

# Component Trapping in Distillation Towers: Causes, Symptoms and Cures

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This article explains the principles behind minor-component trapping, summarizes industry's experience, and provides guidelines for diagnosing and addressing the problem.

**C**OLUMN FEED OFTEN CONTAINS COMPONENTS whose boiling points are between those of the light and heavy key components. In some cases, the top temperature is too cold and the bottom temperature too hot to allow those components to leave the column as fast as they enter. Water, because of its non-ideal behavior with organics, is a common problem. Having nowhere to go, these components accumulate in the column, causing flooding, cycling and slugging. If the intermediate component is water or acidic, it may also cause accelerated corrosion; in refrigerated columns, it may produce hydrates. A large difference between the top and bottom temperature, a large number of components, and high tendencies to form azeotropes or two liquid phases are conducive to intermediate component accumulation.

Although component accumulation has created major problems in many columns, it has not been extensively addressed in literature. This article expands the previous work (1-3) into a more comprehensive review aimed at providing guidelines on anticipating, troubleshooting and overcoming component accumulation problems.

## Principles

From each stage in a tower, the molar upward flowrate of component  $i$ ,  $v_i$  (lb-mol/h), is given by:

$$v_i = Vy_i = VK_i x_i \quad (1)$$

where  $K$  is the K-value at the stage temperature,  $L$  and  $V$  are the total liquid and vapor flowrates (lb-mol/h), and  $x$  and  $y$  are

the component concentrations in the liquid and vapor phases, respectively. The downward flowrate of the same component,  $l_i$ , is given by:

$$l_i = Lx_i \quad (2)$$

When  $v_i > l_i$ , there is a net upward movement of the component; likewise, when  $v_i < l_i$ , there is a net downward movement. Combining this criterion with Eqs. 1 and 2 gives:

$$\text{Net upward movement when } VK_i/L > 1 \quad (3)$$

$$\text{Net downward movement when } VK_i/L < 1 \quad (4)$$

In binary distillation, the light key component (LK) always obeys Eq. 3, while the heavy key component (HK) always obeys Eq. 4. Consequently, there is always a net upward flow of the light key component and a net downward flow of the heavy key component, that is:

$$VK_{LK}/L > 1 \quad (5)$$

$$VK_{HK}/L < 1 \quad (6)$$

For a component with a boiling point intermediate between the light key and heavy key, the following generally applies:

$$K_{HK} < K_{IK} < K_{LK} \quad (7)$$

where  $IK$  denotes the intermediate key.

Now consider a situation where the  $V/L$  ratio is set by the

initial binary separation, the tower produces reasonably pure products near the top and the bottom, and an intermediate key is added into the feed. For a pure top product,  $K_{LK}$  near the top approaches unity. Since  $K_{IK} < K_{LK}$ , the ratio  $VK_{IK}/L$  will be less than 1 when  $K_{LK}/K_{IK}$  exceeds  $V/L$ , suggesting a net downward flow (Eq. 4). Similarly, for a pure bottom product,  $K_{HK}$  near the bottom approaches unity. Since  $K_{IK} > K_{HK}$ ,  $VK_{IK}/L$  will exceed 1 when  $K_{IK}/K_{HK}$  exceeds  $L/V$ , suggesting a net upward flow. With a net downward flow near the top and a net upward flow near the bottom, intermediate components tend to accumulate in the tower.

Figure 1 illustrates the buildup of components in a tower (4). The feed was introduced at stage 10, with the tower bottom at stage 22. The intermediate key component, which tended to concentrate below the feed, was continuously removed as a vapor side draw from stage 13. The heavy key component, which was more volatile than the heavy non-keys that made up most of the bottom stream, steeply concentrated between the bottom stage 22 and the intermediate draw stage 13, peaking at stages 17–18. Over the four stages between 17 and 13, the HK concentration was meant to drop from 50% based on the design. With such a steep concentration gradient of HK, a slight shortfall in the number of stages (by as little as one or two out of eight) caused the concentration of HK in the side draw to increase from 1% to 10%. Here the HK acted as the trapped component.

Intermediate component buildup most frequently takes place over the entire tower, but at times, it is confined to a section. Excessively subcooled feed (or fouling of a feed preheater) can lead to accumulation of an intermediate component between the feed and the bottom. Similarly, excessive preheat (oversurfaced or clean preheater) may lead to an accumulation between the feed and the tower top.

### How much accumulation?

The accumulation continues until the intermediate component concentrations in the overhead and bottom allow removal of these components at the rate they enter, or until a hydraulic limitation is reached.

The factors governing intermediate component accumulation are essentially those that govern the split of intermediate components between the top and bottom products (3):

- the  $VK_{IK}/L$  ratio. A high ratio near the bottom of the column signifies a large

upward movement, whereas a low ratio near the top of the column signifies a large movement downward. When the two come together in the same column, the concentration can be tremendous. Concentrations (“bulges”) 10 to 100 times the feed concentration are common.

- non-ideal equilibrium. A high activity coefficient at the tower bottom can make an intermediate component particularly volatile. For instance, when the tower bottom is mainly water, organic components such as *n*-butanol become highly volatile (high  $VK_{IK}/L$ ). The same organic can become highly nonvolatile if the top is rich in methanol or ethanol. For a methanol/water separation column, *n*-butanol in the feed will tend to accumulate to a large extent (2).

- the number of stages. Each stage intensifies the upward and downward movement. The more stages, the more the intermediate component concentrates toward the middle of the tower.

- the concentration of the intermediate component in the feed. The higher the concentration, the greater will be its tendency to concentrate in the tower.

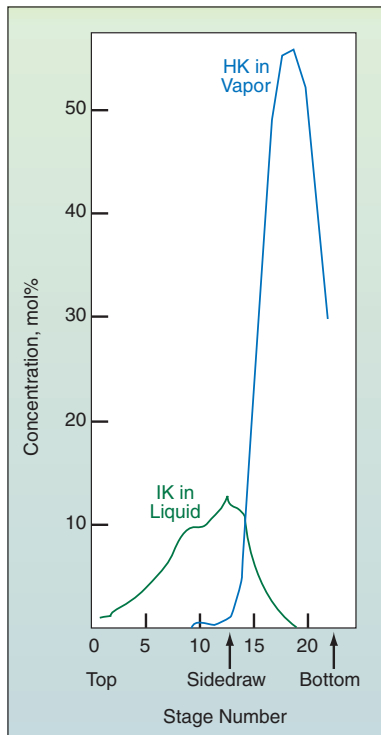
- product specifications. The tighter the specs, the greater the accumulation. Much of this is due to the larger number of stages needed to reach the tighter specs, especially stages at

high purity, where the upward or downward movement of the intermediate component is intensified.

