

# Pt RECOVERY: CATALYST MANUFACTURING INDUSTRY

## REFINING OF PLATINUM CATALYST WASTE

Platinum catalysts are commonly used in the silicone industry for the hydrosilation of alkenes, where Si-H is added across a carbon-carbon double bond. Typically, low levels of highly active Pt(0) catalysts are used, and these can be prepared by the reduction of chloroplatinic acid in the presence of a suitable ligand.

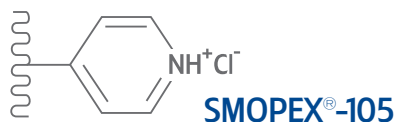


HYDROSILATION REACTION SCHEME

Johnson Matthey manufactures platinum catalysts at their plant in Royston, UK. Some catalyst preparations yield the catalyst as a solution and the waste as a solid. The solid waste can contain as much as 0.5w/w% Pt and a large amount of sodium chloride – amongst other components – hence its name 'salt-cake'. The high value of the residual platinum means it is of benefit to refine the salt-cake. However, the high salt content makes this a difficult material to process using traditional pyrometallurgical refining techniques.

### SMOPEX® FOR Pt REMOVAL

Smopex® offers an easy route for the removal of Pt from salt-cake waste, capturing the Pt in a suitable form for further pyrometallurgical or AquaCat® processing available at Johnson Matthey's Brimsdown plant. The salt-cake is dissolved in water and acid to give a solution containing >1500ppm Pt. This can then be pumped through a column containing Smopex. Tests carried out at Johnson Matthey showed that, using Smopex-105 in a column, >94% Pt removal can be achieved from solution. The solution was heated to 80°C to aid Pt removal, but the process is also effective at room temperature.

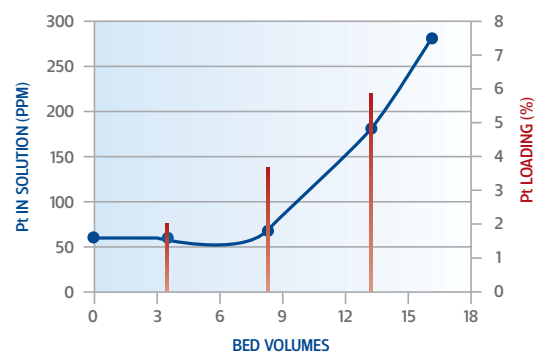


### METAL LOADING IS IMPORTANT

In order to keep costs to an acceptable level, the precious metal loading of the material to be refined should be as high as possible. In the case of salt-cake, the initial Pt content was 0.5w/w%, but after treatment with Smopex, the Pt had been concentrated 32 fold to give a loading of >16w/w% Pt!

### IN THE LAB

500ml solution (1500ppm Pt) was heated to 80°C and passed through a column containing S-105 at a flow-rate of 8ml/min (0.26BV/min).



The graph shows the breakthrough of Pt (blue line), and the % loading of Pt on S-105 (red bars), with bed volume of liquor through the column.

### SCALE-UP

This process for Pt removal has been scaled up to enable treatment of tonnes of salt-cake waste in a batch process, using a polishing Smopex® cartridge to remove the final traces of Pt from solution.

# Rh RECOVERY: OXO-PROCESS

## REFINING OF RHODIUM OXO WASTE LIQUOR

In the rhodium-catalysed L.P. (low-pressure) Oxo process, carbon monoxide (CO) and hydrogen (H<sub>2</sub>) are added across a carbon-carbon double bond to give predominantly straight chain aldehydes. The aldehyde may then be processed further by reduction to an alcohol (e.g. n-butanol or 2-ethylhexanol).

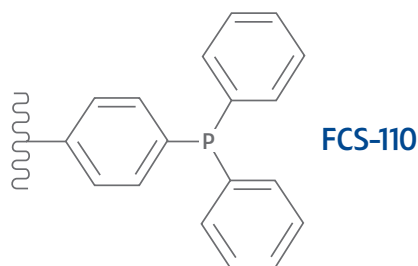


HYDROFORMYLATION REACTION SCHEME

Johnson Matthey supplies a range of rhodium catalysts and precursors for use in the L.P. Oxo process. After separation of the product, the Rh-containing process mother liquor is often concentrated by distillation prior to recovery of the Rh. However, one major problem is that the concentration and shipping of organic waste liquor is costly and time consuming. Furthermore, the refining of small concentrations of Rh from large volumes of liquor is a challenge using traditional processing routes.

### SMOPEX® CAN HELP REDUCE COSTS

Smopex® offers a route for the removal of Rh from Oxo waste liquors. The liquors can be treated at a customer's site and the Rh-loaded fibres are then easily shipped for pyrometallurgical or AquaCat® processing available at Johnson Matthey's Brimsdown plant. Tests carried out at Johnson Matthey showed that, using Smopex® FCS-110 in a column, >94% Rh removal was achieved from solution at 80°C. Furthermore, the Rh content can be concentrated 300 fold from 0.01% (in the organic waste) to 3% (on the fibres), therefore producing a residue that is more economic to refine.



