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MERCURY REMOVAL FROM GAS STREAMS USING NEW SOLID ADSORBENTS

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ABSTRACT

A new process has been developed as a joint collaboration between PETRONAS Research and QUILL, and covers the removal of mercury from natural gas feeds. The process utilises ionic liquids to provide a novel active site for mercury capture. The approach incorporates two key aspects: (i) custom design of ionic liquids with a dual functionality to both oxidise and capture mercury, and (ii) impregnation of the ionic liquids on an inert porous support as solid-supported ionic liquids, SSILs. This allows them to be used directly in existing MRU plants without requiring any changes to process operation, or additional costs associated with plant modification. The efficiency of the SSIL has been explored in direct comparison with commercial sulfur-impregnated activated carbons and, in laboratory trials, increases in bed life-time of up to five-fold have been observed.

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1 MERCURY IN THE PETROLEUM SECTOR

1.1 Mercury compounds and speciation in oil and gas streams

Most naturally-occurring hydrocarbons contain low levels of mercury.[1] Depending on the geological locations, mercury normally exists in natural gas in small quantities as either elemental mercury or mixtures of volatile elemental and organomercury compounds with typical concentrations in the range 0.1-200 $\mu g\ m^{-3}$. However, levels as high as 4400 $\mu g\ m^{-3}$ have been reported. Mercury is harmful to human health and the environment, destructive of process equipment through corrosion, liquid metal embrittlement of aluminium heat exchangers, and also acts as a catalyst poison. Even though the concentrations of mercury can be very low, accumulation within process units *via* condensation, chemical reactions and amalgamation can occur.

1.2 Mercury removal technologies

Mercury removal from natural gas streams is becoming more challenging because of the need to reduce elemental, ionic and organomercury species to very low levels. A number of technologies are commercially available to reduce mercury contents in hydrocarbon feedstocks and products to meet the specifications for downstream processing.[2] The most common of these for treating petroleum gas and liquid feeds use packed beds of activated carbon impregnated with a catalyst, *e.g.* sulfur (for gasses) or iodide (for liquids). Alternative processes include metal sulfides on alumina, and molecular sieves incorporating silver. However, not all systems are capable of treating the full range of mercury species in a single treatment.

The reactions by which mercury is removed are usually rapid, and high levels of mercury are absorbed into the packed bed. However, there are drawbacks:

- Elemental sulfur is soluble in hydrocarbons, particularly in aromatics, which restricts the use of sulfur-impregnated carbons to gas scrubbing.

- Potassium iodide impregnated carbons are sensitive to the presence of moisture, requiring careful plant control and placement of drying units before the mercury removal unit (MRU).

More recent developments have looked at inorganic routes for the removal of mercury from gaseous and liquid hydrocarbons based on the reactivity of mercury with some mixed-valence metal sulfides to form mercury(II) sulfide. These inorganic materials are more expensive than traditional activated carbons, but have a number of advantages including:

- The spent mercury absorbent can be recycled through metal smelters.

- There is little risk of sulfur migration by sublimation or dissolution.

2 IONIC LIQUIDS IN THE PETROLEUM AND PETROCHEMICAL INDUSTRIES

Ionic liquids[3] are liquids composed solely of ions (see Figure 1), in contrast to conventional solvents comprised of covalent molecules, and these, combined with their resultant electrical conductivity,[4] are the defining characteristics of ionic liquids. Their other general properties, such as little or no measurable vapour pressure, have provided the impetus for the investigation of ionic liquids as solvents and catalysts for green chemistry. Most ionic liquids possess a majority of the following properties:

- *Wide liquid ranges (typically over 300 °C)*
- *High thermal stability*
- *Non-volatility at room temperature*
- *Non-flammability of the bulk liquid*
- *Controllable co-miscibility with a range of fluids and gasses (including, by design, immiscibility*

with unsaturated hydrocarbons)
- *Modifiable solubility and extraction capabilities*

There is enormous interest in using ionic liquids to engineer new processes within the petroleum and petrochemical sectors,[5] dating back to the reported use of molten tetraalkylphosphonium and ammonium salts as reaction solvents/catalysts for hydroformylation reactions in 1972.[6] More recent developments have been reviewed by Plechkova and Seddon.[7]

