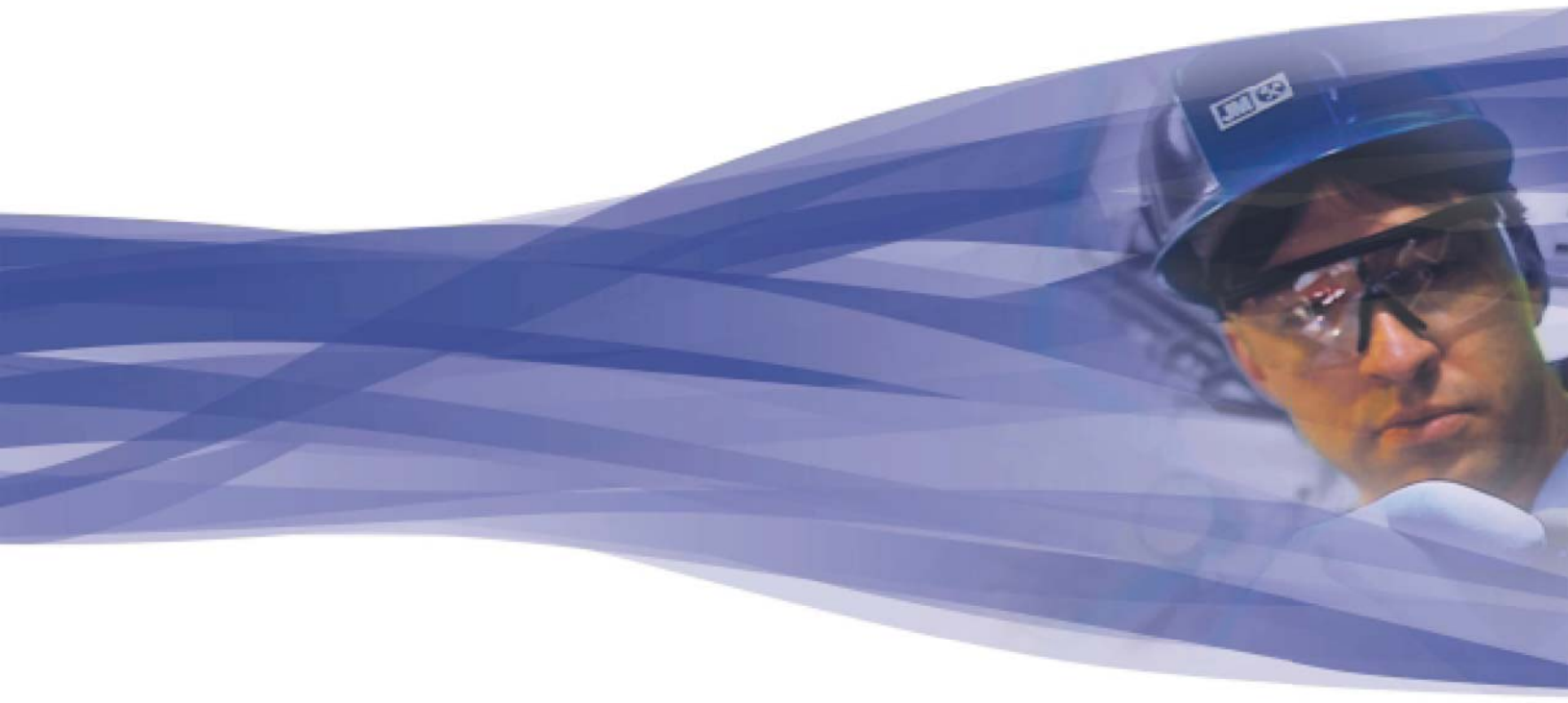
Smopex®

precious metal scavengers

Complete engineered recovery



Johnson Matthey
Catalysts

SMOPEX®

The recovery of precious metals from process solutions is essential for improving process economics, enabling product purification and for the treatment of materials for effluent discharge.

SMOPEX® is a unique metal scavenging system where metal-binding functionality has been grafted onto fibres, allowing the effective recovery of a range of precious metals (PM). The current range comprises of 11 core products, with numerous additional products in development.

