Managing Vanadium from High Metals Crude Oils

Process and equipment design improvements, particularly with regard to crude unit and delayed coker distillation column performance, can reduce metals content. Optimization of components, including vacuum column stripping section and coker main fractionator wash zones, should be considered.

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Managing vanadium in FCC feed streams originating from atmospheric crude, vacuum crude, and the delayed coker is becoming more important as refiners increase the amount of high vanadium crudes imported from Canada, Mexico, and Venezuela. Vanadium reduces hydrotreater run-length and lowers FCC conversion due to its impact on catalyst activity. Total vanadium in FCC feed streams can be as high as 5 to 10 ppmw --- depending on crude oil, vacuum column cutpoint, unit process design, and distillation unit operation and equipment design. Experience shows that total gas oil metals can be reduced by 20 to 50% or heavy vacuum gas oil (HVGO) product yield can be increased for a given metals target by optimizing primary distillation system performance.

A 22.0°API Bachequero Field (BCF) blend will be used to illustrate the potential metals reduction based on optimized primary distillation design and operation. In the following example, 145,000 bpd of BCF is processed through a conventional integrated atmospheric/vacuum unit and the vacuum residue in a delayed coker. The FCC feed consists of atmospheric gas oil (AGO), light vacuum gas oil (LVGO), and heavy vacuum gas oil (HVGO) from the crude unit and heavy coker gas oil (HCGO) from the delayed coker (Figure 1).

**Gas oil metals source**
Vanadium in the distillate products consists of volatile vanadium in the hydrocarbon boiling range and entrainment of non-distillable residues. Volatile metals vaporize at the operating conditions in the unit, thus they are always present. The amount of entrainment depends on the vacuum unit transfer line velocity, coker drum line velocity, and distillation column performance. Entrainment can be nearly eliminated through prudent transfer line and column internal designs. Volatile vanadium depends on the amount of product yielded and the 95 vol% to end point (EP) tail. Process and equipment design has reduced volatile vanadium by up to 30% in the HVGO and HCGO products.

Before revamping a vacuum unit or coker main fractionator to reduce product vanadium, the source of the metals needs to be determined. Proper distillation equipment design can completely eliminate the entrained metals, whereas, volatile metals must be fractionated. Ultimately the value of each incremental barrel of product depends on how much vanadium it contains. With some very high metals crude oils, it is not economic to produce the incremental barrel because the vanadium content is so high that it dramatically reduces hydrotreater run-length.

Residues do not vaporize at the operating conditions, thus they must be entrained with the rising vapor. The simplest method to estimate the quantity of entrainment is to distill 95% of the sample overhead in a laboratory still. A high temperature simulated distillation (HTSD) is then run on the heaviest 5 vol%. Because the HTSD measures atmospheric equivalent temperatures (AET) up to 1380°F, any entrainment will show up as high boiling point material that should not be present at the operating temperature and pressure of the unit. The entrained material is often not detected, if the whole sample is analyzed by HTSD, because it typically represents only be 0.5 to 2% of the total stream.

Table 1 shows BCF 22°API crude (Figure 2), and atmospheric and vacuum residues vanadium content at typical AGO and HVGO product cutpoints. Since these residues contain extremely high vanadium, even small amounts of entrainment will dramatically increase distillate product metals.
For example, 50 bpd of entrained atmospheric residue increases AGO vanadium by more than 40%. Because vacuum residue contains over 800 ppm vanadium, entrainment of less than 0.5% into HVGO product cannot be tolerated. While entrainment from the flash zone into the wash section always occurs; the wash section must be capable of removing all of it, otherwise, vanadium can increase to over 20 ppmw. When refiners switch from low to high metals crude they are sometimes surprised by the HVGO vanadium content. Many vacuum residues have only 40-80 ppmw vanadium compared with 800 ppmw in the BCF 22°API.

Coker unit HCGO contains non-distillable material entrained from the coke drum. As coke drum and main fractionator superficial velocity increase, entrainment goes up. The quantity of entrainment can be estimated by analyzing the HCGO product heaviest 5 vol% with the use of the previously mentioned HTSD. Entrained non-volatile material from the coke drum can contain well over 1,000 ppm vanadium. Entrainment happens during both normal operation and from steaming of the hot coke drum prior to coke cutting.

Volatile material needs to be measured as a function of boiling range so that incremental product yield can be valued. First, the 800°F+ boiling range material must be fractionated into 25°F cuts by ASTM D5236 method or in a continuous flash vaporizer. Metals in the individual cuts are determined by ICP-AES.

