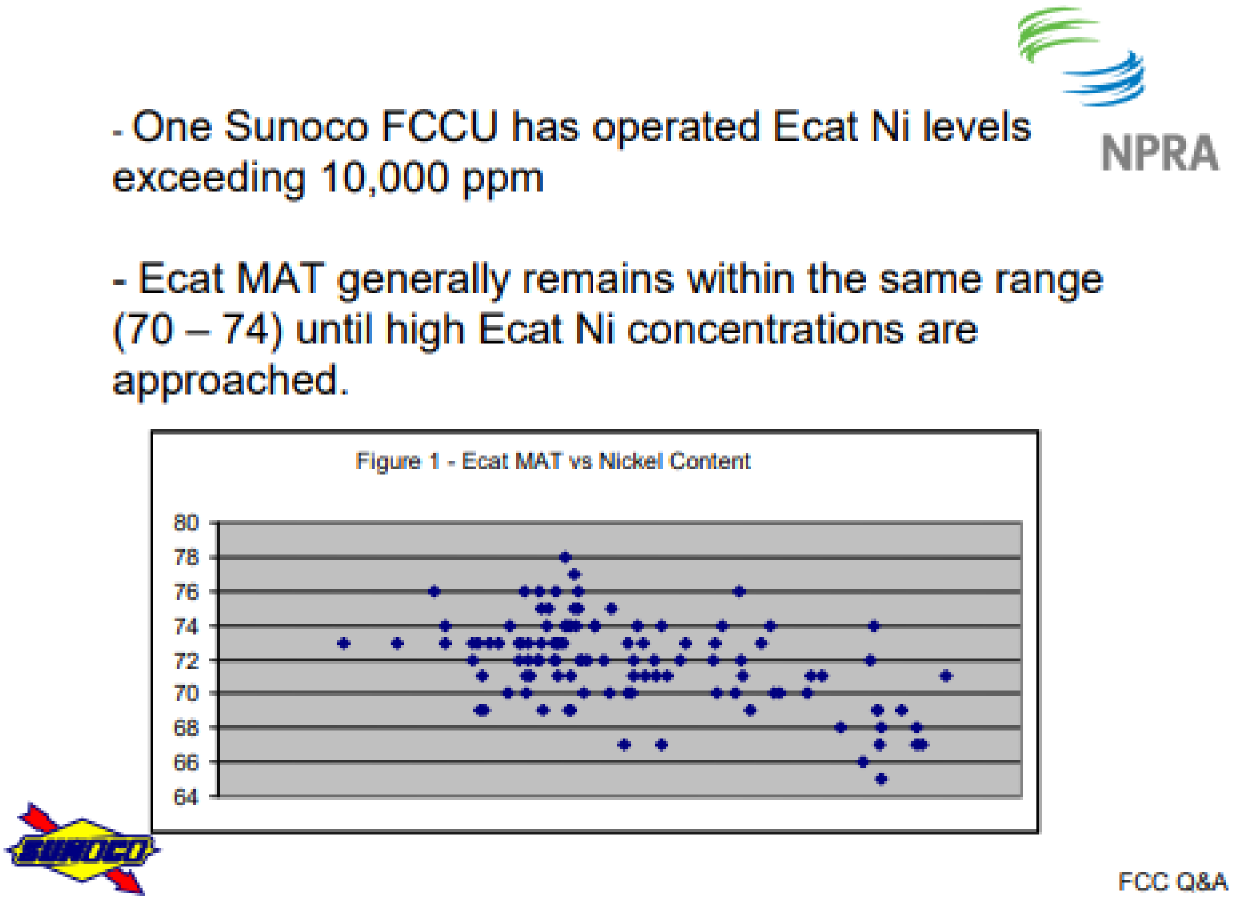
Question 10: What is your recent experience regarding the maximum level of equilibrium catalyst metals (Ni, V, Na, Fe, Ca) in FCC units processing residual feedstocks? Have there been any recent improvements in vanadium passivation technologies? At nickel levels approaching 10,000 ppm, have you experienced increased catalyst deactivation as evidenced by lower equilibrium zeolite surface area?

ASDOURIAN (Sunoco Inc.)

Here we see data regarding one of our FCCUs that operates at e-cat nickel levels exceeding 10,000 ppm. We observe that the MAT generally remains within the same range until high e-cat nickel concentrations are approached.