In accumulation situations, there is always an initial period of non-steady-state intermediate component buildup. The buildup tends toward the equilibrium concentration that reinstates the component balance in the tower. This equilibrium concentration, however, may not always be reached, such as when the  $VK_{IK}/L$  is high near the bottom and low near the top, and/or the number of stages is high, and/or the concentration of the intermediate component in the feed is high, and/or the product specs are tight. Instead, unsteady-state cycling may set in.

### Hiccups and cycling

A typical symptom of unsteady-state accumulation is cyclic slugging, which tends to be self-correcting. The intermediate component builds up in the column over a period of time, typically hours or days. Eventually, the column floods, or a slug rich in the offending component exits either from the top or the bottom. (The end from which the slug leaves



Source: (4).

■ Figure 1. Composition profile pinpoints the concentration of the heavy key between the bottom and side draw.

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often varies unpredictably.) Once a slug leaves, column operation returns to normal over a relatively short period of time, often with minimal operator intervention. The cycle will then repeat itself. Several experiences have been reported in the literature, and those are abstracted in Table 1.

Intermediate component accumulation may interfere with the control system. For instance, a component trapped in the upper part of the column may warm up the control tray. The controller will increase reflux, which pushes the component down. As the component continues accumulating, the control tray will warm up again, and reflux will increase again; eventually, the column will flood. Three cases describing a similar sequence have been reported (DT2.13B, 1213, and 228).

One of the most fertile breeding grounds for intermediate component accumulation is a condition in which some section in the tower operates close to the point of separation of a sec-

ond liquid phase (2). The accumulation itself, or a malfunction of phase separation equipment in the feed route, or simply a change in feed composition, can induce separation of a second liquid phase inside the tower. This changes volatilities and azeotroping, and can generate or aggravate hiccups.

It, therefore, is not surprising that many of the cases in Table 1 involve such a system. Examples include small quantities of water in a refinery or natural gas deethanizer (DT2.10, 1038, 1039, 751, 1001), and oil or other hydrocarbon accumulating in a methanol/water tower (DT2.15). In other cases, such as azeotropic and extractive distillation, the accumulation interacted with the phase separation in the tower and the decanter (*e.g.*, DT2.22 and DT2.23).

Figure 2 illustrates a common configuration of a reboiled deethanizer absorber. The top (absorber) section uses a naphtha lean oil stream to absorb valuable C<sub>3</sub> and C<sub>4</sub> components from

**Table 1. Hiccup experiences reported in literature.**

Case	Ref.	Plant and/or Column	Brief Description
DT2.10	5	Refinery deethanizer	The tower bottom was cooled in an attempt to improve C <sub>3</sub> recovery. This led to water accumulation, causing hiccups and water slugs out the bottom every 2–3 days. The problem was cured by returning to the previous operation mode.
1038	6	Refinery deethanizer stripper	At feed drum temperatures below 100°F, the tower flooded due to water and C <sub>2</sub> accumulation. To unflood, the boilup was cut or the drum warmed, but at the expense of poorer C <sub>3</sub> recovery. Gamma scans showed flood initiation in the middle of the tower, even though the highest hydraulic loads were at the bottom. A retrofit with high-capacity trays produced no improvement. Replacement of the inadequate water-removal facilities by an internal water-removal chimney tray eliminated the water accumulation.
1039	6	Refinery reboiled deethanizer absorber	The tower had no vapor or liquid recycle to the feed drum, two external water intercooling loops, and inadequate water-removal facilities. Water trapping during cold weather led to severe flooding and carry-over. Warming the feed drum and cutting the intercooler duty were cures, but at the expense of lower C <sub>3</sub> recovery. Later, a properly designed water draw tray was installed to eliminate water entrapment.
751	7	Refinery coker deethanizer stripper	The residence time in the downcomer-box water draw was too low to separate water, so no water was withdrawn. The water built up in the tower, periodically hiccuping, disturbing pressure control and contributing to condenser corrosion and fouling in the downstream debutanizer. Replacement with a seal-welded chimney draw tray eliminated the problem.
1001	8	Natural gas deethanizer	Small quantities of water accumulated in a refluxed deethanizer and caused the column to empty itself out from top or bottom, every few hours. This was cured by replacing reflux with oil absorption.
DT2.12	5		
DT2.13A	5	Refinery debutanizer	The tower, processing coker naphtha and straight-run naphtha, experienced a hiccup once every 4 h. The problem was more severe when the preheater fouled. The cure was to operate the top of the tower warm, but at the expense of lower recovery.
DT2.13B	5	Refinery FCC debutanizer	A tray temperature controller manipulated the reboiler steam. Periodically, the boilup rate rose over time without setpoint changes and would continue rising. The cure was to lower the control temperature by 20–30°F for a short time, then return to normal operation.
211	1	Azeotropic	Intermediate components accumulated in the tower, causing regular cycling (hiccups). This was cured by raising the top temperature. Product loss due to the higher top temperature was negligible.
DT2.14	5		
1213	9	Chemicals	A trapped component periodically built up in the upper section of a large distillation column. When it built up, the control temperature rose and increased reflux, eventually causing flooding. Gamma scans diagnosed the problem. Taking a purge side draw solved the problem.

Table 1 continues

gas that goes to fuel. The liquid from the absorber is mixed with fresh feed, cooled and flashed. Flash drum vapor is the absorber vapor feed. Flash drum liquid is stripped to remove any absorbed C<sub>2</sub> and lighter components. Stripper overhead vapor is also combined with the fresh feed prior to cooling.

When the column is properly designed, all the free water in the feed is removed in the flash drum. Only the minute amount of water dissolved in the hydrocarbon should enter. Inside the tower, the water tends to concentrate. The tower top is cool, and the naphtha tends to absorb water, sending it down the tower. The bottom temperature is hot, tending to vaporize the water and send it back up. Overall, the water concentrates in the middle. If the water removal facilities are inadequate, or are not in the region where water concentrates, or the absorber bottoms and/or stripper overhead are internal and not returned

to the feed flash drum, hiccups and floods may result.

