

# Feed Contaminants in Hydroprocessing Units



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## Introduction

**R**efiners are facing many challenges from new regulations on sulfur levels in gasoline and diesel fuel, the rising cost of crude and other raw materials, and directives to decrease the cost of production. In an effort to lower these costs, refineries often find opportunities to purchase lower cost crudes or purchase other feedstocks such as LCO. While these opportunity feeds can help improve profitability, there can be some consequences. Many of these new feeds coming into the refinery may contain unknown levels of common catalyst poisons such as silicon or arsenic. It is important to be aware

of the various contaminants to avoid unfortunate surprises like pressure drop build up or unexpected catalyst deactivation which can both result in shortened cycle length on the hydrotreater and unexpected turnarounds.

In this article, several of the more common feed contaminants that may be present in hydrotreater feeds are reviewed. In some cases guard catalysts can be employed to help mitigate some of the problems caused by catalyst poisons and in other cases, guidelines are suggested to help minimize the potential impact.

## Silicon

Silicon (Si) is probably the most widespread catalyst poison encountered in distillate hydrotreater feeds. The common source of silicon is from a delayed coker operation which uses an anti-foam agent based on polydimethylsiloxane to suppress foaming in the coker drums. The siloxane complex breaks down in the coking process to lighter molecular weight fragments consisting of modified silica gels. These remnants end up primarily in the naphtha range, although small quantities have also been found in the kerosene and diesel fractions. As a result, silicon contamination is a major concern in units treating coker naphtha. In these units, the rate of silicon deposition on the catalyst is usually what determines run length rather than coke deactivation. In extreme cases of contamination, cycle lengths can be as short as three to six months.

Under hydrotreating conditions, the silica fragments present in the feed undergo a condensation reaction with the alumina forming a strong chemical bond as depicted in Figure 1. Thus, once the silicon is bound to the surface it cannot be removed and is considered a permanent poison. The modified gels are associated with the alumina support as opposed to the active metal sulfides, and are dispersed throughout the alumina surface of the catalyst.

As the silicon builds up on the catalyst it begins to restrict the catalyst pores and eventually blocks access to the active sites. This phenomenon is referred to as pore mouth plugging.

Silicon is one of the contaminants which can be trapped by using specially designed catalysts. ART introduced the StART™ Catalyst System for just this purpose. This technology combines a state of the art silica guard material, AT724G catalyst along with the active HDS and HDN

