changed significantly to accommodate feedstock variations in recent years. Operations have become more efficient and treatments have been developed to allow routine, profitable processing of crudes that, until recently, were considered very challenging. Today, some low-API gravity crudes actually sell at a premium because their characteristics are now considered favourable.

Traditionally, challenging or opportunity crudes are those with undesirable properties such as low gravity, high viscosity, high pour point, high nitrogen content, high metals content or high acidity as indicated by total acid number (TAN) in mgKOH/g. These characteristics are often interdependent, confronting the refinery with complex, multifaceted problems.

Refineries in the past were designed and built to process specific crudes or crude blends, many of which have become difficult or costly to obtain. Global markets have become more dynamic and trading

volumes (see Figure 1) are increasingly forcing refineries to become more flexible in their choice of feedstocks. In reality, this is easier said than done, and significant changes must be made to operate profitably under the feedstock constraints most refineries face today.

### Common feedstock constraints

#### Low gravity/high viscosity

Crudes with low gravity and high viscosity are becoming the norm, and they cause significant separation problems in refinery desalters.

The desalting process is governed by Stokes' Law (Equation 1):

$$V_s = \frac{2(\rho_p - \rho_f)}{9\mu} g R^2 \quad (1)$$

where:

$V_s$  = settling velocity

$\rho_p$  = density of particles

$\rho_f$  = density of fluid

$\mu$  = fluid viscosity

$g$  = gravitational constant

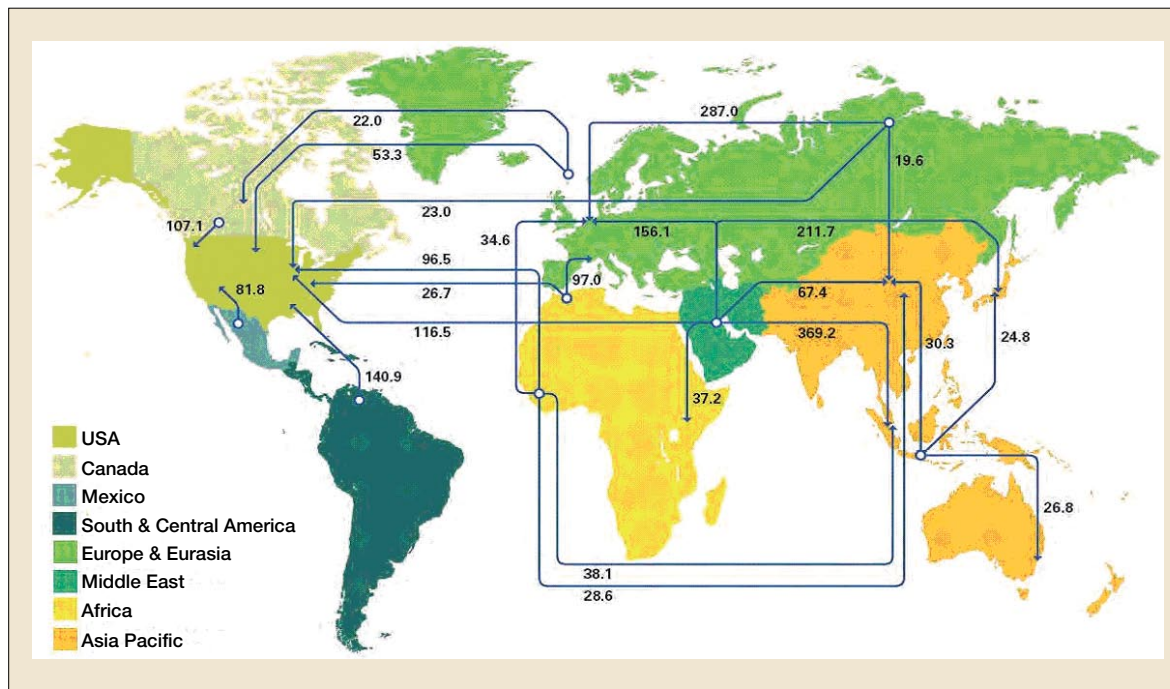
$R$  = radius of spherical object.

According to Stokes' Law, as the density difference between the oil and the water narrows, the settling velocity also

declines, indicating a requirement for extra crude residence time in the desalter.

Desalters are rarely retrofitted to deal with increasing densities. Furthermore, as viscosity increases, higher desalter operating temperatures are required and heat energy balances are often optimised for the design feedstock, not the opportunity feedstock. All of these parameters must be considered to process high-density crudes.