### Metals distribution

Crude oil metals distribution is a function of the source. Many Venezuelan, Mexican, and Canadian crude oils have high vanadium content, and the 800°F+ boiling range hydrocarbon includes volatile vanadium compounds. Some, such as Canadian Lloydminster B, have moderate metals in the whole crude. However, the volatile vanadium in the 800°F+ boiling range is high. Vanadium distribution is crude oil dependent. Therefore, distribution must be known to accurately predict HVGO vanadium content. HCGO product vanadium is a function of the vacuum residue metals, vacuum unit cutpoint, and boiling range of the HCGO product. High vanadium vacuum residues produce HCGO with high vanadium because the volatile vanadium is also high in the coke drum effluent.

### AGO, LVGO, and HVGO vanadium

Combined gas oil vanadium depends on the crude oil metals distribution, processing scheme, and distillation system design and operation. Distribution of vanadium by boiling range will set the minimum amount in the combined gas oil product. However, the vacuum unit process design and distillation equipment design will have a significant impact on the HVGO product 95 vol%-EP, tail which materially influences vanadium.

Vanadium distribution is highly non-linear as is evident by the dramatic increase in vanadium above a 1025°F TBP boiling range shown in Figure 3. Therefore, when operating a vacuum unit at an HVGO cutpoint of 1100°F, there will be a significant amount of vanadium in the HVGO product. Table 2 shows the vanadium distribution in the 950 to 1150°F boiling range for BCF 22°API. Relatively small changes in the TBP cutpoint increase the vanadium content due to the previously mentioned highly non-linear distribution.

### HCGO vanadium distribution

Delayed coker HCGO product vanadium is a function of the crude source and the vacuum unit HVGO cutpoint. Table 3 shows the metals distribution for two different HCGO samples with the vanadium varying significantly in the same boiling range.
HCGO product from a 1060°F cutpoint BCF 22°API vacuum residue is compared with the HCGO from a 920°F cutpoint residue from heavy California crudes. Vacuum unit HVGO cutpoint and crude source have a large impact on HCGO vanadium.

The data shown in Table 3 was generated in the laboratory by fractionating the samples into 25°F cuts and analyzing each cut for vanadium. Table 4 compares the BCF 22°API crude metals distribution with the same boiling range material from HCGO produced from BCF 22°API vacuum residue. Figure 4 shows the TBP and the metals for the HCGO produced from BCF crude. Feedstock properties, coke drum outlet temperature and pressure, coke drum and column superficial velocity, recycle, and delayed coker main fractionator wash zone efficiency all influence HCGO metals.

### Crude Oil/HCGO Metals Distribution

<table>
<thead>
<tr>
<th>TBP Boiling Range, °F</th>
<th>Average, wt ppm Vanadium, wt ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Crude Oil</td>
</tr>
<tr>
<td>950-975</td>
<td>2.0</td>
</tr>
<tr>
<td>975-1,000</td>
<td>2.2</td>
</tr>
<tr>
<td>1,000-1,025</td>
<td>3.5</td>
</tr>
<tr>
<td>1,025-1,1050</td>
<td>8.6</td>
</tr>
<tr>
<td>1,050-1,1075</td>
<td>14.0</td>
</tr>
<tr>
<td>1,075-1,100</td>
<td>22.0</td>
</tr>
<tr>
<td>1,100-1,150</td>
<td>50.0</td>
</tr>
</tbody>
</table>

### Process design

Process design affects the metals distribution in the individual streams. Design and operating variables will affect the product vanadium content. For instance, vacuum units designed with a stripping section produce lower metals HVGO product at the same cutpoint than a dry column because the stripped material is lighter than the same volume vaporized in the vacuum heater. Lowering coke drum pressure and reducing recycle decreases coke production and increases liquid volume yield. However, lower pressure increases coke drum and fractionation column superficial vapor velocity and produces a higher endpoint HCGO product. Reducing recycle also increases HCGO product endpoint. Liquid volume improvements always increase the endpoint and metals in the HCGO product.

Maximum AGO product cutpoint is approximately 800°F when operating at very low pressure, high temperature, and high stripping steam rates. At high cutpoint, the AGO contains volatile metals; however, in most cases AGO product metals are largely a function of entrained atmospheric residue. Poor flash zone, wash section, and stripping section designs can all cause entrainment.

### Vacuum unit design

Three different types of vacuum units are commonly used. A dry design uses no steam in the heater and does not have a stripping section. A damp unit (without stripping) uses steam in the heater coils, but has no stripping section. An optimum design will have both coil steam and a stripping section.