- Be sure of precious metal recoveries from effluent
- of heavy metal removal from effluent
- of minimising hazardous waste volumes for shipment
- overall positive environmental benefits

- SMOPEX® selectively removes ionic and non-ionic precious metal complexes from both aqueous and organic solutions
- SMOPEX® can be used as a filter aid to remove colloidal precious metal particles from process liquors
- SMOPEX® can remove metal from both homogeneously and heterogeneously catalysed reactions
- SMOPEX® allows recovery from liquors containing low levels of precious metal even down to parts per billion (ppb) levels
- The SMOPEX® system offers benefits, including fast reaction kinetics and high precious metal loading on the fibre

SMOPEX® screening

In order to determine fibre affinity and to obtain an indication of the metal recoveries achievable, SMOPEX® is initially tested on solutions at lab-scale using a batch or column type set-up. The process solution can be screened with the SMOPEX® range at Johnson Matthey, or by the customer – Johnson Matthey will supply a SMOPEX® kit and technical advice.

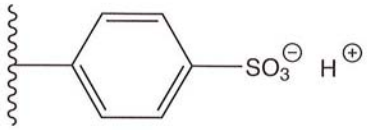
Johnson Matthey can provide the SMOPEX® fibres, in the form that is most suitable for the customer. This can either be for use in stirred batch reactors, or the fibres can be pre-packed in a cartridge or column, also supplied by Johnson Matthey, to offer **a complete engineered recovery of metals.**

SMOPEX® cartridge

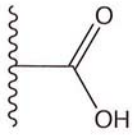
SMOPEX® fibres

Smopex Product Range

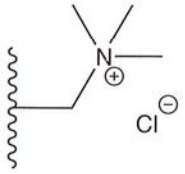
Smopex-101



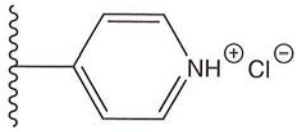
Smopex-102



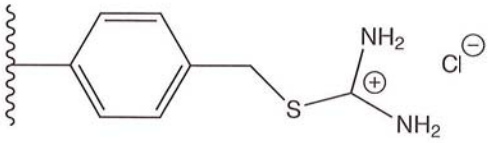
Smopex-103



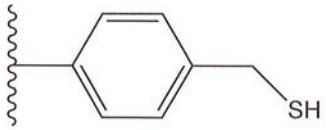
Smopex-105



Smopex-110



Smopex-111



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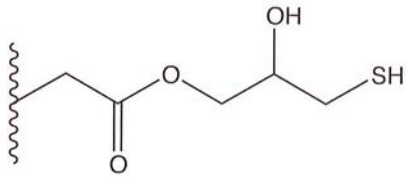
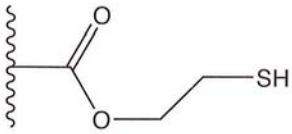


Smopex-234



To find out how Johnson Matthey's knowledge and experience can improve your precious metal recovery visit:

www.smopex.com

Johnson Matthey
Catalysts

SMOPEX® column skid

SMOPEX® for pilot and production scale

Handling

- SMOPEX® fibres are easy to handle and filter.
- The flexibility of the fibres means that they do not break up in stirred reactors – even when high shear agitation is required.
- SMOPEX® can be coated onto a candle filter so that it forms a pre-coat. The PM-containing liquor is then circulated through the pre-coat, enabling easy PM recovery and subsequent separation of the fibres from the liquor.

Cartridges for pilot and production scale

- Cartridges are available in a range of sizes and are manufactured using a selection of materials so that they are suitable for installation in most plants.
- Cartridges can be purchased as individual units, pre-packed with SMOPEX®. They are supplied with a pre-filter attached to remove particulates that may potentially block the SMOPEX® cartridge.
- Where a number of cartridges are required, they can be supplied in multi-cartridge housing – ready to link into the plant.
- After use, the cartridges can simply be returned to Johnson Matthey for refining of the precious metal.

Economics

- Metal loading has a significant impact on the value of the metal recovered per kg SMOPEX®. SMOPEX® metal loadings are usually in excess of 5% due to an excellent accessibility of the metal-binding functional groups, whereas bead type resins typically give lower loadings.
- Johnson Matthey will offer technical advice to help you to optimise your metal loading.

