

Precious Metal Recovery from Spent Catalysts

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A new process called AquaCat[®] for the recovery of precious metals from spent heterogeneous and homogeneous catalysts is described. The process has two stages, the first stage is to determine the precious metal content of a spent heterogeneous catalyst using new direct sampling technology. The second stage involves supercritical water oxidation, during which the carbonaceous material is converted into less noxious compounds, leaving the precious metals as their oxides.

Spent organic-based catalysts which contain precious metals have traditionally been treated by incineration to recover the precious metal content. Incineration destroys the organic content of the catalyst and leaves an ash which, before chemical recovery is started, is sampled to determine the precious metal content. However, a new more environmentally-friendly process, AquaCat[®], jointly developed and patented (1, 2) by Johnson Matthey (3) and Chematur Engineering AB (4), takes a different approach, see Figure 1.

Direct Sampling

AquaCat[®] allows a spent heterogeneous catalyst, such as palladium or platinum on a carbon support, to have the metal content evaluated prior to treatment, directly from the as-received samples. The spent catalyst is received as a wet filter cake with a particle size distribution between 5 and 500 μm . This is added to water and surfactant in a vessel and mixed by agitation and by using a pumped recirculation loop in order to create a homogeneous dispersion. A series of small representative samples of the mixture are then removed from the recirculation loop by automated extraction. These are collected together to form a sample which is sub-sampled in the laboratory and analysed for its precious metal content using standard analytical techniques.

The sampling procedure was extensively validated on a pilot scale before being scaled up for use in production. Over fifty samples of materials representative of typical as-received spent catalyst were evaluated using the direct sampling process.

This was followed by filtration and treatment via the traditional incineration route. Figure 2 shows a graph of the quantity of precious metals found by direct sampling compared to incineration. Samples are monitored against expectations for each batch.

Computational fluid dynamics was used to model the production-scale process. Output from the modelling is shown as a deviation from the average concentration in the vessel and is less than 0.5% throughout most of the mixing vessel, see



Fig. 1 Part of AquaCat[®] at the Enfield site. The direct sampling equipment is on the left. The feed tank and high pressure pump for the SCWO process are on the right

Figure 3. The concentration of material at the outlet and thus in the recirculation loop is equal to the average of the concentrations in the vessel. This ensures that the sample taken from the recirculation loop is representative.

Supercritical Water Oxidation

The water-based slurry is then pumped into the feed tank for the next step in the process: supercritical water oxidation (SCWO). Water becomes supercritical at a temperature above 374°C and pressure above 221 bar, when its viscosity is close to that of the gas phase but with higher density. In this process organic materials become soluble in the supercritical water, which is thus used as a solvent for the oxidation. Inorganic materials, however, become insoluble. If feed materials contain high levels of salts the SCWO process is not suitable.

A flow diagram of the SCWO process is shown in Figure 4. The SCWO process is based on Chematur Engineering's supercritical water oxidation process, Aqua Critox®. Water is pressurised to approximately 240 bar using a high-pressure pump, then heated to about 385°C to be in its supercritical phase. In the SCWO plant heterogeneous (solid) catalysts are fed in a slurry form from the feed tank whereas homogeneous (liquid) catalysts are fed directly into the reactor.

Processing Heterogeneous Catalysts

The slurry containing ~ 5% of spent catalyst is pumped up to a pressure of ~ 240 bar then passed through the economiser (heat-exchanger) into the heater to raise its temperature to 385°C. The material then enters the reactor where sufficient high-pressure oxygen is injected to allow the heat of reaction to raise the temperature to ~ 600°C. Next, quench water is injected to reduce the temperature before a second oxygen injection, which allows the reaction to go to completion. The organic components are converted to carbon dioxide, water and nitrogen and the metals form their oxides.