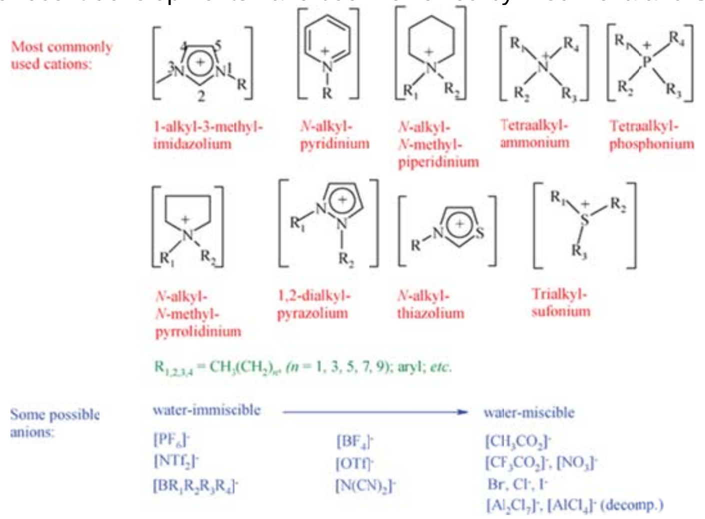

Figure 1: Principle classes of cations (top) and anions (below) that are used to formulate ionic liquids (from Ref. 8)

3 IONIC LIQUIDS FOR MERCURY REMOVAL

The objective of our research program was to determine whether custom-designed ionic liquids can be used as the basis of a new mercury removal and control approach for natural gas streams. Optimal ionic liquids were identified through a screening program and suitable candidates rapidly developed to pilot-scale.

A multistage approach was used to fast-track the program. Firstly, batch contact screening of mercury extraction by ionic liquids from model hydrocarbons was evaluated. Having then selected the most promising ionic liquids, from a set selected with predesigned functionality, a testing régime comprising of four stages was undertaken, as shown below:

First stage:	Rapid breakthrough screening studies with gas streams
Second stage:	Performance validation tests
Third stage:	Laboratory optimisation and scale-up studies
Fourth stage:	Pilot plant trials

3.1 Batch screening from hydrocarbons

Partitioning studies have shown that solvated mercury ions (“Hg^{2+}”) preferentially extract from water to hydrophobic ionic liquids,[9] in contrast to the normal partitioning of most hydrophilic metal ions *to the aqueous phase*. This extraction behaviour can be controlled by incorporating complexing groups (functionality) into the ionic liquid.[10] The high affinity of ionic liquids for aqueous mercury(II) has been used for analytical procedures,[11] and as the basis for optical mercury ion sensors.[12]

Ionic liquids coated onto mesoporous silica have been reported to capture mercury vapour from gas streams at 160 °C.[13-15] In the presence of oxidising agents (for example potassium manganate(VII)[13]) and complexing agents (dicarboxylic acids[14]), oxidation of mercury proceeds efficiently.

Initial distribution studies of elemental mercury in ionic liquid/hydrocarbon mixtures showed a remarkable intrinsic ability of ionic liquids to partition mercury from the liquid hydrocarbons.[16] Mercury extraction was examined using liquid/liquid batch contact tests between liquid hydrocarbons (either a natural gas condensate with mercury concentrations of 250 ppb, or dodecane containing elemental mercury at concentrations of 1000-4000 ppb) and an array of ionic liquids. The mercury concentration in both the ionic liquid and hydrocarbon phases was measured after mixing and separation by direct mercury analysis with a Milestone DMA-80 mercury analyser. Efficient extraction of mercury from dodecane and natural gas condensate was observed with almost all the ionic liquids examined, typically with extraction coefficients greater than 1000, and with the mercury content in the organic phase reduced to <10 ppb (LOC in detection) in a single contact (see Figure 2 for typical results). These results are consistent with the observations of Ji *et al.*[13] at elevated temperatures.