Figure 1

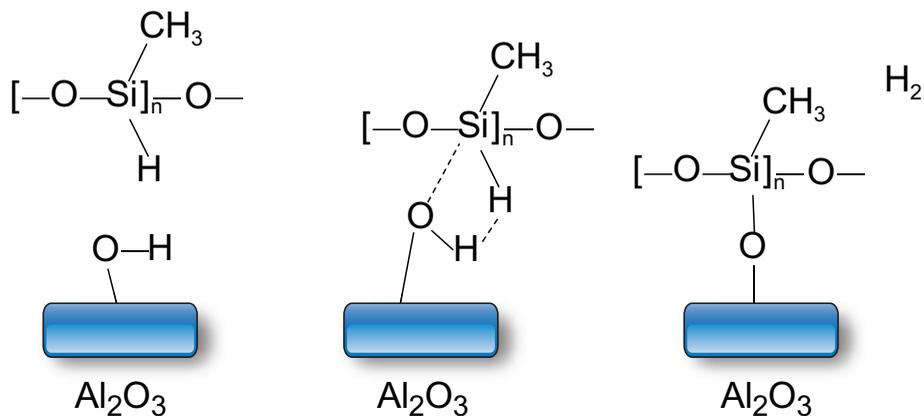


Figure 2  
Same Canister Silicon Capacities

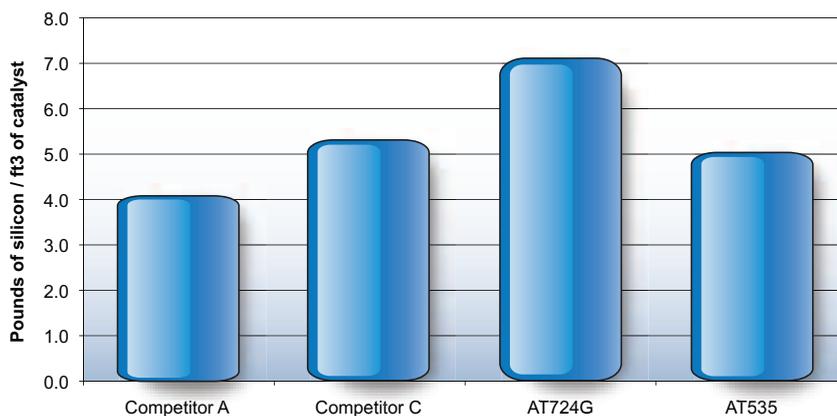
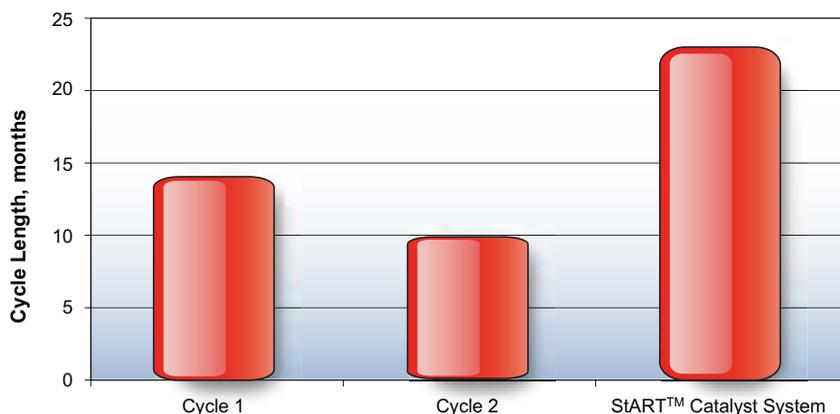
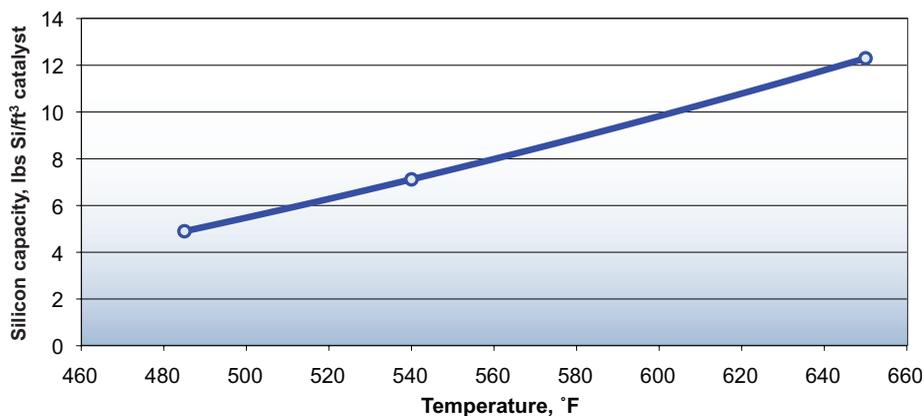


Figure 3  
StART™ Catalyst System Offers Longer Cycles



**Figure 4**  
**Temperature Dependence of Silicon Capacity**



catalyst AT535. The AT724G is a high surface area guard catalyst designed for maximum silicon capacity. Figure 2 compares the Si capacity of AT724G and AT535 with some competitor catalysts. AT535 by itself has essentially the same Si capacity as these materials, while AT724G has over 30% higher Si capacity.

Figure 3 shows a commercial example of the how the StART™ Catalyst System can increase the cycle length over competitive silicon trapping materials. In this case, ART's custom designed system more than doubled the cycle length over the previous cycles with catalyst from competitor A.

Another important aspect to be aware of with silicon poisoning is that the deposition of the modified silica gels on the alumina surface is a catalytic reaction and the ultimate quantity of silicon pick up depends on reactor temperature. The temperature dependence of silicon pick up for AT724G is shown in Figure 4. A catalyst in a guard reactor which is limited to low temperatures will pick up much less silicon than the same catalyst in a main reactor operating at higher temperature.