The product from the reactor next passes through the economiser to preheat the incoming feed and then to a steam boiler (where up to one tonne per hour of steam is generated and fed into

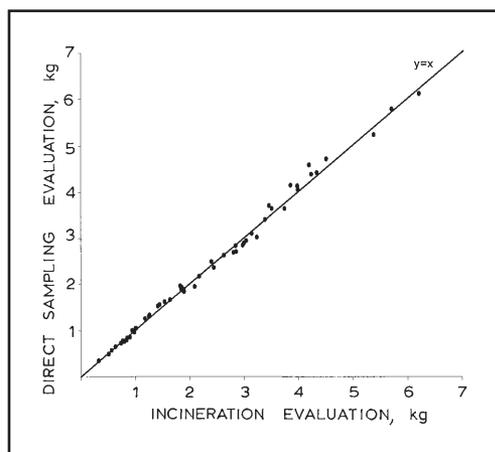


Fig. 2 Pilot scale validation graph of the amounts of precious metal found by direct sampling compared with traditional incineration. Most points fall on or close to line $y = x$, showing that the two evaluation procedures are equivalent. In fact they are statistically equivalent

the site's steam main). The product is cooled to ambient temperature and pressure prior to the combustion gases being separated off. The precious metal oxides along with any other trace elements, such as base metal oxides and silica, are sent on for further refining.

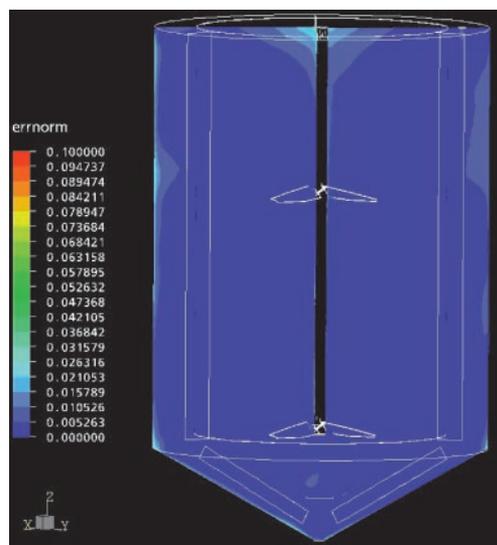


Fig. 3 A computational fluid dynamics model of the sampling vessel is presented. The output from the modelling is shown as the deviation from the average concentration in the vessel and it is less than 0.5% relative throughout most of the mixing vessel