High solids content is a common problem in low-gravity crude oil. The dilbits of Canada and South America contain high levels of solids that pose severe processing problems in the desalter. In addition, the solids can settle as sludge, reducing storage tank capacity and increasing wastewater treatment plant loading. This can result in environmental penalties if unit throughput is not reduced, so solids must be cost-effectively removed as early in the process as possible (in the desalters). Studies have shown that the type and extent of emulsion formed depends heavily on the



**Figure 1** Global oil trade movements

Source: BP, 2012

solids contained in the crude (see Table 1).

### High pour point

Pour point is the lowest temperature at which the crude will flow. Since some paraffins can crystallise at higher temperatures than aromatics, pour point is often an indicator of crude paraffinic content. Table 2 contains examples of high pour point crude oils.

Crudes with higher pour points often require heating in

the crude tanks prior to processing. As a result, refineries may need to hold such crudes in separate tanks, increasing storage space requirements.

Other challenges presented by high pour point crudes include transportation and pumping problems, higher vacuum gas oil and vacuum residue (residue), and desalter dehydration constraints.

### High nitrogen content

Crudes with a high nitrogen

content tend to increase corrosion, degrade kerosene stream quality (aviation turbine fuel in particular) and increase salt loading in FCC units. Nitrogen-containing compounds in crude oil react with chloride ions to form ammonium chloride salts in secondary units. These salts often deposit in the crude unit and FCC main fractionating columns, where they cause pressure drop increases and tray plugging.

High nitrogen streams require hydrotreating for purification to meet final product specifications, and a high nitrogen content also reduces hydrotreater and FCC catalyst life through poisoning.

### High TAN

TAN denotes the amount of acidic species in a crude oil as measured in mgKOH/g. These acidic species are a

**Effect of various solid particles on the type and stability of emulsions**

Solids	Bentonite	Organo-philic clay	Kaolinite	Calcium carbonate	Barite	Water-wet silica	Oil-wet silica
Volume, ml	14.6	15.0	13.4	11.9	11.3	11.0	10.7
Type of emulsion	O/W	W/O	O/W	O/W	O/W	O/W	W/O
Major size range, $\mu\text{m}$	0.1-8	0.1-8	2-18	6-10	6-25	8-15	8-15
Shape	Platelets	Platelets	Platelets	Approx. spherical	Approx. spherical	Approx. spherical	Approx. spherical

Source: Yan, Wang, Jiang, Fan, & Su, 1997

**Table 1**

combination of light organic acids and naphthenic acids.

Naphthenic acids cause the most severe corrosion problems in atmospheric and vacuum units. Ideally, high TAN crudes are processed with sour crudes to provide sulphidation of the metal surfaces, which offers some protection from high temperature corrosion.

However, global standards are imposing increasingly stringent limits on sulphur levels in finished fuels, and fewer refiners are opting for sour feedstock because of the increased demand placed on hydrodesulphurisation units to meet finished product specifications.

### High metals content

Although metals such as iron, nickel, vanadium, magnesium, sodium and calcium are inherent in crude oil in various forms, levels have increased over the years due to deeper exploration and changes in extraction methods. Organic calcium is particularly troublesome because it increases desalting conductivity and causes fouling. In some crude oils, calcium may be present in the carbonate form, which can interfere with desalter operation and cause fouling issues in the preheat train.

Fuel prices factor into the equation, too. Specifications for finished fuels impose limits on metals content, and fuels with higher levels of metals often trade at a discount.

On the other hand, attractive price differentials on high metal crudes offer opportunities to enhance the gross refinery margin, justifying chemical treatment costs.

For all of these reasons, metal

Example high pour point crudes		
Crude	Country	Pour Point, °C
Mandji	Gabon	+9
Oguendgo	Gabon	+9
Zeit Bay	Egypt	+9
Congo Export Blend	Congo	+21
Nile Blend	Sudan	+33
Darr	Sudan	+39

Table 2

movement through the refinery must be monitored and controlled. Fortunately, metals removal technology continues to advance, offering new opportunities for modern refineries. One recent development maintains an acid-free environment in the desalter while effectively removing metal salts.

### Operational constraints

Installation of new units and/or unit upgrades are costly and time consuming, and such changes often involve a cascade of related considerations that add more complexity and increase the cost burden.

Inevitably, the tank farm is the last upgrade considered when refineries choose to increase their refinery capacity, if it is considered at all. Yet tank farm operations are crucial to the successful processing of crude oil.