Columns for pilot and production scale

- Column skid units, containing inserts pre-packed with SMOPEX®, are available that can simply be "plugged" into the customers plant.
- Standard units can be leased for plant trials. With knowledge obtained from the plant trial, Johnson Matthey can then offer column skid units manufactured to customers specifications to buy or to lease. These can be built using a selection of materials to offer units that are resistant to most solvents and operating parameters.
- Each unit is complete with automation, temperature control, and safety devices – ensuring safe and controlled operation.
- After use, the SMOPEX®-containing inserts are returned to Johnson Matthey for refining and the metal is returned to the customer, based on the agreed refining terms.
- Johnson Matthey can offer ongoing technical support whilst the unit is in operation.

SMOPEX® cartridge and housing

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For further information about our products or to talk to us about your individual requirements, please contact your local sales office or contact us at the above addresses

To find out how the knowledge and experience of Johnson Matthey Catalysts can improve your precious metal recovery visit:

www.jmcatalysts.com

Smopex® Pharma Grade Metal Scavengers

Johnson Matthey has developed the Smopex® fibre family based on their unique grafting technology for use as metal scavengers from aqueous and organic media. The fibres are mechanically and chemically very stable, provide a high loading capacity and exhibit compatibility with most solvents used in the chemical industry. Due to their unique structure - thin fibres with externally grafted functional side chains - scavenging kinetics are often very rapid, particularly in comparison with conventional bead technology, where diffusion limits the rate of removal. The fibres are also well suited for use in organic media, where bead resins are frequently ineffective.

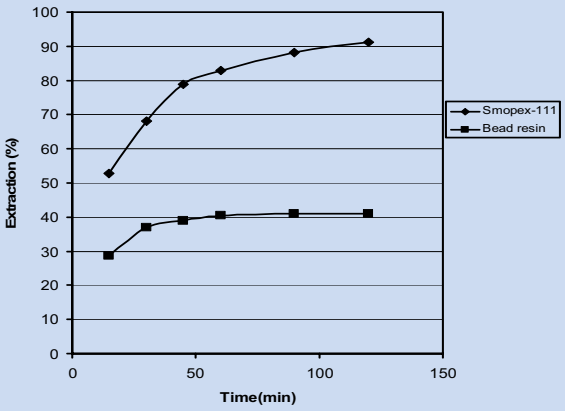
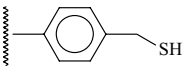
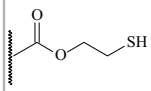
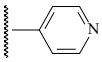


Figure1. Recovery of a homogeneous Pd catalyst in the presence of excess triphenylphosphine and excess dibutylamine using Smopex®-111 and a bead resin containing the same functional group. Reaction solvent is THF

Pharma grade Smopex® fibres used as metal scavengers:

Product code:	**126111**	**126234**	**126102**	**126105**
Product name:	**Smopex®-111**	**Smopex®-234**	**Smopex®-102**	**Smopex®-105**
Description:	Styryl thiol grafted polyolefin fibre	Mercaptoethyl acrylate grafted polyolefin fibre	Acrylic acid grafted polyolefin fibre	Vinyl pyridine grafted polyolefin fibre
Structure:				
Colour and form:	White to beige or yellow fibres	Off white to yellow fibres	Off white fibres	Off white to yellow fibres
Fibre length:	0.3 mm	0.3 mm	0.3 mm	0.3 mm
Fibre tap density:	345 g ± 10 g / dm^3	580 g ± 10 g / dm^3	498 g ± 10 g / dm^3	434 g ± 10 g / dm^3
Functional group capacity:	> 2 mmol / g	> 3 mmol /g	> 6 mmol / g	> 3 mmol / g
Dry content:	> 95 %	> 95 %	> 95 %	> 95 %
Odour:	Mild sulphur smell	Mild sulphur smell	Odourless	Odourless
Stability:	Air stable	Air stable	Air stable	Air stable
Chemical stability:	Stable under normal laboratory conditions	Avoid alkaline conditions	Stable under normal laboratory conditions	Stable under normal laboratory conditions
Max. operating temperature:	120 ° C	120 ° C	120 ° C	120 ° C
Suitable reaction conditions:				
-Aqueous	No	No	Yes	Yes
-Organic	Yes	Yes	Yes	Yes
-Slurry	Yes	Yes	Yes	Yes
-Fixed bed	Yes	Yes	Yes	Yes
Typical applications:	Scavenging of Pd, Pt, Rh, Cu from: - Cross coupling reactions - Hydroformylations - Hydrogenations	Scavenging of Pd, Pt, Rh, Cu from: - Cross coupling reactions - Hydroformylations - Hydrogenations	- Cation scavenger, Ni, Fe, Cr - Colloids with +ve surface charge. - Fines from heterogeneous C catalysts.	- Anionic PGM complexes .- Colloids with –ve surface charge. - PGMs leached from supported catalyst.

