Mercury Removal from Bayer Refinery Condensate

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Mark E. Mullett

25/10/2006
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Summary

The alumina refining industry is one of a number of global industries that produce process waters containing mercury. The research program detailed in this dissertation focuses on processes for removing mercury from Bayer digestion condensate streams.

Bayer refinery digestion condensate is chemically unique because it exhibits high pH and is chemically reducing, thermodynamically favouring the presence of elemental mercury. The temperature of condensate is typically 95 °C, with flow rates up to 490 kL/hour. On the basis of these unique conditions, a literature review of mercury removal processes was conducted. Of the many processes reviewed, three broad process options were selected for further examination. These were:

- Adsorption onto activated carbon or other suitable materials
- Sparging mercury into a gas stream
- Complexation or amalgamation onto modified silica substrates using noble metals or sulphur functional groups as impregnates

A variety of activated carbon types were tested using batch, up-flow column or filtration tests. These carbon types included a granular virgin activated carbon (VAC); granular and extrudate sulphur impregnated activated carbon (SIAC); an extruded silver impregnated activated carbon (AgAC) and a combination of two powdered virgin activated carbons (PAC). The adsorption mechanism for both the VAC and the SIACs was physical and as such the mercury capacity of the carbon was determined to be a function of the concentration of mercury in solution. The sulphur impregnated into the SIAC did not increase the mercury capacity because of sulphur dissolution into the condensate. The removal efficiency and mercury loading demonstrated by these carbon types was poor and did not justify further investigation.
This was primarily because the adsorption and chemisorption processes were interfered with by the digestion condensate matrix.

The PACs were tested in batch mode and were also incorporated into a filter bed, through which condensate was passed. The PACs demonstrated a superior mercury loading and a higher removal efficiency compared to the VAC and SIACs. The volume of condensate required to achieve mercury breakthrough was not determined and it is recommended that further tests be conducted to determine this. In addition to the high removal efficiency demonstrated by the PACs, the short residence times of <30 seconds associated with the filtration procedure, justifies further investigation as a mercury removal process option.

The AgAC demonstrated the highest mercury loading of the granular and extruded carbon types. This may be attributed to the chemisorption or amalgamation of elemental mercury and it is recommended that mercury removal via amalgamation be investigated using a high surface area form of suitable metals such as silver and tin.

A sulphur impregnated silicate material was also tested using batch and up-flow column tests. As was the case for the SIACs, the impregnated silicate material suffered from sulphur dissolution in the condensate. This material is therefore not recommended for further investigation.

Each of the impregnated mesoporous silica based materials, except for the gold impregnated silica, demonstrated poor stability in condensate and should not be considered for further assessment or implementation. Although the gold impregnated silica was stable, and demonstrated effective mercury removal, it would be too expensive to justify for use on an industrial scale unless a process for regenerating the gold was developed. It did, however, further demonstrate the opportunity for tests involving mercury amalgamation.
Gas sparging was the most viable opportunity with ~80% mercury removal demonstrated. The system involves steam sparging to volatilise mercury from the solution phase to a vapour phase, from which the mercury is compressed and re-condensed for collection. It was estimated that the system would cost approximately 4 million dollars to install with annual operating costs of approximately $500 000.
1 INTRODUCTION AND BACKGROUND

The removal of mercury from industrial process waters, groundwater, and other contaminated water bodies has received considerable attention over the last 2-3 decades due to health and environmental risks associated with mercury exposure (Hutchinson and Atwood, 2003; Irukayama, 1966 and WHO, 1976). The US Environmental Protection Agency, for example, has promulgated surface water protection standards significantly below that of drinking water (2 µg/L) (Looney, et al, 2003). The current USEPA standard for discharged water is 10 µg/L (Ku et al, 2002), while the Bulgarian Standard Institute has also set limits of 10 µg/L Hg (II) for discharge into surface waters and a drinking water limit of 1 µg/L (Budinova, et al, 2003). Such stringent standards have particular impact upon industrial operations where discharge into the environment occurs, but also impact on industrial operations that are net consumers of water, where re-use of water streams within the processes is maximised. The stringent environmental standards have led to research into the development of a number of chemical and physical processes to remove mercury from process waters (See Table 1).

