THE ROLE OF CATALYST IN FCC TROUBLESHOOTING

SUMMARY

Fluidized Catalytic Cracking is a complex process where problems are not easily defined or isolated. This paper presents some background regarding the effects of catalyst properties on operating problems. In commercial operations it is essential to separate these effects from the influence of hardware malfunctions or changes in process conditions. This requires a basic understanding of fresh catalyst management and the implications of E-cat analyses.

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1. INTRODUCTION TO CATALYST MANAGEMENT

Continuous addition of fresh catalyst to the FCC is essential for at least three reasons:

- to maintain optimum catalyst activity and selectivity
- to keep metals on E-cat at an acceptable level
- to make up unit catalyst inventory to compensate for catalyst losses

The primary criterion governing fresh catalyst addition is activity maintenance. The following factors may serve as guidance for catalyst management:

- the optimum E-cat activity level, determined by feed quality, unit limitations and yield/product quality requirements
- the range of metals, primarily Ni, V, Na, to be tolerated on E-cat, on a temporary or permanent basis
- the response of E-cat activity to fresh catalyst addition

The optimum catalyst activity level must be determined for any specific operation. Generally, cleaner feeds allow higher E-cat activity to boost conversion. Heavier and more contaminated feeds lead to more moderate catalyst activities, due primarily to heat balance constraints (i.e., delta coke).
In principle, three alternative catalyst management policies exist:

1. **Balanced addition:** amount of fresh catalyst added equals catalyst losses. Optimum catalyst activity and selectivity is often not obtained with this policy.

2. **Catalyst withdrawal:** fresh catalyst addition equals the sum of catalyst losses and withdrawal. This type of operation is practiced to reduce metals poisoning, or to enhance catalyst replacement for more optimum system activity.

3. **Catalyst flushing:** the addition of E-cat or low activity flush catalyst is applied to avoid excessive equilibrium activity or delta coke, and reduce total catalyst costs especially during periods of high losses or high metals.

Another parameter to be considered is optimum catalyst particle size distribution in the circulating system. Catalyst ranges from 1 to 150 microns in size. Catalyst fines in the 0-20 micron range, either entering with fresh catalyst or generated by attrition, are quickly lost through regenerator and reactor cyclones. In some cases even particles above 40 microns are not retained properly, indicating cyclone problems. This influences not only catalyst losses, but also replacement efficiency of fresh catalyst and circulation properties of the E-cat.

### 2. CALCULATION OF CATALYST REPLACEMENT

A catalyst switch is usually made by adding the new type of fresh catalyst on top of the old inventory. The rate of replacement depends on the size of the inventory and the catalyst addition and withdrawal rates. Calculation of the replacement is not straightforward due to the continuous losses of fresh catalyst together with the E-cat. With the following equation, the replacement rate can be estimated (figure 1):

\[
\text{FRACTION REPLACED} = 1 - e^{ -\text{EFF} \times \text{CAD} / \text{INV}}
\]

with:  
EFF = replacement efficiency factor  
CAD = new catalyst added since switch (tons)  
INV = catalyst inventory (tons)

For properly operating cyclones the replacement efficiency is about 0.80, indicating that some 20% of the fresh catalyst is not retained. With a typical addition rate of 2% of inventory per day, 60% will be replaced in about 60 days. In most cases the effect of the catalyst switch should be visible after 60% replacement, when most of the active E-cat is then the new catalyst. Remaining prior catalyst is substantially inactive.
A different approach is to compare the equilibrium analyses with the analyses of the fresh catalyst before and after the switch. In this approach it is assumed that the composition of the catalyst lost is equal to the composition of the equilibrium mixture. The parameters to calculate the replacement are usually the alumina and rare earth contents. Other (trace) elements can also be applied, such as separate RE elements like Ce or La, or additives such as TiO₂.

3. CONTROL OF METALS POISONING

In principle all metals entering the FCC reactor with the feed are deposited on the catalyst. A simple mass balance adequately describes the effect of catalyst addition on equilibrium metals. This is illustrated in figure 2. In some cases the buildup of metals is different due to increased pickup of metals by the catalyst fines that leave the system, or volatility of some metals at high regenerator temperatures.