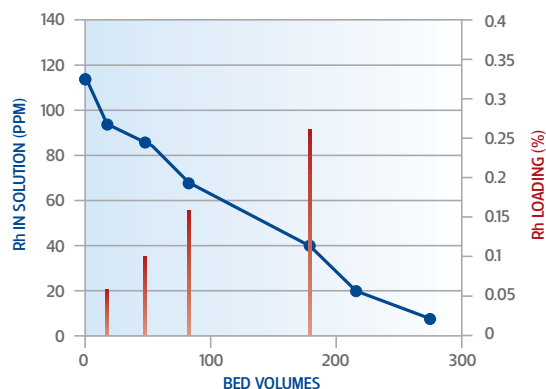
### LONG RESIDENCE TIME?

Precious metal scavenging with Smopex® often has fast kinetics, due to the accessibility of functional groups at the exterior of the fibre. However, the nature of the liquor (solvent, pH, ppm

speciation, and presence of competing ligands or ions) can sometimes dictate that Smopex® scavenging requires an increased contact time for the reaction to go to completion. One easy way to achieve complete metal removal under these conditions is to cycle the mother liquor in a closed loop – between a holding vessel and a column of Smopex®.

### IN THE LAB

500 ml solution (>100ppm Rh) was heated to 80°C and passed through a column containing FCS-110 at a flow-rate of 10ml/min (0.22BV/min), giving a 4.5 minute residence time. The liquor was cycled through the column for 20h to achieve 94% Rh removal.



The graph shows the decreasing Rh concentration, and increasing % loading of Rh, as the liquor is cycled through the column.

### SCALE-UP

This process runs commercially for the treatment of large quantities of Rh bearing liquor in a continuous recycle through a column (pumping rate of 350l/h and residence time of 22 minutes). Rh levels of <5ppm are regularly achieved.

# Pd RECOVERY: PHARMACEUTICAL AND FINE CHEMICAL INDUSTRY

## PALLADIUM REMOVAL FROM PROCESS MOTHER LIQUOR

Palladium-phosphine catalysts are widely used in the pharmaceutical and fine chemical industries for carbon-carbon bond forming reactions, also known as cross-coupling reactions. These include Heck, Stille, Suzuki, and Sonogashira. Highly active Pd catalysts are also used in the Buchwald-Hartwig reaction, which is a carbon-heteroatom coupling.

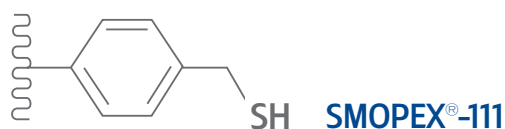


### BUCHWALD-HARTWIG CARBON-HETROATOM CROSS-COUPLING

Johnson Matthey supplies a range of catalysts and precursors for cross-coupling reactions. Whilst the activity of the Pd catalysts is of major importance, a further critical step is the removal of Pd to low levels (typically <5ppm) to ensure that the product is free from metal contamination. A number of techniques can be used for separating contaminants from product streams, such as: precipitation, crystallisation, solvent extraction or adsorption. While these are commonly used in the chemical industry, they can contribute to high losses of valuable product and wasteful use of reagents.

#### SMOPEX® FOR PRODUCT PURIFICATION

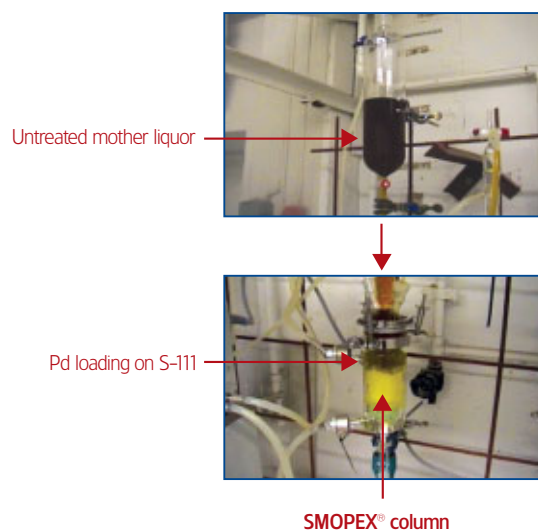
Smopex® offers a simple, neat route for the removal of Pd from product process streams. In this case study, a Pd precursor and a large excess of triphenylphosphine were combined in-situ and used as a catalyst. After reaction 30ppm Pd was left in the THF mother liquor. At lab scale, Smopex®-111 removed >99% Pd from solution at 55°C and, more importantly, the Pd concentration was reduced to <1 ppm.



The loading of Pd on fibre was 2w/w%, this is sufficient for pyrometallurgical or AquaCat® processing available at Johnson Matthey's Brimsdown plant. Repeating the same experiment in a column would generally result in higher loadings being seen.

#### IN THE LAB

The solution (30ppm Pd) was heated to 55°C and passed through a column containing S-111 at a flow-rate of 10ml/min (0.07BV/min), residence time of 14 minutes. More than 99% of Pd was scavenged from solution.



#### SCALE-UP

This process has been scaled up and the fibres used in multi-tonnage quantities on the plant. Results to date indicate a Pd loading of 6w/w% on the Smopex® fibre.