Heavy crudes are difficult to vaporize. Therefore, rarely will a dry vacuum unit meet the HVGO product yield target. Heater outlet temperature needs to be high and the flash zone pressure very low to vaporize heavy crudes in a dry unit. Generally, coil steam is required to keep the vacuum heater from coking. A damp column without a stripping section will always produce higher vanadium HVGO than a damp column with stripping for the same cutpoint. An optimized vacuum unit processing high vanadium feeds will have a stripping section and use coil steam. Because total steam sets the ejector size, it must be balanced between the heater coils and the stripping section. Coil steam should be kept to the minimum needed to prevent coking and stripping section efficiency maximized by using design principles that raise tray efficiency.

### Delayed coker

Delayed coker revamps to improve liquid volume yields are common. Higher yield raises EP because lower operating pressure vaporizes heavier material and increases coke drum and main column superficial velocity. Lower recycle also improves yields, but it requires using a spray chamber in the wash section to meet the lower recycle target. When the main fractionator vapor C-factor exceeds approximately 0.25 to 0.28 ft/sec through a spray chamber, the amount of non-distillable hydrocarbons and coke fines in the HCGO increase. Some revamps have raised vapor C-factors to 0.32 ft/sec or higher. While spray chambers allow low recycle, entrainment also increases.

### Equipment Design

Distillation equipment design effects entrainment and the product distillation 95% to EP. Good atmospheric crude and vacuum crude flash zone designs will eliminate entrainment, while poor designs cause very poor quality distillate. Commonly, shed trays are used in the bottom of coker fractionators. Shed trays actually increase the amount of entrainment because they reduce column cross-sectional area for vapor flow by at least 50%. Because liquid rates are so low, there is no liquid curtain for the vapor to flow through. Therefore, there is little contact-

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**Figure 4.** HCGO Product TBP Distillation and Metals Distribution

**Figure 5.** Flash Zone Entry

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ing between liquid and vapor. Yet, they continue to be used in many cokers. Understanding the fundamental equipment design principles is essential to meeting both yield and quality targets, while ensuring unit reliability.

**Atmospheric column**

Atmospheric crude column internals design varies greatly. When processing high metals crude it is important that the equipment eliminate all entrainment. AGO vanadium depends on the flash zone, wash section, and stripping section design. Poorly designed flash zone internals are the most common cause of black high vanadium AGO. Flash zone internals need to dissipate the high-energy two-phase feed without creating high velocity areas that promote entrainment. Minimizing atmospheric residue entrainment from the flash zone reduces the load on the wash section.

Wash zone efficiency determines whether entrainment reaches the AGO product. Columns with trays require higher liquid rates to produce low vanadium AGO. Sufficient liquid rate is also needed to avoid low flow areas that cause severe fouling. Packed columns require very little liquid to remove entrainment and atmospheric columns operating temperatures are rarely high enough to generate coke. Trays require minimum overflash rates of about 3 to 4 vol%. Operating trays below 2 vol% causes blowing, which lifts the liquid off the tray. Thus, high vanadium residue is carried into AGO product. On the other hand packing removes entrainment at less than 0.5 vol% overflash. Stripping sections vaporize a portion of the liquid from the flash zone, but when they flood residue is entrained into the AGO product.

**Vacuum unit design**

Flash zone, stripping section, and wash zone design all affect the HVGO product yield and vanadium content. Feed enters the column at 400 ft/sec. The flash zone internals need to help separate the two-phase feed and distribute the rising vapor across the column cross-sectional area. Stripping vaporizes the front-end of the flash zone liquid and a portion of the overflash, and the wash section removes entrainment and fractionates the 95 vol%EP tail.

In a typical vacuum column, the feed enters tangentially (Figure 5) and the swirling motion must be broken or the vapor and entrained residue will tend to travel as a cyclone up the column along the vessel shell. A good vapor horn design helps provide initial vapor distribution to the wash section to reduce the velocity gradient. High velocity areas entrain residue through the wash section packing into the HVGO product.

**Stripping section**

Stripping trays reduce oil partial pressure of the liquid flowing across the tray, which vaporizes the lightest portion. The material vaporized has a lower distillation boiling range than an equivalent amount of vaporization from the vacuum heater. Hence, the vanadium content is much lower because vanadium distribution is highly non-linear. Maximizing stripping section efficiency will increase vaporization for a given amount of steam or reduce the steam for the targeted amount of stripping section hydrocarbon vapor. Five or six trays and maximum efficiency will lower steam rate and reduce ejector system capital and utility costs.