The alumina refining industry is one of many world-wide industries including chlor-alkali (Kirk-Othmer, 1981; Patterson, 1985), dental (Vandeven and McGinnis, 2004), municipal waste treatment (Pollution Prevention Resource Exchange, 2005; USEPA, 1997), gold mining (Reese, 1997), lead and copper smelting (Patterson, 198; USEPA, 1997) and weapon’s making facilities (Stewart and Roberts, 1998) that produce waters containing mercury. Alumina refinery condensate streams contain relatively low concentrations of mercury and current technology does not specifically target treatment of mercury at these levels; however due to a combination of increasingly stringent environmental discharge standards and the alumina industry’s desire to minimise its environmental impacts, there has been increased interest in processes capable of removing mercury at low concentrations.
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<tbody>
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</tr>
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</tr>
<tr>
<td>(Anoop Krishnan and Anirudhan, 2002a; Anoop Krishnan and Anirudhan, 2002b; Gomez-Serano et al, 1998; Nucon International, Inc., 1997)</td>
</tr>
<tr>
<td><strong>Waste rubber</strong></td>
</tr>
<tr>
<td>(Griffith, 1975; Gunasekara et al, 2000; Knocke and Hemphill, 1981; Rowley et al, 1984; Tharin, 1974)</td>
</tr>
<tr>
<td><strong>Lignites / coals / biomass</strong></td>
</tr>
<tr>
<td><strong>Silica based materials</strong></td>
</tr>
<tr>
<td>(Bibby and Mercier, 2002; Bonnissel-Gissinger et al, 1999; Delacour et al, 1999; Feng et al, 1997; Fisher et al, 2000; Mahmoud and Gohar, 2000; Mercier and Pinnavai, 1998; Radi, et al, 2000)</td>
</tr>
<tr>
<td><strong>Iron oxide based materials</strong></td>
</tr>
<tr>
<td>(Bonnissel-Gissinger et al, 1999; Manju, et al, 2002)</td>
</tr>
<tr>
<td><strong>Precipitation / Coagulation / Complexation / Chelation agents</strong></td>
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<tr>
<td><strong>Functionalised adsorbents</strong></td>
</tr>
<tr>
<td>(Barron-Zambrano et al, 2002; Celis et al, 2000; Mercier and Detellier, 1995; Manohar et al, 2002; Monteagudo et al, 2003; Nam, et al, 2003)</td>
</tr>
<tr>
<td><strong>Sulphide and hydrogen sulphide gas</strong></td>
</tr>
<tr>
<td>(Cowling et al, 1992; Nebit and Davis, 1994)</td>
</tr>
<tr>
<td><strong>Cementation / reduction / amalgamation</strong></td>
</tr>
<tr>
<td>(Biester et al, 2000; Moeller, 2003; Ku et al, 2002; Patterson, 1985)</td>
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<tr>
<td><strong>Ion Exchange / solvent extraction</strong></td>
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<tr>
<td>(Becker and Eldridge, 1993; Chiarle et al, 2000; Larson and Wiencek, 1992; Larson and Wiencek, 1994; Monteagudo and Ortiz, 2000; Patterson, 1985; Ritter and Bibbler, 1992)</td>
</tr>
<tr>
<td><strong>Fly ash</strong></td>
</tr>
<tr>
<td><strong>Microorganisms</strong></td>
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<tr>
<td>(Wagner-Dobbler et al, 2000)</td>
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<tr>
<td><strong>Filtration</strong></td>
</tr>
<tr>
<td>(Barron-Zambrano et al, 2002; Broome et al, 1994; Patterson, 1985)</td>
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<tr>
<td><strong>Air stripping</strong></td>
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</tbody>
</table>
Alumina refinery process waters are increasingly re-used to reduce refinery water consumption. This re-use may expose the water to situations where mercury emissions can occur within the immediate working environment. In addition, waters are often stored in lakes prior to returning to the process. Mercury emissions could also occur from the surfaces of storage lakes.

Although there have been numerous processes investigated for removing mercury from aqueous solutions, there have been no published studies on the removal of mercury from alumina refinery process waters. As such, the main aims of this project were to develop a better understanding of the types of mercury species present in a specific alumina refinery process water, commonly referred to as digestion condensate, and to use this information to investigate and develop a suitable mercury removal process. A sound knowledge of the type(s) of mercury species present is required to select the most appropriate treatment options for this specific application. Understanding conditions, such as solution Eh, pH, temperature, flow characteristics and inorganic and organic species, was also an aim of this project as these are important aspects in determining the most appropriate process options.