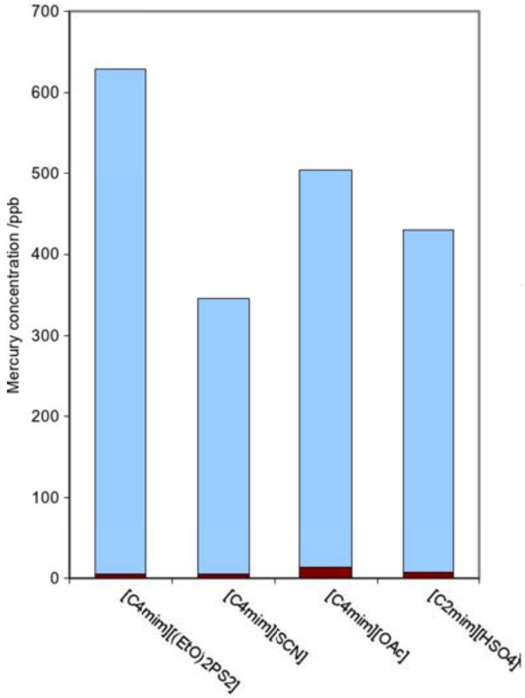

Figure 2: Total mercury concentrations measured in the two phases (open bars, ionic liquid; filled bars, natural gas condensate), after liquid/ionic liquid contacting, of a natural gas condensate sample (mercury concentration = 250 ppb) with four representative ionic liquids ($[C_4mim][(EtO)_2PS_2)]$, 1-butyl-3-methylimidazolium diethoxydithiophosphinate; $[C_4mim][SCN]$, 1-butyl-3-methylimidazolium thiocyanate; $[C_4mim][OAc]$, 1-butyl-3-methylimidazolium ethanoate; $[C_2mim][HSO_4]$, 1-ethyl-3-methylimidazolium hydrogensulfate). Excellent partitioning of mercury from the hydrocarbon phase to the ionic liquid extractant is demonstrated in each case.

However, the limiting feature was found to be the relatively poor solubility of elemental mercury in the ionic liquids. Even in the best cases, such as with commercially available, 1-butyl-3-methylimidazolium thiocyanate ($[C_4mim][SCN]$), the maximum mercury solubility was determined to be <1 wt% in the ionic liquids. This is too low for practical *in situ* scrubbing.

3.2 Reactive extraction using ionic liquids containing oxidising anions

The solubilities of mercury(II) ions and compounds in ionic liquids are much higher than that of elemental mercury. Ionic mercury species are readily extracted from hydrocarbons to ionic liquids. The extraction processes of Ji *et al.,*[13] using an oxidising agent to perform a reactive extraction of elemental mercury as mercury(II), offered an alternative approach to conventional mercury capture processes with sulfur or sulfide-impregnated supports.

Based on these observations, it was anticipated that an ionic liquid designed to incorporate an oxidising function would lead, on reaction with elemental mercury, to the formation anionic mercurate(II) species. ^{199}Hg NMR spectroscopy[16] can be used to examine the formation of mercurate(II) anions in ionic liquids after reaction with elemental mercury. Figure 3 shows the ^{199}Hg NMR spectra of two ionic liquids, used for gas scrubbing (as described below), after contacting with elemental mercury. In both cases, a single mercury signal is observed (other than the external standard) and corresponds to the chemical shifts obtained for the respective anionic species, demonstrating that (i) mercury is dissolved in the ionic liquids and (ii) it is in a unique complexed Hg(II) form.

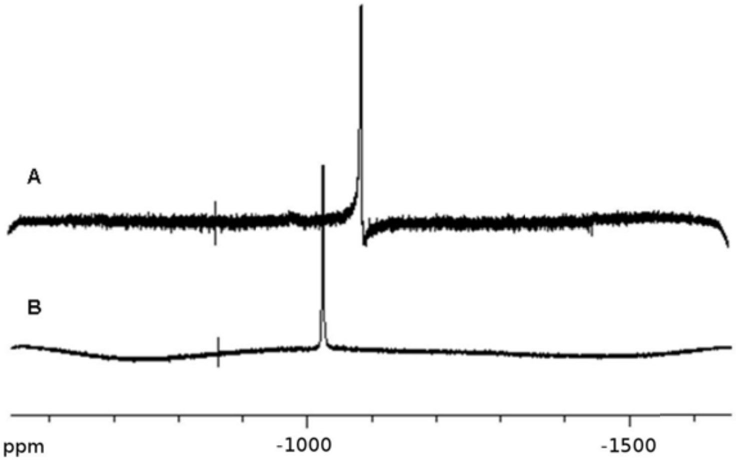

Figure 3: ^{199}Hg NMR spectra of two ionic liquids, A and B, after contacting with elemental mercury, showing distinctive ^{199}Hg NMR signals with chemical shifts corresponding to those from pure ionic liquids.

4 SCRUBBING ELEMENTAL MERCURY FROM GAS STREAMS WITH SSILS

4.1 Heterogenisation as solid supported ionic liquids (SSILs)

The process of immobilising ionic liquids on solid supports is well established.[18] Simple physisorption was selected to immobilise essentially non-volatile ionic liquids on porous silica (see Figure 4), alumina and activated carbon supports. The ionic liquids were loaded using wet impregnation and showed no leaching in contact with hydrocarbons.

4.2 Bench-scale testing of SSILs for mercury removal

We used a laboratory-scale test rig to evaluate the mercury adsorption capacity and extraction efficiency of the materials. Key features of the test rig are shown in Figure 5. Tests were run in parallel, comparing SSIL performance directly against commercial materials.

In the first generation (**SSIL-1**), an ionic liquid capable of simultaneously oxidising and capturing elemental mercury has been deployed in an existing MRU pilot-plant with no changes in day-to-day operational parameters.