Means of improving C<sub>3</sub> and C<sub>4</sub> recovery include cutting boilup, cooling the feed, or increasing the naphtha rate, each of which cools the tower and shifts the water concentration downward. The system in Figure 2 (Case DT2.10) had no water removal facilities below the feed. Attempts to recover more C<sub>3</sub> and C<sub>4</sub> led to concentration of water below the feed and to hiccups. The hiccups led to slugs of water in the stripper bottoms, which went into a hot debutanizer downstream, rapidly vaporizing and causing a pressure surge there. In Cases 1038 and 751, the water removal facilities did not have enough residence time for water separation, and were unable to mitigate the water accumulation and hiccups. In other cases, poor functioning of the feed water removal facilities caused hiccups.

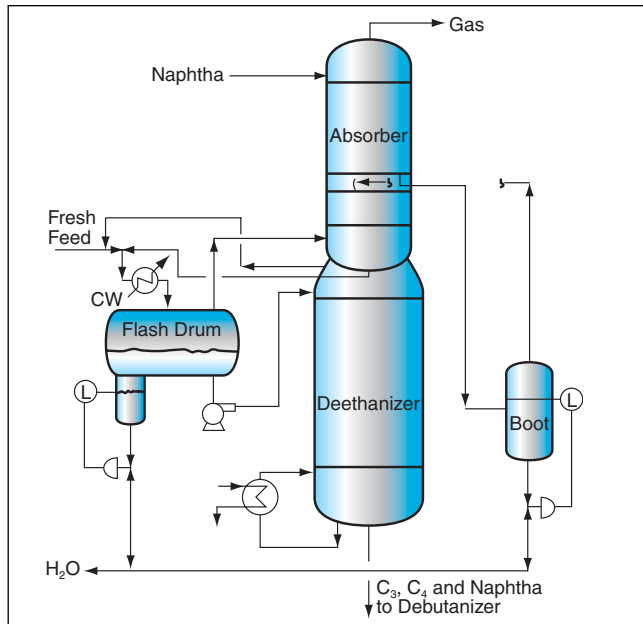
Figure 3 shows a methanol/water tower (Case DT2.15)

**Table 1. Hiccup experiences reported in literature — continued.**

Case	Ref.	Plant and/or Column	Brief Description
228	10	Multi-component	The capacity of a packed tower dropped to almost zero in 3–4 days. A shutdown and restart reestablished full capacity and the cycle repeated. The cause was accumulation of a trace intermediate component in the stripping section. It was cured by a vapor side draw between the beds.
DT2.15	5	Methanol/water	Several cases were reported in which oil, hydrocarbon and heavier alcohols caused hiccups in this separation. In one case, separation of an oil or liquid phase could have played a role.
DT2.16	5	Ammonia stripper	Small quantities of methanol accumulated, causing hiccups every 2–3 days. This was cured by increasing the overhead temperature.
DT2.22	5	Azeotropic dehydration	Hiccups every 2–3 days were caused by accumulation of an aromatic alcohol that was recycled into the tower with the benzene entrainer. This was cured by adding water to the decanter to extract the alcohol.
DT2.23	5	Extractive distillation	A pilot-scale tower separating aldehydes and ketones from alcohols using water as a solvent experienced hiccups every 2 h when one heavy ketone was at >1% concentration in the feed and at the same time the water/feed ratio was low. Modeling showed two liquid phases on most rectification trays. Foaming could have played a role. The cure was a higher water/feed ratio.
DT22.14	5	Solvent recovery	The tower separating organics from water periodically foamed due to accumulation of heavy alcohols just above the feed. The foam (which was seen in sight glasses) raised the tower dP. The cure was opening the side draw above the feed and temporarily cutting steam.
DT15.2	5	Formaldehyde	Premature foaming and flooding occurred near the feed. Cause was products of in-tower reactions forming an intermediate-boiling azeotrope that induced foaming. Enlarging downcomers, adding an antifoam, and minimizing feed acidity helped alleviate the problem.
202 DT2.17	8 5	Natural gas lean oil still	An added preheater that performed better than design caused the column to hiccup and empty itself every few hours either from the top or bottom. A bypass around the preheater eliminated the problem.
229	6	Refinery deethanizer stripper	Chronic and severe flooding occurred at low (70–80°F) feed drum temperatures. Gamma scans showed the flood initiated above the internal water-removal chimney tray, eight trays from the top, even though hydraulic loadings were higher further down in the tower. C <sub>2</sub> accumulation and foaming were possible causes. Adding a feed preheater cured the problem.
221	12	Refinery deethanizer stripper	Cold feed temperatures caused ethane condensation and accumulation, leading to hiccups once per week during the winter. This was solved by bypassing some of the feed around the feed cooler.

Note: DT indicates cases taken from “Distillation Troubleshooting,” by Kister, H. Z., to be published by Wiley, Hoboken, NJ, 2005 (5).

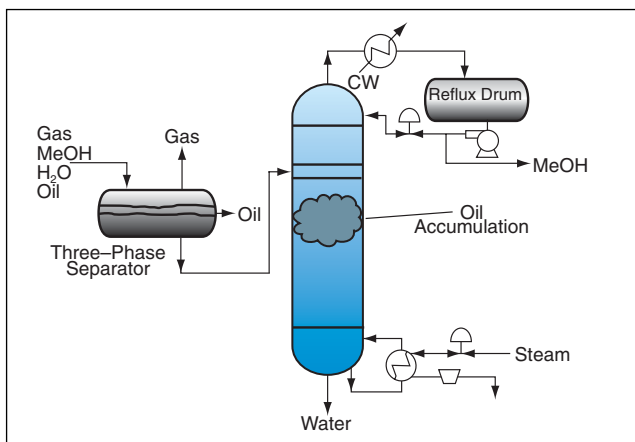
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■ Figure 2. Reboiled deethanizer absorber system that experienced water accumulation.

(11). Some of the oil phase from the separator was entrained in the feed, in addition to the oil dissolved in the methanol/water phase. Oil components rapidly became less volatile as they went up the tower, where methanol concentrations were higher, and rapidly became more volatile in the water-rich lower sections. Light oil components escaped overhead and heavy ones out the bottom, while mid-range oil components accumulated, leading to intermittent flooding and hiccups.

Figure 4 illustrates a solvent recovery tower that experienced hiccups even though phase separation did not appear to be an issue (Case DT2.14). The tower separated a low-boiling organics/water azeotrope from a water bottom stream. The tower experienced hiccups, at times due to concentration of *n*-propanol (cold cycle), at other times due to concentration of a



■ Figure 3. Oil accumulation in a methanol/water tower.

