

## The ART of Trapping Silicon and Arsenic



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In an effort to lower costs and improve refining margins, refiners often look for opportunities to purchase lower cost crudes or other feedstocks. While these opportunity feeds can help improve profitability, there can be some unpleasant consequences. Many of these new feeds contain unknown levels of catalyst poisons such as silicon (Si) and arsenic (As). ART has seen an increase in the number of units experiencing poisoning from these contaminants in recent years as significantly more of these opportunity feeds are processed.

### Silicon

Silicon is probably the most widespread catalyst poison encountered in hydrotreater feeds. The main source of silicon is from delayed coker operations which use an anti-foam agent based on polydimethylsiloxane to suppress foaming in the coker drums. The siloxane complex breaks down in the coking process to primarily cyclic methylsiloxane trimers. These species are volatile at coker temperatures with boiling points ranging from 270-475°F (132-246°C). As a result, these compounds tend to concentrate in the overhead products and, as a general rule of thumb, 70-80% of the silicon at the coker ends up in the coker naphtha fraction. More recently, even refineries that do not have cokers are experiencing silicon poisoning of hydrotreating catalysts once thought unlikely since their feed source comes directly from the refiner's crude unit. These refineries have begun processing synthetic or other opportunity crudes and the process of making synthetic crude often involves a coking step. In addition, it is becoming more common to use silicon additives in the drilling process, and for pipeline companies to use them for both flow enhancing performance and foaming issues. It has also been found that silicon additives are sometimes used in barge unloading.

In the hydrotreater the silica fragments from the antifoam agent undergo a condensation reaction with the alumina surface of the catalyst forming a strong chemical bond. Once the silicon is bound to the alumina surface it cannot be removed by regeneration or other means. It is a more moderate poison compared to contaminants like sodium or arsenic, but it nonetheless results in activity loss of the order of 5-10°F (3-6°C) for each 1.0 wt.% Si deposited on the hydrotreating catalyst. The impact is worse for other catalysts which are used in processes downstream from the hydrotreater (i.e. reformers, isom units). Figure 1 shows the results of pilot plant testing which demonstrates the activity loss due to silicon contamination.

