Recovering Precious Metals from Spent Chemical Processing Catalysts

When selecting a precious metals refiner, it’s important to first understand the basics of sampling, assaying and environmental issues, as well as the concept of leasing metal.

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Many chemical and petrochemical processes use precious-metal-bearing catalysts for facilitating and/or speeding chemical reactions. Precious-metal-bearing catalysts are also used for end-of-pipe pollution abatement applications, mainly to eliminate atmospheric emissions of volatile organic compounds (VOCs) and other harmful pollutants.

Most catalysts used for these applications are composed of platinum group metals (PGMs), which include platinum, palladium, ruthenium and rhodium. In some applications, these metals are used in combination, and could also include rhenium, gold and silver. Various carriers, or supports, for these metals are employed depending on the application, including carbon, soluble or insoluble alumina, silica, zeolites, or metal alloys. Homogeneous catalysts in aqueous solution are also common.

Regardless of how catalysts are used, or whether they take the form of monolithic structures, pellets, beads, extrudates, powders or solutions, most chemical process industries depend on precious metals refiners to recover the valuable metals from their spent catalysts.

Many businesses facing profit squeezing overlook the potential to maximize returns for the remaining precious metals in spent process and pollution abatement catalysts. This is unfortunate, since working with the right refining organization can be a rewarding and profitable experience.

Perhaps more important, though, is the fact that working with the wrong refiner can have serious — and costly — consequences. For example, many catalyst users may not be aware of the legal requirements concerning environmental discharges by the refiners they select, and violations are taken seriously by regulatory agencies at all levels.

This paper will help you select and work effectively with a precious metals refiner. It describes some important activities performed in precious-metals recovery and refining, and discusses sampling, assaying, processing turnaround time, environmental concerns, and metals leasing and financing.
Precious metals sampling

To accurately determine the amount of precious metals present in materials for recovery, three different sampling techniques are typically used — melt sampling, solution sampling and dry sampling. Each technique offers specific advantages, and determining the most appropriate sampling method depends on the type of material being processed as well as its estimated precious metals content.

The fundamental principle of sampling involves reducing large quantities of precious-metal-bearing catalysts (as much as many tons) into small representative samples (which may consist of as little as a few grams). Sampling begins by converting precious-metal-bearing scrap into as homogeneous a state as possible so that the concentration of precious metals and other constituents is evenly distributed. Results of sampling the homogeneous mass thus represent an accurate ratio of the precious metals content in the overall matrix.

Melt sampling (Figure 1) employs a collector metal, such as copper that is melted along with the precious-metal-bearing material. The resulting molten metal is poured into ingots, which are sampled at the beginning, middle and end of the pour. Subsequent processing steps yield an extremely high degree of accuracy, with tolerances as close as ±0.1% relative between samples. Metal mesh pollution-abatement catalysts may be sampled in this fashion.

Solution sampling (Figure 2) is used for precious-metal-bearing solutions, such as homogeneous catalysts, and is cost-effective as well as extremely accurate in determining precious metals content. This technique also involves achieving a homogeneous dispersion of precious metals and other constituents to the molecular level with precision comparable to melt sampling. Multiple samples are taken from different parts of the solution for further analysis.

Dry sampling (Figure 3) is used whenever materials cannot be dissolved in solution or are inappropriate to melt, either because of their structure or because of the cost associated with melting vs. the possible return. Because it is difficult to achieve homogeneity, dry sampling is more complex and potentially less precise than melt or solution sampling and therefore requires more judgmental skills than the other sampling methods. Materials for dry sampling are homogenized, generally by grinding large pieces into smaller and ever-finer particles. The material is allowed to free-fall into a full-stream, cross-cut, timed automatic sampler. Representative samples are taken periodically and sampling accuracy is typically ±2% relative. Most industrial precious-metal-bearing catalysts fall into this class because of the support material and are designated as heterogeneous catalysts. They are usually sampled with this technique.

Although inorganic supported catalysts could conceivably be sampled by melting the entire lot, this is not a practical approach. Ceramic-based catalysts require a high melting temperature that normal fossil fuels or induction furnace melting cannot achieve, and electric arc furnaces must generally be used. Maintaining lot integrity
while concentrating the precious metal in a collector metal, pouring off the slag layer, and finally pouring the precious metal bullion layer is, in most cases, unrealistic, since many electric arc furnaces cannot be completely emptied. Therefore, most of these catalysts are dry sampled after they have been prepared to be free flowing and relatively void of volatile components.

Carbon-supported catalysts present a special case for sampling. Carbon catalysts cannot be melted, because carbon doesn’t melt and its high loss-on-ignition characteristics (typically 80–90%) essentially prevent obtaining an accurate sample as received. Instead, the carbon must be burned off and the remaining residue dry sampled or possibly melt or solution sampled. More discussion on this subject will follow.