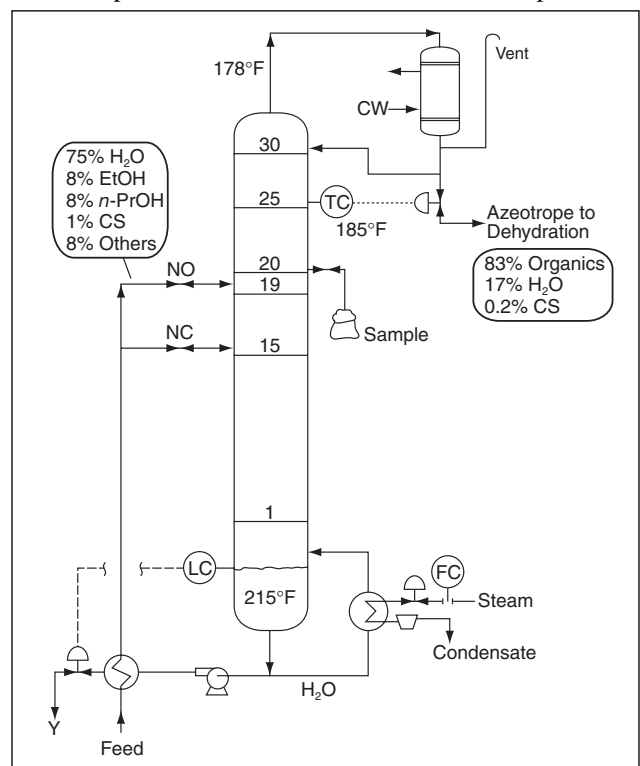
higher-boiling component designated CS (warm cycle). Both were very volatile in the water-rich bottom section, and became non-volatile in the cold ethanol-rich upper part of the tower.

Ross and Nishioka (13) showed that foam stability is at a maximum at the plait point, *i.e.*, just before the solution breaks into two liquid phases. In many cases, the intermediate component accumulation will drive the tower toward the plait point, foaming will break out, and the tower will foam-flood. Sometimes, the foam flood entrains the accumulating components into the top product, permitting the tower to return to normal. Foaming due to component accumulation occurred in Case DT22.14, and possibly also DT2.23 and 229. The interactions between intermediate component accumulation and foaming are discussed at length in Ref. 2.

As stated earlier, intermediate component buildup may take place over a section of the tower rather than over the entire tower. In Cases 202, 221, 229, and possibly DT2.13A, 1038 and 1039, the buildup occurred between the feed and either the top or the bottom. The buildup between the feed and top was caused by excessively hot feed, and that between the feed and bottom by excessively cold feed.

### Freeze-ups, corrosion and separation issues

Minor-component accumulation may lead to other problems well before the accumulation reaches or even approaches the hiccup concentration. In some cases, the buildup reaches



■ Figure 4. Solvent recovery column that experienced hiccups.

steady state, and the problem occurs due to steady-state concentration. The most troublesome problems include hydrates, corrosion, instability and purity issues (Table 2).

Tower hydrates are common in ethylene plant C<sub>2</sub> splitters and gas plant demethanizers. Small amounts of water in the feed (which is usually dried to less than 1 ppm) concentrate in

**Table 2. Tower hydrates, corrosion and other accumulation experiences reported in literature.**

Case	Ref.	Plant and/or Column	Brief Description
1020 DT2.20	14 5	Olefins C <sub>2</sub> splitter	Hydrates between the feed and the interboiler eight trays below occurred 2–3 times per week. Stepping up methanol injection and dryer regeneration gave only limited improvement. Methanol and dissolved hydrates got trapped in the kettle interboiler, from which they slowly batch-distilled back into the splitter. This was mitigated by draining methanol/water from the interboiler.
1024	15	Natural gas demethanizer	An ice plug prevented liquid draw from a chimney tray. The plug location was found by using radioactive spot density measurements along the pipe. The ice plug was melted by external heat.
DT29.1	5	Olefins C <sub>2</sub> splitter	The tower operating close to its natural flood limit flooded every two months. Natural floods were often mistaken for hydrates and were countered by methanol injection, which aggravated them. Installing separate dP recorders over the top and bottom sections permitted distinguishing natural floods from hydrates, and allowed early corrective action, reducing flood episodes to once a year.
DT2.9	5	HCl and chlorinated hydrocarbons	With less than 3 ppm water in the feed, the 15 middle trays severely corroded, needing replacement once a month. The top temperature was too cold, the bottom too hot, so the water was trapped and concentrated near the feed. The cure was to upgrade the tray metallurgy.
1040	29	Natural gas ethane recovery column (ERC)	An upstream constraint caused excessive water vapor in the feed gas to the extractive distillation column. The water peaked at the side reboiler in the middle of the stripping section, forming carbonic acid and corrosion. Increasing solvent circulation, or surges in inlet gas, pushed the water up, causing hydrates in the chilled condenser, with off-spec product for up to a week. Extensive methanol injection and column thawing dissolved the hydrates.
DT2.11	5	Refinery deethanizer	The tower bottom was cooled in an attempt to improve C <sub>3</sub> recovery. This led to water accumulation. The bottom trays in the absorber and most of the stripper trays experienced severe corrosion and required frequent repair and replacement.
1010	16	Refinery alkylation depropanizer	The column feed contained strongly acidic components, which dissolved in small quantities of water and caused a severe and recurring corrosion failure problem. The rate of corrosion failure was greatly reduced by adopting an effective dehydration procedure at startup. To dehydrate, acid-free butane was total-refluxed, while drains were intermittently opened until all water was removed.
15143	17	Refinery alkylation deisobutanizer	The distillate was C <sub>3</sub> /iC <sub>4</sub> , bottoms C <sub>5</sub> –C <sub>8</sub> , and side purge was nC <sub>4</sub> . The purge rate, adjusted per daily lab analysis, was minimized to minimize iC <sub>4</sub> loss. An insufficient purge led to nC <sub>4</sub> buildup. This and variable C <sub>5</sub> in the feed impeded temperature control and destabilized the unit. Stabilization was achieved by inferential model control.
210 DT2.8	4 5	Chemical	The vapor side-product impurity content was 10% (design 1%) due to a non-forgiving concentration profile. Over the eight design stages in the bottom bed, the concentration rose from 30% at the bottom, to 50% four stages below the side draw, then dipped to 1% at the side draw. A miss by 1–2 stages would bring the concentration to 10%.
216	18	Ethanol extractive distillation	Heavy alcohols (fusel oils) were side-drawn, cooled, then phase-separated and decanted from the tower's ethanol/water mixture. Depending on the draw tray temperature and composition, the cooled side draw did not form two liquid phases. The problem was diagnosed with the help of process simulation, and was solved by adding water to the decanter to ensure phase separation.
217	19	Alcohols/water	An intermediate component buildup caused the formation of a second liquid phase inside a column. The problem was solved by decanting the organic phase and returning the aqueous phase to the column.
136	20	Ethylene depropanizer, debutanizer	Small amounts of radon-222 (boiling point between propylene and ethane) contained in natural gas concentrated several-fold in the C <sub>3</sub> fraction. It decayed into radioactive lead and contaminated the towers and auxiliaries, as well as polymer deposits on trays and wastewater from reboiler cleaning. This caused problems with waste disposal and personnel entry into the towers. Ref. 20 describes the contamination survey, how it was tackled and the lessons learned.