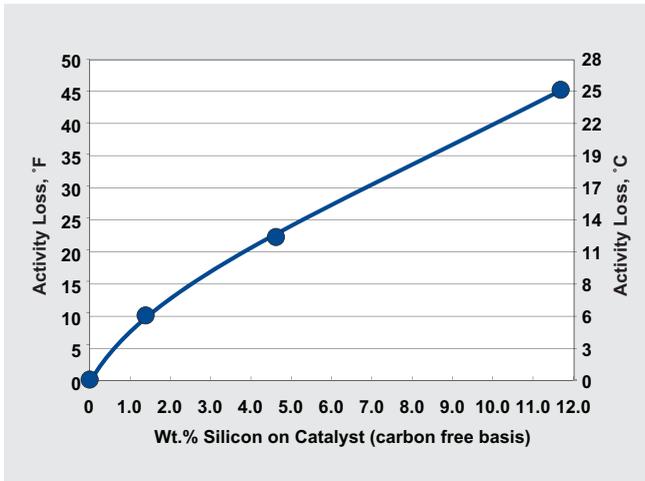


FIGURE 1: Impact of Silicon Poisoning on Activity

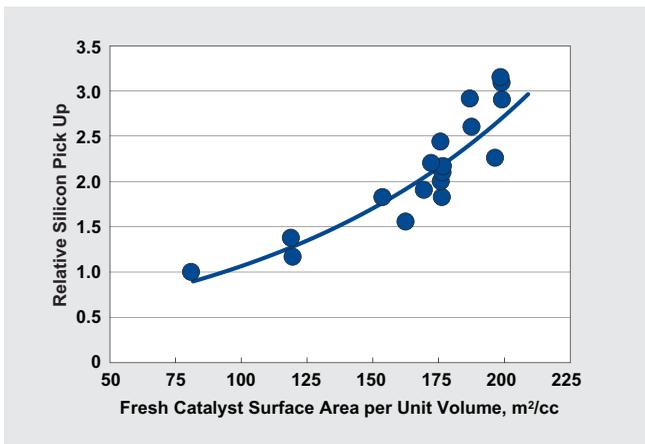


FIGURE 2: Silicon Pick Up Depends on Catalyst Surface Area

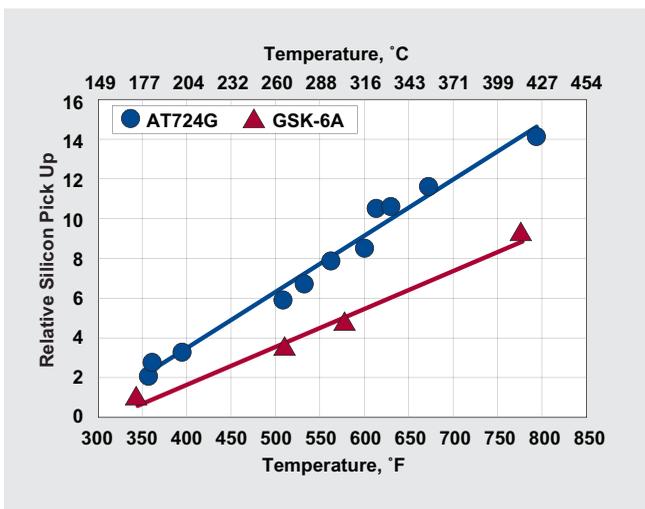


FIGURE 3: Silicon Pick Up Depends on Temperature

A variety of analytical techniques have been applied to silicon poisoned catalysts, and this confirms that the silicon is associated with the alumina support as opposed to the active metal sulfides of the catalyst. Furthermore, the silicon is dispersed throughout the available alumina surface as opposed to poisoning only the exterior of the catalyst pellet. As a consequence, the available alumina surface area of a catalyst has a significant impact on silicon capacity of a catalyst. This is shown in Figure 2 for a number of different ART catalysts. It is a plot of the relative silicon contamination observed on spent catalyst following a careful regeneration as a function of the fresh catalyst surface area. The capacity for silicon increases by a factor of 3 or more as the surface area per unit volume increases from roughly 100 m<sup>2</sup>/cc to over 200 m<sup>2</sup>/cc.

Another important aspect of silicon poisoning is that silicon pick up depends on unit operating temperature. Figure 3 shows the temperature dependence of silicon pick up for ART's GSK-6A, an active ring used in top bed grading, and AT724G, ART's premier silicon guard catalyst. The data represent spent catalysts and baskets samples from a variety of applications ranging from low temperature guard reactors to higher temperature applications like ULSD units.

The data clearly show that the operating temperature of the application must be considered when discussing silicon pickup capacity and when designing effective guard catalyst systems. The maximum capacity of the catalyst needs to be considered as well as the capacity at the operating temperatures of the specific unit in order to accurately predict the point at which silicon will break through into the next bed of catalyst or refinery unit.



## Arsenic

Another poison which is becoming more common with the increase use of some synthetic and opportunity crudes is arsenic. Arsenic is also a permanent poison, so once it is on the catalyst it cannot be removed. It is a much more severe poison than silicon with roughly 60°F (33°C) of activity loss per 1.0 wt% arsenic on the catalyst. Figure 4 shows the results of pilot plant testing which clearly demonstrates the detrimental effects of arsenic on catalyst activity.

Unlike silicon, it is believed that arsenic reacts with the metal sulfide sites on the catalyst, and in particular, has an affinity for the nickel on the catalyst forming nickel arsenide. This suggests that catalysts containing high levels of nickel will pick up higher levels of arsenic. Figure 5 demonstrates this nicely. It shows the relative amount of arsenic pick up as a function of the nickel content on the fresh catalyst. This data represents a variety of ART NiMo catalysts which were retrieved from different hydrotreating applications which explains some of the scatter, but the trend is clear. Catalysts containing higher levels of nickel can pick up six times or more arsenic compared to catalysts with lower nickel levels.

