AT734G: A Combined Silicon and Arsenic Guard Catalyst

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Refiners are often looking for opportunities to purchase lower cost crudes and other feed-stocks, and while these opportunity feeds may help improve profitability there can be some consequences. Many of these new feeds coming into the refinery contain unknown levels of catalyst poisons such as arsenic and silicon and, in fact, ART has seen an increase in the number of units experiencing poisoning from these contaminants in recent years as more of these opportunity feeds are processed.

Arsenic (As) is found in many crudes including some from West Africa, Russia, Venezuela and many synthetic crudes. Unlike the silicon from antifoams, evidence suggests that arsenic is distributed throughout the whole boiling range. Table I shows examples of the arsenic content for several crudes and the distribution through various cuts.

Arsenic is a permanent catalyst poison which means once it is on the catalyst it cannot be removed via regeneration or other means. It is a severe poison since a small amount results in significant activity loss. The arsenic is believed to bind with the metal sulfide sites, and in particular the active nickel on the catalyst forming nickel arsenide.

To demonstrate the impact of arsenic on catalyst activity, ART obtained a series of spent catalyst samples from a refiner. The catalyst samples had different levels of arsenic because of their location in the reactor. These samples were carefully regenerated in the laboratory and then activity tested using a diesel

Table I
Arsenic in Crude Oils

Oil Type	Total Arsenic (ppb)
Almein	2.4
Alberta	2.4 to 111
California	63 to 1112
Libya	77 - 343
Louisianna	46
Venezuela	20 -284
Wyoming	111

Distillation Cut	Percent of Total	Distillation Cut	ppm
Total	20 ppm (Venezuela)		4.6 ppm (Shale Oil)
Desalter	15	Naphtha	<DL
LVO	4	Light Distillate	1.4
HVO	25	Heavy Distillate	4.4
Residuum	56	Residuum	2

Tang, W. T., J. Gumulka and P. Y. Sun, 1994. Source *Control and Treatment of Contaminants Found in Petroleum Tank Bottoms.* API Publication No. 4606. American Petroleum Institute. Washington, D.C.

feed containing 50% FCC LCO under conditions producing <500 ppm sulfur. Figure 7 summarizes the results of that work. The catalyst had lost 15°F of activity after only 1000 ppm of arsenic poisoning, and the activity loss quickly increases to about 60°F at 1 wt.% arsenic on the catalyst.

The ultimate arsenic capacity of a catalyst is strongly dependent on temperature, similar to silicon pick up. Figure 8 shows how the arsenic pick up varies as a function of catalyst temperature for an ART NiMo catalyst. These results were obtained by analyzing spent samples retrieved 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