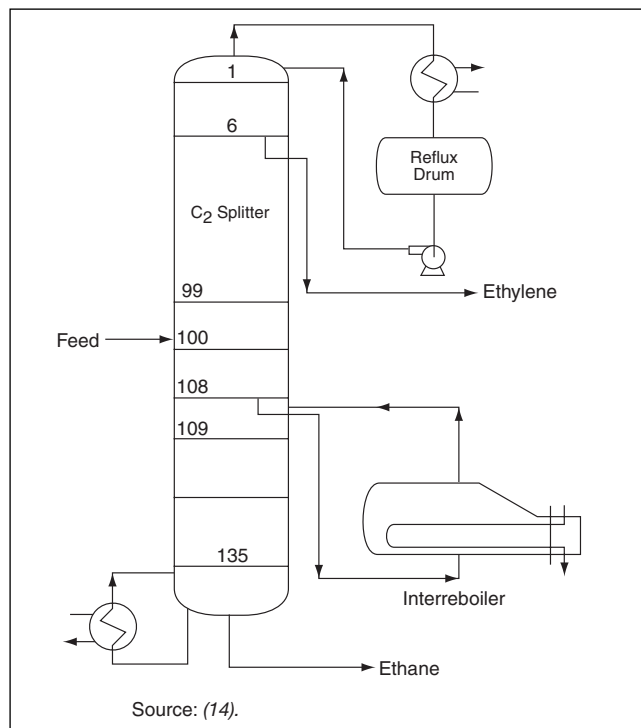
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the tower. Under the high-pressure, low-temperature conditions in the tower, the water combines with the light hydrocarbons to form solid ice-like crystalline molecules known as hydrates. The hydrates precipitate, plugging tray holes and valves and eventually restricting flow through the tray. Liquid accumulates above the plugged tray and the tower floods. A common cure is to dose the tower with methanol, which acts like anti-freeze and dissolves the hydrates.

The presence of an interboiler (or side reboiler) can interfere with hydrate removal. In the system in Figure 5 (Case 1020), the methanol and dissolved water were trapped by the interboiler. Over time, the water batch-distilled back into the tower, causing the hydrate to return. A blowdown from the reboiler removed the methanol and dissolved water.

Trapping and concentrating minor quantities of water, as minor as a few ppm, has caused major corrosion problems in towers handling hydrocarbons together with acidic components. It is common in refinery reboiled deethanizer absorbers (Figure 2). In a well-designed tower, the entering hydrocarbons are saturated with dissolved water. Any concentration or water entry beyond that will lead to a free water phase. If it persists, it will dissolve acidic components, resulting in weak acid circulating through the tower, which is death to carbon steel. A typical symptom is corrosion in the middle of the tower (sometimes also further down), fouling with corrosion products in the lower part, while the upper trays remain in good condition.



■ Figure 5. C<sub>2</sub> splitter with interboiler that experienced stubborn hydrates.

## Trapping of lights

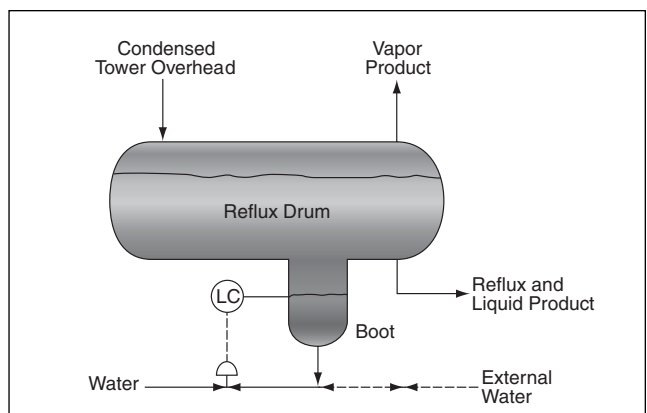
In many hydrocarbon towers, where water is an impurity, the reflux drum has a boot to remove the water (Figure 6). The heavier water phase descends to the boot, from where it is removed, typically on interface level control. If the amount of water is small, an on-off switch is sometimes used. If the boot level control malfunctions, water can be refluxed to the tower, causing fouling and corrosion in the tower as described in two cases (1004 and 15157) in Table 3.

Plugging may be a problem in the water outlet line from the boot because of low flowrates and because solids and corrosion products tend to become entrapped in the boot and the water stream. The converse problem is leakage rates across the water outlet control valve exceeding the rate of water inflow into the boot. This makes maintaining the level inside the boot difficult and causes loss of product in the water stream.

Both the plugging and leakage problems are most troublesome when there is a high pressure difference across the water-outlet control valve. A high pressure difference promotes valve leakage; it also tends to keep the valve opening narrow, which promotes plugging. Both problems can be overcome by adding an external water stream (which may be a circulating stream) to the boot outlet (Figure 6). This stream boosts velocity (21, 24) and safeguards against a loss of liquid level. The external water flowrate should be low enough to prevent excessive water backup from overflowing the boot during fluctuations. It is also important to pay attention to good level monitoring.

In some columns, the overhead is totally condensed and then decanted to form an aqueous stream and an organic product. The product is sent to a stripper to remove traces of the aqueous phase. The stripper overhead is recycled to the condenser inlet.

When a light condensable organic enters the column, it will end up in the organic phase. In the stripper, it will be stripped and returned to the condenser. Thus, it will become entrapped in the system, traveling back and forth between the condenser and the stripper. The stripper temperature controller will act to keep



■ Figure 6. Reflux drum boot arrangement.