Just like silicon, arsenic poisoning is an activated process, thus the arsenic capacity of a catalyst is strongly temperature dependent. This is demonstrated in Figure 6 which shows the arsenic pick up as a function of temperature for an ART NiMo catalyst. The arsenic pick up increases by a factor of 14 as temperature increases from 270-650°F (132-343°C).

## Silicon Trapping

ART has long held a strong position in applications dealing with silicon contamination, and this was strengthened by technology advances like the StART® (Silicon tolerance by ART) Catalyst System now with a decade of operating experience<sup>1</sup>. Figure 7 shows the results of basket testing for AT724G and AT535, key components of a

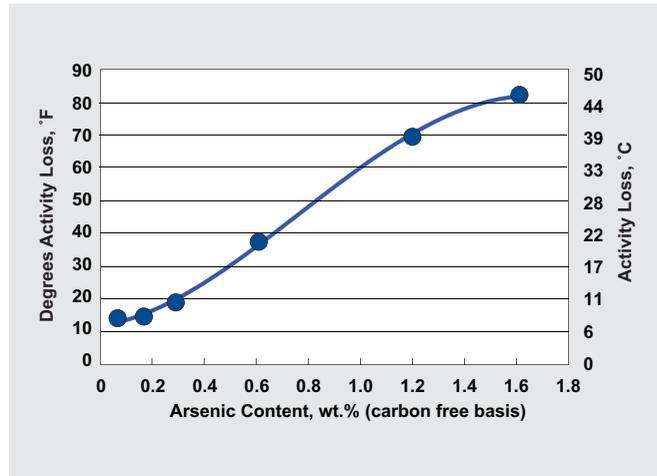