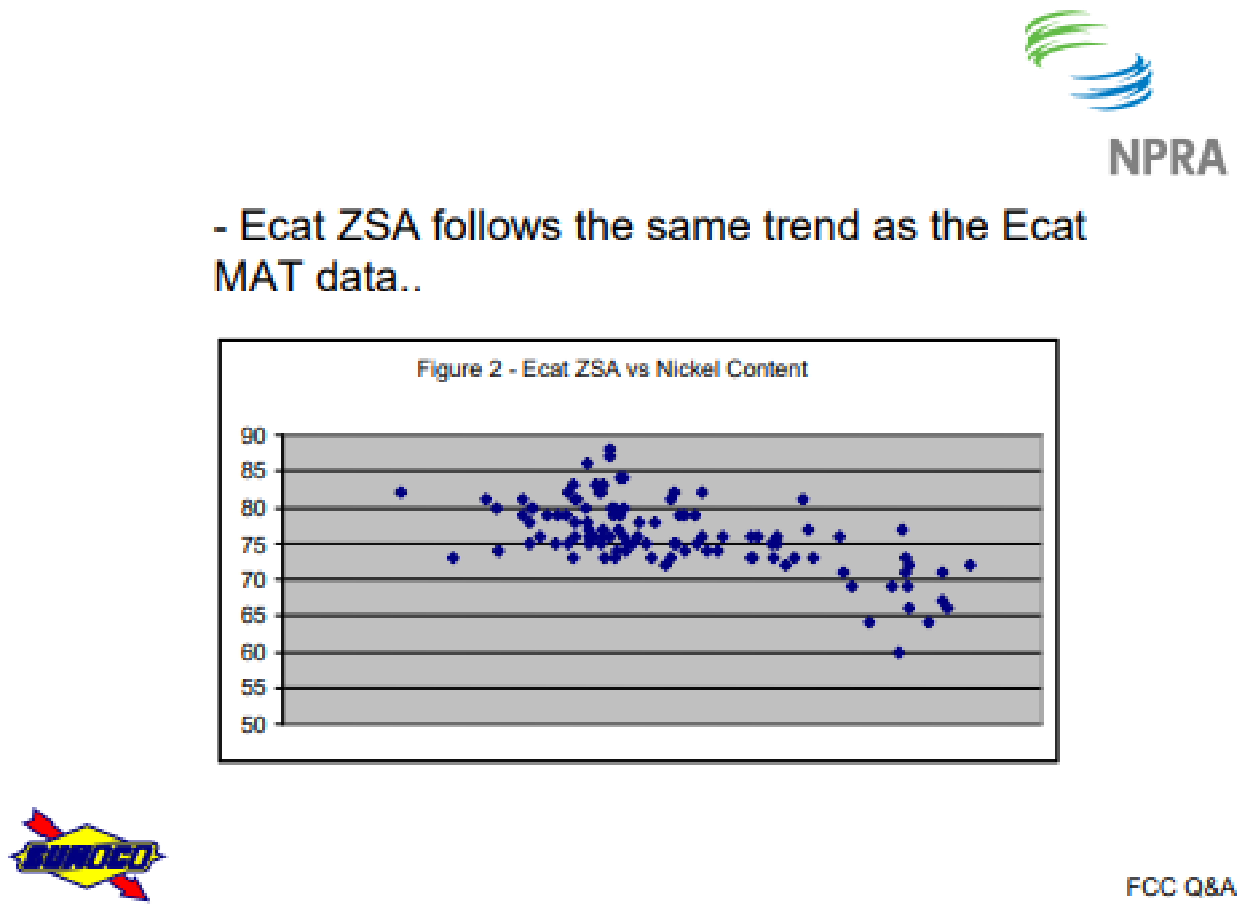
- One Sunoco FCCU has operated Ecat Ni levels exceeding 10,000 ppm

- Ecat MAT generally remains within the same range (70 – 74) until high Ecat Ni concentrations are approached.

Figure 1 - Ecat MAT vs Nickel Content

FCC Q&A

The relationship between the zeolite surface area versus nickel content is shown in the next plot. Again, it follows the same trend as the MAT versus the nickel content.



- Ecat ZSA follows the same trend as the Ecat MAT data..