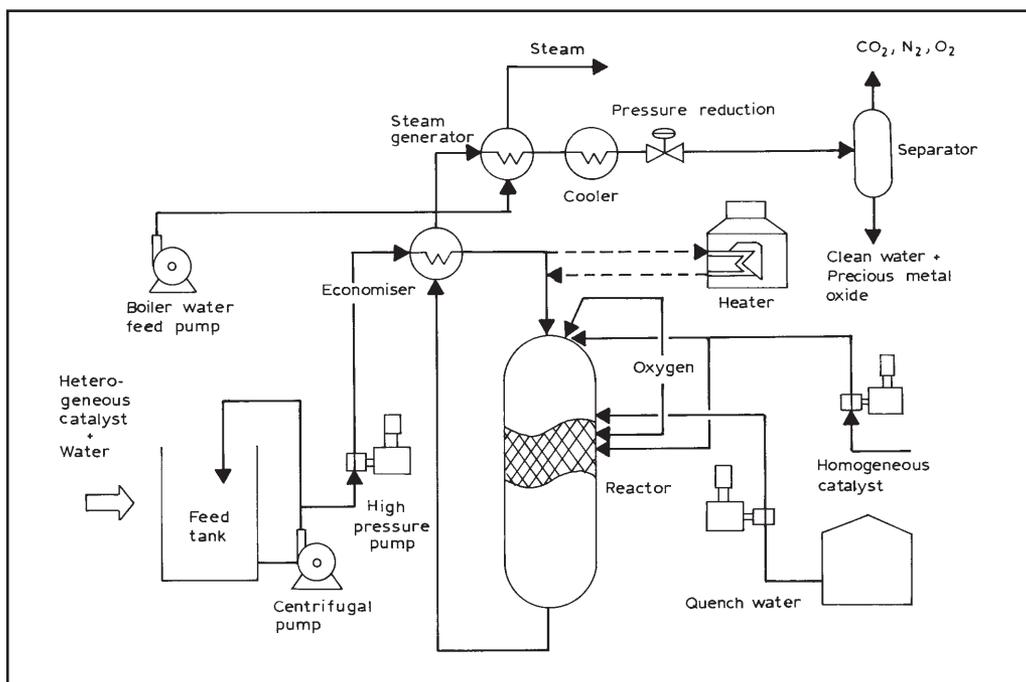


Fig. 4 Flow diagram of the supercritical water oxidation process, based on Chematur Engineering's supercritical water oxidation process, Aqua Critox[®]. Water is pressurised to ~ 240 bar using a high-pressure pump and then heated to ~ 385°C so that it is in the supercritical phase. Heterogeneous (solid) catalysts are fed in a slurry form from the feed tank. In contrast, homogeneous (liquid) catalysts are fed directly into the reactor

Processing Homogeneous Catalysts

Homogeneous catalysts are processed similarly to heterogeneous catalysts except that only high-pressure water is fed into the economiser. The homogeneous catalyst is injected directly into the reactor after the oxygen injection points because it is not miscible with subcritical water and it often contains phosphorus which would pyrolyse in the preheating equipment when oxygen is not present.

The Benefits of AquaCat[®]

Several environmental benefits result from using the SCWO process instead of traditional incineration. In part these are because the process is totally enclosed and so prevents the release of any harmful substances and metal loss. As such it achieves efficiencies for organic destruction close to 100%. Additional benefits include:

- Lower CO₂ emissions – less fuel is required.
- No CO emissions – the reaction goes to completion.
- No NO_x emissions – lower reaction temperature.

- No SO_x emissions because sulfur remains in the liquid effluent, and is treated off site as sulfate.
- No dioxins or furans due to effective oxidation.

The process is also more energy efficient as the energy from the exothermic reaction is used to preheat the incoming feed and generate steam. The process is continuous giving a greater degree of control than in batch incineration. SCWO can oxidise the organics in metal-organic compositions, particularly heterogeneous or homogeneous precious metals catalysts, and produce metal oxides with few byproducts and low loss of precious metals. Catalysts containing higher levels of residual organics can thus be treated more safely.

Benefits from direct sampling include the acceptance of material in intermediate bulk containers, as well as drums, thus hazardous materials are handled less. Incoming residues are checked and sampled before any processing – demonstrating confidence in the process efficacy. The prior sampling also gives earlier evaluation than in traditional processing.

References

- 1 S. Collard, A. Gidner, B. Harrison and L. Stenmark, *World Appl.* 01/83,834
- 2 *Filtration & Separation*, June 2003, 40, (5), 16 and references therein
- 3 <http://www.chemicals.matthey.com/>
- 4 <http://www.chematur.se/>

The Author

Piers Grumett is the Production Manager for Aquacat[®], Johnson Matthey Catalysts, at the Enfield site, U.K. He has managed Aquacat[®] from its initial stages, through installation, to current day-to-day operations. His interests include continuous improvement of process operations and implementing operational changes. Other interests are environmentally-friendly procedures and safety.

Hydrogen Economy Forum in Russia

SECOND INTERNATIONAL SYMPOSIUM ON SAFETY AND ECONOMY OF HYDROGEN TRANSPORT

IFSSHT-2003 was held from 18th to 22nd August at Sarov, Russia, where about 250 delegates from 12 countries attended a range of presentations on various aspects of hydrogen (H). The symposium also commemorated the 60th anniversary of pioneering H utilisation by Boris Shelishch who, during the Siege of Leningrad, devised H-powered vehicles. Selected papers, some relating to the platinum metals, are reported here.