Nickel (to a lesser extent vanadium and other metals) causes a large increase in the production of hydrogen and consequently the volume flow to the wet gas compressor. The addition of passivator (e.g. antimony) to reduce dehydrogenation is a proven technology and is recommended for units operating at extremely high nickel levels. For units at modest Ni levels, or operating periodically with Ni-rich feed, the installation of an antimony dosing system may not be justified economically. In such cases the nickel tolerance of the catalyst is an important factor. Albemarle has catalyst zeolite and matrix technology that has demonstrated excellent nickel tolerance. In this technology, proven superior at Ni levels over 4000 ppm on catalyst, the nickel is encapsulated and deactivated in large pores with low acidity.

Figure 1: Effect of catalyst addition on replacement
If the production of $C_1$ and $C_2$ increases, the compressor power requirement also goes up. A reduction in the amount of dry gas is obtained by minimizing thermal cracking in the riser and reactor. A low regenerator temperature is beneficial, which makes the delta coke performance of the catalyst important. A higher catalyst activity can also be considered because it improves the balance between catalytic and thermal cracking, provided that the delta coke does not increase substantially (figure 3).

Finally, a higher compressor inlet temperature or lower inlet pressure increases both the gas volume and the power required. It is clear, therefore, that the term “compressor limited” is too broad to properly define the FCC downstream processing in terms of adjusting the catalyst management. A more thorough analysis is needed to establish the actual limits. This requires, among other things, accurate monitoring of the gas yield breakdown and the E-cat analysis.
The effects of metals, especially Ni, V, and Na, can be minimized by adding high levels of fresh catalyst, or blends of fresh and E-cat or flush cat, to reduce metals concentrations in catalyst inventory. A plot of Na on E-cat surface area, which reflects catalyst activity, is shown in figure 4. Vanadium also reduces catalyst activity, depending on regenerator conditions, and can be combated with metal traps in the catalyst.

Figure 4: Effect of sodium on equilibrium surface area

4. SPENT CATALYST STRIPPING

Poor spent catalyst stripping causes an increase in delta coke, and especially in amount of hydrogen in coke, which result in a decrease of catalyst circulation rate at a given heat balance duty. The regenerator temperature will increase, and eventually the feed rate may have to be decreased, or feed quality improved. A stripping problem may be apparent from an increase in hydrogen in coke calculated from the flue gas analysis, but care is needed to ensure the flue gas is properly sampled and analyzed.

The optimum steam rate to ensure proper stripping depends on the catalyst circulation rate, the stripper design, the catalyst porosity and its equilibrium catalyst surface area. Good stripping occurs when the delta coke is minimized. For a given design, the stripping steam rate is optimized by adjusting it to a value slightly above the one which minimizes the regenerator temperature. This is determined by ramping steam rate upward until regenerator temperature stops dropping.

The catalyst architecture can directly affect the observed stripper performance. Entrainment of hydrocarbons in the catalyst pores and the resulting carry-over to the regenerator will be minimized by use of a large-pore catalyst. With such a catalyst, it is easier to remove the hydrocarbons from the catalyst. An example of surface area impact is shown in figure 5.
5. ANALYSIS OF EXCESSIVE CATALYST LOSSES

The E-cat fines content decreases with deteriorating cyclone performance. This usually results in a continuous rise of the average E-cat particle size (figure 6). The replacement efficiency drops as well. A procedure to troubleshoot this problem is provided in FCC Manual 5.5; in this section we summarize the issues.

Catalyst is usually lost through the reactor cyclones to the slurry oil or through regenerator cyclones to the stack (or downstream catalyst removal devices such as third stage separators or ESP). The losses are acceptable as long as they are less than target fresh catalyst makeup rate, slurry oil is within specification on ash and metals content, and flue gas dust emissions are within legal limits. Total catalyst losses can be calculated by unit and hopper inventories, taking the ABD as an indication of catalyst density:

Total losses = Initial inventory + Fresh catalyst loaded – Final inventory
To monitor cyclone performance, periodic analyses of the particle size distribution of the E-cat and fines samples are required (figures 7 and 8). For units with a turbo expander on the flue gas, the regenerator fines are taken from the third stage separator underflow. Reactor fines can be sampled by hot slurry filtration or ashing.