Figure 2 - Ecat ZSA vs Nickel Content

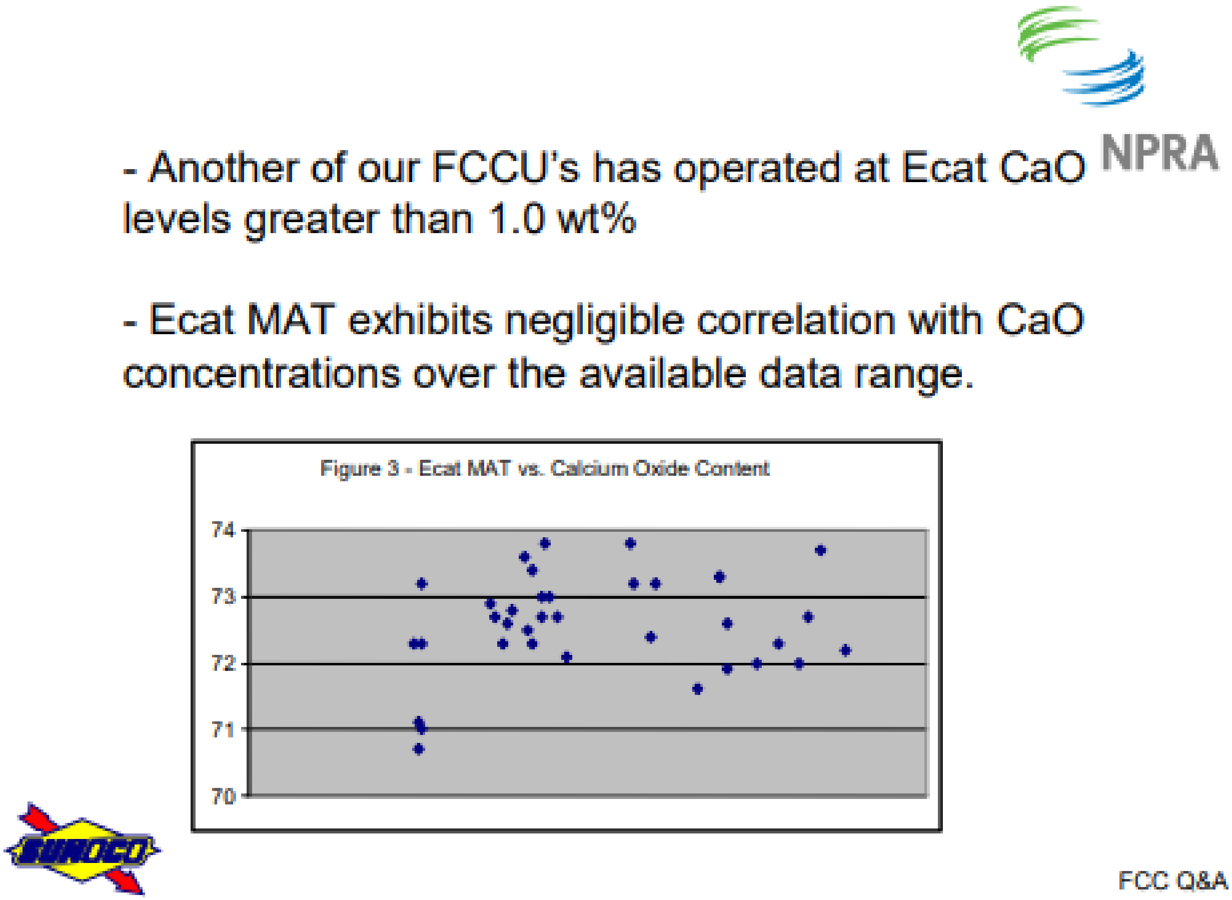
FCC Q&A

The decline in catalyst activity with increase in nickel levels has been observed, although we do not believe that a loss in zeolite surface area is directly related to nickel content; rather, it is a result of other contaminate matters being present. As a result of elevated nickel levels, we believe that mass transfer becomes inhibited due to catalyst pore obstruction that also contributes to a loss in catalyst performance.

Our primary concern with nickel deposition on e-cat is the resulting increase in dehydrogenation reactions. I should point out that iron behaves in the same manner, although it is not as active as nickel in terms of catalyzing these dehydrogenation reactions.

Increased hydrogen production is undesirable since it increases gas production and decreases the mole weight of the wet gas. The negative effect can be minimized by the addition of antimony, which passivates nickel. Feed and e-cat nickel content and e-cat antimony and nickel ratios are closely monitored. The antimony addition rate is adjusted accordingly.

Another of our FCCUs has operated at e-cat calcium oxide levels greater than 1 wt%. Here we see a plot of the MAT versus calcium oxide content.



- Another of our FCCU's has operated at Ecat CaO levels greater than 1.0 wt%

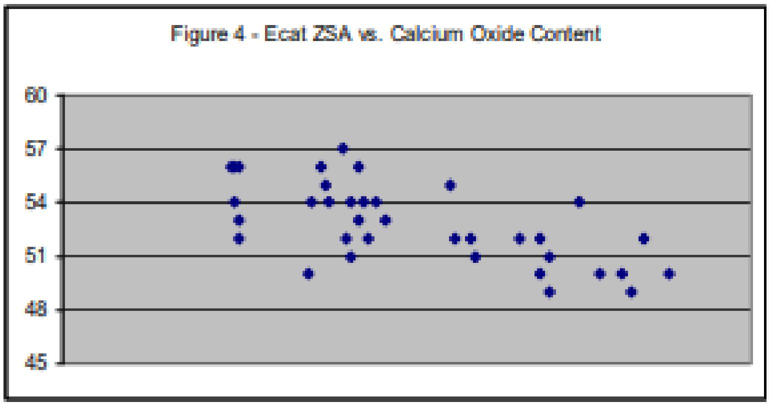
- Ecat MAT exhibits negligible correlation with CaO concentrations over the available data range.

Figure 3 - Ecat MAT vs. Calcium Oxide Content

FCC Q&A

The MAT exhibits negligible correlation with the calcium oxide concentration over the available data range. The e-cat zeolite surface area begins declining at high calcium oxide levels. Perhaps the feedstock used in the laboratory testing is less sensitive to this change and therefore the MAT shift is small. We would suspect the cracked stock, like coker products, is the more difficult to crack and/or heavier feed would show a decline in the MAT as in the ZSA plot.

- The Ecat ZSA declines at high CaO levels.



FCC Q&A

High levels of calcium on e-cat can lead to formation of eutectics; and depending on regenerator conditions, it can result in a decline in catalyst performance. I should point out that sodium, which behaves in the same manner, is an even worse actor, since it also attacks the zeolite structure of the catalyst. We control calcium oxide levels on our e-cat by manipulating catalyst additions.

Yet another of our FCCUs has operated at e-cat vanadium contents of several thousand ppm, and that elevated iron content. Here we see a plot of the MAT versus the vanadium content. We also have a plot of the zeolite surface area versus vanadium content, which shows the same correlation.

