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## **Question 87: Iron contamination of CCR, cyclic, and semi-regen reformer catalyst is a common problem. What level of iron concentration typically justifies catalyst replacement due to poor catalyst performance?**

### **METKA (Sunoco, Inc.)**

Typically, iron levels up to approximately 12,000 ppm can be tolerated before a change-out is required. Iron is a support modifier that can affect both the metal and acid sites. There is more of an impact on the acid sites, and iron can impede chloride pick-up and trap sulfur on the catalyst. Iron typically impacts the first reactor in a fixed-bed unit and is primarily a result of upstream corrosion in the naphtha hydrotreater. The catalyst will turn orange. Iron levels can be managed in semi-regen units by moving the first reactor catalyst to the back of the unit during dump-and-screen operations.

### **ZMICH (UOP LLC)**

I think that John has summarized this very well. First, I'd like to add that this topic was discussed back in the Year 2000 NPRA Q&A, so there's some additional discussion that you can refer to.

Iron contamination in the catalytic reforming: Yes, it's common for people to see iron accumulation on the catalyst. In fact, sometimes people will see the catalyst turning orange. If you take a sample from a reactor and you put it in your hand, you'll see that there is an orange-ish tinge and some, at high concentrations, will show up on your fingertips.

I agree that the levels of around 12,000 ppm (1.2 wt%) should have a minimal effect, in general, on the catalyst performance. Iron will have some effect on the ability of the catalyst to retain chloride. It does have an effect on the chloride retention. In rare cases, we have also seen some effect on the metal function through severe regeneration with high concentrations of iron on the catalyst.

Iron also will oxidize and reduce during the regeneration part; and in a fixed-bed unit, this may lead to additional water generation during the reduction of the platinum/rhenium type catalyst system. We have seen samples of both CCR Platforming and fixed-bed Platforming with iron contamination. At UOP, we don't have much experience with cyclic reforming units and concentration limits or concentration amounts that they see of iron, but I suspect it's similar to fixed-bed Platforming units.

The final comment is: Large amounts can adversely affect flow distribution in the reactor. This really means that if you get some scale that was coming into the reactors, it may lead to plugging of the scallops in a radial floor reactor and could lead to some flow distribution issues.

### **QUINTANA (Valero Energy Corporation)**

As Joe alluded to, we see the impact of iron primarily being an indirect function through the production of higher moisture levels during the catalyst reduction step of regeneration. So in a fixed-bed unit, whether it's semi-regen or cyclic, that will require a longer reduction step to dry down the catalyst sufficiently. Or if the reactor is put online prematurely, then the release of that residual moisture into the reactor circuit will result in higher cracking and coking and most likely a shorter cycle length on the next run.

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In a CCR unit, the impact is similar; but of course, you may be able to tolerate it to a greater degree if the recycle gas moisture level remains below about 30 wppm. As to what level of iron justifies replacement, we don't see that there's a fixed level at which you might change out; but rather, replacement is going to be based on overall catalyst performance, which is addressed later on in Question 92.

**SONI OYEKAN (Marathon Oil Company)**

I'm a little curious about the 12,000 ppm iron on the catalyst that was discussed. Is this iron contamination really from a semi-regen-type unit? And if it was, was it in the top part of the lead reactor? Or, is this 12,000 ppm iron uniformly distributed in a CCR Platformer catalyst system? Now, the concern here is that sometimes people hear about such high numbers and might suggest that we should run the reformers until 12,000 wppm is exceeded in the refineries because they don't want to spend the money on catalyst. And of course, we need to assess unit economics and other factors before making the decision to operate at such a high catalyst iron content. 12,000 ppm iron on a CCR catalyst would be a tremendous amount of iron on that catalyst. I would expect that such a level of iron contamination would negatively impact the reformer productivity and economics.

**ZMICH (UOP LLC)**

My comment about 12,000-ppm iron is based on observation of samples from operating CCR Platforming units. And, 1.2 wt% with no reported problems in yield performance, reformat production or hydrogen production, no problems maintaining normal reactor performance—that is, reactor inlet temperature to achieve the target octane or target paraffin conversion. It's empirical. We've seen it in the commercial units.

**HAZLE (NPRA)**

John, you mentioned 12,000. Do you have any issues?

**METKA (Sunoco, Inc.)**

No, nothing really more to add, Jeff.

**BOB RODDEY (Roddey Engineering Services, Inc.)**

Joe, was that a CCR or a fixed-bed unit?

**ZMICH (UOP LLC)**

The number that I'm quoting was from CCR Platforming catalyst, but we've seen numbers on fixed-bed units also approaching those high levels and equally with no apparent effect on catalyst performance. And in fact, we've taken samples and tested them in our pilot plants. We see, effectively, the same performance as far as temperature requirements, yield performance, and stability in fixed-bed-type service.

**NEWTON (Roddey Engineering Services, Inc.)**

Just a way of planning: Whenever we go to the semi-regen units and are doing dump-and-screens, we see the high level of iron in the first reactor bed. So you want to make sure that you segregate every reactor. When you're dumping and screening, you want to make sure that the catalyst people don't mix in the catalyst because if you need to replace a first bed or move it to somewhere else, you want to have it segregated so you're not mixing it with your second, third and fourth reactors; although, we have seen the iron get all the way into the second reactor bed. So any time we dump-and-screen, we get samples

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of the catalyst and send them off the catalyst vendor and have them test for iron.

**HAZLE (NPRA)**

And that 12,000-ppm or 1.2-ppm, that's just in the first bed? That's the concentration there?

**NEWTON (Roddey Engineering Services, Inc.)**

Yes. You're going to get iron scale coming from your feed effluent exchanger and your charge heater. It's going to deposit in your scallops and your first reactor bed on the fixed-bed unit.

**ZMICH (UOP LLC)**

I just want to clarify this 1.2 wt% number in that it is not a hard-and-fast limit. That's an observation that we have. It could be that 1.3 wt% or 1.4 wt% is acceptable. So this 1.2 wt% is just simply an observation and not to be considered a hard limit on contaminant levels.

**LEE TURPIN (Turpin Consulting)**

There definitely is a point when the iron will kill the first reactor; and in one particular incident that I know of, it was about 2%.

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