### Arsenic

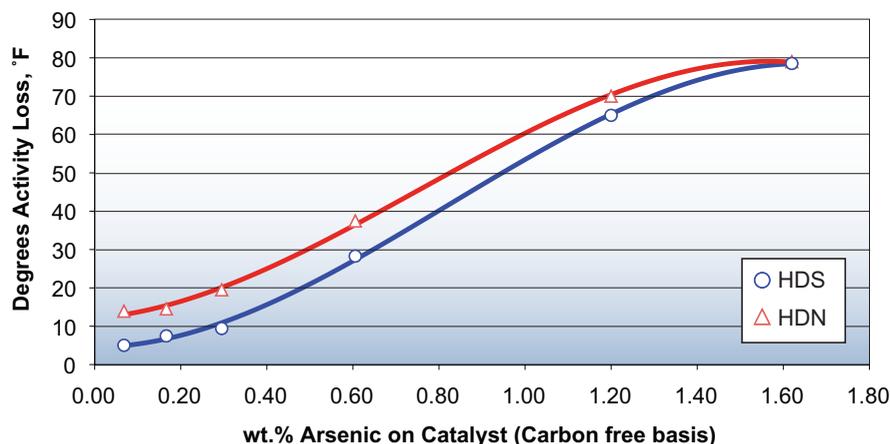
Arsenic (As) is found in many crudes including some from West Africa and Russia as well as many synthetic crudes. It is frequently becoming a common contaminant

as use of these crudes, especially synthetic crudes from Canada, has increased in recent years. The Arsenic is believed to bind with the metal sulfide sites, and in particular the active nickel on the catalyst forming nickel arsenide. This has a dramatic impact on catalyst activity. To demonstrate the impact of arsenic on catalyst activity, ART obtained a series of catalysts containing different levels of arsenic. These samples were carefully regenerated in the laboratory, and were then activity tested using a diesel feed containing 50% cracked stocks under conditions producing <500 ppm sulfur. Figure 5 summarizes the results of that work. At 1000 ppm arsenic the catalyst shows 5°F HDS activity loss and nearly 15°F loss in HDN activity. The activity loss quickly increases to over 50°F at 1 wt.% arsenic on the catalyst.

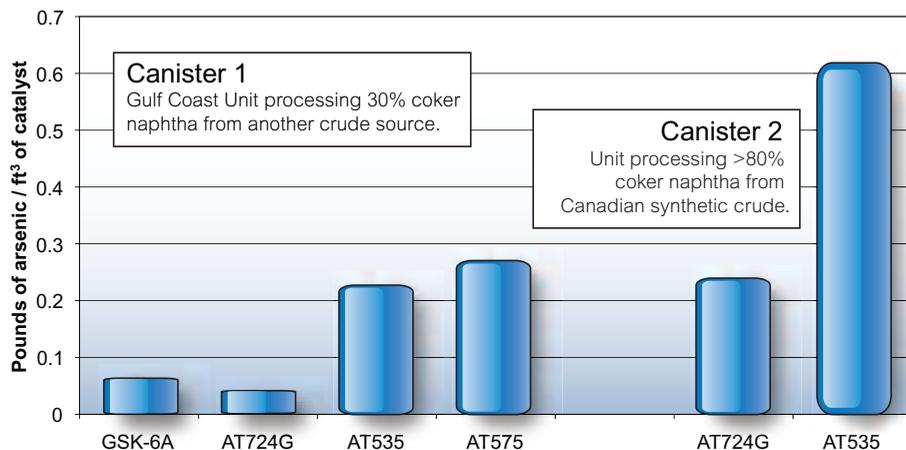
Canister data for a variety of ART catalysts indicates that catalysts containing nickel are more effective for trapping arsenic. Figure 6 summarizes the arsenic pick up values for several ART NiMo catalysts. As this data shows, both AT535 and AT575 are quite effective for trapping arsenic. Note that the difference between canisters 1 and 2 are the level of arsenic in the feed (canister 2 was in a unit processing >80% coker naphtha) and the temperature of the reactor containing the canister.