Because precious-metal-bearing catalysts are made in many sizes and configurations (pellets, beads, monolithic structures, and extrudates, for example), determining the best sampling technique is crucial to recovering the most value from a spent catalyst.

**Assaying**

Accurate and repeatable assaying procedures depend on both classical and instrumental techniques for measuring the precious metals content of the materials being reclaimed.

A well-equipped analytical laboratory utilizes x-ray fluorescence equipment, atomic absorption (AA) and inductively coupled plasma (ICP) emission spectroscopy, and also incorporates classical volumetric, gravimetric and fire assay techniques. When all methods are used together, they provide the most thorough and precise approach for determining precious metals content in spent catalysts, thus assuring the highest possible returns.

In general, the specific techniques used for assaying are determined by the types of materials being processed. For example, alumina-substrate catalysts can’t easily be dissolved and instead must be subjected to fire assay methods that flux out the non-metallic materials, leaving the precious metals behind. The matrix (the material other than the precious metals) always affects the assay method used. As in all analytical chemistry procedures, the matrix of the sample, as well as the particular mix of analytes, will determine such things as the collector metal used in fire assay, or which wavelength (or combination of wavelengths) is used in ICP analysis.

One major difference between the typical analytical laboratory and the laboratory experienced in precious metal work involves the region of accuracy and precision needed for satisfactory results. Many laboratories routinely perform very high-accuracy, high-precision analyses when the level of the analyte is also quite high (10% or higher). Many other laboratories, especially environmental labs, are capable of analyzing extremely low analyte levels of ppb and lower, but at relatively low precision (e.g., ±20% relative).

Precious metal labs are usually not concerned with the extremely low analyte levels, because the resulting value of the metal usually does not justify reclamation. For
example, 100 ppb of platinum in a lot as large as 10 tons is worth only about $50. Precious metal labs similarly seldom need to produce results with extremely high precision, since the system is often limited by the precision of the sampling protocol. Rather, the precious metal laboratory must be capable of producing highly accurate results at moderately high precision (±1% relative) at analyte levels on the order of 0.1%. These assays will be applied to lot sizes of several tons and will result in payments of hundreds of dollars per troy ounce contained. For example, the platinum in a 10-ton lot of material containing 0.1% Pt would be worth about $500,000.

**Processing turnaround time and your bottom line**

The speed at which spent catalysts are processed and their precious metal recovered (known as the reclamation turnaround time) is the third key factor in maximizing returns. Faster reclamation turnaround minimizes the interest charges a user accrues for leasing replacement precious metals to eliminate process downtime.

The costs for PGMs have been fluctuated wildly over the past decade, at one point reaching as high as $1,100/oz for palladium and up to $2,200/oz for platinum. While prices have moderated since those highs, there still is good reason to seek out a precious metals refiner who will return maximum value to you.

Typically, it could take as long as three months to have a new catalyst fabricated, and just as long to have the spent catalyst reclaimed — a period of six months during which new metals may have to be financed. Consider a simple (and realistic) example involving a 40,000-lb shipment of 0.6% platinum catalyst with platinum at $1,600/oz, at a lease rate of 2.5%. Leasing the metal contained in this material would cost in excess of $2,700/wk. Therefore, if one refiner has a 6-wk turnaround and another a 12-wk turnaround, the additional six weeks would cost more than $16,200 in lease charges.

The variations in lease rates are governed by worldwide production for primary (mine production) sources and the immediate, local availability of the physical metal. For the catalyst user, PGM lease rates usually represent a significant cost, since “new” precious metals are often financed while spent catalysts are being recovered and refined. By providing faster spent-catalyst-reclamation turnaround times, substantial cost savings may be realized, in many cases translating into thousands or hundreds of thousands of dollars each year. These are serious numbers, so there is a clear trend in industry toward establishing independent asset-recovery programs (or departments) functioning as profit centers for the recovery of precious metals within an organization.

**Avoiding legal and environmental problems**

When selecting a refiner, be aware of how the materials will be processed as well as those of the refiner’s other customers. Determine how any solid, liquid or gaseous by product is handled at the processing facility.
Ideally, there should be no hazardous waste materials shipped from a precious-metals processing facility, although some plants will ship them under approved procedures and conditions. Minimal pollutants should be emitted before, during and after refining. Exhaust air quality should be managed with state-of-the-art pollution control systems. The process water recovery procedure should minimize all sources of pollution. While each of these functions is fundamental, many potential pitfalls with regard to environmental compliance exist.

