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Consider Offshore Recovery of Remaining Precious Metals in Spent Process Catalysts

ver the past few years many APAC hydrocarbon and petrochemical processing industries planned for significant growth with new upstream and downstream projects to add domestic capacity. China and India, in particular, planned major production expansion projects by both government-and privately-owned refineries. India held nearly 5.7 billion barrels of crude oil reserve at the beginning of 2014. Domestic production has not kept pace with demand in recent years, leading to exploration of deep water and marginal fields and investment in improving recovery rates of existing fields. India is also a significant importer of crude oil, as demand continues to out-shrink domestic supply growth. The Indian government projected a 1.25 million bpd capacity expansion within the next three years. According to a recent article in this magazine, China, for example, produced approximately 4.50 million bpd of oil last year, almost all of it for domestic consumption. Projections for Chinese capacity additions were estimated at 3.5 million bpd within the next three years. Now, however, many Indian, Chinese, and other APAC refineries' expansion plans may be halted.

The US. Energy Information Administration (EIA) considers India the world's fourth-largest consumer of oil; with China as the world's second- largest consumer of oil. In fact, the country was also projected to move from second-largest net importer of oil to the largest

last year. The U.S. EIA also points out that "substantial oil demand growth and geopolitical uncertainties have increased pressure on China to import greater volumes of oil from a wide variety of sources." Most of APAC's new refining capacity growth has been in China and India, while other industrialized APAC countries experienced, "No growth in refining capacity..." according to information from research firm Gaffney, Cline & Associates.

Capacity Additions Planned For an Additional Six Million Bpd

Most APAC countries with domestic oil production demand over 200,000 bpd are self-sufficient in refining capacity; exceptions are Malaysia, Indonesia, Pakistan, and Vietnam where refining capacity is below demand. Since 2003, of these four countries, only Vietnam has added some incremental refining capacity. Overall plans in these and other APAC countries call for total capacity addition: of 6.0 million bpd. Most of the capacity addition: were expected from China (55%), India (24%) and the rest of Asia (21%), Within these growth plans, almost three-quarters of new crude distillation unit (CD1) capacity additions was planned for national oil companies, with local private and foreign companies contributing about 15% and 10%, respectively.

Now, it appears as though many of these expan-

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sion plans are being postponed because of global economic and geopolitical changes. There are many reasons for these changes (not the least of which has been the worldwide decline of crude oil prices) however, there is also a paradigm shift occurring in two major regions: Asia Pacific and the Middle East. Many APAC countries that had been net importers of refined products—including China and India had been looking to become self-sufficient within the next few years.

A Few Typical examples

Malaysia is the second largest oil and natural gas producer in Southeast Asia with the area's fourth highest known oil reserves. In Indonesia, the international majors—especially Chevron and Total dominate the country's upstream oil sector, while the state owned energy company Pertamina must balance its needs against its mandate as a government owned oil company to meet domestic demand. Well production in 2013 actually declined in Indonesia and recent discoveries have yet to reach full capacity. This is the impetus for building new infrastructure in this country to serve a growing domestic market.

A Realistic Look to the Future

As previously mentioned, the six million bpd growth predictions for all APAC nations' refining capacity appears now to be unrealistic, considering current market conditions: lower global crude prices coupled with less global demand, and production overcapacity in some APAC countries. It's a new game out here for many APAC hydrocarbon and petrochemical refineries. In fact, participation in APAC countries by private and foreign refiners is now not only slowing, it has come to a full stop in some areas. If market demand did not decline, refinery additions in China and India would have exceeded the combined expected growth in consumption in their respective countries in the next five years by almost 2.5 million bpd.

Another APAC refinery trend (which parallels the Mideast hydrocarbon refining industry as well) is the fact that more APAC refineries have become involved in other "value-added" products in the chemical and petrochemical arenas. Many have moved towards increased production of non-fossil fuel products such as fine and specialty chemicals (as well as a variety of other petrochemical end products). This not only provided additional profit opportunities but also flexibility for their profit structures (both upstream and downstream). It is especially true of older industrialized countries such as Japan. However right now it looks as though this trend might also be reversing with some major APAC petrochemical producers reducing production or even shutting down. All of them, however, must deal with the prospect of obtaining maximum value from the precious metals that remain when the catalysts lose their efficacy.