Continued..

Smopex®
precious metal scavengers

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www.jmcatalysts.com

Scavenging from Catalyst Solutions

Effective removal of metals from catalyst solutions depends critically on the nature of the metal complex and the type and excess of ligands present. The scavenging fibres must have a stronger affinity for the metal than any other ligands in solution.

Modelling a scavenging appliction using simple metal complexes such as Pd acetate can often be misleading, in view of the changes to metal catalysts that will take place during the reaction. It is always worth testing 'real life' solutions to confirm the best conditions for metal recovery.

Figure 1 is based on data from a real solution resulting from a Pd catalysed coupling reaction. Metal recovery is effective even in the presence of excess phosphine ligands and amine base (both of which compete with the scavenger).

Table 1 shows some more examples on how the nature of the catalyst complexes affect the choice of the correct Smopex® fibre. The pyridine based Smopex®-105 is very effective for complexes containing weak ligands whereas the thiol based Smopex®-111 is needed for catalyst complexes containing stronger ligands.

Metal complex	*Recovery - % with*	
	Smopex®-111	*Smopex®-105*
$t\text{-}PdCl_2(PPh_3)_2$	100	1
$t\text{-}PdCl_2(CH_3CN)_2$	100	99
$Pd(PPh_3)_2$	96	56
$RhCl(CO)(PPh_3)_2$	95	32

Table 1. Recovery of some homogeneous catalyst complexes using Smopex®-105 or Smopex®-111 from a 100 ppm solution at 60 C.

Guidelines for use:

Batch test for fibre affinity with the metal complex:
Use 0.5 g fibre per 50ml of solution (this should give a metal loading of approx. 1 wt-% for 100 ppm of metal in solution). Stir for 2 hours at 60°C. Good indication of metal uptake is a colour change in the solution. Once the optimum fibre is selected, a loading of 2-10 wt-% would be expected from organic solutions and up to 25 wt-% from aqueous solutions. The quantity of fibre should be decreased according to this.

Laboratory scale column set-up: Slurry 0.25 mm fibres in a suitable solvent and allow to swell for 15 minutes. To pack the column, cover the bottom plate with glass wool and filter the slurry whilst maintaining a head of solvent. The bed should be packed to a dry density of about 250 g/l. We recommend the use of a chromatography column equipped with a flow adapter, which can be used to gently compress the bed further. Allow solvent to flow through the column and discharge the first 2-4 bed volumes to wash out any extractives before elution of the metal-containing sample. Normal flow rates should be in the range of 0.1-2 bed volumes per minute depending on the sample. If needed, the liquor can be cycled through the bed in a closed loop to enhance the recovery. After the run, wash the bed with the reaction solvent.

Johnson Matthey has developed Smopex®-fibres for a wide variety of markets and applications. Johnson Matthey is ready to help you evaluate Smopex®-fibres for your application. We offer samples and technical support.

Smopex®-111 fibres are listed in the US-FDA under DMF No.: 18099
Smopex®-102 fibres are listed in the US-FDA under DMF No.: 18441
For Smopex®-105 and Smopex®-234 filing has been submitted.

