

Rhenium: A Hidden Asset



Robert T. Jacobsen, Sabin Metal Corp., USA, discusses how rhenium in spent precious metals bearing process catalysts can prove a hidden asset, enhancing hydrocarbon processing profits.

Hydrocarbon processing catalysts typically include one or more precious metals such as platinum, palladium, ruthenium, and rhodium (commonly referred to as platinum group metals or PGMs). To function in hydrocarbon processes, these metals are deposited on a variety of substrates, or carriers, to meet specific requirements. In addition to PGMs, many of these catalysts also contain another valuable precious metal, rhenium (Re), which is usually used in combination with platinum. The most common use of this particular catalyst formulation is for reforming naphthas into other desirable products. No matter what their precious metals composition, all PGM and rhenium bearing catalysts eventually lose their efficacy to facilitate and/or speed process reactions, and must be 'changed out' and replaced with fresh catalysts to continue an uninterrupted process/ production flow.



Figure 1. Water treatment facilities such as this plant consume aluminum sulfate or sodium aluminate, common byproducts of rhenium from spent hydrocarbon processing catalysts.

Recovering Rhenium

While all precious metals refiners are capable of recovering the PGMs from spent process catalysts, until now refiners have been unable to recover all of their Re content. There are many reasons for this, but the main reason concerns the inability to separate the remaining Re with a practical process for its recovery and subsequent refining. In fact, most precious metals catalyst refiners recover rhenium by dissolving their carriers (typically aluminum oxide) using strong caustic or acidic chemicals in a process that is commonly referred to in the industry as 'digesting'. This process is capable of recovering the soluble platinum and Re content in spent catalysts, but a significant portion of the desirable 'pay metals', sometimes as much as 20%, remains due to the insolubility of part of the substrate. The reason for this is that the substrate is hardened as a result of overheating during operation, and cannot be dissolved, even with the strongest solvents. As a result, working with a precious metals refiner that employs the digesting method for a particular spent Re bearing catalyst will not return the full value of the remaining Re in a platinum (Pt)-Re composition. The bottom line for the catalyst owner is simple: less return value for its Re content. The digester does typically send the insoluble residues out to a conventional copper smelter so that the Pt may be more completely accounted for. However, this is not true for the Re, since these smelters lose it in the smelting process.

The rising cost of Re over the past 5 – 6 years has rendered this deficiency in precious metal recovery particularly significant. Right now, catalyst grade ammonium perrhenate (typically the form in which recovered Re is returned to catalyst manufacturers' specifications) is valued at approximately US \$ 3700/kg.

Putting this in context, using the digestion process to recover the PGM and Re content of a 100 000 lbs (50 t) lot of spent catalyst would produce 175 t of aluminum sulfate or somewhat less of sodium aluminate. Fortunately for the digesters, the global water purification industry (Figure 1) uses and will pay for these byproducts, thereby relieving the digesters of the task of disposing of these byproducts as waste. Any hardened substrate that will not dissolve still carries its Re and Pt and as mentioned above is usually sent to a conventional copper smelter who will recover and return the Pt but lose the Re.

Enhancing Rhenium Returns

There is now a significantly more productive method of recovering virtually all of the Re content in spent process catalysts, a method that allows the accounting to be based on total Re content in the catalyst lot for the first time. This recently developed method,

known as Pyro-Re®, is based on a unique, proprietary pyrometallurgical technique that permits recovery of virtually all Re content from spent semi-regenerative and cyclic fixed bed catalyst lots, especially from catalysts' substrates that cannot be dissolved with caustic chemicals. The Pyro-Re® process provides a key advantage with regard to maximizing total return value of all precious metals in spent catalyst lots, and must now be given serious consideration when evaluating and selecting a precious metals refiner.



Figure 2. Contaminants in spent catalysts are removed with an indirectly fired rotary kiln, enhancing sampling accuracy and reducing overall refining costs.

Recovering and Refining Rhenium and PGMs

With regard to the recovery and refining process for spent PGM/Re bearing catalysts, the following is a brief description of the procedures involved. Typically, a precious metals refiner will assign a tracking number to incoming spent catalyst materials which are tested for carbon, sulfur, moisture, or other impurities acquired during use in harsh environments. Impurities must be removed to maximize accurate sampling and assaying procedures (which will be described below) as well as helping to verify that the catalyst materials pose no workplace hazard to the refiner and will be free flowing, so as to determine the most appropriate sampling approach.