Enhance Profits by Maximizing Precious Metals Returns

Now that we've got this background sorted out, under current circumstances, how can these APAC hydrocarbon processors, chemical, and petrochemical refiners maintain profitability under domestic and international market pressures-not only dealing with lower crude prices but also less demand, tough competition, and increasing margin squeezes? How does a prudent hydrocarbon processor acquire better bottom line numbers? One way to do this is to maximize recovery of the precious metals that remain in its spent process catalysts. Typically these high value metals, commonly referred to as PGMs, which include platinum, palladium, ruthenium, and rhodium are recovered and refined by a precious metals refining organization using a variety of process techniques to maximize recovery of what could be millions of dollars of PGMs in large spent catalysts lots (100 metric tons would not be uncommon for example).

Enhancing profitability through obtaining highest values for remaining precious metals from spent catalysts is especially important for industries at less developed countries that are moving up the socio-economic ladder and competing with other countries around the world. Let's face it: All governments want to become self-sufficient both upstream and downstream and many are looking to become net exporters as well.

How exactly does a precious metals refiner work to assure maximum recovery of PGMs and other precious metals? How can you profit most by working closely with one? And how do you find the best precious metals refiner to fit into your precious metals asset management program?

Full-service, in-house recovery/ refining capability

First, consider that in many APAC countries, there are few-if any-precious metals refining organizations that provide the unique combination of sophisticated equipment, advanced technology, and years of experience required to extract maximum return value of remaining PGMS from spent catalysts (including rhenium, another valuable precious metal which we will discuss later). Your goal is to find a refiner who has the capability to maximize returns of all precious metals, since many millions of dollars will likely be involved. And in order to maximize return values, the catalyst owner may have to look towards distant shores for the right refining organization-even if added transportation costs are incurred, along with expenses to send or hire an independent representative to the refiner's facility to witness the processing of its spent catalyst materials. Only in this way can a catalyst owner be virtually guaranteed of receiving maximum return value. understandably, recovery/refining turnaround time is an important consideration: everyone wants quicker settlements for obvious reasons. however, the financial advantages of maximizing return metals value may outweigh the added transportation time to and from a refiner's facility. Also, a refiner with full in-house capabilities will provide quickest possible turnaround time for processing spent PGM-bearing catalyst materials.

Procedures and Policies for Recovery and Refining

The precious metals recovery and refining process involves complex procedures and policies that include logistics, materials documentation, contamination removal, sampling, assaying, recovery, refining, processing turnaround time, financial services, and environmental considerations. An experienced precious metals refiner will coordinate all these activities for its customers, with he goal to arrive at a successful-and mutually rewarding-conclusion. The refiner's efficiency in executing these functions can determine the amount of PGMs recovered from spent catalysts, the turnaround time, and the value returned to the catalyst owner. To understand the criteria in selecting a precious metals refiner (see sidebar) it is important to understand the equipment, sampling/assaying techniques, and environmental considerations involved in precious metal catalyst recovery. In simplistic terms: Achieving the highest possible return value from all remaining precious metals in the spent catalyst lot, and doing it in an environmentally safe manner.

As an operator, how do these circumstances affect you? It's simple, really: It is in the best interest of any hydrocarbon refining organization to look carefully at its asset recovery program with regard to acquiring highest possible value for remaining precious metals in spent catalyst lots. Consider this typical example: A large spent catalyst lot from a major refiner might contain ten million dollars in recoverable platinum at today's market price of over \$1400/Troy ounce; clearly this represents a significant contribution to any organization's profit picture—even if five or six years pass between changeout cycles.



Figure 1. Oversized materials (after re-working) are inspected to assure sample particle sizes under -40 mesh.

Most refiners use a wide variety of equipment to process spent catalysts. This equipment includes rotary and crucible furnaces, kilns, roasters, thermal processors, pulverizers, regulators, screens, blenders, auto samplers, reactors, dissolvers, precipitators, electrolytic scales, filter presses, and more (Figure 1). When selecting a precious metals refiner for a "partner relationship," a catalyst owner should be aware of some of the key steps within the refiner's process and how its technologies are applied to recover highest possible remaining PGMs—including virtually all remaining rhenium—from spent catalyst lots. Here's a good example:

All hydrocarbon and petrochemical refiners believe they know the precise composition of their precious metal-bearing process catalysts at the start of a campaign. But how many know their precise composition at the end of the campaign, after years of working under extreme conditions? In addition to many common problematic factors in spent catalysts (moisture, sulfur, coke, carbon, benzene, excessive fines, and support media) there are also other extraneous elements present such as silicon, iron, and others. While the troublesome contents and traits have little or no value themselves, they can have a significant effect on the total precious metals return value one receives from one's refiner.