In the U.S., both the Resource Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), or Superfund Act, address the direct responsibility of the generator (customer) and the operator (refiner). These laws mandate that both the company that is the source of the precious metals being recovered and the precious metals refiner share in the “cradle-to-grave” responsibility, as well as future liability, for the proper treatment and/or disposal of any waste materials. If the refiner commits any violation of environmental laws or regulations, the catalyst user could incur high legal costs and be subject to heavy fines.

One of the more recent—and comprehensive—series of laws associated with precious metals under the overall umbrella of the U.S.A. PATRIOT ACT could also have significant negative impact on both precious metals owners and their refiners. The PATRIOT ACT mandates that virtually all transactions involving precious metals must be fully traceable. The scope of this law is so broad, that it would make good sense to review it thoroughly before engaging any precious metals refiner. (See sabinmetal.com to review this and other applicable regulations.)

Requesting detailed documentation on environmental compliance can help determine whether the refiner violates any applicable law or regulation. Check its use of appropriate pollution-abatement technology, such as afterburners, baghouses, wet scrubbers and liquid-effluent neutralizing equipment. Also, evaluate the refiner’s approval status with all applicable agencies at the local, state and federal levels. Most precious metals refiners willingly provide copies of environmental documentation.

Many interrelated variables associated with recovering precious metals from spent catalysts must be considered when evaluating a precious metals refiner. Consider the relationship with a precious metals refiner as a partnership — mutually profitable and based on trust and fair treatment. To achieve — and maintain this kind of relationship — consider the issues discussed here when evaluating and selecting a precious metals refiner.
Figure 1. In a typical melt sampling process, a collector metal is melted along with the precious-metal-bearing material. The molten metal is poured into ingots, which are sampled at the beginning, middle and end of the pour.

Figure 2. Solution sampling achieves a homogeneous dispersion of precious metals and other constituents, down to the molecular level, with precision comparable to that of melt sampling.
Figure 3. In dry sampling, the material is ground into smaller and smaller particles, which are allowed to free-fall in a stream. A timed automatic sampler cuts across the entire stream, producing a representative sample.
Leasing and Pool Accounts

Typically, precious metals used in catalytic processes — especially platinum and palladium — are not purchased on an outright basis by their users. Instead, they are “leased” by their users and held in a “pool account” at one of a number of physical locations, where the metal is commingled with other owners’ or lessees’ metal. Owners or lessees of these metals draw from this material on an as-needed basis or are provided with credit from a pool account on which to draw. From this pool, users can request delivery of metals for incorporation into catalysts.

Leasing platinum group metals (PGMs) for catalyst production is a financial transaction where the user has no desire to purchase the metal, but rather “borrows” it, the same as borrowing money from a bank. Lease rates vary widely depending upon supply and demand. In fact, the rate fluctuation is substantially greater than the interest rate on money, which is generally fairly constant and much more predictable. Most businesses can usually borrow money from lending institutions at one or two points above prime. However, metal leasing rates in the past have been as low as 1% per annum and as high as 200%! That incredible difference is caused purely by supply and demand.

Another common practice in the precious metals industry might be referred to as “metal banking.” Owners of metals will “lend” them to institutions or other businesses, which pay interest charges to the owners just as a bank would pay interest on dollar deposits. These institutions, in turn, lease out these metals to users as a method of generating profits.

Banking is not very common with regard to PGMs employed by catalyst users, but is more closely associated with metals speculation or accumulation for future consumption. For example, a speculator or consumer may purchase metal today, but not require it physically for 6–12 months in the future. In order to defray some of the financing costs, they may “lend” this metal back to the market.

Most users make the lease vs. buy decision based on their perception of prevailing lease rates and trends over extended time periods. Many catalyst users prefer not to “own” precious metals, since they don’t want the costs to appear on their balance sheet as inventory or as a fixed asset; consequently, they are willing to incur the added expense of leasing. They also may be averse to assuming the risk associated with metal price variability. Typically, people who lease precious metals are not consuming them, but instead using them to produce their products or having others fabricate them into catalysts. Since much of the precious metal in catalysts is recoverable, users get their metal back after the recovery and refining process.

Because of these operating practices, it is in the best interest of precious-metal-catalyst users to obtain the highest possible recovery for their precious metals, and then to work with a refiner that offers the fastest possible processing turnaround time in order to minimize lease charges.
When Selecting a Precious-Metals Refiner...

