Incineration is the traditional method used to recover precious metals from spent catalysts, but it has a number of drawbacks, particularly from an environmental point of view. Now a British-Swedish joint venture, involving Chematur Engineering AB and Johnson Matthey, has developed a process that uses supercritical water oxidation to recover the precious metals. The technology, called AqauCat®, offers organic destruction efficiencies of close to 100%, but without any of the problems associated with incineration.

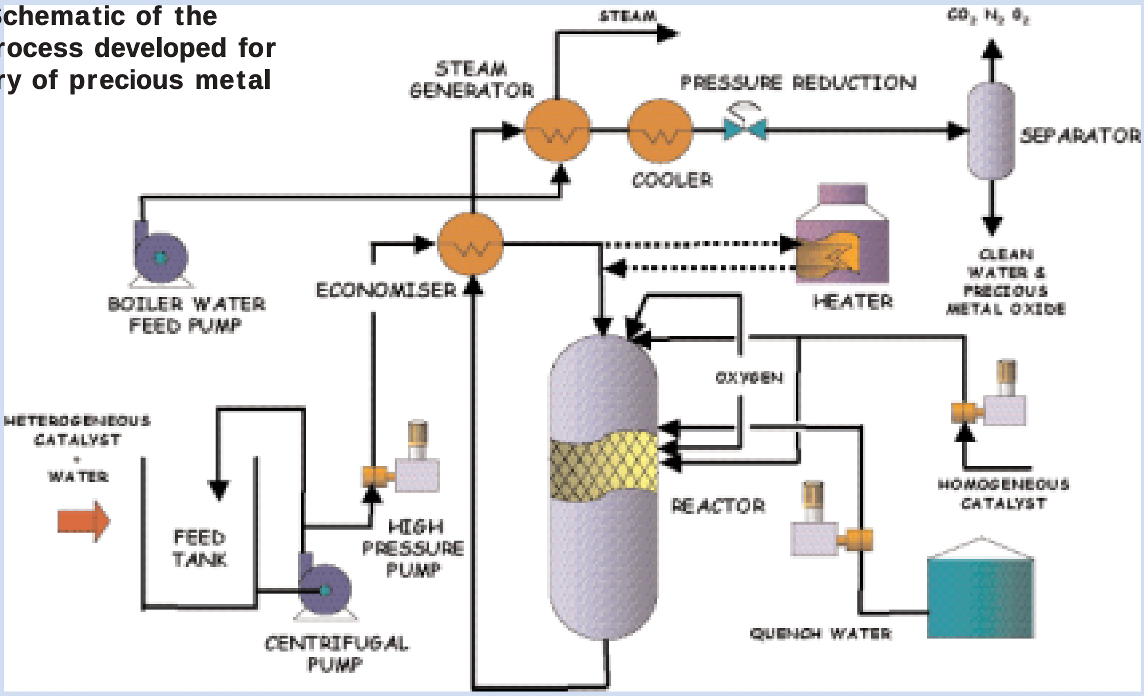
Recovery of Precious Metal Catalysts with Supercritical Water Oxidation

Precious metals are used extensively as catalysts in a wide range of industrial chemical processes. They can be used in a homogeneous form, but more commonly they are heterogeneous, i.e. they are fixed to a solid support for ease of handling. In many applications only a precious metal catalyst can provide the necessary speed or selectivity to the reaction, while in others these attributes, together with a long catalyst life make the overall system the most cost effective choice. However, precious metals, such as platinum, palladium or rhodium, constitute a huge investment, so a key factor in the economics of these processes is the ability to recover the precious metal content from the catalyst once it is spent. Quick and efficient retrieval of the metals is therefore very important. However, spent process catalysts are typically contaminated with organic materials that were present in the reaction mixture. These organics, which are often hazardous, as well as any carbon present in the support, have to be removed before the complex process of metal recovery can begin.

What is Supercritical Water Oxidation?

The precious metal recovery process has almost exclusively used incineration to destroy the organic content of the catalyst material, followed by a chemical treatment of the remaining

Figure 1: Schematic of the AquaCat process developed for the recovery of precious metal catalysts.



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metal oxides. However, incineration as a process suffers from a number of drawbacks, including incomplete combustion and the subsequent need to scrub the stack gases to remove environmentally hazardous substances such as dioxins.

Now through a joint venture between Johnson Matthey (UK), and Chematur Engineering AB (Sweden) a new recovery process, called AquaCat, has been developed (Figure 1). The process utilizes supercritical water oxidation (SCWO); a technique previously patented by Chematur Engineering.

When water's temperature and pressure are above 374 °C and 221 bar, respectively, it enters a supercritical condition or 'fourth phase', i.e. an additional phase to its more familiar solid, liquid and gaseous phases. Under these conditions the physical properties of water change. For example:

- its density is less than that of the liquid;
- its viscosity is the same as the gas; and
- its diffusivity is mid-way between the liquid and the gas.

Most importantly the solubility of gases and organic compounds are increased to almost 100%, while inorganic compounds become insoluble. When oxygen is added to organic contaminants under these conditions, a very rapid reaction occurs, resulting in the almost complete destruction of the organics.

Unlike incineration, the only gaseous emissions from this process are carbon dioxide (CO_2) and nitrogen (N_2) at room temperature.