Figure 2 The continuous catalyst sampling system generates homogenous, consistent, and reproducible intermediate samples. Automated systems produce samples that accurately represent entire lots of spent catalysts. To help assure materials balance accountability, independent dust collection systems (one for the primary sampler and one tor the secondary sampler) are employed.

The reason for this is that precious metal refiners typically use one of two discrete methods to recover PGMs, rhenium, or other remaining precious metals from spent process catalysts. These methods use hydrometallurgical or pyrometallurgical technologies. After a spent precious metal-bearing catalyst lot is homogenized (the sampling process-(Figure 2) and representative samples are drawn, a series of sophisticated laboratory instrument analysis procedures is conducted, commonly known as assaying. As saying enables the refiner and the catalyst owner to agree on the value of the recoverable precious metals contained in the spent catalyst lot (Figure 3). Once this is done, the actual refining can begin The process that extracts the precious metals by one of the two previously mentioned techniques (Note: Sampling and assaying procedures art outside the scope of this article because of space constraints; however, full details are available a www.sabinmetal.com.)



Figure 3. Atomic absorption analysis (AA)

Pyrometallurgical vs. hydrometallurgical technology

There are fundamental differences between hydrometallurgical and pyrometallurgical processing, but one of the key advantages of pyrometallurgical technology (the Pyro-Re® process, for example) is the ability to fully recover the spent catalysts' rhenium content, while the hydrometallurgical process can only recover the rhenium that is acid soluble. There are many reasons for this, but the main reason concern: the inability to separate the remaining rhenium with a practical process for its recovery and subsequent refining. That's because most precious metals refiners recover rhenium by dissolving their carriers (typically gamma aluminum oxide) with strong caustic or acidic chemicals (the hydrometallurgical or digesting process). While this process is capable of recovering the soluble PGMs and rhenium content in the spent catalyst, an unknown portion of the desirable "pay" metals-sometimes as much as 20%-remain behind due to the insolubility of the substrates or carriers. That insolubility occurs because the substrates are hardened as a result of overheating during years of operation, preventing their dissolution, even with strong solvents.

What happens when spent catalysts contain a significant quantity of rhenium? It's usually present in about a third of precious metals-bearing hydrocarbon processing catalysts; for example, in combination with platinum for reforming naphthas into other desirable products. A precious metals refiner with the ability to recover virtually all of the remaining rhenium in the spent catalyst lot may not exist in any APAC country. In fact, there may be only a few refiners in the world that can offer this capability. That alone will have a significant effect on processing time, costs, and, of course, the return value you receive.

With the value of rhenium rising over the past few years, the technology to recover virtually all of it from a spent catalyst lot has become increasingly important-especially when petroleum refiners are facing increased profitability pressures. Typical value of rhenium today is approximately USS. \$3,000/kg. With regard to this issue, precious metal refiners using hydrometallurgical techniques typically send these insoluble materials to third parties (smelters) to recover whatever precious metals remain. In this situation the catalyst owner is generally paid only for the acid soluble rhenium content and not necessarily the total rhenium content. This in itself could be a valid reason to consider sending large spent catalyst lots overseas for recovery and refining since, in some cases, recovery of the rhenium content alone will more than make up for any additional transportation charges. The refiner that uses pyrometallurgical technology can recover virtually all the rhenium content from spent catalyst lots (semi-regenerative and cyclic fixed bed), particularly from catalysts on substrates that cannot be dissolved with caustic chemicals.

It is difficult to put a precise value on the rhenium in question when comparing these two technologies. The reason for this is due to the circumstances within the catalyst's lifecycle. The final coke and carbon content, the amount of heat the catalyst may have been exposed to during years of processing, and perhaps even additives that may have been used to extend the catalyst's life cycle. However, when spent catalysts are processed by hydrometallurgical techniques these factors become more critical since they can interfere



Figure 4. Slag from the dual electric arc furnaces—containing trace amounts of precious metals—is poured into slag pots which are set aside tor cooling. The slag is shipped to SMC (Canada) Ltd. for subsequent refining, Dual electric arc furnaces double pyrometalurgical processing throughput to help assure maximum recovery of remaining PGMs in spent catalysts including rhenium.