- Select a refiner that uses state-of-the-art techniques and equipment.
- Choose a refiner that has a long and successful history and good reputation in the industry.
- Discuss the refiner’s performance and policies with its customers.
- Request appropriate reference material, including environmental documentation.
- Determine whether the refiner has the financial resources to pay you in a timely manner.
- Select a refiner that has full in-house capabilities. The use of outside subcontractors might affect your returns, in terms of values and timeliness.
- Ask the refiner about laboratory techniques and replications.
- Request detailed weight and analysis reports on your shipment.
- Ask if you are allowed to be present during sampling of your material and whether you can appoint an independent organization to represent you.

Accurate sampling helps assure fair market value

Sampling procedures for spent catalyst materials are perhaps the most critical elements with regard to maximizing the recovery of precious metals from spent process catalysts. As a catalyst user, it is in your best interest to understand how sampling processes help refiners determine the precious metals content of spent catalysts and, ultimately, the amount (and value) of these metals that is returned to you.

Fundamentally, sampling spent catalysts containing precious metals is similar to sampling any homogenous mass. The problem is, even new catalyst on substrates (carriers) such as soluble and insoluble alumina, alumino-silicate, zeolite or carbon supports are not homogenous masses. After years of exposure in the harsh environment of a catalytic reaction process, spent catalysts are far from homogenous. They accumulate many different contaminants of various densities, including sulfur, carbon, solvents, oils and water, during their useful lives (typically 5–6 yr).

A portion of the spent catalyst must first be reduced to a size amenable to laboratory analysis. This involves working with large quantities of spent catalysts (as much as many tens of tons) and ultimately extracting quantities as little as a few grams, while maintaining a precious metal concentration representative of the original lot. During
this process, contaminants that might interfere with that determination must also be eliminated.

The goal, therefore, is to obtain a sample that is as precisely representative of the overall material lot as possible, and as homogenous as possible, in order to make as accurate a determination as possible of the actual value of recoverable precious metals within the lot. Clearly, this is easier said than done, since there are many processes, evaluations, equipment and systems involved in the sampling process, and there are also vastly different sampling methods used depending on circumstances. Another critical factor is the refiner’s experience and expertise, since some sampling procedures — and their ultimate outcome — are affected solely by judgment. No matter what, all of these steps must be accomplished to arrive at an accurate, final value determination.

Dry sampling spent chemical process catalysts

Because of their composition and chemistry, precious-metal-bearing catalysts are usually sampled using dry sampling processes. Dry sampling is employed whenever materials cannot be dissolved in solution or are inappropriate to melt either because of their structure or because of the cost associated with melting vs. the possible return.

Because it is difficult to achieve homogeneity, dry sampling is more complex and potentially less precise than melt or solution sampling. In fact, this method requires more judgment and skill than the others.

An ideal dry sampling system would be capable of drawing representative samples from free-flowing catalyst at a rate of 2,000–3,000 lb/h according to the principles of Pitard (2) and Gy (3) and the practices of Merks (4).

Because sampling is considered the most important procedure in the precious-metals recovery and refining process, it must be viewed from the perspective of the refiner as well as the catalyst user (the refiner’s customer). Clearly, the customer’s goal is to receive the maximum possible value for the remaining precious metals in its spent catalyst materials. The refiner, on the other hand, must not only consistently meet that goal for its customer, but it must also provide the customer with detailed documentation as to how that value was determined. The refiner and the customer each have responsibilities that must be met to ensure a mutually rewarding relationship.

As previously mentioned, dry sampling procedures involve converting many tons of spent catalyst materials to as little as a few tens of grams with the same precious metal concentration as was in the original lot of material. This is essentially a statistical process, and the laws of random sampling must be observed closely.

Pretreatment

Any sampling method requires a free-flowing material. If the catalyst is agglomerated into large balls because of oil or residual coke, or if it is covered with standing liquid, etc., it simply cannot be sampled. Pretreatment is then necessary.
The sampler

While a grain thief (a device consisting mainly of a long tube used to take samples at various depths) can produce a fairly representative sample if proper precautions and multiple samples are taken (4), it becomes impractical when the lot size to be sampled is greater than a few hundred pounds. Large lots require some means of drawing the sample from a flowing stream that ultimately contains all of the material. The design characteristics of these continuous samplers (auto-samplers) vary considerably, but all must have certain characteristics:

1. The device that extracts the sample periodically must cut across the entire flowing stream of particles, taking an equi-volumetric sample from all portions of that stream. (This is often violated in commercial automatic samplers.) Many factors in a flowing stream cause the material to segregate, for example by particle size, shape, density, surface charge, etc. Thus, if one portion of the stream is favored in the selection process, it will inevitably bias the sample and, therefore, its apparent precious metals content).

2. The extraction device must be large enough that the size of the particles being collected is small by comparison. If this is not the case, the sample will be biased against the larger particles in favor of the smaller pieces. Many refiners consider that the ratio of the smallest part of the collector to the largest particle size should be a minimum of a factor of ten.