Tank farm capacity provides settling time, reducing the amount of water entering the refinery and enhancing desalter operations. As attempts are made to increase refinery throughput without adding tank capacity, settling time decreases, allowing more water and salt into the refinery and making operations more difficult. With this in mind, many refiners rely on chemical

additives to increase throughput when additional tank farm capacity is not an option.

### Demulsification chemistry with metals removal

A refinery in Europe was considering alternative feedstock processing to increase refinery margins by processing residuum along with crude. Its ideal blend to deliver target returns was 70% crude with 30% residuum.

To accomplish this, the refinery invested in chemical treatment to process the heavy feedstock. A demulsifier helped it maximise the removal of impurities in the residuum. However, the low gravity of the feedstock degraded desalting efficiency, causing catalyst contamination downstream as well as coking issues.

Residuum naturally contains metals, which, if not removed efficiently in the desalter, can cause serious problems. Metals are a prime cause of rag layer build-up in the desalter. They can form naphthenate soaps that upset desalter operation, increasing water toxicity in effluent water treatment.

When desalted crude contains too much calcium, catalyst poisoning can occur, interfering with FCC operation. A high calcium content also causes fouling problems in the hydrodesulphurisation (HDS) system and increases ash content, degrading coke quality.

This refinery's increase in residuum processing also increased the amount of feed routed to the downstream cracking units that produce lighter, more valuable products. In turn, this increased the

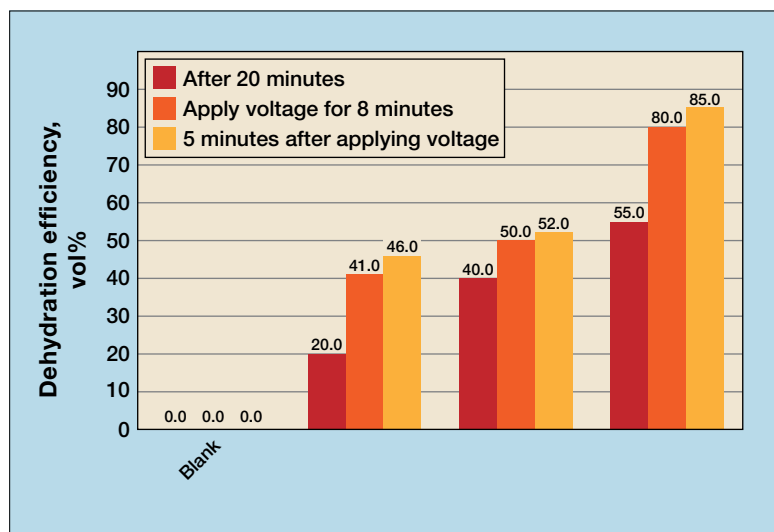


Figure 2 Dehydration efficiency at a European refinery

amount of phenolic water routed to the sour water stripper (SWS).

As with tank farms, SWSs are rarely upgraded when making other changes to refinery configurations. Loading increases, performance suffers and this reduces efficiency elsewhere in the refinery.

In this case, the concentration of impurities to be removed in the SWS increased and the quality of the water rerouted to other units within the refinery declined, causing desalter performance problems.

The refinery was suffering from a vicious cycle. The residuum it was processing increased the load on its downstream cracking units, which increased the load on the SWS. As a result, the stripper sour water pH increased.

This stripper sour water served as the refinery's source of desalter wash water. Since alkaline desalter environments tend to stabilise desalter interface emulsions, desalting efficiencies degraded as wash water pH increased. This, in

turn, made it more difficult to process the residuum, and the cycle continued to repeat.

To solve the problem, the refinery opted for a demulsifier with a uniquely formulated metals removal agent specially engineered for heavy crude blends (<22° API). The demulsifier controlled the emulsion and the metals removal agent featured a neutral pH that helped improve desalter performance in spite of a high wash water pH.

Conventional metals removal products range from highly acidic (pH <1) to moderately acidic (pH 3 to 4). Refiners are understandably concerned that although such products can control desalter wash water pH, they may also attack the metallurgy of the lines.

Corrosion is already a problem in many refinery units, and refiners want to make sure that additive usage will not make these problems worse. In this case, the product selected was a unique, neutral (approximately pH 6) metals removal agent developed by Dorf Ketal

that allows refiners to use additives for pH control and metals removal without corrosive side effects.

Desalting and dehydration efficiencies improved, allowing the refiner to process the residuum and crude in the desired proportions. Figure 2 shows the results.