- Yet another of our FCCU's has operated at Ecat Vanadium content of several thousand ppm

-The Ecat MAT remains fairly steady over the range of Vanadium content

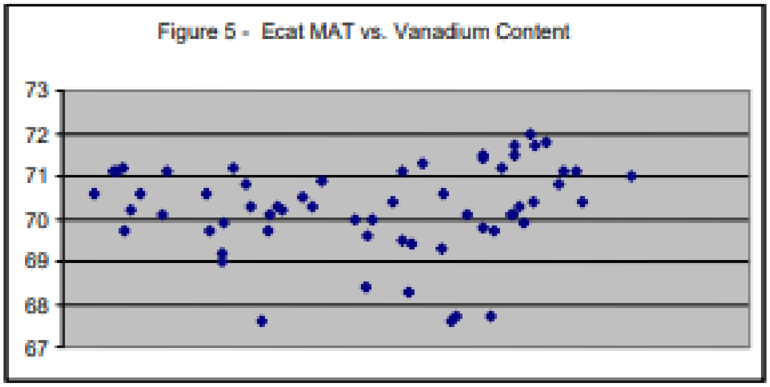


Figure 5 - Ecat MAT vs. Vanadium Content

- Ecat ZSA follows same trend as MAT

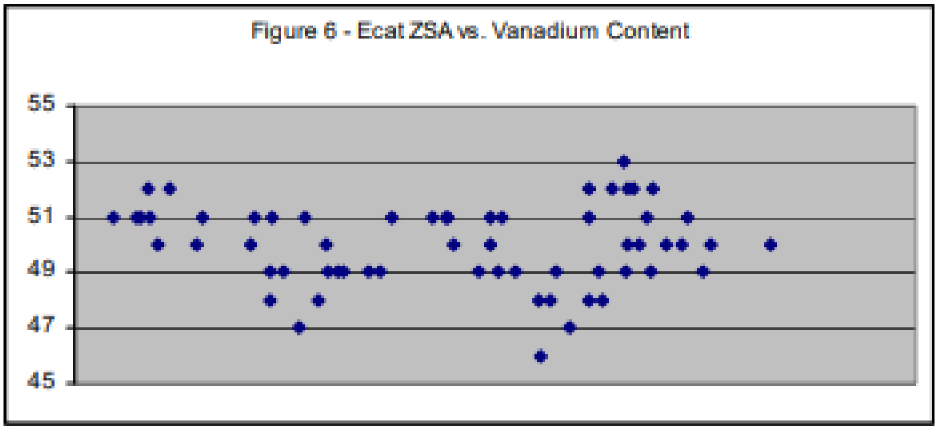


Figure 6 - Ecat ZSA vs. Vanadium Content

Vanadium forms acidic compounds in the regenerator, which then interact with the catalyst zeolite structure, causing deactivation. Vanadium passivation has been accomplished via deeper partial burn, adding matrix surface area, adding sacrificial zeolite, examining higher rare earth and zeolite ratios, and using a vanadium catalyst trap. These aforementioned approaches are not new.

Fresh cat adds are adjusted based on feed metals content to manage contaminant metal levels. We work closely with our catalyst suppliers to formulate catalysts specific for each one of our FCCU operations with regard to metals trapping, zeolite and matrix surface area, and fresh cat activity.

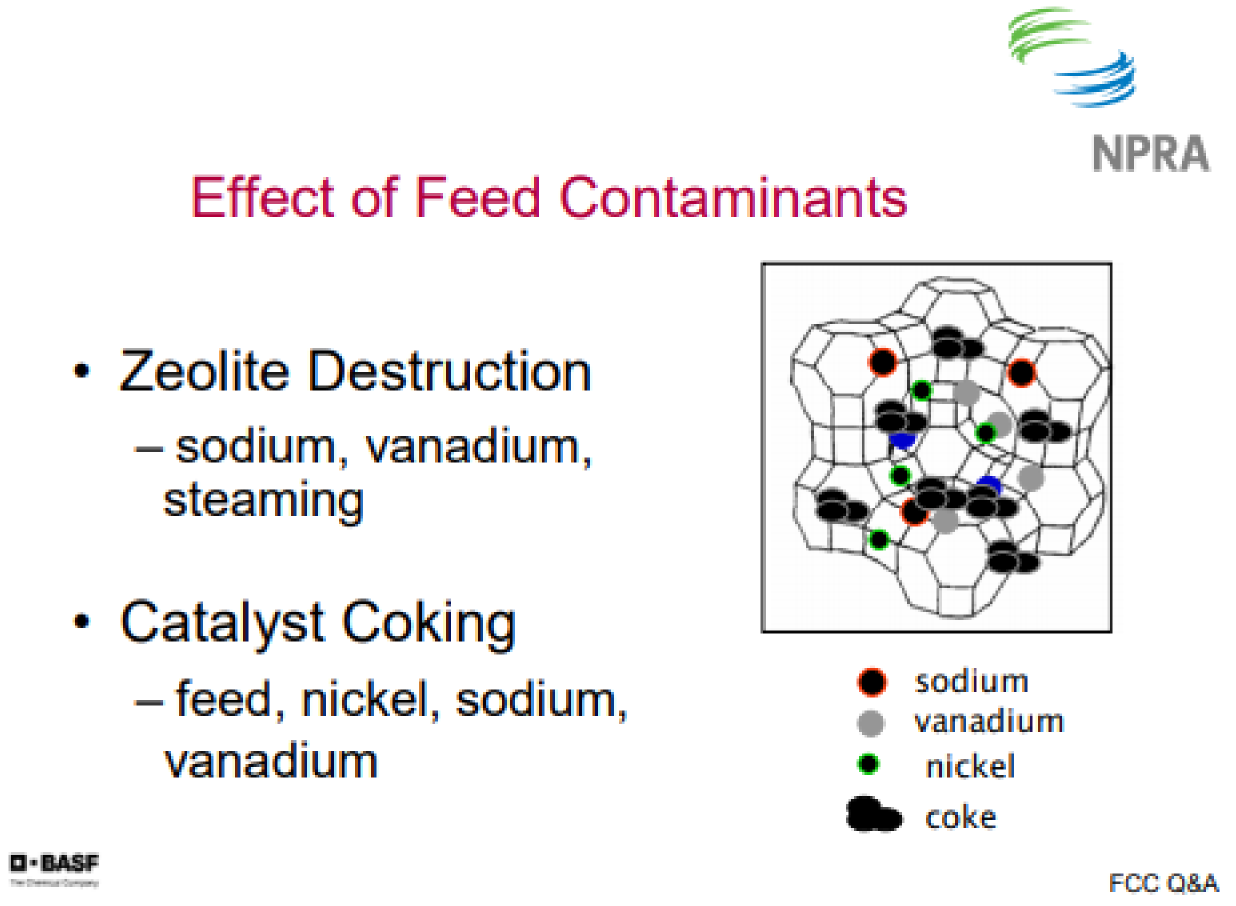
HEATER (BASF Catalysts)