3. Many collections, or cuts, of the stream (increments) should be taken at regular intervals during the passage of the entire lot through the device. The number should be well into the hundreds at a minimum to avoid the vagaries that the statistics of small numbers might introduce to the sample.

4. All of the material contained in the subject lot of catalyst must end up either in the collected sample or in the uncollected material bin (the reject). This may appear to be obvious, but it is not always realistic.

For example, material may be ejected from the system by higher-speed parts of the device or might fall between collection bins. In either of those cases, a biased sample would result because some difference in the particles would make it more likely that a certain type of particle is missed and therefore biased against, and there is no way of knowing whether those particles were higher or lower in precious-metals content.

Dust collection makes it very difficult to keep all of the material in the sampler as either sample or reject. Most samplers employ integral dust collection for reasons of health and safety, as well as material conservation. This material should be collected in an easily observed manner and sampled separately, with credit given to the customer for its value. The precious metals concentration (grade) of this fine material may be substantially different (higher or lower) than that of the bulk lot.

5. The sampling system should be easily cleanable to avoid cross-contamination.
6. Finally, the sampling system should be easily observable by its operators and by the customer or his or her representative. Customer representation at precious-metals refiners is a generally accepted standard in the industry. It is a false economy to minimize representation to save a few dollars. Sampling is a complex process, and small mistakes or misunderstandings can be very costly.

**Sub-lot size**

Sampling is not as simple as merely loading an arbitrarily large lot of catalyst of arbitrarily sized particles into the device and reduce its size to a sample bag suitable for laboratory analysis.

Consider first the lot size itself. Assume that we can achieve a sample that represents the lot to a precision and accuracy of 1%. Also assume that the total lot size is 100 tons and that the grade is approximately 0.3% platinum. (These assumptions are typical.) The total platinum value in the lot — at current Pt prices of about $1600 per troy ounce — is about $14 million. One percent of that value is $140,000. Most organizations would not tolerate such a variance.

Most refiners and customers will insist that the original lot be broken up into sub-lots of more manageable value, perhaps a few hundred thousand dollars each. For example, the 100-ton $14-million lot could be divided into 28 sub-lots that would then be sampled independently. Assuming the error is unbiased, the 28 independent determinations, each at ± 1%, would yield a much lower financial risk than if the material were treated as a single lot at the same relative error. This assumes that the 28 determinations are unbiased — that is, the chance of error on the high side is equal to the chance of error on the low side of the true content.

**Particle size vs. sample size**

Once it has been established that the sampling system is unbiased and that the sub-lot size is appropriate, the next task concerns producing a laboratory sample from a lot of 10,000 lb.

To illustrate this point, consider the following extreme analogy: Assume a 40,000-lb truckload of a mixture of bowling balls, some of which are made of glass and some of black ebonite plastic. We want to determine the percentage of glass in the mixture. We have a large auto-sampling system that meets the specifications above and can produce a random sample — to a point. Obviously, we cannot continue to split the lot down to a laboratory sample-bottle size, since a bowling ball will not fit in a typical sample bottle. The solution is to crush the bowling balls into small particles and then analyze the powdered mixture. But how small a sample should the bowling balls be split into before crushing them? Crushing is expensive and time-consuming, and therefore optimization of that grinding point is essential to efficient sampling.

The point to which the balls should be crushed is greater than one might suppose. For instance, assume that 10% of the original truckload of balls were made of glass and we
wish to determine the percentage to the 2% level. Assume as well that the bowling balls each weigh 16 lb. Now let us take a 10% unbiased sample with our hypothetical bowling ball auto-sampler. We now have 4,000 lb in the sample and 36,000 lb in the reject bin. Since 4,000 lb of bowling balls is still a lot of bowling balls, we will take a 10% sample of the 4,000-lb sample to obtain a 400-lb bulk sample. If we now crush the 400 lb to a powder and properly split out a laboratory sample, can we possibly hope to have achieved our desired 2% accuracy?

Remember that in this hypothetical example we know the actual percentage (grade) of the glass balls to be 10%. Therefore, 10% of the balls in the 400-lb sample should be glass. But 10% of 400 lb is 40 lb, and each ball weighs 16 lb. Therefore, the number of glass balls in the sample should be 2.5, which is impossible, since we have not yet ground the balls. Even after discounting random sampling aspects that the entire 400-lb sample had only 25 balls in it, the best we could do would be either 2 of 25 (8%) or 3 of 25 (12%). In either case, we have a 20% relative error.