**Table 3. Experiences of lights trapping.**

Case	Ref.	Plant and/or Column	Brief Description
1004	21	Refinery debutanizer	Column internals and reboiler tubes severely corroded after the water draw-off control valve on the reflux drum boot plugged. Manual draining was too inconsistent to prevent water (saturated with H <sub>2</sub> S) refluxing to the tower. Continuous flushing of the water draw line with an external water source prevented recurrence.
15157	22	Refinery FCC main fractionator	A plugged tap on the boot's oil/water-interface level transmitter locked the transmitter's reading at about 50%. Water refluxing to the fractionator over time caused cavitation and damage to the reflux pump, and deposited salts that plugged the top internals. Water in the naphtha destabilized the gas plant. The problem was eliminated by blowing the level tap.
111	23	Refinery HF alkylation depropanizer	The depropanizer overhead went to an HF stripper. The stripper bottoms was the propane product, while the stripper overhead was recycled to the depropanizer overhead. When ethane entered the depropanizer due to an upstream unit upset, it became entrapped in the overhead system and could not get out. The depropanizer pressure climbed and excessive venting was needed. This was cured by dropping the stripper bottom temperature to allow ethane into the propane product.

the light in the system, because its presence will reduce the control temperature, which in turn will increase the stripping heat input. The trapped light will raise column pressure, as well as the heat loads on the column condenser and stripper reboiler.

To provide an outlet for the light, either venting from the reflux drum or reducing the stripper heat input (thus allowing it to leave from the stripper bottom) is necessary. Reducing stripper heat input is more effective when the light is only slightly more volatile than the organic product. In Case 111, reducing the stripper heat input effectively provided an outlet for ethane trapped in the overhead of an alkylation unit depropanizer, where venting was relatively ineffective.

### Trapping by recycle

Table 4 reports cases of component trapping due to recycling of product to the feed, usually to improve product recovery. There are two solutions — adding some removal facilities to take out the component, or increasing the purge rates.

### Diagnosing component trapping

Key to the diagnosis, especially where hiccups are encountered, is the symptom. With hiccups, the symptom is cycling that tends to be self-correcting, taking place over a long time period. This is seldom less than 1 h, which distinguishes hiccups from other, shorter-period cycles, such as those associated with flooding or hydraulic or control issues, which typically have periods of a few minutes.

Typical cycle periods for component accumulation range from about once every 2 h to once every week. The cycles are often regular, but if the tower feed or product flows and compositions are not steady, the cycles may be irregular.

Drawing internal samples from a tower over the cycle (or over a period of time) is invaluable for diagnosing accumulation. Even a single snapshot analysis can show accumulation of a component. In the tower in Figure 4, a

sample drawn from a downcomer was key to the diagnosis. Two snapshot samples had concentrations of the accumulating components (*n*-propanol and CS) of about 50%, compared to less than 10% in the feed. Unfortunately, safety, environmental and equipment constraints often preclude drawing internal samples.

Tracking and closely monitoring temperature changes is also invaluable for diagnosing component accumulation. Temperature changes reflect composition changes. Since the accumulation is that of an intermediate key component, it tends to warm the top of the tower and cool the bottom of the tower. This tendency will be countered or augmented by the control system and by the rise in tower pressure drop, and these interactions need to be considered when interpreting temperature trends. In any case, one symptom is common. At the initiation stage, temperature deviations from normal are small, often negligible. As the accumulation proceeds, and the concentration of the intermediate key grows, systematic temperature excursions become apparent. Close to the hiccup point, temperature excursions become large.

The solvent recovery tower in Figure 4 was well-instrumented, with a temperature indicator every five trays. The tower experienced two types of cycles: a cold cycle, predominantly due to the accumulation of *n*-propanol, and a warm cycle, mainly due to the accumulation of CS. During the cold cycle, with the control temperature set at 185°F and bottom at 215°F, temperatures below the control tray began to creep down. The deviations were largest on tray 20, diminishing toward the bottom of the tower. Over a 2–3-h period, initially the deviations on tray 20 were small, but they became larger. Then, suddenly the column showed flooding signs and the temperatures dropped throughout. The operators tackled the problem by reducing the feed to about 40%, while maintaining the steam flowrate, which allowed the accumulated component to be purged from the top.



Table 4. Trapping by recycle.

Case	Ref.	Plant and/or Column	Brief Description
1019 DT2.18	25 5	Natural gas absorber and deethanizer (in series)	Modifications to recover the deethanizer overheads (previously sent to fuel) compressed, chilled, then recycled it to the absorber feed. Small quantities of water, previously going to fuel, returned to the absorber feed. The absorber top was too cold, and the deethanizer bottom too hot, to allow the water to escape. The water built up until freezing at the recycle chiller. For years, the chiller was thawed to flare once per shift. This was cured by adding a small glycol dryer at the compressor discharge.
139	26	Olefins C <sub>3</sub> splitter	The frequency of propylene product going off-spec with methanol increased following installation of a system that enhanced BTX and methanol recovery out of the plant wastewater. The recovered materials concentrated in the process. Corrective action was routing some water away from the process and stripping some with fuel gas into a waste gas burner.
DT2.19	5	Ethanol/water	Heads (light non-keys) and fusel oil (intermediate keys) products were mixed with cold water, then decanted, with the aqueous layer returned to the tower. Every 2–3 days the product alcohol developed an undesirable smell due to buildup of an impurity. This was cured by cutting the feed rate, while keeping the fusel oil and heads rates the same.

Note: DT indicates cases taken from “Distillation Troubleshooting,” by Kister, H. Z., to be published by Wiley, Hoboken, NJ, 2005 (5).

During the warm cycle, the temperatures near the bottom rose. The initial rise was slow. Then the bottom temperature suddenly jumped to 230°F (normal 215°F) and, at the same time, the bottom pressure went up by 2–4 psi, indicating flooding. The rise in bottom pressure accounts for much of this boiling point rise (about 3°F/psi). This occurred regardless of whether the tower temperature controller was in automatic or manual mode. The overhead temperature went up to about 190°F, indicating that the tower was emptying itself out. At the same time, the bottom flowrate did not change much. The operators tackled that by cutting the steam flow by about half and diverting the bottoms to an off-spec tank. This emptied the accumulation from the bottom rather than from the top, preventing problems in the dehydration system downstream and reducing product losses.