The specific aims of this research project were as follows:

- Review available mercury removal technologies in terms of -
  - Target mercury oxidation state(s)
  - Developmental maturity
  - Mercury capacity and adsorption kinetics
  - Stability in environments similar to those encountered in alumina refining
  - Functional pH range
• Review mercury solution chemistry to determine the likely mercury speciation in specific aqueous environments

• Investigate the physical and chemical properties of digestion condensate to determine the most appropriate removal options

• Conduct experiments to investigate candidate removal options

• Conduct capital and operating cost estimates for favourable process options

• Make recommendations for treatment options

It is highly desirable to find or develop a process that enables the mercury to be chemically immobilised and stabilised in a concentrated form rather than moving it to other process streams or to the environment. The scope of this project was confined to developing a mercury removal technology that involved a minimal number of process stages and produced little or no discharge or waste to landfill facilities.

1.1 Bayer Process

Karl Bayer created an alumina extraction process in 1887. Bayer made use of the amphoteric nature of aluminium and treated bauxite with sodium hydroxide solution so the aluminium hydroxides and oxyhydroxides would dissolve to produce a sodium aluminate solution, leaving the iron oxides and other insoluble species as gangue material. By lowering the temperature and seeding the solution, aluminium tri hydroxide (Al(OH)₃) crystallisation is encouraged, allowing the sodium hydroxide leachate to be re-cycled. The modern Bayer Process (see Figure 1, Buckett, 2000) begins with comminution of the bauxite through crushing and grinding followed by a hot, high-pressure alkaline digestion stage in some refineries. The solid phase of the post-digest slurry is split into sand and mud fractions, which
are washed to recover leachate and are deposited in tailings disposal areas. The aluminate-rich digest liquor is further clarified and aluminium trihydroxide (gibbsite) is crystallised. Gibbsite crystals are washed to remove residual process liquor and calcined to dehydrate the gibbsite to produce alumina, \( \text{Al}_2\text{O}_3 \). Spent liquor is recycled from gibbsite crystallisation to digestion. During this recycle the liquor is evaporated to remove excess water introduced during the circuit and sodium hydroxide is added to make up for leachate losses.

![Simple flow diagram of Bayer Process](image)

**Figure 1** Simple flow diagram of Bayer Process

### 1.2 The Australian alumina industry

The combined Australian alumina and aluminium industries account for \( \sim 0.54\% \) of the Australian gross domestic product and about 4.5\% of manufacturing gross product (Australian Aluminium Council, 2000). In 2004 - 2005, total exports were $7.8 billion, the third largest commodity export (Colebatch, 2005). To maintain this substantial contribution to the Australian economy while maintaining its environmental responsibilities, the Australian alumina refining industry is constantly trying to minimise the adverse environmental impacts.
of its processes. To reduce emissions and still remain an economically sustainable industry, cost-effective impurity removal technologies are required.

Much of Australia’s alumina industry is situated in regions where there is a scarcity of available water. Evaporation from holding ponds and losses from steam discharges creates conditions whereby some refineries are net water consumers and, as such, the industry is often forced to recycle water streams to minimise water use. Water recycled for re-use often requires “cleaning” to remove species that may have deleterious performance or safety impacts on the process and the environment in general. The removal of mercury from stored process waters may reduce global health impacts associated with mercury emissions to the local work environment and the atmosphere and hence make these process waters safer for re-use.

1.3 **Mercury and Bayer process water streams**

Digestion of alumina bearing compounds occurs at 145 – 300 °C in autoclaves. The digestion temperature depends on the mineralogy of the alumina bearing compounds in the bauxite. The temperature required to digest gibbsite (Al(OH)$_3$, ~145 °C) < boehmite ($\gamma$-AlOOH, ~250 °C) < diaspore ($\alpha$-AlOOH ~300 °C).

In many alumina refineries digestion heating is carried out via the injection of superheated steam which directly contacts the bauxite slurry within autoclaves. Following the required digestion contact time, the heated slurry is cooled in a series of flash vessels (see Figure 2, Buckett, 2000) and the evolved steam is condensed in heat exchangers to recover heat back to the digestion process. This heat conservation is known as continual regenerative digestion or CRD. The flash vapour is saturated with respect to water vapour, volatile organic carbons
(VOCs) and other volatile species, and these species co-condense into a predominantly aqueous phase known as CRD digestion condensate (condensate).