The difference between canisters indicates that like silicon pick up, the ultimate arsenic pick up is strongly dependent on temperature. Figure 7 shows the As pick up as a function of temperature for an ART NiMo catalyst. These results were obtained by analyzing spent samples of the catalyst from a three reactor unit processing 100% cracked naphtha from a synthetic crude source. The first reactor was operated at very low temperature (~275°F) in order to saturate diolefins. The second reactor was designed to saturate mono-olefins and operated at about 430°F. The last reactor had an inlet of 570°F and an outlet temperature of approximately 650°F. The arsenic content on the catalyst correlated with the temperature of the reactor as depicted in the figure. The data demonstrate that a high nickel cata-

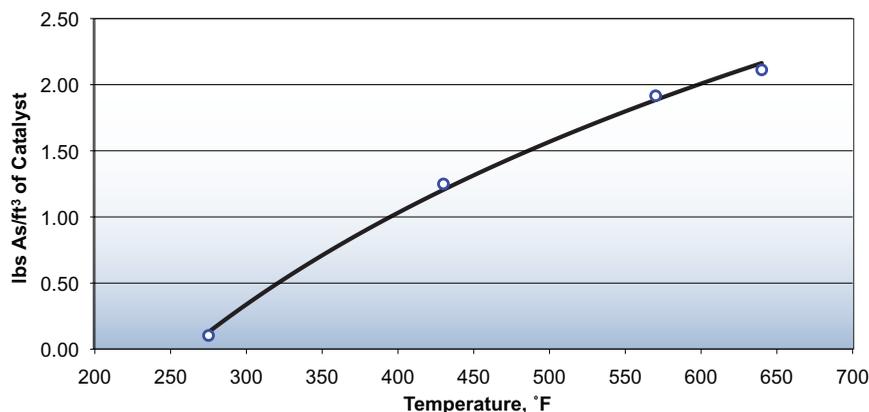
**Figure 5**  
**Effect of Arsenic on Catalyst Activity**



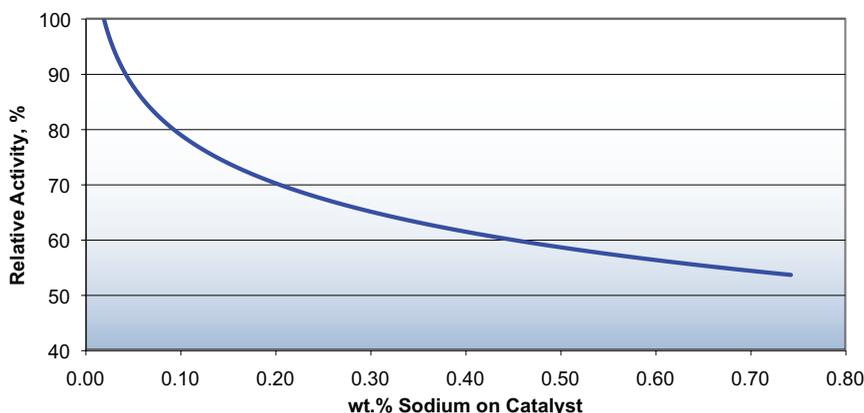
**Figure 6**  
**Arsenic Pick-Up in Basket Testing**



**Figure 7**  
**Temperature Dependence of Arsenic Capacity**



**Figure 8**  
**Impact of Sodium Contamination on Activity**



lyst can pick up very high arsenic levels if the operating temperature and feed concentration are high enough.

### Sodium and Calcium

Sodium (Na) is a severe catalyst poison that can cause significant activity loss even at low levels. It works by promoting the sintering of catalytic metals and neutralizing acid sites. Typical sources of sodium include a malfunctioning desalter, sea water contamination or caustic contamination. Depending on the source of sodium, the signs of poisoning include rapid activity loss and an increase in pressure drop. Figure 8 shows the effects of sodium poisoning on catalyst activity. The figure indicates that for a sodium content of 0.5 wt.% the activity is at most 60% of fresh catalyst activity. This translates to roughly 30°F loss in activity for 1 wt.% sodium on the catalyst.

Calcium (Ca) is a similar poison to sodium and is found in some West African crudes. There is some evidence that it is an even stronger poison with roughly 1 wt.% calcium resulting in 50°F or more activity loss. It is therefore critical to keep these out of the hydrotreater feed with a suggested maximum of 0.5 ppm of either sodium and calcium.

### Phosphorous

Phosphorous (P) contamination in oil has been traced to fractionation fluids that are often used in crudes from the Western Canadian Sedimentary Basin. The source is diphosphate esters which are soluble in the crude oil. Refineries that run large percentages of light Western Canadian crude have reported crude column and crude furnace fouling for many years. Improvements made to crude columns to minimize fouling have transitioned the depositing of phosphorous to the downstream hydrotreaters.