Figure 7 shows an azeotropic distillation system in which an organics/water azeotrope is dehydrated by injecting a hydrocarbon entrainer. The hydrocarbon is more volatile than the organics, so once the water is gone, it distills up, leaving an organic bottom stream. The water and hydrocarbon leave in the tower overhead, are condensed, then phase-separated in the reflux drum, with the hydrocarbon returned to the tower and the water (with some organics) removed. In this system, water descended to about Tray 10, forming two liquid phases on the trays above.

Figure 8 is based on actual operating charts for the system in Figure 7. The steam flowrate to the reboiler was temperature controlled. Initially, there was a good temperature gap between Trays 8 and 12, which is typical of the region where the second liquid phase disappears. As the accumulation proceeded, the second liquid phase descended toward Tray 8. It was countered and pushed back by the control action, but later came back. With time, the movement became more intense. In this case, only the temperatures on Trays 8 and 12 were prob-

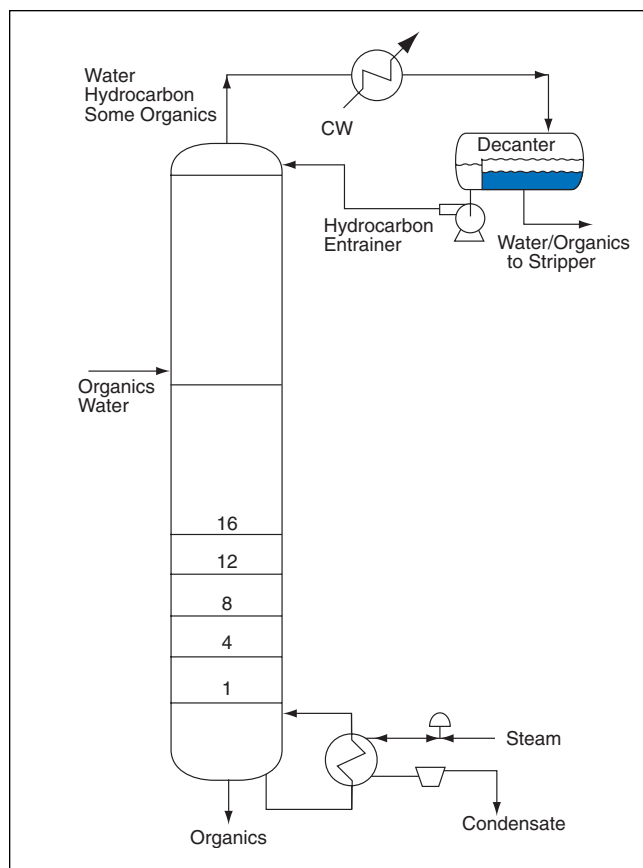
lematic; the temperatures on Trays 4 and 16 did not change much. This is typical, and for best diagnostics, the relevant temperatures need to be monitored. In most situations, this is readily achievable even if thermocouples are not present, since with today’s surface pyrometers, column wall temperatures can be reliably measured (27).

Item 3 of Figure 8 shows what happens when the temperature control was placed on manual — it no longer countered the accumulation, so the swings stopped. The temperature in this case was set high enough to push the accumulation up the tower. This provided temporary relief only. Eventually the buildup returned, requiring a further increase in steam. The only way to clear the buildup in the long term was to make drastic changes (analogous to those described for the Figure 4 system) that allowed the impurity to get out.

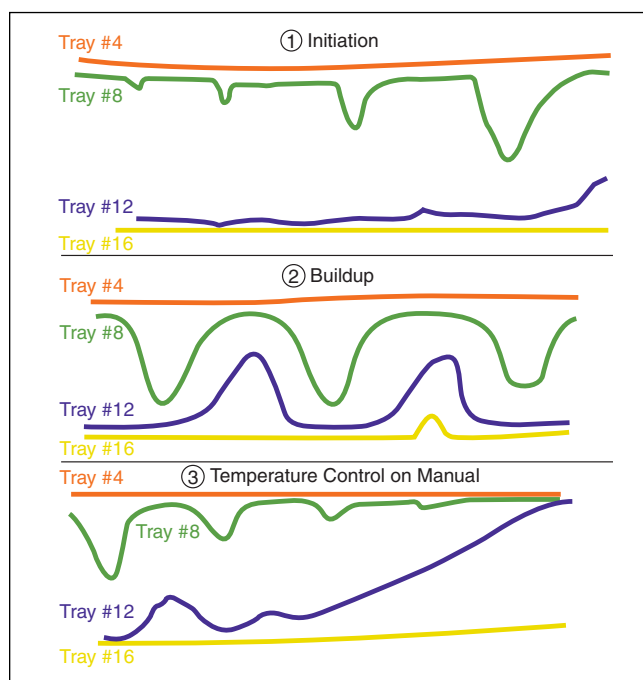
Simulations are also invaluable for diagnosing component accumulation. Steady-state bulges can be readily simulated and recognized on a plot of component concentration against stage numbers (Figure 1). But since most accumulation problems are non-steady-state, it is necessary to “trick” the simulation to avoid convergence problems (which may reflect the physical reality that the conditions specified do not lead to a stable steady-state solution.)

The main trick to overcome this is to study a related system that can converge. One example is to reduce the concentration of accumulating component in the feed to the point where convergence is readily reached. Then the concentration of the accumulating component in the feed is gradually increased, and the changes tracked by means of a tower concentration versus stages diagram for each step.

In the case of a second liquid phase, many stages in the simulation may alternate between a single liquid phase and two liquid phases, making convergence problematic. There,



■ Figure 7. Azeotropic distillation system that experienced hiccups.



■ Figure 8. Temperature changes accompanying component accumulation in an azeotropic dehydration tower.

either increasing or decreasing the concentration of the second liquid phase can help stabilize the simulation.

Gamma scans and dP measurements are also useful for detecting intermittent flooding. Gamma scans showing flood initiating in mid-column, away from feeds or draw points, provide evidence supporting accumulation, especially if the tower hydraulic loadings are higher near the top or the bottom. Gamma scans taken at different points in the cycle can help trace the accumulation from initiation (at which the trays operate normally) to flood. If enough nozzles are available on the tower, dP transmitters can be just as informative. Finally, sight glasses are extremely useful when safety requirements permit.

In each specific situation, one of the above techniques can be particularly valuable. For instance, Case DT29.1 (Table 2) describes a situation in which recording the dP across each section of the C<sub>2</sub> splitter permitted excellent diagnosis of hydrates. The hydrates were encountered below the feed, in a tower section that was not operated at maximum load, so a rise in dP of the bottom section signified hydrates, while a dP rise in the loaded top section signified regular flooding.