**Particle size determines minimum sample size**

Ignoring this rule is one of the most common errors associated with dry sampling in general and catalyst sampling in particular. Pitard (4) and Gy (5) have derived formulae for estimating the minimum sample size from the physical parameters of the particulate system that are beyond the scope of this paper. A graphical representation of the theory calculated for a “specific hypothetical catalyst” is shown in Figure 4. The abscissa is maximum particle size and the ordinate is sample size. For this particular hypothetical catalyst, points to the left of and above the “safe line” have a probable relative standard deviation ≤1%, while those to the right and below are ≥1% relative.

It has happened that a 5,000-kg lot of catalyst with obvious color in homogeneities and a maximum particle size of 1 cm was split all the way down to 1 kg before it was ground to ~100 mesh and further split to laboratory size. Laboratory analysis agreement between customer and refiner was assured, but agreement between the sample and the lot in question was not. The refiner ground the bulk catalyst lot that was left down to the size required to achieve a sampling precision of 1–2%. Since the particle size was not appropriate prior to that, there is no assurance that the final material that was ground was, in fact, a representative sample to the degree of precision required.

**Sampling procedure**

A typical sampling procedure for a lot of spent catalyst materials sent to a precious-metal refiner begins when incoming catalyst materials are inspected, weighed, assigned tracking numbers and stored prior to sampling. The assignment of tracking numbers is critical; each lot — from the time it enters the refiner’s plant — is segregated from all other materials at the facility to eliminate all possibility of mixing with other lots.

When removed from a reactor, spent catalysts are often contaminated with organic materials, which must be removed to ensure accurate evaluation of the remaining precious metals. The catalysts must first be processed to remove those contaminants
and achieve free-flowing properties that will ensure accurate sampling, provide a reproducible settlement weight, and also permit safe and efficient operation of the process that will ultimately recover the remaining precious metals.

After any necessary pretreatment, the lot or sub-lot is screened to separate any oversize, or “tramp,” material and any fines from the bulk of the catalyst. The tramp material is inspected by the refiner and the customer’s representative to confirm that it may be discarded. The fines fraction is sampled separately, since it obviously is very different from the bulk of the catalyst in particle size and possibly in precious metal grade.

The main portion of the catalyst lot, which typically consists of extrudates of the order of 1 cm in length, is then divided by an automatic sampler into one or two bulk samples of a size suitable to achieve the desired precision. This is often in the region of 100 lb. This may require two or more passes through the sampling system, depending on its design.

If two bulk samples were cut from the lot, one of them is used for drawing an approximately 1-Kg sample that is known as a loss-on-ignition (LOI) sample. Alternatively (though less preferably), a portion of the single bulk sample is taken for that purpose. LOI samples are not analyzed for precious metal content, but are ignited to an agreed-upon temperature (usually around 900°C) to remove volatiles and oxidizables. This provides a reproducible basis for laboratories and a settlement weight for the lot. The LOI concept is discussed below and is treated in some detail by Helm, et al. (7).

The other bulk sample (or the balance if there was only one) is then ground to a particle size suitable for further splitting to approximately 1 Kg. For a typical catalyst, 100% –40 mesh is suitable and can be achieved in a ball mill. A rotary divider can then safely split –40-mesh material down to about 1 kg. Before dividing the material into 120-g laboratory samples, it should be ground to approximately 100-mesh, typically in a ring-and-puck mill. Several of these so-called quality samples are packaged and sealed for the customer, the refiner, an umpire, and for reserves.

The owner of the material and the refiner usually assay the quality samples (on an LOI basis) independently for the precious metals of concern. If these assays agree to within predetermined limits, they are simply averaged to arrive at the payable settlement. If they do not agree, then the sealed sample (called the umpire sample) is sent to an independent laboratory (the umpire). The three resulting assays are used (again by an agreed-upon procedure) to determine the settlement. Many times this involves averaging the two closest assays or using the middle assay to determine the final settlement. The reserve samples (usually sealed by both the catalyst owner and the refiner) are held and analyzed, if needed.

Keep in mind that throughout the sampling procedure, the refiner must adhere to all applicable environmental codes and standards with regard to effluent disposal and atmospheric emissions. Therefore, a typical ideal sampling system is enclosed for dust control and evacuated under a low-volume flow into a dedicated baghouse. In addition
to the obvious reasons for preventing atmospheric discharge of toxic and/or noxious fumes, the dust collected during this sampling process is also recovered and sampled separately, with its value — which is often substantial — returned to the catalyst owner.