FIGURE 4: Arsenic is a Severe Catalyst Poison

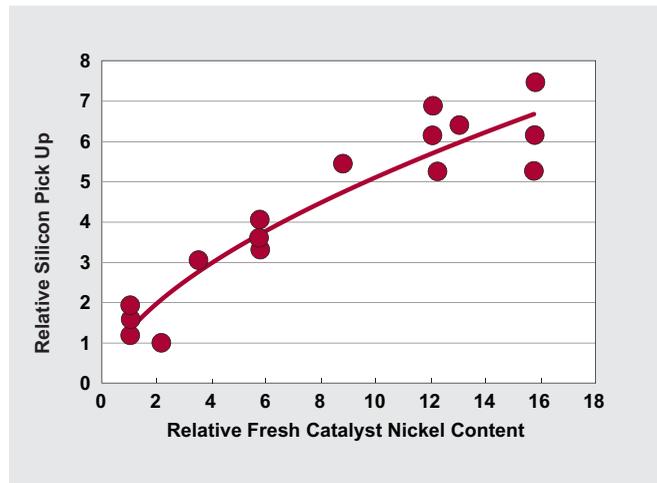


FIGURE 5: Arsenic Pick Up Depends on Catalyst Nickel Content

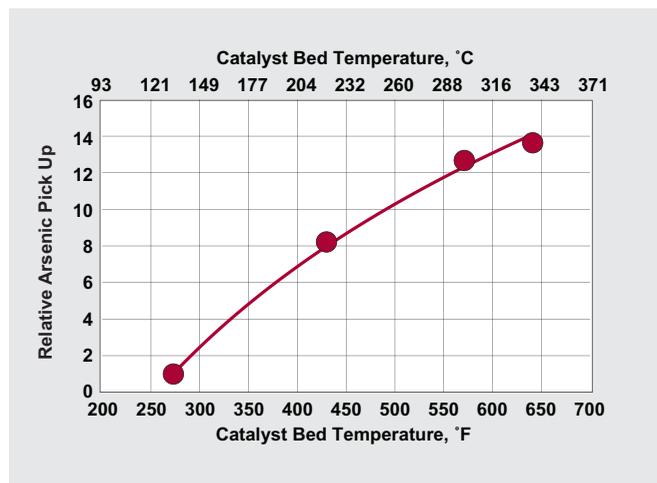


FIGURE 6: Arsenic Pick Up is an Activated Process

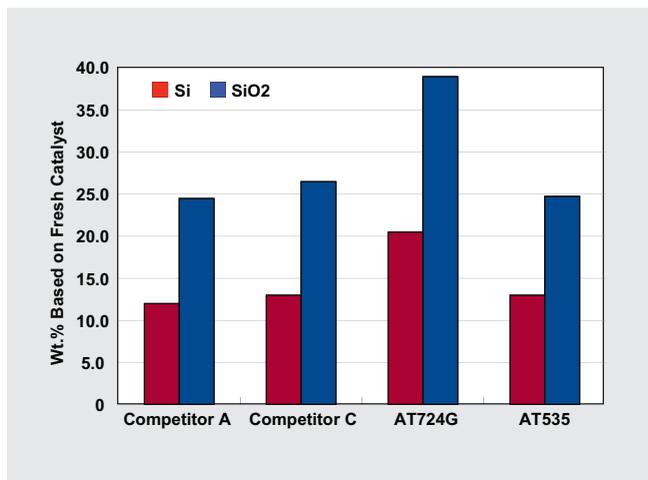


FIGURE 7: AT724G Excels

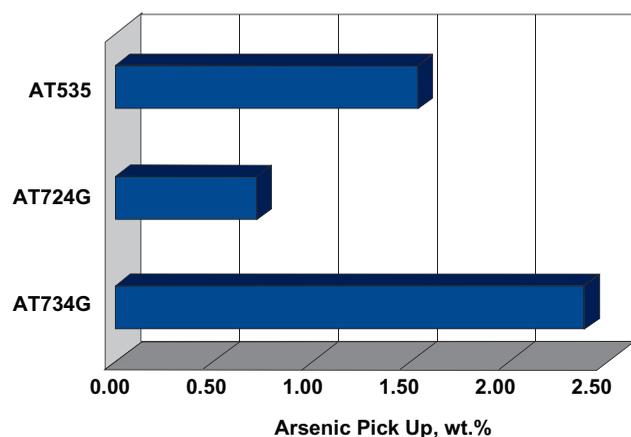


FIGURE 8: AT734G Has High Arsenic Capacity

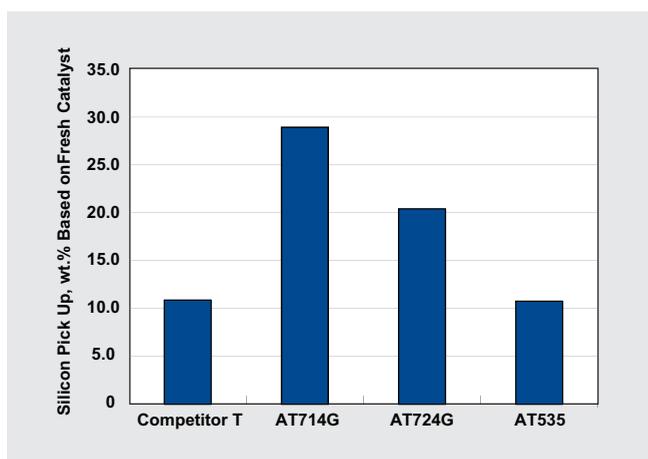


FIGURE 9: AT714G Picks Up Significantly More Silicon

StART system, against some competitive catalyst offerings. AT535 alone has essentially the same Si capacity as the competitor catalysts while AT724G has over 30% higher Si capacity; the data show the combination of AT724G and AT535 has the highest capacity and activity.