Figure 7
Impact of Arsenic Poisoning on Catalyst Activity

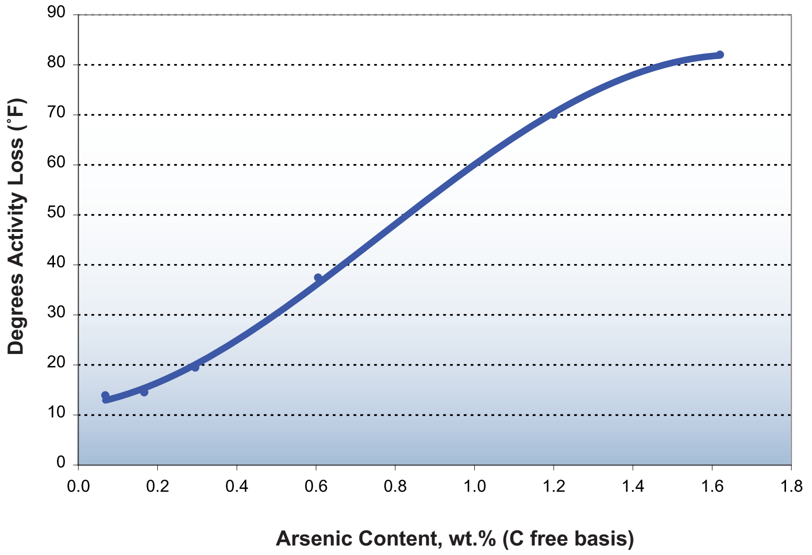


Figure 8
Temperature Dependence of Arsenic Pick Up

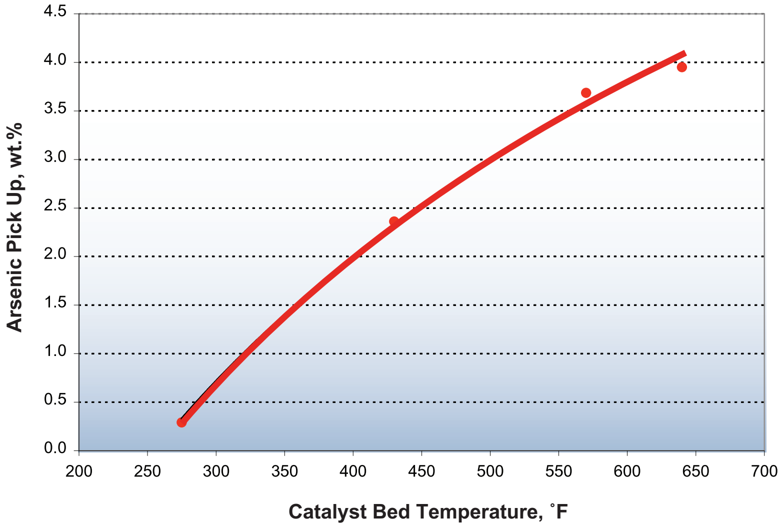
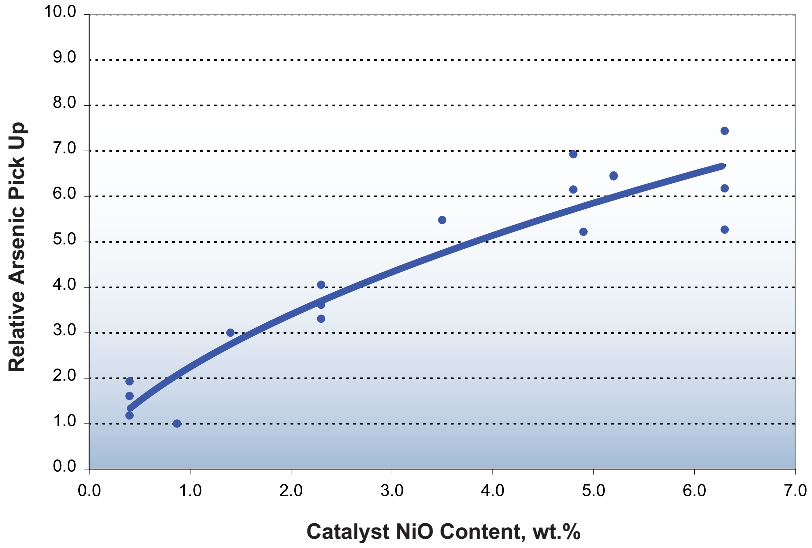


Figure 9
Relative Arsenic Pick Up Improves with Catalyst Ni Content



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 demonstrates the temperature dependence of arsenic pick up, and further indicates that a high nickel catalyst can pick up very high arsenic levels if the operating temperature and feed concentration are high enough.

A number of catalyst basket tests and spent catalyst data have provided additional evidence that catalysts containing nickel are much more effective for trapping arsenic, and Figure 9 summarizes some of this data. The figure shows that the relative arsenic pick up observed on a variety of catalysts correlates well with the catalyst nickel content.

These data, combined with the increasing incidence of catalyst poisoning from arsenic, prompted ART to develop a high surface area arsenic guard catalyst utilizing the highly successful AT724G catalyst technology platform. The goal of the development was to provide a single catalyst for applications suffering from both silicon and arsenic poisoning. In those types of units catalyst suppliers have typically recommended two guard catalysts, one each for silicon and arsenic. With the commercialization of AT734G catalyst, one guard layer is sufficient for both contaminants leaving more reactor volume available for the active catalyst.