Figure 7: Particle size distributions of equilibrium catalyst
Figure 8: Particle size distributions of equilibrium fines

Attrition = increased catalyst losses due to attrition problems
Cyclones = increased catalyst losses due to cyclone malfunction

There can be several reasons for deteriorating cyclone performance:

- increased loading, either solids or vapor
- holes in cyclone body, outlet, dipleg, or plenum chamber
- erosion of cyclone internal lining
- lost dipleg seal, dipleg blockage or blocked flapper or trickle valve

An increased load can be caused by poor air distribution, leading to localized high velocities and catalyst entrainment. Increasing regenerator bed level may help to combat the maldistribution. Once cyclones are badly eroded, little can be done to keep the unit operational for long periods with controllable losses. If there are holes near the bottom of diplegs, it may be possible to raise bed level to seal them and reduce losses.

Measured bed levels are actually pressure drops, and require calculations to determine the physical height of catalyst. This requires two separate dp-cell transmitters, one to determine bed density and the other to determine total bed pressure drop. For proper troubleshooting, these must be calibrated and free of blockages. A change in catalyst type can cause a change in catalyst bed level if the catalyst density differs. Cyclone efficiency and fines retention usually improves with increase in E-cat density (figure 9), though fluidization actually is better with lower catalyst density.
6. CATALYST CIRCULATION PROBLEMS

Proper fluidization of catalyst, both in the beds and transfer lines, is essential to the operation of the FCC unit. A basic measure of the fluidization properties of FCC catalyst is given by the ratio of minimum bubbling ($U_{mb}$) and minimum fluidization ($U_{mf}$) velocity as described by the following equation*:

$$U_{mb} / U_{mf} = 2300 \left( \frac{\rho_g^{0.126} \mu^{0.523} e^{0.716F_{45}}}{D_p^{0.8} ((\rho_p - \rho_g) g)^{0.934}} \right)$$

with:
- $\rho_g$ = gas density, kg/m$^3$
- $\mu$ = gas viscosity, kg/m-s
- $F_{45}$ = fraction of fines < 45 microns
- $D_p$ = mean particle size
- $\rho_p$ = particle density
- $g$ = gravitational constant


The ratio $U_{mb} / U_{mf}$, also called bed expansion, is larger than 1. The bed expansion (figure 10) increases with this ratio and favors smooth circulation. The required ratio is not an absolute value, but depends on unit characteristics and operating conditions.
The following factors appear to improve fluidization, according to the above correlation:

- low mean particle size
- low particle density
- high fines content
- high density / viscosity of fluidizing gas

Figure 10: Typical bed expansion curve of FCC catalysts

The E-cat fines have a positive effect on fluidization as they influence both the F45 fines fraction and the mean particle size. The fines content depends on the balance between cyclone design, unit attrition sources, fresh catalyst fines content, fresh catalyst attrition index, amount of E-cat fines recycled, and other factors which determine cyclone loading, e.g. operating pressure, temperature, solids concentration and gas velocity.

If a unit displays fluidization problems the following approaches are recommended:

- localize problem by measuring the pressure profile through the unit
- increase fines concentration, by adding more fresh catalyst, using softer catalyst, recycling E-cat fines, and/or a flow improver
- increase density/viscosity of fluidizing gas if possible (e.g. less steam content)

Fines can be returned to the reactor/regenerator by recycling the main column bottoms, however this stream has a negative impact on unit heat balance and yield distribution. Use of slurry settlers, electrostatic separators or sintered metal filtration to recover such fines from slurry for return to the riser will minimize such impacts. Recycling fines from third stage separators is also an option, though a method to permit frequent re-injection is required to permit regular return to the regenerator (e.g., use of a separate fines addition hopper). The fresh catalyst PSD and attrition properties can be adjusted to some degree to improve the fluidization properties of the E-cat circulation system.