Papers looked at atomic H energy, nuclear ways to produce H from water, the H economy, and the Kyoto agreement effects on Russia. Safe ways to process H from the H₂S trapped in the Black Sea were described by V. G. Kashiya (Sukhumi Physical-Technical Institute, Tbilisi, Georgia). More traditional H production using electrolyzers in fuelling stations for various projects in Europe (ECTOS, CUTE and CEP) was examined by A. Cloumann and K. Sollid (Norsk Hydro Electrolyzers, Norway). Modules to extract pure H from industrial gas mixtures, using palladium (Pd) alloy (Pd-In-Ru, Pd-Cu and Pd-Y) thin foil membranes, diameter 50–150 mm, were evaluated by D. I. Slovetsky, E. M. Chistov and N. R. Roshan (A. V. Topchiev Institute, Moscow).

Micro- and nano-patterning of silicon (Si) wafer substrates by sputtering Pd and platinum (Pt) for H separation membranes in reformers for fuel cells were discussed by H. Presting and colleagues from Daimler-Chrysler, Germany, and the Institute of Microelectronics Technology, Chernogolovka, Russia.

Work on H in metals and alloys began with a survey of H diffusion coefficients in Pt, Pd and their alloys, presented by J. Čermák (Institute of Physics, Prague) and F. A. Lewis (Queen's University, Belfast). Problems with residual stress in hollow cylinders related to diffusion problems were described by N. M. Vlasov and I. I. Fedik ("Louch" Research Institute, Russia), while the role of segregation at dislocations and grain boundaries in Pd and some other metals was discussed by Yu. S. Nechaev and G. V. Filippov (Bardin Central Research Institute of Ferrous Metallurgy, Moscow).

Stable and unstable equilibria in metal-H systems, such as rhodium-H, were examined by V. E. Antonov, I. O. Bashkin and E. G. Ponyatovsky (Institute of Solid-

State Physics, Chernogolovka) who looked at the phase equilibria at high pressures.

The influence of H and vacancies on the evolution of structure in thermodynamically open Pd-based alloys was discussed by A. A. Katsnelson, V. M. Avdyukhina, A. A. Anishchenko and G. P. Revkevich (Moscow State University). B. A. Spiridonov and V. N. Ermilin (Voronezh State Technical University, Russia) described chemical deposition of a catalytic Pd layer for a H sensor. Generation of a colloidal layer of Pd was involved.

Mechanical instability in concentrated non-homogeneous M-H media, M = Pd, Nb, V, was examined by L. V. Spivak and N. E. Skryabina (Perm State University, Russia). Equilibrium deuterium pressure over Pd and its alloys was described by S. V. Dyomina, M. V. Glagolev and A. I. Vedenev (Russian Federal Nuclear Centre, Sarov). An analysis of stationary isotherms of H permeability in Pd alloy membranes was described by L. L. Murav'yov, A. B. Vandyshev and M. Sh. Gadel'shin (Institute of Engineering Science, Ekaterinburg, Russia).

A. L. Gusev (Russian Federal Nuclear Centre, Sarov) described research underway on low-temperature H detectors and absorbers, including one based on palladised manganese (Mn) dioxide with a protective antioxidant membrane of thin-walled quartz shells. He further described work with Voronezh State University into the effect of H on the electrical properties of metal oxide films alloyed with Si. Lastly, work with the Institute of Problems of Chemical Physics, Chernogolovka, on the production of palladised films of Mn and Co oxides, which can serve as the basis of H sensors, was mentioned.

Abstracts of the proceedings have been published in English and Russian as an *International Scientific Journal for Alternative Energy and Ecology* (ISJAEE) Special Issue, ISSN 1608-8298, <http://isjaee.hydrogen.ru/>, available from the Scientific Technical Centre "TATA", PO Box 787, Sarov, Nizhni Novgorod Region, 607183 Russia; Fax: +7 (83130) 63107; E-mail: gusev@hydrogen.ru.

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Fred Lewis is retired from Queen's University, Belfast, after many years of research into hydrogen diffusion in palladium and palladium alloys. These are still his main interests.