This refinery exemplified many of the noteworthy changes in refinery operations that have taken place in the past 10 years (see Figure 3):

- Crude (and residuum) compatibility because the refinery was not designed for the target blend
- Reduced tank preparation time did not allow the water to settle out effectively
- Increased water recycles increased water stream pH because sour water stripping was inefficient
- Increased crude viscosities due to residuum processing
- Increased contaminants in the residuum from the refining process.

Finished fuel specifications are a complicating factor that reduces refinery flexibility in such feedstock changes. Flash point specifications for diesel limit the amount of kerosene in the blend. Low end point naphtha results in colder overhead conditions and a higher probability of corrosion. Refiners must take all of these factors into account when evaluating discounted feedstocks.

### Impact of oilfield chemical treatment on feedstock and unit operations

A large Asian refinery faced related problems that were even more complex. This refinery typically processes more

than 12 crudes in a single blend, and the blend changes at least every three days and often more frequently. Crude compatibility is often compromised, increasing the likelihood of fouling in the crude unit and contaminant ingress.

Many heavy crudes today are treated with several chemicals in the oilfield to improve production rates. These oilfield chemicals end up in the refinery units and, due to their acidic and/or aminic nature, they often show up first in the crude unit overhead when unexpected peaks are seen in pH, chlorides and iron content, indicating foreign species in the crude. A full ionic analysis may be needed to identify the species causing these fluctuations.

Heavy oil upgraders in the Orinoco region have been known to use emulsifiers such as calcium hydroxide in high TAN crudes like Merey-16 (Orinoco bitumen and Mesa crude oil). High TAN crudes contain naphthenic acids of varying molecular weights.

Generally speaking, the more naphthenic acids in the crude, the higher the TAN of that crude. Naphthenic acids are not corrosive in the liquid phase, but they are harmful at their boiling point, which in most refineries happens to be in the heavy vacuum gas oil cut of the vacuum distillation unit. At certain temperatures, fluid velocities are high and liquid impinges on process surfaces in transfer lines, return bends and restricted flow areas.

In addition to the amount of naphthenic acid present, other factors that can contribute to

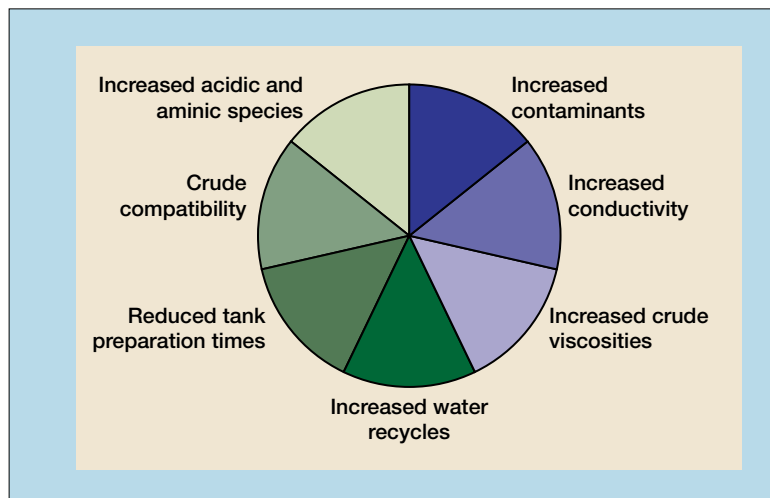


Figure 3 Recent changes in refineries

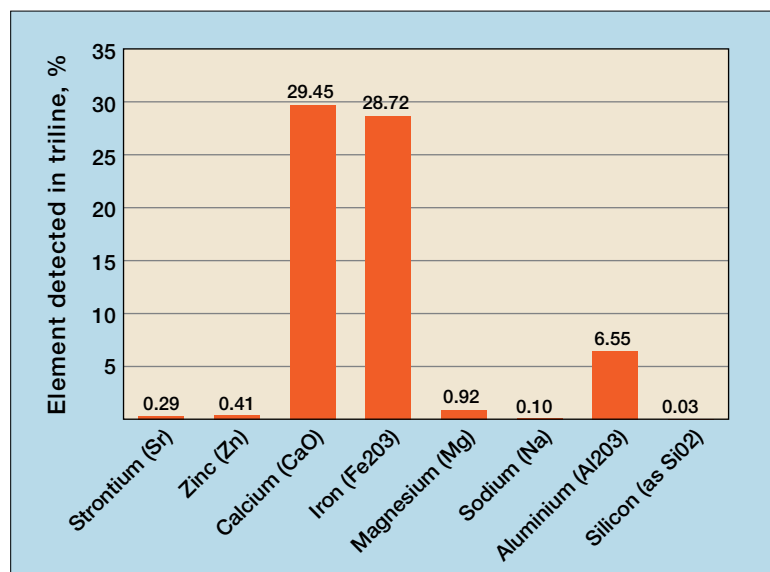


Figure 4 ICP test results for metals in desalter interface following Merey-16 processing