Figure 2 Schematic diagram of heating processes for a typical bauxite digestion process

The digestion process is chemically reducing, due mainly to the presence of organics dissolved from the bauxite and from within the recycled liquor stream, which are readily oxidised. Gases exiting these processes include hydrogen, nitrogen, methane, ammonia (Chiappalone, 2001), water (J Lochore [Alcoa World Alumina] 2002, Pers. Comm., 20 May) and some volatile organic carbons (Leeder, 2002) with the balance being nitrogen. Ammonia dissolves into the condensate, and together with some caustic carry over from digestion vapours, contributes to a relatively high pH. Mercury is present in bauxite in trace quantities, originating from sulphide minerals such as pyrite. Following digestion, mercury vapour is liberated and can be saturated in the digestion gases according to Henry’s law (Lide, 1979; Sanemasa, 1975; Waite et al, 2002). Dissolution or co-condensation with water leads to
significant quantities of dissolved species, including mercury, in condensate. This has also been observed in condensate waters from kilns used to distil HgS in the mercury mining industry (Defence National Stockpile Centre, 2005).

Much of the condensate exits the refinery to reside in storage lakes, often via a counter current decant washing process used to recover dissolved products from the solid gangue materials. The fate of mercury within these storage lakes is not comprehensively understood and removal of mercury prior to discharge is preferred to avoid release of mercury into the environment. In addition, the waters are brought back into the plant as make-up water or for washing and cooling purposes, which allows for the opportunity of further exposure to mercury laden sources.

Within the alumina refining industry, condensates are generally similar in terms of their chemical matrices and physical characteristics, although the relative dilutions of analytes may vary. For example, digestion condensate samples from Alcoa’s Kwinana and Wagerup refineries were analysed at the commencement of this study. The results of these analyses, as well as general analytical data collated from other sources, are shown in Table 2.
### Table 2 Characteristics of typical Bayer digestion condensate

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical flow rates (kL/hour)</td>
<td>150 – 490</td>
<td>Armanios et al, 2001; Armanios et al, 2002a; Armanios et al, 2002b</td>
</tr>
<tr>
<td>Volatile Organic Compounds (mg/L)</td>
<td>1.8</td>
<td>Leeder, 2002</td>
</tr>
<tr>
<td>Aldehydes and ketones (mg/L)</td>
<td>50</td>
<td>Leeder, 2002</td>
</tr>
<tr>
<td>Phenols (mg/L)</td>
<td>1</td>
<td>Leeder, 2002</td>
</tr>
<tr>
<td>Lignins and tannins (mg/L)</td>
<td>2.3</td>
<td>Leeder, 2002</td>
</tr>
<tr>
<td>Mercury µg/L as (Hg)</td>
<td>4 - 35</td>
<td>Armanios et al, 2001; Armanios et al, 2002a; Armanios et al, 2002b; McGuiness, 2001</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>210 – 230</td>
<td>Leeder, 2002</td>
</tr>
<tr>
<td>Ammonia as (mg/L N)</td>
<td>110</td>
<td>Leeder, 2004a</td>
</tr>
<tr>
<td>Kwinana Wagerup</td>
<td>100</td>
<td>Leeder, 2004b</td>
</tr>
<tr>
<td>Total Organics as C (mg/L)</td>
<td>61</td>
<td>Leeder, 2004a</td>
</tr>
<tr>
<td>Kwinana Wagerup</td>
<td>70</td>
<td>Leeder, 2004b</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>95</td>
<td>J.Lochore, 2004, pers. comm., 24 November.</td>
</tr>
<tr>
<td>pH</td>
<td>10.2</td>
<td>Hoang et al., 2004</td>
</tr>
</tbody>
</table>

### 1.4 Chemistry of mercury species in aqueous solution

Mercury in aqueous solution can exist in three oxidation states (0, +1 and +2). As the types of species present in alumina refinery condensate are unknown, it is necessary to discuss the chemistry of each of these species in detail.