## Arsenic Trapping

The StART portfolio was further strengthened several years ago with the introduction of AT734G which is a combined silicon and arsenic guard<sup>2</sup>. The new catalyst is built on the AT724G platform and exploits the different poisoning mechanisms for silicon and arsenic. It has very high alumina surface area for high silicon capacity and a higher nickel content imparting high arsenic capacity. AT734G has over four times the arsenic capacity of AT724G with similar silicon capacity. Figure 8 shows an example of the arsenic pick up capabilities observed in a basket test comparing AT724G, AT734G and AT535. The basket was installed in a cracked naphtha unit at a refinery processing synthetic crudes.

## Even Higher Capacity

With the increasing incidence of silicon and arsenic poisoning, ART saw the need to make further improvements to the StART system portfolio. This led to the development of AT714G, a very high surface area guard with lower active metals content compared to AT724G. The new guard has extremely high silicon capacity, and the lower activity makes it ideal for activity grading. In addition, AT714G does not need to be activated in order for the silicon guard functionality to be effective. Figure 9 shows catalyst basket results comparing the silicon pick up of AT714G with AT724G, AT535 and a competitor catalyst. In this example AT714G picks up over 40% more silicon than AT724G which significantly increases the silicon capacity of the StART system.

## Silicon Tolerant Catalyst

The main component of the StART system is AT535, a high activity NiMo catalyst. It has been widely recognized as one of the leading catalysts for naphtha and cracked naphtha applications as evidenced by over 300 units worldwide since its introduction. Even with this excellent track record, ART recognized a need for a high activity catalyst that is even more silicon tolerant than AT535. Utilizing the knowledge gained from numerous basket studies and spent catalyst analysis, some of which are outlined above, has allowed ART to design a new silicon tolerant catalyst, AT525. Figure 10 summarizes the results of a basket study comparing AT525, AT535 and a competitor catalyst. In this case both AT535 and AT525 outperform the competitor catalyst for silicon pick up by at least 15%, and it is readily apparent that AT525 significantly outperforms all catalysts in the test.

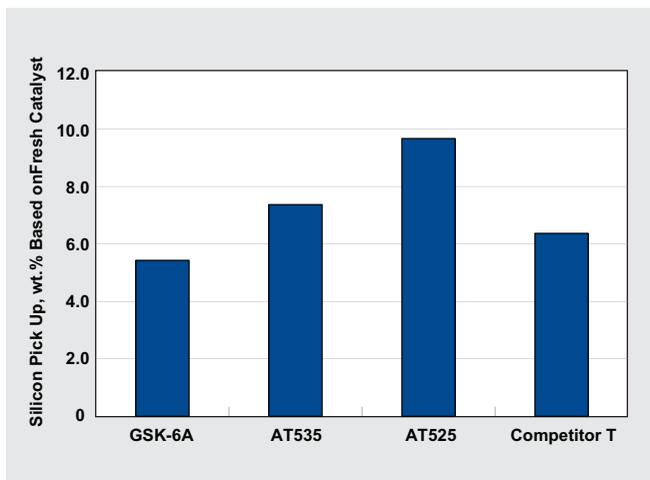


FIGURE 10: AT525 Has High Activity and High Silicon Capacity

Advanced Refining Technologies has significantly enhanced its already strong position in naphtha and cracked naphtha applications, and has added another tool for silicon and arsenic trapping in ULSD and other applications. The StART system now includes an improved stand alone silicon tolerant catalyst AT525, and a new high-performance silicon guard material AT714G. These new additions combined with AT724G and AT734G offer unparalleled protection from silicon and arsenic allowing refiners to further extend unit cycle length under the most adverse conditions. This technology can be applied across a wide range of distillate hydrotreating applications enabling refiners to be better prepared to deal with the unexpected. Let the ART technical group custom fit these products into your process for improved reliability and performance.

## References

1. D. Krenzke, C. Olsen, and B. Watkins, *Catalagram*® No. 90, 2002.
2. C. Olsen, *Catalagram*® No. 108, Fall 2010.