Figure 10
Comparison of Arsenic Pick Up

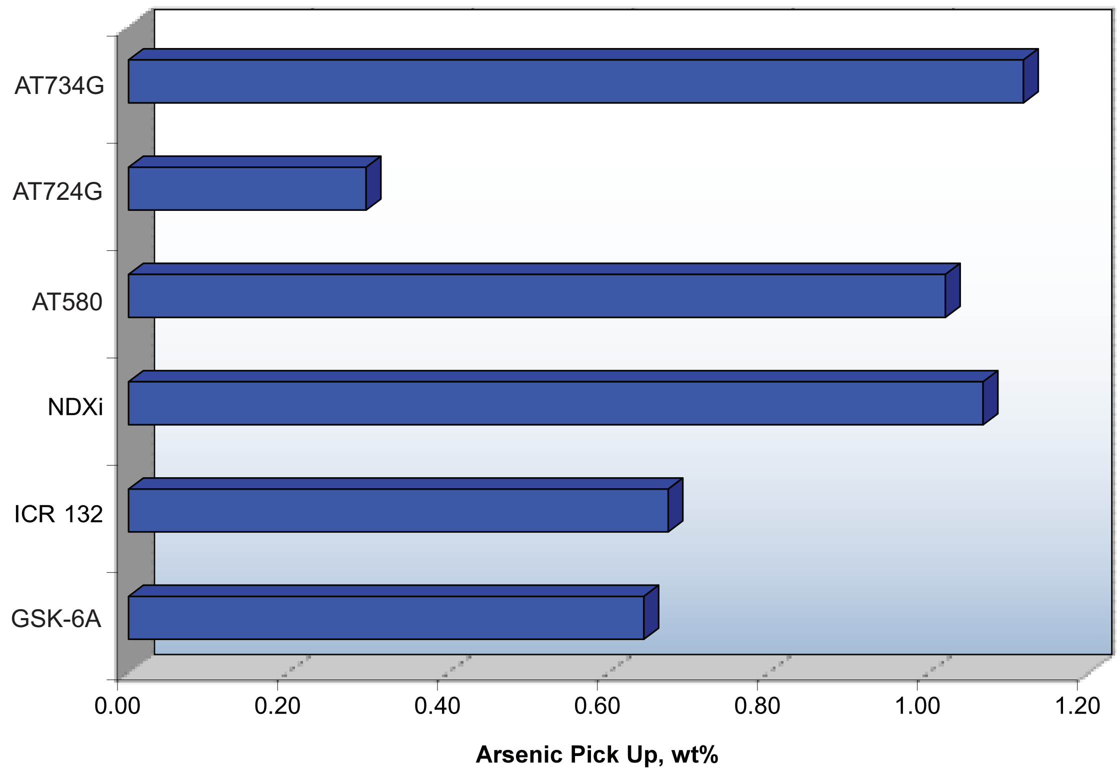


Figure 10 summarizes some results from a catalyst basket where several ART catalysts were evaluated along with AT734G. AT734G picks up about four times more arsenic compared to AT724G, and even picks up more than some high Ni catalysts like NDXi and AT580.

Data from another catalyst basket is shown in Figure 11. This basket was installed in a unit processing cracked naphtha from a synthetic crude. Again, AT734G significantly outperforms AT724G and AT535 in terms of arsenic capacity.

Catalyst basket data confirms the superior arsenic pick up of AT734G, but what about silicon pick up? Figure 12 compares the Si pick up of AT734G and AT724G observed in a number of different catalyst baskets.