A sampling system built to these specifications is shown in Figure 5. On the right are loading facilities for totes, drums and bags; to the left are vibrating screens to remove oversize tramp material and fines, which are treated separately. Three automatic samplers cut dual bulk samples of 1% each. One of these is further split into 4 portions of approximately 250 grams each for LOI determination. The other 1% sample, which may be as large as several hundred pounds, is ground in a batch ball mill to 100% –40-mesh. The –40-mesh material is split by another auto-sampler followed by a 24-pan carousel. This approximately 2-lb portion is ground in a ring-and-puck mill to 100% –100-mesh and split on a small rotary sampler into eight laboratory-sized samples. These approximately 150-g samples are packaged and sealed for the customer, the refiner, the umpire and reserves.

Note that the entire bulk sample of 1% of the batch is ground to –40-mesh before any further splitting occurs. This is quite important if there is any significant inhomogeneity in the sampled material (3). A secondary grinding in the ring-and-puck mill is performed later for the same reasons. The system is enclosed for dust control and evacuated into a baghouse, and the customer is credited with the metal values contained in the dust.

**The role of assaying**

In conjunction with this comprehensive sampling process, accurate and repeatable assaying procedures also play a major role in determining precise values of precious metals remaining in spent catalysts. Once the final samples are obtained, sophisticated instrumentation is used to measure their precise precious-metals content as previously described.

What may seem to be a simple analysis of a few elements in an inorganic matrix can be deceptively complex. Remember that the goal is to determine the precious-metal content to an extremely high accuracy at analyte levels of around 0.1% and many times much lower than that. Interferences and matrix effects are very common, and therefore only a laboratory with extensive precious-metals experience should be used.

**Recovery of the precious metal**

When sampling is complete, the spent catalyst lot is blended with a mix of flux and a carrier metal such as copper or iron. The proportions in this mix are determined by the calculated concentration of recoverable precious metals in the lot and the desired slag chemistry, which takes into account its electrical conductivity, corrosivity, morphology, melting temperature and other parameters.
This mix, called the charge mix, is then smelted, usually in an electric arc furnace (Figure 6). The furnace produces a two-layer molten pool. One layer is slag, which is the reaction product of the catalyst’s ceramic support and the added fluxes. This layer floats on a pool of collector metal in which the precious metals have dissolved. After the slag is poured off, the remaining layer of metal is poured into molds of a suitable size. The resulting ingots are then sent to a conventional hydrometallurgical or electrorefining facility for separation and production of the market grade precious metals. The slag, which contains trace amounts of precious metals, is usually also processed for further recovery and refining.

Reactions and Separations

![Particle size determines sample size.](image)

Figure 4. Particle size determines sample size.

![In an automated sampling system enclosed for dust control, dust generated during the sampling process is captured and sampled later to recover the precious metals.](image)

Figure 5. In an automated sampling system enclosed for dust control, dust generated during the sampling process is captured and sampled later to recover the precious metals.
Spent precious-metal-bearing catalysts may exhibit high loss-on-ignition (LOI) characteristics due to moisture, volatile hydrocarbons and contaminants such as sulfur and carbon. Removal of the substances is critical to the downstream sampling process and to the efficiency, safety and environmental compliance of the subsequent refining processes.

Any sampling system, especially one designed to handle large lots, requires materials that are free-flowing. This is often not the state of the catalyst when it is removed from the process unit. Instead, the spent catalyst is often moist or sticky and will not flow through an automatic sampler. Heavy carbon deposits, known as coke balls, are often present, and can be as large as a grapefruit. Pre-burning will remove these physical impediments to achieving a representative sample.

**Loss-on-ignition analysis**

The analysis of the sample's precious-metal content must be adjusted for any changes in the material's weight during handling. This is usually accomplished by determining the loss of weight upon ignition of a sample at a high temperature. Samples should be drawn as close to the net weighing of the lot as possible and in an undisturbed state. Although loss on ignition analysis may be handled at an independent organization (at
the discretion of the catalyst owner), it is advisable to have this procedure done at the refiner's facility. The reason for this, is because of possible physical and/or environmental changes to the sample which may occur during shipment.

This is in contrast to the sample drawn for precious-metal analysis, which is subjected to many conditions that the bulk of the lot (sometimes called the reject) is not. For example, the sample material will be repeatedly ground and exposed to significant airflow during screening; these and other handling conditions during sampling can cause weight loss through evaporation of volatiles or weight gain due to the absorption of moisture from the atmosphere.

An LOI sample is preferably ignited immediately (at approximately 900°C) at the refiner’s facility (and under observation by the owner or his representative) or placed in hermetically sealed containers for later analysis by both the customer and the refiner. The LOI of the sample is expressed in weight percent. This factor is then applied to the net weight of the lot to calculate the ignited, or “settlement,” weight of the lot. Later, an analytical laboratory will subject a quality sample to the same conditions and determine the precious-metal content on an ignited basis. Even if a representative sample is taken, the presence of volatile components and/or moisture may cause a weight change during transit to the laboratory. The loss on ignition procedure described above will compensate for this possibility. LOI determination is inherently less precise and less accurate than a settlement assay, and its variance must be as low as possible when samples are sent to the assay laboratory. The average precision of an LOI measurement is about 2% relative, although the range can be substantially more (up to 10%).