There is a balance between catalyst management; that is, fresh addition rate, purchased e cat and withdrawal rate, and the penalty associated with the decline a reactor yields. Regarding nickel, we believe that it is a secondary effect. High nickel increases delta coke, which in turn increases regenerator temperature and results in catalyst deactivation.

Vanadium and the alkaline metals have a direct deactivation impact. There is been a lot of recent development in commercialization of vanadium-trapping technology by BASF and our competitors. This technology has been very well received by refiners, and development is ongoing.

In the Answer Book, I have included a number of histograms on nickel, vanadium, sodium, iron, and calcium to show the relative population of FCC units at varying levels of metals.

This is a diagram of how contaminants deposit on the catalyst particle. You may not be able to see it really well from the back, but it will be in the Answer Book. Sodium, vanadium, nickel, and coke all deposit slightly differently on the catalyst particle. Zeolite destruction is affected by sodium, vanadium, and steaming. Catalyst coke deposition is affected by feed properties, nickel, sodium, and vanadium.



NPRA

Effect of Feed Contaminants

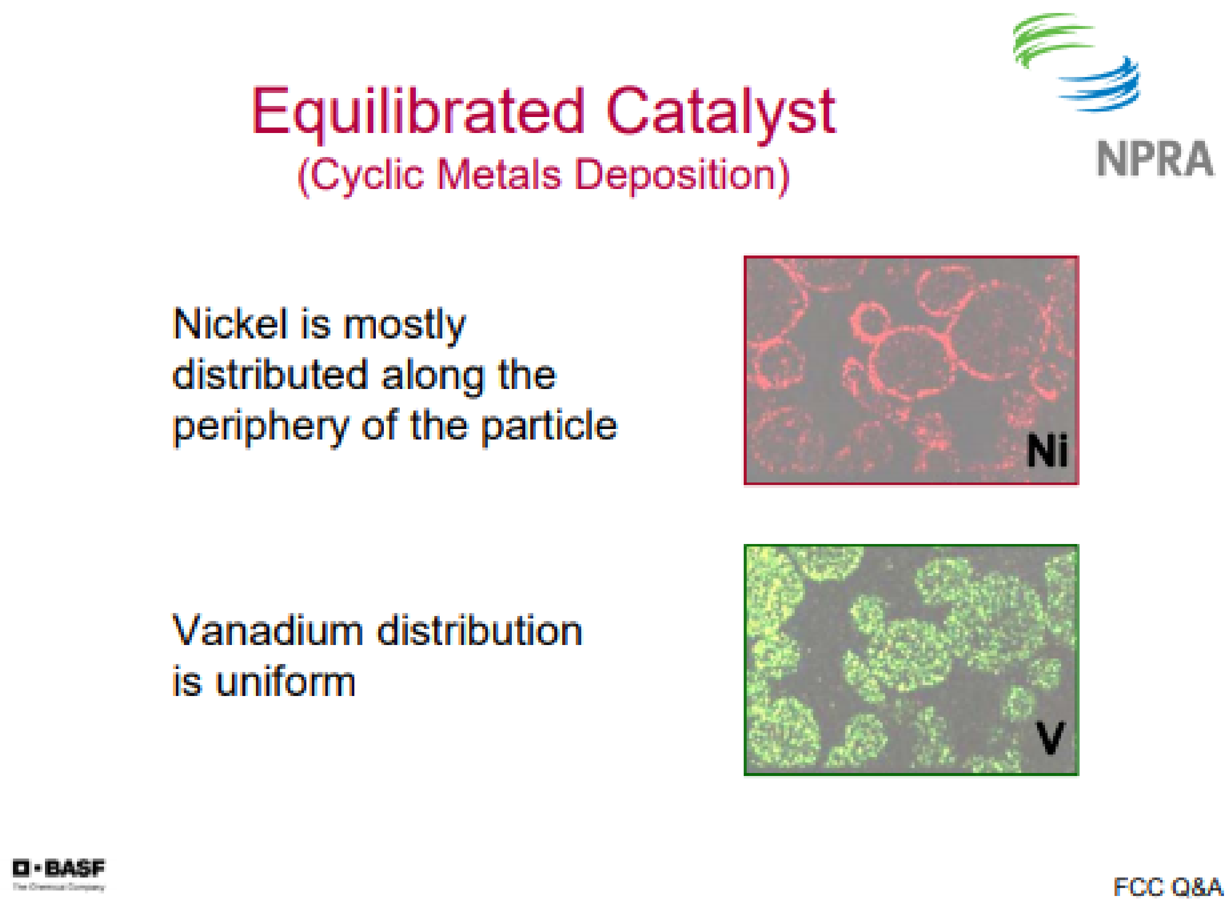
- Zeolite Destruction
  - – sodium, vanadium, steaming
- Catalyst Coking
  - – feed, nickel, sodium, vanadium

● sodium
● vanadium
● nickel
● coke

BASF

FCC Q&A

These are images of equilibrated catalysts that have had metals deposited on them. The top picture is nickel. You can see that nickel is distributed primarily along the edge of the catalyst particle. The bottom picture is vanadium. You can see vanadium distribution is very uniform throughout the catalyst particle.