Other sources of phosphorous include gasoline slop tanks, imported feeds and lube oil wastes. If phosphorous does manage to make its way into the hydrotreater, it will poison the active sites of the catalyst causing a loss in activity. A level of 1 wt.% of phosphorous on the catalyst results in roughly 10°F loss in activity. ART recommends that a feed content of < 0.5 wppm be maintained whenever possible, as well as the use of feed filters to assist in trapping of phosphorous sediment.

A case study of the detrimental impacts of feed poisons on hydrotreater performance involved a ULSD unit which had recently started up with ART catalysts. Shortly after start up the unit began to experience extremely rapid catalyst deactivation. It was so severe that within a few months the unit required an unplanned turnaround and fresh catalyst was installed. Samples of spent catalyst were collected representing catalyst throughout the bed, and these were analyzed in the laboratory. The results are summarized in Table I. It is apparent from these results that the catalysts were exposed to high levels of several poisons including arsenic, sodium, phosphorous and iron. The contaminants penetrated well into the catalyst bed. Catalyst at the bottom of the reactor was not yet poisoned, but the coke content was extremely high for catalyst which had been onstream such a short time. The level of contaminants indicates the catalyst in the top half of the bed had lost over 60°F of activity, while the bottom was providing most of the HDS conversion. This required very high temperatures, which is reflected in the high carbon content for the catalyst at the bottom of the bed.

### Iron

Iron (Fe) works its way into hydrotreater feed as rust and iron scale from corrosion of upstream equipment and piping, as well as from unfiltered particulates present in the feed. Iron naphthenates can

form from corrosion due to naphthenic acid in the feed, and the iron readily precipitates out in the presence of heat and H<sub>2</sub>S. These iron particulates fill the interstitial spaces in the catalyst bed which will result in a higher than expected pressure drop. To help mitigate the pressure drop associated with iron, ART uses a series of grading materials (GSK-19, GSK-9, GSK-6A and GSK-3A) which have high void space to accumulate and 'store' these particulates. GSK-9 is also an iron trapping material which has high internal void space for trapping soluble iron inside its large pore network. These measures are helpful for delaying pressure drop buildup, but they do not prevent or eliminate it. Effective feed filtration to remove particulates (at least 25 microns) in combination with high void grading provides a longer lasting way in helping mitigate pressure drop buildup from these sources.

### Nickel and Vanadium

Nickel (Ni) and Vanadium (V) contamination have been found in resids and the heavier fractions of vacuum gas oils. They are a more significant problem in FCC pretreat units and other applications processing heavier feeds, and not often encountered in diesel or other light feeds. The deactivation mechanism of these poisons is pore mouth plugging. Nickel and

vanadium are usually contained in large porphoryin molecules which are too big to penetrate into the pores of typical hydrotreating catalysts. Therefore, the nickel and vanadium end up depositing on the outside of the catalyst ultimately blocking access to the active sites within the pores. Pilot plant testing with heavy feeds by ART on a widely used FCC pretreat catalyst, AT575, indicates that a 1 wt.% Ni+V on the catalyst results in 5-9°F loss in activity. AT575 is a catalyst designed for treating heavy feeds, so the activity loss will be greater for a smaller pore (relative to AT575) catalyst.

Nickel and vanadium are treated by using specially designed catalysts for removing metals. These catalysts have pore size distributions which are tailored to provide very high capacities for nickel and vanadium. ART has vast experience with treating resid and resid containing feeds, and offers a wide array of ICR and HOP series catalysts with differing metals capacities and HDS activities. Using these in conjunction with ART AT or DX™ Catalyst Platform are an effective way of dealing with nickel and vanadium in cases where they are known to be present.

**Table I**  
**Spent Catalyst Analysis**

	As, wt.%	Fe, wt.%	Na, wt.%	P, wt.%	C, wt.%
<b>GSK-19</b>	0.00	0.72	2.43	0.60	0.0
<b>GSK-9</b>	0.00	1.23	1.71	4.43	0.5
<b>GSK-6A</b>	0.11	0.11	0.21	2.29	3.9
<b>Top</b>	0.10	0.64	1.66	2.29	6.6
<b>Middle</b>	0.07	0.08	0.20	1.05	7.5
<b>Bottom</b>	0.04	0.00	0.02	0.68	11.1