**Wash zone**

Vacuum column wash section efficiency and unit reliability need to be balanced. Improved wash section efficiency reduces metals by 15 to 20%. However, as wash section efficiency increases so does the

<table>
<thead>
<tr>
<th>Packing Efficiency</th>
<th>HETP, inches</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grid (most efficient)</td>
<td>84+</td>
</tr>
<tr>
<td>Random</td>
<td>60+</td>
</tr>
<tr>
<td>Structured</td>
<td>48+</td>
</tr>
</tbody>
</table>

*Table 5.*
likelihood of coking. Because deepcut vacuum columns operate at flash zone temperatures as high as 785°F, packing will quickly coke unless it is kept sufficiently wetted in the middle of the bed. Overflash is material that is vaporized and is returned to the flash zone as liquid. This rate must be high enough to keep the middle of the packed bed wetted. Often, the liquid rate leaving the bottom of the wash section is interpreted as overflash. Yet, it contains both entrained residue from the wash zone and overflash. Because wash oil flow rate is often controlled based on the metered flow rate of liquid leaving the packing (Figure 6), assuming all this metered liquid is only overflash, it results in low wash rates and dry areas in the middle of the bed. As the packed bed depth or efficiency increases, it becomes more important to maintain adequate wash oil flow to avoid coking in the middle of the bed.

What is sufficient wetting? Industry accepted values range from an aggressive target of 0.05 gpm/ft² leaving the packing to the more conservative value of 0.2 gpm/ft². In a short, low efficiency packed bed, it is possible to operate at low liquid rate because entrained residue wets the bottom 1 to 2 feet of the packing. It may be possible to operate at 0.3 gpm/ft² to the top of the bed when the bed is only 2 to 3 feet deep. When operating at 0.3 gpm/ft² to the top of the bed, 98% of the liquid will be vaporized removing the flash zone vapor superheat. Operating at 0.05 gpm/ft² leaving the packing and meeting a four-year superheat. Operating at 0.05 gpm/ft² leaving the packing and meeting a four-year run with essentially overflash is only possible when the flash zone temperature is low or the bed depth is 3 feet or less. Yet when processing high vanadium crudes, deeper beds are required and packed bed efficiency must be increased.

Wash zone efficiency depends on the type of packing used. Grid has poor fractionation efficiency because it has low surface area. Structured packing has high surface area and much better efficiency. However, as surface area goes up the amount of liquid needed to wet the packing increases. Very low liquid rate areas have high residence time, which raises the likelihood of coking. Table 5 shows wash zone packing efficiency estimates.

Many deepcut vacuum units produce good quality and high yields of HVGO product for the first six months after start up. Then the wash section pressure drop begins to increase and eventually HVGO product quality deteriorates. When coking occurs, pressure drop increases because coke is reducing the open area for vapor flow. Once sufficient coke is deposited to increase bed pressure drop by 3-5 mmHg across the wash section, HVGO product vanadium begins to rapidly increase because vacuum residue is entrained with the rising vapor. Most deepcut vacuum units revamped in the last 15 years have high residence time, which raises the likelihood of coking. Table 5 shows wash zone packing efficiency estimates.

Coker main fractionators
Wash zone section designs depend on the recycle and HCGO quality targets. Increasing liquid volume yield requires minimum recycle. Therefore, spray chambers are used. However, they have very low efficiency and once vapor capacity factor Cf rises above 0.25 to 0.28 ft/sec, entrainment of non-distillable material and coke fines into HCGO increases. While ultra-low recycle requires using a spray chamber, the HCGO quality is lower. Meeting low levels of both non-distillable material and coke fines in the HCGO product requires higher efficiency internals than a spray chamber or low column vapor velocity.

Generally, revamps to lower coke yields raise column superficial velocity and reduce recycle. High vapor capacity factor revamps require vapor distribution into the wash section even if a spray chamber is used. The vapor distributor needs to be
entrainment. By modifying the atmospheric 50 bpd of atmospheric residue improved coker wash section efficiency. coil and stripping steam rates, and column wash zone efficiency, optimizing to the AGO product, increasing vacuum will be reduced by eliminating entrainment.

The metals level of the total gas oil pool and the metals in the combined gas oil.

**Table 6** shows the base case unit yields and Vanadium.

<table>
<thead>
<tr>
<th>Wash Zone No. of Stages</th>
<th>HVGO (wt ppm Va)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.8</td>
</tr>
<tr>
<td>2</td>
<td>7.4</td>
</tr>
</tbody>
</table>

**Table 7** shows AGO product vanadium can be lowered from 3.1 to 1.8 ppmw by eliminating entrainment.

- Atmospheric gas oil is black. ASTM-1500 color is 8+ (typical of many refiners).
- HVGO TBP cutpoint of approximately 1030°F
- All vacuum residue processed in the delayed coker
- Delayed coker recycle 5%.
- Spray chamber only
- Vacuum unit with no stripping section.