Equilibrated Catalyst

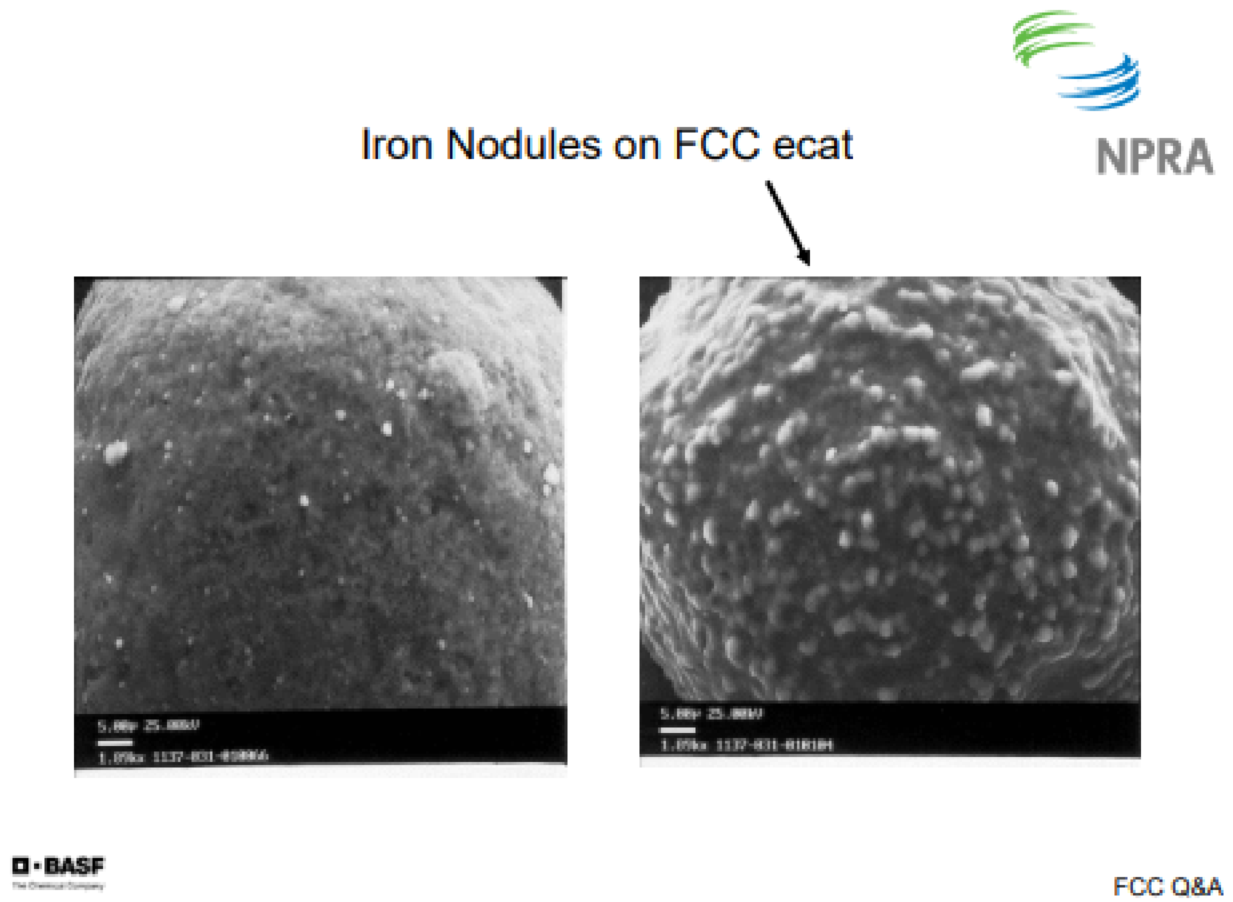
(Cyclic Metals Deposition)

Nickel is mostly distributed along the periphery of the particle

Vanadium distribution is uniform

FCC Q&A

These are two pictures of equilibrium catalyst particles. On the left is a normal catalyst particle with relatively low iron levels. On the right side is a catalyst particle with very obvious iron nodules. The iron nodules can sometimes lead to fluidization and circulation problems, but not always. Typically, you will see a drop in the e-cat ABD at very high iron levels.