The table illustrates the effect of pre-burning on the precision of the entire settlement, even if the LOI can be determined to ±2%. When the entire lot of catalyst is pre-burned, the LOI of the remaining material is reduced to about 1.5% of the lot. The uncertainty is thus 2% of 1.5% (0.03%), so the settlement weight is accurate to ±18 lb (60,000 x 0.0003). If, however, the LOI is determined on the catalyst as received, and it is still possible to achieve 2% relative precision (which is doubtful when the LOI is as high as 40%), the settlement weight would only be accurate to ±800 lb (0.008 x 100,000). Of course, this effect would be much larger if the accuracy of the LOI determination were lower. These uncertainties are separate from, and in addition to, the sampling precision and the analytical precision.

**On-site vs. off-site pre- burnings**

Pre-burning is often done in an indirectly fired rotary kiln (figure 7). The typical rotary kiln will remove carbon and sulfur contaminants at catalyst throughput rates of 300–1,000 lb/h. The contaminants may also be removed in a multiple-hearth furnace or fluidized-bed furnace. An indirectly fired rotary kiln is more versatile and controllable than other methods, in that it is easier to control the throughput time (the time in a
reaction chamber), the dust and finer particulates, the temperature and the oxygen supply to the reaction.

Also important — at least from a financial perspective — is where the contaminants are removed. Overall refining costs can be reduced significantly when the kiln is located at the refiner’s facility. Many catalyst users must first ship their large lots of spent catalysts (as much as 35,000–500,000 lb) to an independent facility. There, strip burning removes hydrocarbons and coke burning removes carbon. In addition, another furnace may be required to dry fine particulates and other materials to eliminate moisture content.

Added turnaround time and additional costs are two major disadvantages of off-site strip and coke burning of spent catalysts. If these capabilities are not available at the refiner’s facility, catalyst users must pay substantial transportation charges to ship the catalyst to an independent off-site facility, where it might remain up to a month before it is processed. Then it would have to be shipped to the refiner to start the actual sampling, analyzing, recovery and refining process. During this time, the precious metals are unavailable to the catalyst user, and new metal must be acquired at current market prices and lease rates which was discussed earlier.

In addition, the indirectly fired kiln used for contamination removal must incorporate accurate, multiple temperature zones programmed for the specific catalyst type and contaminants present. And, the kiln should be part of a system that incorporates downstream air-pollution control equipment such as scrubbers, baghouses and incinerators to comply with applicable environmental regulations.

Perhaps the most important advantage of having the refiner handle the pre-burning in-house is the control the refiner has over every catalyst lot. This accountability eliminates the possibility that your materials could be mixed with unrelated materials from another organization. When that happens, it is not possible to accurately calculate its actual value.

**The devil is in the details**

The keys to obtaining maximum value — that is, recovering all possible remaining precious metals — from spent catalysts are detail, detail, and more detail: the thoroughness and accuracy of the materials sampling process, with assaying of the sample lots close behind. When you are seeking a precious-metals refiner for your spent catalyst materials (or working with one presently), you must look carefully into these areas, and work closely with the refiner whenever possible. These steps, as well as the refiner’s overall policies with regard to environmental compliance, should provide you with the knowledge and confidence to select (or work with) the proper precious metals refiner.
Figure 7. A rotary kiln at the refiner’s facility removes contaminants from spent catalyst materials prior to sampling.

<table>
<thead>
<tr>
<th>Table. Pre-burning improves the accuracy of sampling.</th>
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<tbody>
<tr>
<td><strong>Sampling with Pre-Burning</strong></td>
</tr>
<tr>
<td><strong>Net Weight Received</strong></td>
</tr>
<tr>
<td><strong>After-Burn Weight</strong></td>
</tr>
<tr>
<td><strong>LOI After Pre-Burn</strong></td>
</tr>
<tr>
<td><strong>LOI Without Pre-Burn</strong></td>
</tr>
<tr>
<td><strong>Settlement Weight</strong></td>
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<tr>
<td><strong>Settlement Pt Assay</strong></td>
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<td>Pt Content, troy oz</td>
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**Pt Accuracy**

**Literature Cited**


Note: Weight measurements are in avoirdupois pounds; 1 avdp = 14.583 troy oz.

**About the author:**

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