The AquaCat Process in Detail

The AquaCat process, which took three years to develop, is based on Chematur's AquaCritox® process, where water is heated up to approximately 400 °C and pressurized to 250 bar. It then enters the supercritical condition, where it can 'burn' organic materials extremely quickly and efficiently through the addition of an oxidant, leaving no harmful residues.

In the AquaCat process hydrocarbons are converted to CO_2 and water, with a guaranteed extent of conversion of at least 99.99%. Early experiments confirmed the AquaCat process has an extremely rapid reaction rate because the presence of the catalyst assists the oxidation process.

The majority of materials that come for catalyst recovery are heterogeneous in form. In the AquaCat recovery process, these heterogeneous materials are first made into a slurry in water. After sampling to determine precious metal content the mixture is pumped to supercritical pressure and heated to supercritical temperature and transferred to the reactor (Figure 2). Oxygen is then added, and the organic backbone of the spent catalyst is immediately burnt off, leaving behind almost clean water containing a fine particulate phase of precious metal oxides (Figure 3). The solid precious metal oxides are then separated from the water, and are ready for refining and use in the preparation of fresh catalysts.

Benefits Over Incineration

The AquaCat process solves many of the problems associated with traditional incineration. From the environmental and economic points of view it is more energy-efficient because it does not require an external source of energy. It also eliminates the need for complex and expensive exhaust gas treatment and

Figure 2: View of the AquaCat reactor.

reduces the amount of physical handling of the catalyst materials, which again makes containment easier.

From a customer's point of view, the biggest advantage of AquaCat over incineration is that it allows pre-treatment sampling of the material. This is important because precious metal catalyst materials are very expensive. Therefore, it's important to know exactly how much is being processed and to be able to move it through as quickly as possible, i.e. speed can save money.

On-Site Recovery Plants

Johnson Matthey, which specialises in the field of catalyst recovery, can use the AquaCat method to retrieve the metals and make new catalysts for their customers.

In addition to providing this as a service carried out in its own plants, AquaCat now makes it possible for the company to offer the processing equipment itself to certain customers. In some cases, for example in pharmaceutical manufacture, the residues are strongly bioactive and must be handled with extreme care. In other situations, such as in a petrochemical plant, large volumes of organic residue are generated, which are both costly and difficult to transport. For customers like these, Johnson Matthey and Chematur are now be able to provide an on-site SCWO plant, so that these hazardous materials can be treated at the point of generation, avoiding additional handling or transport of the residue. According to Johnson Matthey, the delicate control required by classical incineration techniques meant that on-site units using that technique were never a viable option.

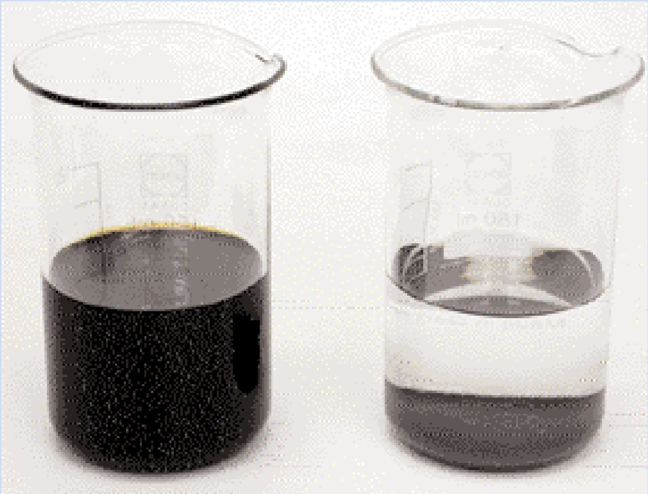

Figure 3: Homogeneous catalyst before (left) and after (right) treatment with the AquaCat process.

Figure 4: The first commercial scale AquaCat system at Johnson Matthey's Brimsdown site in the UK.

Johnson Matthey's first commercial scale AquaCat plant is based at its Brimsdown site in the UK and was commissioned in late autumn 2002 (Figure 3). The company has future plans to install more of the plants in their facilities worldwide.

Is this the End for Incineration?

With all the obvious benefits of AquaCat, does it mean the end of incineration in this field? Johnson Matthey does not believe so. While it believes that the AquaCat process will be the benchmark for precious metal recovery from spent catalysts there is still a role for classical incineration. Certain materials, particularly those contaminated with extraneous material or plant debris, will not be suitable for the AquaCat process, and will continue to be burnt in the traditional way. Furthermore, classical incineration remains the most suitable technique for treating other forms of material, which contain precious metals, such as scrap electronic components.

Other Applications for AquaCritox

In addition to the AquaCat application, Chematur Engineering are optimistic about further developments for its AquaCritox technology. One area is in the treatment of sludge from municipal treatment plants. The process can be easily incorporated into the sewage treatment plant operation. In pilot studies both raw and digested sludge can be treated at 15-20% dry solids, which means simplified dewatering. The effluent chemical oxygen demand (COD) level is less than 5 parts per million (ppm), so no further treatment is necessary. The inorganics settle as an inert, non-leachable residue. The high purity and fine grain appearance of the residue make it a viable starting material for the recovery of coagulants and/or phosphorous.

Chemtur has also been involved in a number of paper recycling projects, looking at oxidising de-inking sludge to recover valuable inorganic materials, such as paper filler. The de-inking sludge contains organic material (ink and fibres), as well as inorganic matter (mainly paper filler). When the sludge is treated with the AquaCritox process, the organics have been destroyed, while the white filler is left behind to be recycled.

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