Figure 11
Arsenic Pick Up from Synthetic Crude

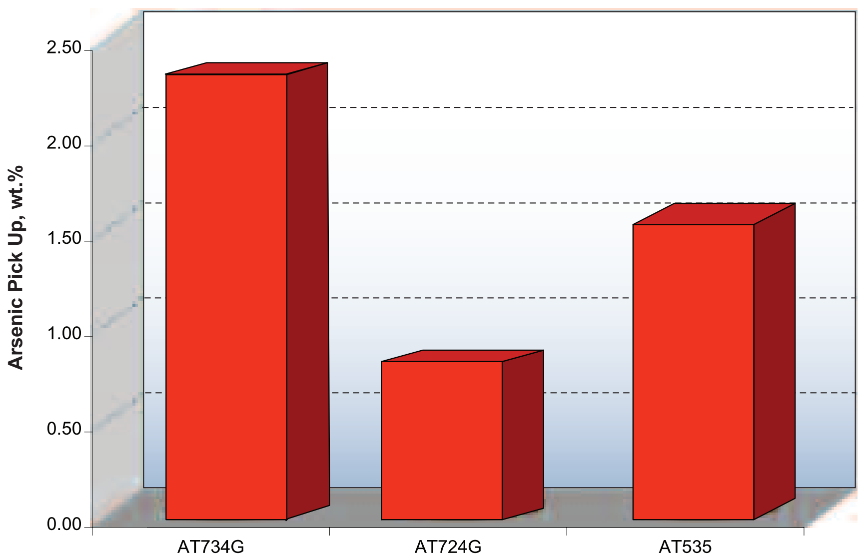
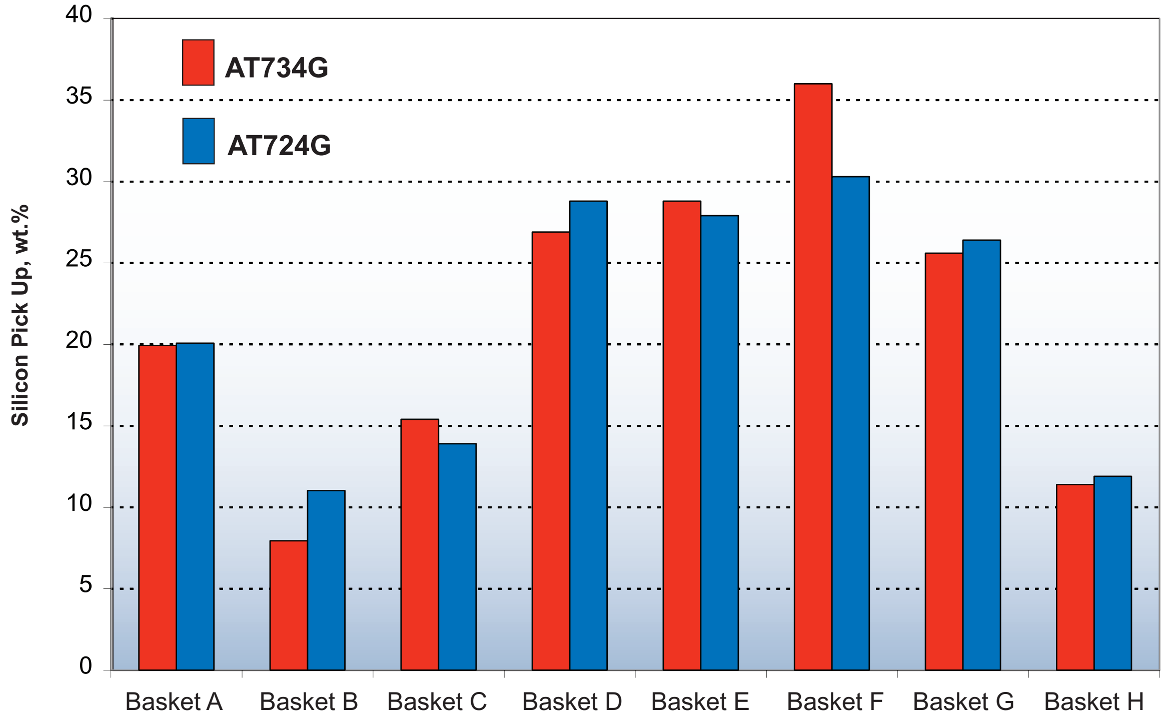


Figure 12
Comparison of Silicon Pick Up



These baskets were installed in coker naphtha units as well as diesel units which suffer from Si poisoning. The data show that the Si pickup of AT734G is on average the same as the Si pick up of AT724G. Notice a few basket samples show extremely high Si pick up, in excess of 25 wt.% Si. These were installed in diesel units and experienced much higher temperatures than some of the baskets showing lower Si values.

The data demonstrates that ART has successfully commercialized a combined silicon and arsenic guard catalyst, AT734G. Like AT724G, it has moderate activity making it suitable for activity grading in applications processing cracked stocks. Several refiners have already selected AT734G because of its high capacity for both silicon and arsenic; it has 4 times the arsenic capacity of ART's highly successful AT724G silicon guard, but with the same silicon capacity making it an excellent new addition to the StART™ Catalyst System.