the corrosivity of crudes include the concentration of sulphur compounds, the velocity and turbulence of the flow stream in the units, and the liquid/vapour interface location in the unit.

When calcium hydroxide is used during the production of these acidic crudes, an even more aggressive compound is produced: calcium naphthenate. In reservoirs where

alkalinity is high in produced water, calcium naphthenate may also occur naturally.

Calcium naphthenate has the unusual property of not being soluble in oil or water. As a result, calcium naphthenate compounds accumulate at the oil-water interface within the desalter, creating a thick interfacial pad/emulsion that substantially degrades the desalting process.



Along with calcium naphthenate, compounds such as calcium hydroxide, calcium carbonate and other solids resembling ankerite and kaolinite have been identified in desalter interfaces and triline samples. A study recently conducted at a refinery processing high percentages of Merey-16 indicated the presence of such solids through inductively coupled plasma (ICP) testing (see Figure 4).

If the crude has a naturally high TAN but is low in metals content, treatment for metals removal typically is not considered necessary. However, as the crude is processed, calcium naphthenate decreases desalting and dehydration efficiencies while increasing the oil content in the brine water and posing significant environmental threats.

Once this problem has been

Examples of high TAN crudes		
Crude	Location	TAN, mgKOH/g
SJV	California, USA	4.3
Marlim	Brazil	1.1
Dalia	Angola	1.2
Lokele	Cameroon	2.7
Heidrun	North Sea	2.9
Shengli	China	1.39

**Table 3**

identified, a metals removal agent can be used in conjunction with conventional emulsion-breaking technology. The product is injected into the desalter wash water so that it mixes thoroughly with the crude and reacts with the calcium naphthenate to form water-soluble metal salts, controlling the interfacial emulsion. This is sound in theory, but as experience showed at the refinery in Asia, it is considerably more complex in practice.

As mentioned earlier, high

TAN crudes are frequently processed along with high sulphur crudes to provide protection from high temperature corrosion. High temperature corrosion inhibitor functionality often depends on sufficient inherent sulphur in the crude to assist with sulphiding metal surfaces.

When this refinery processed high TAN crude with high sulphur crudes, a thick interfacial pad formed in the desalter. A conventional metals removal agent was then added to control the emulsion, but, like most such products, it was ineffective due to the presence of  $H_2S$ .

The result can be seen in Figure 5. Black insoluble particles were formed that deposited in the desalter and contaminated the brine water. These particles further degraded desalter performance and had a dramatic negative impact on effluent treatment plant loading.

To solve the problem, Dorf Ketal engineered a new product to bypass the reaction pathway that produced the black insolubles, providing optimum solubility for the salts in the brine water and preventing effluent treatment problems. The results are apparent in Figure 5 (right-hand photo). A patent application has been approved for this new metals removal process in  $H_2S$  environments.

### Impact of high TAN crudes on unit metallurgy

The ability to remain flexible when processing crude blends is a key consideration in managing refinery operating margins. In South America, refineries often process high



**Figure 5** Black particles forming due to the presence of  $H_2S$  (left) and after treatment with Dorf Ketal additive (right)

TAN crudes because they are readily available locally, along with ample supplies of sweet crudes. The difficulty there is with the availability of the high sulphur crudes they need to help control corrosion. If these crudes are not readily available then the cost of importing them may exceed the return from refining domestic sweet crude.

A refinery in Brazil faced such a problem. The refinery wanted to process high TAN crudes with sweet crudes in the blend, but high sulphur crudes were not consistently available at an acceptable cost.

Naphthenic acid is most dangerous at its boiling point (broadly between 200-350°C). The naphthenic acid reacts with the scale chemistry on the metal surface in order to form corrosion products. This then exposes fresh metal and the cycle begins again.

The corrosion cell with naphthenic acids is shown in Figure 6, in which iron (Fe) represents the metal surface of the pipe to be protected. As can be seen in the figure, reactive sulphur can be present in a number of forms that adhere to the metal surface.