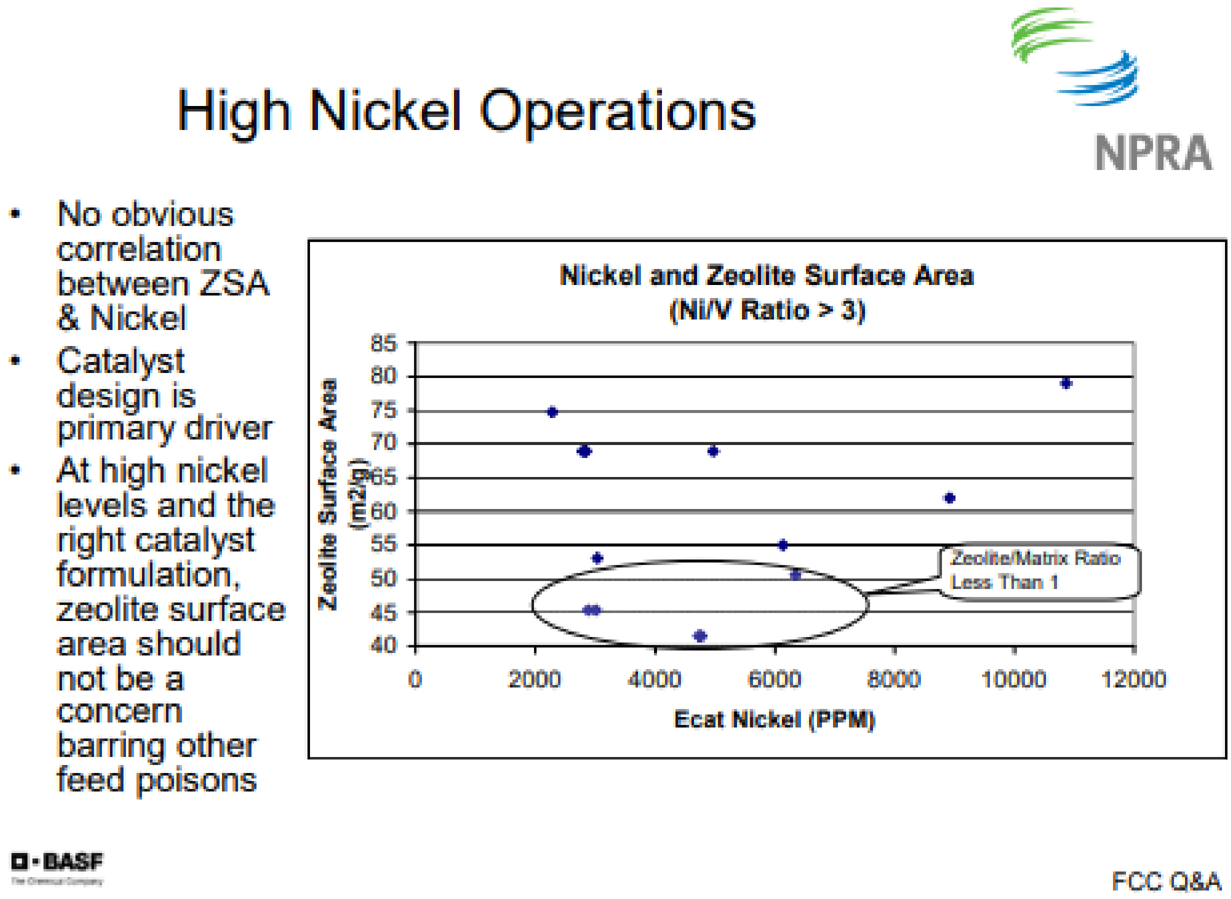
Iron Nodules on FCC ecat

FCC Q&A

The next slide is taken from our e-cat database. What we are showing here is high nickel levels where the nickel-to-vanadium ratio was greater than three. This is to filter out the impact of vanadium on the zeolite surface area and represents points from all three U.S. catalyst suppliers.

The key points here are:

- There appears to be no obvious correlation between ZSA and nickel;
- Catalyst design is a primary driver because each of these points is using different catalysts; and,
- At high nickel levels and the right catalyst formulation, zeolite surface area should not be a concern, barring other feed poisons.



High Nickel Operations

- No obvious correlation between ZSA & Nickel
- Catalyst design is primary driver
- At high nickel levels and the right catalyst formulation, zeolite surface area should not be a concern barring other feed poisons

FCC Q&A

THOMPSON (Chevron)

We have only a few units that process high levels of metals on equilibrium catalyst. At the levels that we see 5,000 to 6,000 ppm each of nickel and vanadium, we do not see the kind of effects that some have mentioned earlier. We do process crudes with considerable iron, calcium, and mercury. We have a lot of experience with processing high iron crudes and reduced crude gas oils. Iron on catalysts generally affects catalyst circulation and tends to yield higher slurry. It basically coats the catalyst particle, as Rex’s slide showed. We see these effects at less than 1% iron on catalyst.

WARDINSKY (ConocoPhillips)

ConocoPhillips has two FCCs in our system with e-cat iron levels in the range of 1 wt%. The iron is believed to be in the feed in the form of a microcolloidal iron sulfide scale since it does not appear to hinder the diffusional capabilities of the catalyst. In other words, we have not seen loss of catalyst activities at these iron levels. If you are seeing iron in that range on your e-cat, you might want to look and see what type of iron is coming in. Is it coming in the form of a scale or porphoryn-type type of iron?

JIM WEITH (Mustang Engineering)

Some time ago, I was an advisor on a unit in Wyoming on a startup and they were having desalter problems. Fortunately, this was a small unit because on the initial startup, we were watching the sodium content climb on the e-cat slowly but continuously. About the time it got to 0.7 wt% sodium, we literally—overnight—saw the activity of the catalyst fall from the 60s in the surface areas down into the 50s. As I said, fortunately it was a small unit so we were able to recover rather quickly with massive fresh cat additions.

