Question 7: What are your typical precious metal recoveries from reforming catalysts? What factors impact this?

BILL KOSTKA (AXENS NORTH AMERICA)
Reported platinum recoveries from reforming catalyst following commercial utilization have typically ranged between 90 and 100 wt% and have rarely been less than 80 wt%. The magnitude of this range is both frustrating and at least somewhat explainable.

How one defines recovery greatly impacts the variability of its outcome. The number of variables necessary for tracking a reforming catalyst from cradle to grave is significant with each of these variables carrying some level of error. The largest errors tend to be associated with physical loss of catalyst and bookkeeping. Physical loss of catalyst typically occurs anytime the catalyst is handled (loading, unloading, transferring containers, screening, transporting, etc.), reactor containment is compromised or the catalyst is misplaced. The sum of these catalyst losses can range from nearly nothing to several percent. Recoveries based solely on analysis of the platinum content for fresh and spent catalyst samples neglect catalyst loss and only reflect possible in service loss.

Several errors are associated with the determination of a catalyst's platinum content. Most catalyst fills contain billons of pieces of catalyst with some minor inhomogeneity in platinum content. Proper sampling technique and size are critical to limit the size of this error. Even the best protocol can result in a 0.5% sampling error. Platinum analysis accuracy can introduce another 0.5% error. Measurement of LOI (Loss on Ignition) to bring the platinum analysis value to a "dry catalyst" basis can introduce a 2% error. These errors double since they apply to both the fresh and spent catalyst analyses. Spent catalyst can contain a substantial amount of coke if not burned prior to unloading and can adsorb a substantial amount of moisture if left exposed to humid air for even a short period of time. The resulting significant increase in LOI can easily amplify the LOI error.

Although fresh catalyst seldom contains the exact nominal amount of platinum, its platinum content will be within the purchase specification. Multiple platinum assays are used to determine the size of this deviation for each Lot of catalyst produced. A Lot typically contains 10-20 klbs of catalyst, but can be any size. Large orders consist of multiple Lots that are individually assayed. The buyer is reimbursed for any difference between the amount of platinum supplied and the actual amount of platinum present in the manufactured catalyst. Using fresh catalyst nominal platinum content to determine platinum recovery tends to result in inaccurate recovery values. Assay values must be used to calculate accurate recoveries, even though the several-year-old fresh catalyst assays may not be readily available. The accuracy of platinum recovery calculations for CCR reformers are further complicated by the periodic addition of fresh make-up catalyst to compensate for catalyst fines removal and other forms of catalyst loss.

Some platinum loss from the catalyst while in service may be possible. Studies of platinum and palladium volatilization to recover these precious metals from automotive exhaust catalysts clearly show they can be efficiently recovered in the presence of chlorine gas (Cl_2) at temperatures above 700 °C. Volatilization still occurs at 500 °C, but at much lower rates. Palladium chloride species are more

volatile than platinum chloride species. These same studies also show the presence of CO, NO and SO2 creates species such as Pt(CO)2Cl2, Pt(NO)2Cl2 and PtSO2Cl2 which are more volatile than their respective binary chlorides.

In service platinum loss most likely results from reformer catalyst regeneration. At around 500 °C, reformer catalyst regeneration temperature is high enough to volatilize certain platinum species. Chlorine, a key component of all reforming catalysts and an integral component in platinum redispersion, is certainly present during catalyst regeneration. Most refiners add PERC (C2Cl4) to the unit to maintain the appropriate chlorine level during the regeneration. Decomposition of PERC in oxygen is difficult even at 500 °C and proceeds through a phosgene (COCl2) intermediate before conversion to HCl and CO2 in the presence of water. CO and SO2 can be generated in low concentrations at various times during the regeneration. As a result of the species present and the operating temperature, one should not be surprised if some degree of platinum volatilization occurs during reformer catalyst regeneration. In fact, subjecting a palladium-containing catalyst to multiple commercial reformer on-oil/regeneration cycles resulted in a palladium loss that far exceeded the highest losses of platinum. Greater in service platinum loss should be expected at higher temperature, higher chlorine, CO, SO2, etc. concentrations and increased regeneration time (number of regenerations).

Finally, precious metal reclaimers do not return the assayed amount of platinum. Those utilizing hydrometallurgy return 99.5% of the assayed platinum while those utilizing pyrometallurgy return somewhat less.

ABIGAIL SLATER (HollyFrontier)
Precious metal recoveries can range from unit to unit, but we typically observe an 80% or higher recovery. Factors that can impact precious metal recoveries are accounting issues, operational issues, and external reclamation losses.

Accounting issues usually occur during catalyst handling activities, such as delivery truck transfers, screening, loading/unloading, catalyst fines collection, warehouse movements, unit equipment maintenance, etc. During these activities, catalyst can be spilled and lost (or not picked up). Operational issues that can occur are reactor containment issues, precious metals volatilization, catalyst fines trapped in reactor/regenerator internals, etc.

The actual reclamation process is also not perfect, and typically will not recover 100% of the precious metal on the catalyst. Some reclamation methods are better than others, but none will recover all precious metal.

THOMAS PORRITT (Chevron U.S.A.) (3)
Our precious metals manager uses a rule of thumb for metal losses in the 8-12% range for the total life cycle of the catalyst. Factors that impact recovery are: handling of catalyst during loading and dumping, what happened to the catalyst in the unit, the presence of carbon and the moisture content of the catalyst.

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