#### 1.4.1 Mercury (0)

Elemental mercury is only slightly soluble in pure water at room temperature (56.2 – 63.9 µg/L at 25 °C, Lide; 1979, Sanemasa, 1975; Waite et al, 2002). Its solubility depends primarily on solute concentration², temperature and the concentration of mercury vapour above the water according to Henry’a law (Sanemasa, 1975). The majority of publications on aqueous elemental mercury presented in the open literature (Amyot et al, 1994; Amyot et al,

---
² The solubility of elemental mercury is lower in high ionic strength solutions such as seawater (54.9 µg/L at 25 °C, Sanemasa, 1975).
1997; Lalonde et al, 2001; Mason et al, 1994; Vandal et al, 1991; Yamamoto, 1996) discuss the reactions of aqueous elemental mercury in natural waters such as seawater. The reactions of aqueous elemental mercury in seawater are particularly important as they contribute significantly to the amount of gaseous mercury released into the atmosphere. The oceanic recycling of gaseous mercury accounts for ~30% of the current total flux of mercury to the atmosphere (Lalonde et al 2001), of which >90% is elemental mercury (Waite et al, 2002).

Aqueous elemental mercury can undergo various reactions in natural waters. Schroeder et al (1992) proposed that aqueous elemental mercury can be oxidised by hydrogen peroxide produced from UV-induced transformations of dissolved organic matter in surface waters (Cooper et al, 1994). Lalonde et al (2001) reported that aqueous elemental mercury is rapidly and completely oxidised (to $\text{Hg}^{2+}_{\text{aq}}$) in the presence of chloride, benzoquinone and light (UV-B lamp) in water at pH 8. No reaction occurs for the same system in the absence of light. This reaction (Equation 1.1, Schroeder et al, 1992) however would most likely not occur in Bayer refinery process waters due to the higher solution pH and also would not occur in waters retained in the refinery circuit that are not exposed to light.

$$\text{H}_2\text{O}_2 + 2\text{H}^+ + \text{Hg}^0 \rightarrow 2\text{H}_2\text{O} + \text{Hg}^{2+}_{\text{aq}}$$  \hspace{1cm} \text{Equation 1.1}

Lalonde et al (2001) also found that aqueous elemental mercury is oxidised in the presence of chloride, fulvic acid and light. A similar oxidation process to this may occur in Bayer process storage lakes if humics/fulvics and chloride ions are present. Although condensate solution is generally free of such species, influx from other Bayer liquors into storage lakes containing predominantly condensate may contain humic/fulvic acids and chloride ions. This process
could lead to a steady state mercury concentration because $\text{Hg}^{2+_{(aq)}}$ is significantly more soluble than elemental mercury (Lide, 1979; Sanemasa, 1975; Waite et al, 2002).

### 1.4.2 Mercury (I)

Monovalent mercury, which is only found in a dimer form, $\text{Hg}_2^{2+}$, can also exist in aqueous solution. Monovalent mercury species are usually not as soluble ($\text{Hg}_2\text{Cl}_2 = 2$ mg/L at 25°C (Lide, 1979) and 10 mg/L at 43°C (Weast, 2005) or stable as divalent mercury species. At high pH, monovalent mercury is not stable as it readily reacts with $\text{OH}^-$ forming elemental mercury and $\text{HgO}$ (Equation 1.2, Cotton and Wilkinson, 1980). In condensate solutions, aqueous monovalent mercury would most likely be converted into elemental mercury and mercuric oxide.

$$\text{Hg}_2^{2+} + 2\text{OH}^- \rightarrow \text{Hg} (l) + \text{HgO(s)} + \text{H}_2\text{O} \quad \text{Equation 1.2}$$

A number of other reagents such as $\text{NH}_3$, amines, $\text{CN}^-$, $\text{SCN}^-$ and $S^{2-}$ react with monovalent mercury leading to the formation of elemental mercury and a mercury (II) species (Equations 1.3a and 1.3b, Cotton and Wilkinson, 1980). Mercury (I) can also form complexes with oxygen donor ligands such as oxalate and succinate. Although mercury (I) can form a number of different compounds, very few stable mercury (I) complexes exist. This is mainly because mercury (II) will form even more stable complexes with most ligands (Cotton and Wilkinson, 1980).
1.4.3 Mercury (II)

Divalent species of mercury (Hg$^{2+}$) are quite soluble in aqueous solution (HgCl$_2$ = 69,000 mg/L and HgO = 53 mg/L at 20°C (Lide, 1979)). Different species of mercury (II) are found in aqueous solution in the presence of chloride ion and nitrate ion respectively (see Figures 3 and 4). According to Knocke et al (1981), at a pH above 6, mercury (II) is present exclusively in the form of Hg(OH)$_2$. Below a pH of 6, a range of mercury (II) species exist. The types of mercury (II) species that are found below pH 6 are dependant on the other ionic species that are present in solution.