Sampling, as the name suggests, reduces a large batch of spent catalyst (perhaps as much as 500 000 lbs) into smaller amounts suitable for accurate analysis. The goal of any materials sampling method is to maintain the relative amounts of component materials in the mix while reducing the amount of the material to a practical level to permit accurate determination of the remaining precious metals content in the catalyst.

Removing Contaminants

Regardless of how the Re is recovered, and at what level, all spent catalysts share a common trait: they are contaminated to some degree with materials such as sulfur, carbon, moisture, and other unwanted elements. To assure accurate evaluation, spent catalysts are first pre-burned to remove their accumulated contaminants and to help provide the free flowing properties necessary for highest possible sampling accuracy, which ultimately means highest possible return values for their Re and PGMs.

Removing contaminants and moisture from ceramic based catalysts (typically aluminum oxide) is generally accomplished with indirectly fired rotary kilns (Figure 2), multiple hearth furnaces, or fluidized bed furnaces. As many spent precious metal bearing catalysts exhibit significant loss on ignition (LOI), these processes burn off moisture content. Accurate LOI data are necessary to account for any weight changes from the time spent catalysts are received at a refiner's facility, during the pre-burning process, and while the final sample is in transit to a laboratory for assaying.

Pre-burning may be performed at the refiner's site or elsewhere. However, if pre-burning is handled by a third party, the spent catalyst (perhaps as much as 500,000 lbs) must be shipped to that facility, which may use various types of kilns depending on the nature of the contamination: hydrocarbons, carbon, sulfur, moisture or some combination. When completed, the reduced lot is then shipped to the refinery for sampling, assaying, and final recovery and refining of its precious metals.

Most hydrocarbon processing catalysts are sampled by a process known as dry sampling. Dry sampling involves use of mesh screens, vibratory feeders, rotary samplers, and other specialized equipment. Accurate sampling of hydrocarbon processing catalysts involves tight process control, to ensure that each sample has the representative composition of the initial material lot.

The Importance Of Assaying

Once accurate samples are obtained, the precious metals refiner and the catalyst owner may assay the samples for their precious metals content independently. Ideally, their independent assays provide values in close agreement. If both assays are within prescribed tolerances their values can be averaged to arrive at an agreed upon figure for valuation of the PGMs in the spent catalyst. In cases where the values of the two independent assays are far apart, a third sample may be sent to an independent umpire laboratory to determine a settlement amount. Standard industry practice requires that both parties, the catalyst owner and the precious metals refiner, agree by contract on how an independent umpire's assay is used to arrive at a final settlement.

After sampling, Re-bearing catalysts must be assayed to determine the amount of PGMs and Re in the samples that were generated. Most precious metal refiners' laboratories perform assays in triplicate by more than one method to ensure accuracy. Assaying methods require specialized instruments, including x-ray fluorescence systems, which can identify precious metals as well as any remaining contaminants which might degrade the accuracy of a precious metal determination. X-ray fluorescence spectroscopy can semiquantitatively analyze over 80 elements within a few minutes per sample. In addition, such equipment as atomic absorption (AA) and inductively coupled plasma (ICP) emission spectroscopy systems can support accurate assaying methods along with classical volumetric and gravimetric assaying techniques. As with sampling, the type of spent catalyst materials being analyzed will dictate the type of assay procedure to be used.

Once again the recovery method, digestion or pyrometallurgical, plays a key role in the precision and accuracy with which the contractual agreement can be met. If pyrometallurgical recovery is used, the contractual return to the customer may be made on the actual content of Re in the catalyst. Therefore, the most accurate methods of rhenium analysis may be used and do not need to be specified.

If, however, the recovery method is digestion, only the soluble portion of the rhenium counts. Thus, all the details of the analytical method have to be agreed upon, such as: the solvent to be used; the concentration; the temperature; how long to stir, etc. Even the shape of the stirring bar can cause a difference in the result, and therefore the amount of Re that the refiner owes the customer.

Environmental Concerns

Responsibly recovering and refining precious metals requires that a refiner use well controlled processes that comply with applicable environmental regulatory agencies. There are virtually hundreds of them throughout the world that concern effluent disposal and atmospheric emissions. A properly equipped refiner will have the technology appropriate to comply with all international requirements, along with approved status from appropriate governing environmental agencies.

Conclusion

All things being equal with regard to the other considerations described here, it is wise to seek out a precious metals refiner that provides maximum returns on total remaining Re content in your spent catalyst lot, in addition to the PGMs. Doing your homework before you contract for recovering PGMs and Re from your next spent catalyst lot may pay off in big dividends.