PHILLIP NICCUM (KBR)

I just want to make a comment. If you are comparing data from different operations with respect to an inactivity, such as vanadium level, you really have to be careful to consider the makeup rate on the unit. For instance, in one case, you might have a unit with a lower vanadium content feed, but they are just very frugal with respect to their catalyst budget. So you can have a fairly high vanadium level. In another case, you might have someone charging a very heavy resid but making up catalysts at a very high rate to come to the same vanadium concentration on the equilibrium catalyst. These can give a very different result in terms of activity.

BP DAS (Indian Oil Corporation)

Regarding the spent catalyst disposal, our nickel plus vanadium levels are about 9,000 ppm, our refinery has not been in operation, and the FCC has not been in operation for the last five years. Because the generation of spent catalyst is almost 8 tons per day, do people know of another way by which I can dispose of the spent catalyst besides landfill with this lower metals level?

WALKER (UOP)

We do get this question a lot. As you mentioned, there are certain industries that will take low metals catalyst; but for high metals catalyst, I am not aware of any solution other than landfill.

WARDINSKY (ConocoPhillips)

Within our system, we are selling to or hiring the cement manufacturers to take spent catalysts. We also landfill it. I think there were some processes a couple decades ago where people looked at extracting metals from catalysts using different processes. I do not know if any of those have been implemented anywhere or not.

DOC KIRCHGESSNER (W.R. Grace Refining Technologies)

I would just like to make a couple of comments about catalysts and activity as you operate in these high metal regions. It has to be remembered that when you are operating in these types of situations, you are going to be processing obviously heavy resids; therefore, probably a lower activity and lower surface area will be beneficial, for a number of reasons. The lower activity allows you to maximize your conversion through cat-to-oil severity rather than through catalytic severity, which was normally the case in an air-limited operation.

Furthermore, the lower surface area helps to improve stripping in a resid operation, so higher surface area catalysts will have a tendency to create problems in terms of carryover of hydrocarbons. I guess just to emphasize what Mike said about the spent catalyst disposal issues, I think the fly ash substitute into the cement operations is probably the number one outlet for spent catalysts, including catalysts with very high metals levels. It is encapsulated in the calcining process.

REZA SADEGHBEIGI (RMS Engineering)

It is generally beneficial to use antimony if the nickel on the e-cat is about 1,000 ppm; but in most cases when you do that, the NOx goes up. I would like to ask the panel and also maybe the audience: How many of you do not use antimony because of the NOx issue?

WARDINSKY (ConocoPhillips)

I believe we have a couple of units that do not use it because of this issue; it is kind of a mixed response within our system. We have some units that do run higher nickel feeds, so they are using antimony. On the units currently using antimony, we have not seen any increase of NOx emissions. I did ask the Phillips Petroleum Company scientists that invented antimony passivation years ago if they had looked into this, and they had not done any work on that. So the mechanism as to why antimony may increase NOx emissions has not been reported, to my knowledge, in the literature.

JIM WEITH (Mustang Engineering)

The process you are talking about catalyst removal or extraction, I think, was the Magna Cat process. We were looking at a process in South America last summer that was going to be using on the order of about three pounds of catalyst per barrel of feed. We inquired into that Magna Cat of the licenser and discovered that the company was no longer supporting that technology.

On another aspect: You talked about sending e-cat to the fly ash. The problem is that the small refiners just do not have the volume to interest the cement kiln people, so they are left with only landfill options.

TERRY GOOLSBY (MCAT Services, LLC)

There is some equilibrium catalyst treatment out there now using magnetic separation for the e-cat market. We are using the same type of process that Magna Cat was using, but we are treating it by physically separating the old from the new. There are processes out there that treat the e-cat.

RAY FLETCHER (Albemarle Catalysts)

I would like to add one comment in response to one of the questions that came to the floor related to discontinuing the use of antimony due to high NOx formations. One rather elegant solution that can be applied to these unique situations is the use of specific high crystalline aluminates in conjunction with antimony. The nice thing about this type of a solution is that the high crystalline aluminum, plus the antimony, are additives, so you get an enhancement in the nickel trapping. The result is that you are often able to cut the antimony additions by half or more and are thereby able to use antimony without such a high NOx level in the flue gas stock.

DAVID OYARCE (ENAP Chile)

I would like to know if anyone in the panel has any experience with losing fluidization of the catalyst because of high metal contents on the e-cat.

HEATER (BASF Catalysts)

Iron nodules—as in the picture I showed earlier—can have the impact of destabilizing the fluidization in units that are extremely sensitive to fluidization. We do not often see it, but it can happen.

THOMPSON (Chevron)

We have seen that on a couple of units.

PHILLIP NICCUM (KBR)

We have seen this at very high levels of alkaline metal sodium or calcium, which can result in the catalyst particle size becoming very large, causing catalyst circulation difficulties.

BOB LUDOLPH (Sunoco Inc.)

We have seen that in the cases of calcium or any sort of material that may lead to eutectic formation where the particles fuse. There is a change in the physical properties. We have also seen losses in ?P across slide valves; not severe, but just taking up any little margin you might have had.

Print as PDF:

Tags

- Coker
- Desalting
- Hydrogen
- Poisoning

Submitter

- Consultant
- Licensor
- Operator
- Vendor