The speciation predicted by Knocke et al (1981) (see Figures 3 and 4) is for an oxygenated aqueous system. Hg (0) is the thermodynamically stable phase in solutions with reducing conditions where the oxygen pressure is less than $10^{-20}$ atm, the point at which HgO and Hg (0) are at equilibrium (Baes and Mesmer, 1976; Pourbaix, 1973). The potential defining the redox couple Hg(0)/HgO is dependant upon solution pH and mercury concentration according to Equation 1.4 (Pourbaix, 1973). Above neutral pH, the speciation changes and Hg (OH)$_2$ predominates.

$$E_0 = 1.034 - 0.0591 \text{ pH} + 0.0295 \log C$$ 

Equation 1.4
The Hg$^{2+}$ ion has a strong tendency to form complexes. Hence, the complexity of the chemistry of Hg$^{2+}$ in a water source will depend upon the anionic species present. A number of complexes of Hg$^{2+}$ with C, N, P and S ligands are known. For sulphur species, Hg—S bonding always occurs (Cotton and Wilkinson, 1980). In the presence of excess sulphide and hydroxide, the Hg—S transforms into a soluble complex, HgS$_2^{2-}$. Paquette and Helz (1997) examined the solubility of mercury from 6 g/L cinnabar (HgS) from pH 1-12 in the presence
of 0.3 - 0.9 mg/L excess sulphide. Between pH 2 and neutral pH the mercury concentration was relatively stable at 0.05 ng/L. As the pH increased towards 11, the mercury concentration increased to 50 µg/L. Greenwood and Earnshaw (2002) report a pK_{sp} for HgS in neutral solutions as 51.8 ± 0.5, whereas in a weak base with excess sulphide pK_{sp} = 1.5. Kirk-Othmer (1981) report that the solubility of HgS in water at 18 °C is 12.5 µg/L, whereas in a strongly alkaline environment, 9.5 g/L Na_{2}S addition increases the HgS solubility to 2.5 g/L.

The strong tendency of sulphur to form complexes with Hg^{2+} led to the name “mercaptan” for R-S-H compounds. Hg^{2+} forms complexes with a variety of amines. The affinity of Hg^{2+} for nitrogen ligands in aqueous solution exceeds that of the transition metals (Cotton and Wilkinson, 1980). Several mercury (II) oxo ion complexes also exist, including [Hg(SO_{3})_{2}]^{2-} and [Hg ox_{2}]^{2-} (ox = oxalate).

Mercury (II) can also form complexes with large molecules, such as humic acids. Scholtz et al (2002) and Turner et al (1989) reported that abiotic reduction in water of aqueous mercury (II) into elemental mercury can be initiated by humic substances. According to Turner et al (1989), this abiotic reduction could account for as much as 10-70% of the volatile Hg(0) released from some contaminated streams.

### 1.4.4 Mercury species in Alumina refinery digestion condensate

Condensate is created in a chemically reducing environment; however it is difficult to predict with a high degree of confidence the types of mercury species likely to exist in condensate. In particular for condensate stored in a lake, it is feasible that stratification of mercury species could occur with elemental mercury thermodynamically favoured at the lower levels of the water column where the oxygen concentration is very low. At the surface where diffused oxygen would increase the oxidation potential of the solution, both Hg(OH)_{2} and HgO may
predominate, however these species could in turn be reduced to Hg(0) by humic substances (Scholtz et al, 2002; Turner et al, 1989).

There is a significant gap in the scientific literature regarding mercury speciation in complex, highly alkaline solutions with a low redox potential. Hg(0) may well predominate in these solutions, however only a thorough investigation of condensate chemistry will allow a better prediction of the speciation.

1.5 Existing mercury Removal Processes

1.5.1 Activated carbon

Activated carbon has historically been the most common material used to remove mercury from aqueous solution. Activated carbons make up a group of materials that possess highly developed internal surface area and porosity. Scanning electron micrographs of the surface and cross section of an activated carbon prepared from flax shive (Cox et al, 1999) are shown in Figures 5 and 6. Activated carbons are made from a variety of carbonaceous materials such as wood, peat, lignite and coal (Cox et al, 1999). A number of other cheaper carbonaceous materials have also been used to prepare activated carbon such as flax shive (Cox et al, 1999, Cox et al, 2000), sugarcane bagasse pith (Anoop Krishnan and Anirudhan, 2002a; Anoop Krishnan and Anirudhan, 2002b), nut wastes, onion skin, coffee grounds, scrap rubber (Aoyama et al, 2001), rice husk, moss, human hairs, chitosan beads and sawdust (Mohan et al, 2000).
Activated carbons are usually prepared by heating the starting carbonaceous material at high temperatures (800 – 1200°C) but can also be prepared by chemical activation. One method of preparing activated carbon by chemical activation involves dehydration with sulphuric acid at
155 - 160°C (Cox et al., 1999). Another popular method for producing activated carbons is via steam pyrolysis.