**Table 8** shows the impact of increasing distillation column internals, the entrainment can be eliminated. Table 7 shows AGO product vanadium can be lowered from 3.1 to 1.8 ppmw by eliminating entrainment.

Vacuum column optimization requires both improved wash section efficiency, and the coil and stripping steam needs to be balanced to produce the best quality product. Increasing wash section efficiency involves flash zone and wash section modifications. Poor flash zone design causes localized high velocity areas and high entrainment into the wash section. Both increase the HVGO vanadium content. Table 8 shows the impact of increasing wash section efficiency from 1 to 2 stages at the same HVGO product cutpoint. HVGO product metals are reduced by 1.5%

Coil and stripping steam rates need to be optimized. In this example, a total steam rate of 15,000 #/hr has been assumed. Moving steam from the coils to the stripping section affects heater oil residence time and heater radiant section design needs to be thoroughly reviewed. However, if 5,000 #/hr of steam is moved from coil to stripping then the furnace outlet temperature actually decreases when a stripping section is added. Table 9 summarizes the HVGO vanadium reduction for the same cutpoint when the column has a stripping section.

**Table 9.**

<table>
<thead>
<tr>
<th>Case</th>
<th>Vanadium, wt ppm</th>
</tr>
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<tr>
<td>No Wash Section</td>
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</tr>
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In this example, delayed coker HCGO product vanadium is 3.5 ppmw prior to making modifications. The delayed coker has no wash section packing (only a spray chamber). All the non-distillable material and coke fines from the drum end up in the HCGO product because the vapor capacity factor (Cl) exceeds 0.3 ft/sec. Reducing coke fines and entrainment requires a grid bed (Figure 9) and higher recycle. The challenge is to design for enough wash to maintain the packing wetting above the coking point without excessive recycle. All wash section equipment including collector trays must be designed for very low hold-up and the design needs to prevent condensation of heavy hydrocarbon on the underside of the tray. Table 10 summarizes the HCGO product quality improvement associated with a 2.0 % increase in the unit recycle.

**Quality versus yield**

In this example, optimization of the primary distillation system will decrease vanadium levels in the total gas pool over 40%. Alternately, the gas oil yield can be increased over the base case by increasing HVGO cutpoint from 1030 to 1060 °F, while maintaining the base case metals of 5.7 ppm vanadium. This raises total gas oil yield by 2.5 vol% on crude after taking into account higher coker recycle. While hydroprocessing will continue to handle the bulk of the vanadium removal, primary distillation plays a significant role.

**Table 10.**

<table>
<thead>
<tr>
<th>HCGO Product Quality-Delayed Coker Improved Wash Section Efficiency</th>
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</tr>
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<tr>
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**Optimized yield and quality**

Ultimately reducing vanadium in the total gas oil (AGO+LVGO+HVGO+HCGO) stream or increasing yield is the objective. Gas oil quality is a function of both volatile and entrained metals and primary distillation revamps can reduce the vanadium content substantially. Figures 7 and 8 show the atmospheric and vacuum crude unit schematic, and the delayed coker main fractionator systems that are being evaluated in the article’s example. The conditions before revamping the primary distillation column internals were:

- Atmospheric gas oil is black. ASTM-1500 color is 8+ (typical of many refiners).
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- Spray chamber only
- Vacuum unit with no stripping section.

Table 6 shows the base case unit yields and the metals in the combined gas oil.

The metals level of the total gas oil pool will be reduced by eliminating entrainment to the AGO product, increasing vacuum column wash zone efficiency, optimizing coil and stripping steam rates, and improved coker wash section efficiency.

AGO product is black due to an estimated 50 bpd of atmospheric residue entrainment. By modifying the atmospheric column flash zone and wash section can be eliminated. Table 7 shows AGO product vanadium can be lowered from 3.1 to 1.8 ppmw by eliminating entrainment.

Vacuum column optimization requires both improved wash section efficiency, and the coil and stripping steam needs to be balanced to produce the best quality product. Increasing wash section efficiency involves flash zone and wash section modifications. Poor flash zone design causes localized high velocity areas and high entrainment into the wash section. Both increase the HVGO vanadium content. Table 8 shows the impact of increasing wash section efficiency from 1 to 2 stages at the same HVGO product cutpoint. HVGO product metals are reduced by 1.5%

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**THE AUTHOR**

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