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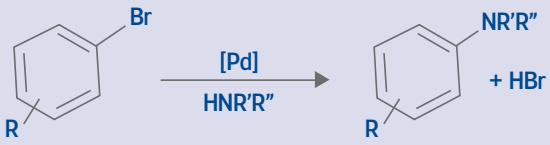
Pd RECOVERY: PHARMACEUTICAL AND FINE CHEMICAL INDUSTRY

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.

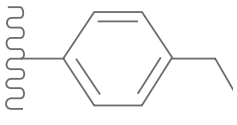


BUCHWALD-HARTWIG CARBON-HETROATOM CROSS-COUPLING

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.

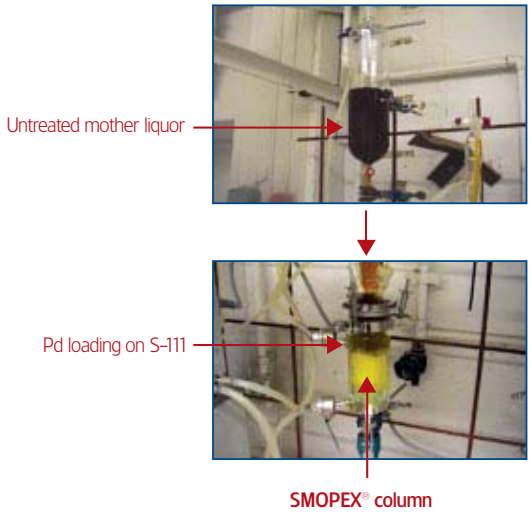


SMOPEX®-111

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.

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Pt RECOVERY: CATALYST MANUFACTURING INDUSTRY

REFINING OF PLATINUM CATALYST WASTE

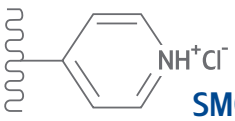
Platinum catalysts are commonly used in the silicone industry for the hydrosilation of alkenes, where Si-H is added across a carbon-carbon double bond. Typically, low levels of highly active Pt(0) catalysts are used, and these can be prepared by the reduction of chloroplatinic acid in the presence of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



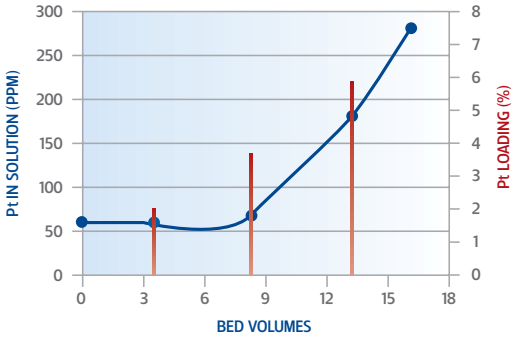
SMOPEX®-105

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.

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Rh RECOVERY: OXO-PROCESS

REFINING OF RHODIUM OXO WASTE LIQUOR

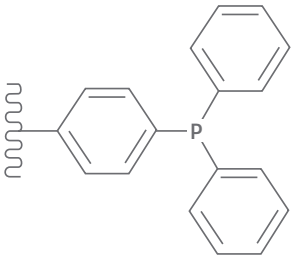
In the rhodium-catalysed L.P. (low-pressure) Oxo process, carbon monoxide (CO) and hydrogen (H_2) are added across a carbon-carbon double bond to give predominantly straight chain aldehydes. The aldehyde may then be processed further by reduction to an alcohol (e.g. n-butanol or 2-ethylhexanol).

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.



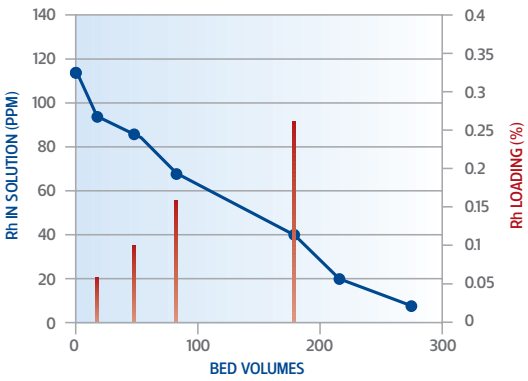
FCS-110

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, pgm 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.

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