Figure 4: An example of an SSIL on silica.

Figure 5: A typical screening reactor for SSIL evaluation in PETRONAS.

Data are presented here, and compared against a commercially available sulfur-impregnated adsorbent under the same conditions. Typical mercury outlet concentration profiles over the duration of a screening trial are shown in Figure 6. The tests were performed using high mercury concentrations in the gas stream in order to stress-test the materials in a relatively short time-frame. As can be seen, mercury was scrubbed with high efficiency; the ionic liquid system affords excellent performance with complete mercury capture and continued to scrub mercury for three times longer before breakthrough than the commercial material.

Having established that the concept and experimental approach was successful, a range of solid supports were examined. Key variables for optimisation that were addressed include:

- Support type and structure (material type, surface area and pore size)
- Ionic liquid composition
- Ionic liquid loading on support

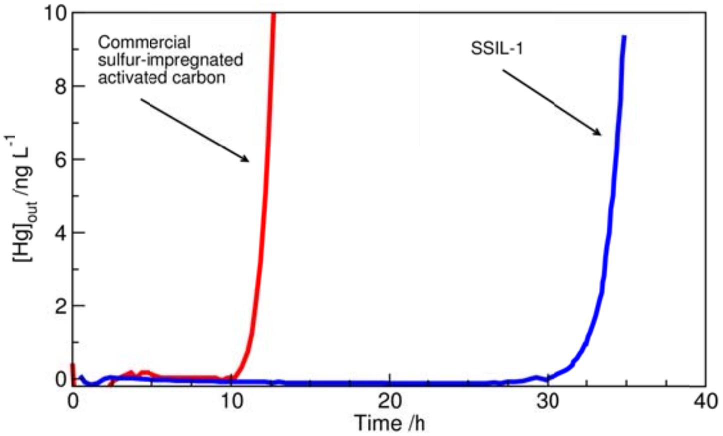

Figure 6: Comparison of mercury capture profiles with commercial carbon based and SSIL materials.

Supports were impregnated with ionic liquid and screened for mercury extraction. The mercury contents, measured after breakthrough, are shown in Figure 7. The SSILs show good capacity for mercury capture. At breakthrough, the mercury captured by the SSILs approaches 70-75% of the theoretical capacity based on the oxidation to mercury(II) and incorporation into the ionic liquid structure.

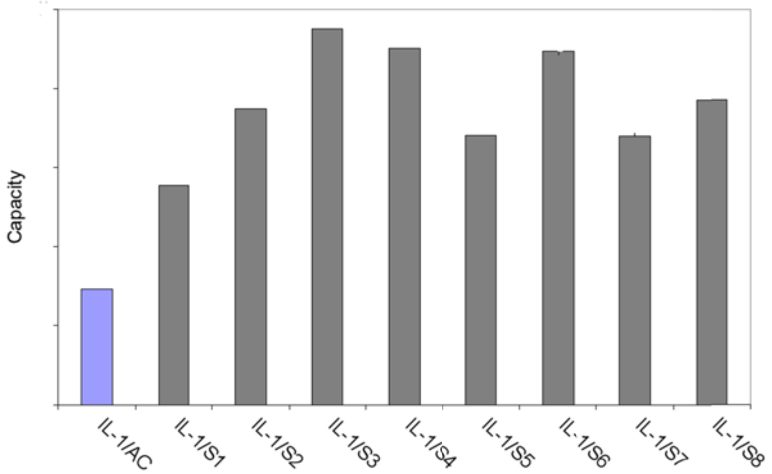

Figure 7: Relative mercury uptakes on a range of SSILs (carbon in blue, silica in grey).

Having defined the optimal support and ionic liquid combination from the initial screening, material was then taken through extensive laboratory optimisation and characterisation, and subsequently progressed to pilot testing.

5 OUTCOMES

Pilot plant studies are in progress. SSILs are effective for mercury extraction from gas feeds, retaining the extractive capability of the parent ionic liquids. SSILs can be used as a direct replacement for the current adsorbents in existing MRUs without process or plant modification. Benefits of our new generation of mercury adsorbents are higher efficiency, service longevity and robustness, and they represent both a significant improvement to the health and safety of the workforce, and added protection for the environment. We believe this will be the first commercial demonstration of ionic liquids in this field.

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List of Figures

List of Abbreviations

1.	PRSB	PETRONAS Research Sdn Bhd
2.	QUB	The Queen’s University of Belfast
3.	QUILL	Queen’s University Ionic Liquid Laboratory
4.	SSIL	Solid Supported Ionic Liquid
5.	MRU	Mercury Removal Unit
6.	IL	Ionic Liquid