Several options other than managing crude blend TAN and sulphur can provide high temperature corrosion control. Metallurgy upgrades can help, but would have been too expensive and time consuming in this refinery. The full metallurgy of the entire crude unit (atmospheric and distillation columns) would have required assessment prior to processing high acid crudes. Such a survey would have been extremely complex because refinery metallurgies vary in susceptibility to

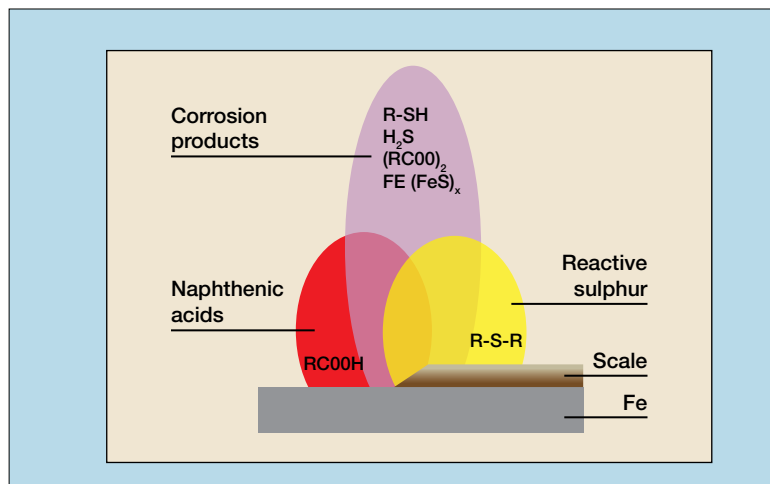


Figure 6 Naphthenic acid corrosion cell

acid corrosion, and suitable metallurgy is costly.

To compensate for the corroding effects of sulphur and naphthenic acid in this case, an austenitic stainless steel with approximately 2.5% molybdenum (minimum) would have been beneficial. Figure 7 illustrates the benefits.

However, a high temperature corrosion inhibitor was clearly a simpler, lower-cost alternative for this refinery and so a number of corrosion inhibitors were tested in field trials.

Conventional high temperature corrosion inhibitors are

based on phosphate or thiophosphate esters, but these compounds form reaction products that can cause fouling. One of the products tested was a patented, new-generation inhibitor that was very different from the others.

This new chemistry was effective under the required low sulphur, high TAN conditions because it did not rely on sulphur-containing crudes to pre-sulphide metal surfaces. The product is stable at high temperatures and works in synergy with metal surface chemistry to prevent fouling.

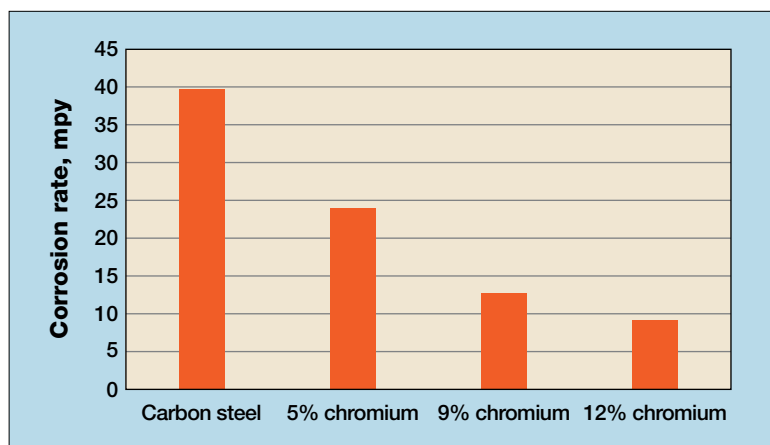


Figure 7 Corrosion rates with different metallurgies

As a result, the refiner gained the feedstock flexibility it needed to operate profitably and manage corrosion without high sulphur crudes.

## Conclusion

Refineries confront many challenges in today's dynamic markets. Opportunity crudes are just one of many, along with increasingly stringent global environmental restrictions on sulphur, mercury, arsenic, lead and other components in process streams.

As this article has shown, treatment chemistry is evolving to meet these challenges and, as new problems arise, innovative chemistry will provide effective solutions. These include powerful chemical tools for processing opportunity crudes, which enhance feedstock flexibility and prevent costly shutdowns and throughput reductions.

One thing seems certain:

many of the crude oils that today are considered challenging opportunities for adventurous refiners will become so desirable that they will trade at a premium tomorrow.

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