There are five classes of cures to hiccup and tower accumulation problems: reducing the column temperature difference; removing the accumulated component from the tower; removing the accumulated component from the feed; modifying tower and internals; or living with the problem.

### Reducing the column temperature difference

This can be done either by raising the top temperature or lowering the bottom temperature, or both. This enables the accumulating component to escape with a product stream.

The effectiveness of this technique may be limited, and it can cause off-spec products and/or excessive product losses. It was successfully applied in several of the experiences reported in Table 1. In some of these (DT2.10, DT2.13A, DT2.13B), there was a significant product recovery penalty. In the others (1001, 211, DT2.16), the penalty was negligible.

A special case is accumulation between the tower feed and the top or between the feed and the bottom. Here, the feed temperature is often lowered to prevent accumulation of the component in the top section or raised to prevent accumulation in the bottom section. Similarly, a feed point change may encourage the component to leave the column at one end or another. Proper bypasses around preheaters and precoolers are invaluable for this purpose (e.g., Cases 202 and 221).

### Removing the component from the tower

Usually, this technique involves drawing a small liquid or vapor side steam from the column, removing the intermediate component from the side stream externally, and returning the purified side stream to the column. If purification is not economical, the side stream may be processed elsewhere, blended

## Distillation

with a slop stream, or just purged. The side stream drawn should be large enough to remove the amount of the component entering in the feed. Since at the draw-off location the component is normally far more concentrated than in the feed, the stream drawn is usually small.

A typical example of this technique is using an external boot for removing water from inside a hydrocarbon distillation column (Figure 2). Only a small portion of the tray liquid goes to the boot. This portion must be large enough to prevent water accumulation in the tower, but small enough to permit adequate hydrocarbon/water separation in the boot. Proper design of the draw box, as well as the piping to and from the boot, are essential for avoiding siphoning, choked flow, and excessive downcomer backup. As with the reflux drum boot, an external water supply may be desirable. Alternatively, the water/hydrocarbon separation can be performed inside the tower, but this requires a large chimney tray to provide enough settling time for the entire liquid flow. Cases 1038, 1039, 751 and 2.10 (normal C<sub>3</sub> recovery) report successful water removal from deethanizers.

Another typical example is removal of higher-boiling alcohols (“fusel oil”) from ethanol/water columns. Unless removed, they will concentrate in the column, and upon reaching their solubility limit form a second phase and cause cyclic flooding as described earlier. Fusel oil is commonly removed by a similar scheme to that in Figure 2, except that the side stream is usually cooled prior to phase separation and the aqueous phase (rather than the organic phase) is returned to the column.

Another application of this technique is in the separation of ethyl ether from aqueous ethanol, where benzene tends to build up in the bottom section. Removal of a small benzene-rich side stream out of the bottom section effectively increased the column’s overall capacity (28).

The component removal technique need not be confined to gravity settling. Other separation techniques, such as stripping and adsorption, may also be employed. Ref. 2 mentions the use of a side dryer to prevent hydrates in a C<sub>2</sub> splitter.

The best location for the side draw point can be determined by simulation, but changes in composition and simulation inaccuracies can alter the optimum feed point. Case 2.10 in Table 1 (Figure 2) describes a scenario in which the optimum draw point shifted down the tower over the years, as the economics for recovering C<sub>3</sub> from refinery fuel gas improved. A flexible solution often employed is to install draw facilities on several trays, which permits online optimization. While this is easy to do with tray towers, it may be more difficult with packings, where side draws are normally taken from collectors or vapor spaces between the beds, which limits the alternatives.

Another question that needs to be addressed is what

purge rate is required. Often the side draw contains good product that needs to be recycled after the accumulating impurity is removed. If most of the good product is recovered from the side draw, there is little issue with drawing a larger side draw flowrate than needed. But if some of the product cannot be recovered from the side draw, there is an incentive to minimize the side draw flowrate. This is achieved at the risk of not removing enough to fully mitigate the accumulation. Good control can play an important role here, as shown in Case 15143.

Cases 2.10 (during normal operation), 1038, 1039, 751, 1213, 228 and DT22.14 (Table 1) report success with side draws.

### Removing the component from the feed

It is surprising how often this can be the best solution. The tower in Figure 4, in its initial years of operation, experienced no hiccups. The problem started when the solvent composition changed. During the initial operation, the tower feed had twice the ethanol concentration and half the *n*-propanol concentration, making *n*-propanol accumulation far less.

A similar experience occurred in an ethanol/water separation tower that normally received feed from a process that hydrated ethylene and was lean in heavier alcohols (like propanol and butanol). Occasionally, the plant processed a low-cost feedstock from fermentation rich in the heavier alcohols. With this feedstock, severe hiccups were experienced.

Cases DT2.22 and DT15.2 in Table 1 and 217 in Table 2 are also cases in which an accumulation problem was cured by removing the accumulating component from either the feed or the reflux drum. This is also the cure contemplated for Case 1040 (29).

### Modifying the tower and internals

A large number of stages is conducive to accumulation. In one case, doubling the number of separation trays tremendously intensified tower hiccups. In another, hiccups were avoided in a new tower by reducing the number of stages (more reflux, well above the normal optimum), which allowed the same product purities to be maintained.

In some cases, (e.g., DT15.2) accumulation led to foaming. Addressing the foaming issue (for instance, by enlarging downcomers or injecting antifoam) helped alleviate the adverse effects.

When the main issue with the accumulation is corrosion, changing materials of construction has effectively mitigated the effects in many cases (e.g., DT2.9, DT2.11). Several refinery deethanizers containing stainless steel internals experienced no significant corrosion, whereas those with carbon steel internals often do.

## Living with the problem

In many situations, it is uneconomical to cure the problem. At times the product loss is minimal and the problem is just an operating nuisance. Steps such as improving controls, minimizing the accumulating component in the feed by trimming upstream units, reducing or rerouting recycle streams, changing product specs, and providing off-spec and storage facilities have helped to reduce hiccup frequency and intensity and minimize product losses.

## Epilogue

Regardless of whether you decide to live with an accumulation problem or attempt to solve it, accumulation remains a potential source of erratic operation, flooding, cycling, foaming and corrosion. It is therefore important to understand the principles, be familiar with the industry's experience, and correctly diagnose and address accumulation each time it appears.

CEP

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