How to Select a Precious Metals Refiner

To ensure that a relationship with a precious metals refiner will be mutually profitable and based upon trust and fair treatment, you must address several key questions. This checklist may help:

- Select a refiner that uses state-of-the-art techniques and equipment
- Select a refiner that has a long and successful history and good reputation within the industry
- Discuss the refiner's performance and policies that it maintains with its customers
- Ask your refiner if there will be any "hidden charges" not described in a contract proposal
- Request appropriate reference material, including environmental regulation documentation
- Determine whether the refiner has the financial resources to arrive at a settlement in a timely manner
- Select a refiner that has full in-house capabilities —without use of outside subcontractors which might affect returns in values and timeliness
- Ask the refiner for detailed weight and analysis reports on shipments
- Ask the refiner if sample materials are assayed in triplicate
- Ask the refiner if it is allowable to be present during materials sampling, and whether an independent analysis can be conducted, if desired

with the digesting method and its ability to capture the total rhenium content. The trace elements that may or may not be present and the status of the catalyst substrate base can have a dramatic effect on how much precious metals will dissolve. Pyrometallurgical processing, however eliminates this issue; in other words, everything in an electric arc furnace melts. As a result, then is no need for processing of any insoluble or unmeltable material (Figure 4).

Responsibly recovering and refining precious metals from spent process catalysts requires a refiner to use well controlled processing methods that comply with appropriate environmental standards and reg-Hydrocarbon Asia, APR-JUNE 2015



Figure 5. Minimizing harmful atmospheric emissions is both mandatory and critical. Baghouses such as this prevent discharge of noxious, toxic, or annoying fumes or odors, while capturing remaining precious metal particulates prior to atmospheric discharge.

ulatory agencies everywhere in the world. In other words, the refiner must adhere to all applicable environmental codes and standards covering effluent disposal and atmospheric emissions. Therefore, a properly equipped and environmentally responsible refiner will have the technology appropriate for pollution abatement, including afterburners, baghouses, scrubbers, and legal effluent disposal and/or neutralizing equipment.

For example, any systems used for thermal oxidation must be able to combust organic contaminants completely. Off-gases resulting from thermal oxidation should be processed through a baghouse/ scrubber system designed not only to eliminate pollution but also to capture precious metal particulates that would otherwise be discharged into the atmosphere

This publication thanks Bradford M. Cook, Vice President, Sales and Marketing at the Sabin Metal Group of Companies. Cook has an extensive background in the precious metals industry, having served for 22 years at Inspectorate America Corp, Houston, TX where he began as a field representative for the northeastern US. and Canada and advanced to sales and marketing management positions in both North America and Europe. In 2006 he was named general manager for the company's Precious Metals division, and advanced the following year to senior general (Figure 5). Atmospheric discharges must be managed with pollution control systems that result in few or no pollutants being emitted before, during, and after the refining process; a refiner's water treatment process should also minimize all causes of pollution.

A precious metal refiner should have approved status with all appropriate governing environmental agencies, and will generally provide copies of the required documentation stating such. One thing to remember is that a refiner must be responsible for all its customers; the violation of a pollution control law by a refiner can have legal implications for all of the refiners' customers anywhere on the globe.

Conclusion

Eventually crude oil prices will rise; demand will grow; and capacities at most APAC countries will increase. However, competition will also get tougher, and bottom line profits will still be harder to come by. For now, however, based on current conditions: lower costs for crude feedstocks, reduced market demand for finished products, overcapacity facilities, slower growth and increased competition, it makes good sense for prudent APAC refiners to look long and hard at partnering with a well-established, well experienced precious metals refining organization, no matter where it is located. When the circumstances improve you will be that much ahead of the game.

(1) Exports or imports-—The future of Asian refining; Gaffney, Cline & Associates, October 2014; republished from an article by GCA in Chemical Industry Digest/March 2014

manager for Inspectorate's North American Metals and Minerals Group where he was responsible for over 40 employees and 80 subcontractors throughout North America. Prior to his affiliation with Inspectorate, Cook was a supervisor at Boliden Metech in Mapleville, RI where he was responsible for settling precious metals lot contents with the company's customers and representatives. He has been a member of the International Precious Metals Institute Executive Committee since 2007 and has also served as president of that organization.