Activated carbons can also be impregnated with various elements/compounds to increase mercury removal efficiency. Sulphur is the most common impregnate used to aid removal of mercury from aqueous solution. Sulphur impregnated carbons can be prepared by steam activation in the presence of a sulphur containing gas such as H₂S or SO₂ (Anoop Krishnan and Anirudhan, 2002a). The removal of mercury from aqueous solution by sulphur impregnated carbon is discussed in detail in the proceeding section.

### 1.5.1.1 Chemistry / Removal mechanisms

Activated carbons can remove mercury from aqueous solution via four main mechanisms: ion exchange; reduction/precipitation; complexation (sulphur impregnated activated carbons) and pore capture.

The ion exchange mechanism involves the release of protons from the carbon surface and reaction between the deprotonated surface sites and oxidised mercury species (Hg²⁺, Hg₂²⁺, Equation 1.5, Cox et al., 2000). Oxidised mercury species can also exchange with H⁺ from carboxylic acid groups, which may form on the activated carbon surface. The ion exchange mechanism is strongly reliant on solution pH. Optimum ion exchange usually occurs at pH 5-7. Ion exchange is also affected by other light metal ions (K⁺, Na⁺, Ca²⁺, Mg²⁺) in solution. These ions can decrease mercury removal by competing for the cation exchange sites.

\[
2C-H + Hg^{2+} \rightarrow (C-)_{2}Hg + 2H^{+}
\]

Equation 1.5

Activated carbons can remove mercury from aqueous solution via a reduction/precipitation mechanism. This mechanism firstly involves the reduction of mercury (II) at the carbon
surface via Equations 1.6 and 1.7 (Cox et al, 2000), which results in a loss of carbon from the surface, and equations 1.8 – 1.10 (Cox et al, 2000), which results in the formation of new carbon functional groups on the surface.

\[
C + 2H_2O + 4 Hg^{2+} \leftrightarrow CO_2 + 2 Hg_{2^{+}} + 4H^+ \quad \text{Equation 1.6}
\]

\[
C + 2H_2O + 2 Hg^{2+} \leftrightarrow CO_2 + 2 Hg^0 + 4H^+ \quad \text{Equation 1.7}
\]

\[
>C-H + Hg \text{ (oxidised)} + H_2O \leftrightarrow >C-OH + Hg \text{ (reduced)} + H^+ \quad \text{Equation 1.8}
\]

\[
>C-H >C-OH + Hg \text{ (oxidised)} + H_2O \leftrightarrow >C=O + Hg \text{ (reduced)} + H^+ \quad \text{Equation 1.9}
\]

\[
>C-H >C-OH + Hg \text{ (oxidised)} + H_2O \leftrightarrow >COOH + Hg \text{ (reduced)} + H^+ \quad \text{Equation 1.10}
\]

The mercury (I) produced from reduction can be reduced further to elemental mercury (which is sparingly soluble in aqueous solution). If chloride ions are present the mercury (I) formed from the initial reduction step can react to form mercury (I) chloride (which is also sparingly soluble in aqueous solution). It was proposed by Cox et al (2000) that in the presence of chloride ions, Hg(I) chloride crystallites precipitate onto the carbon surface and within the pores of the carbon. The precipitated crystallites then migrate from the reduction site towards earlier deposited sites for crystal growth. This proposed mechanism is supported by scanning electron microscope images of activated carbon used to remove mercury in the presence and absence of chloride ions (see Figures 7 and 8, Cox et al, 2000).
Figure 7 SEM of carbon after Hg (II) sorption in the presence of chloride ions, showing Hg (I) Cl crystals formed from the reduction/precipitation mechanism.

Figure 8 SEM of carbon after sorption of Hg (II) in the absence of chloride ions. Only droplets of elemental mercury are formed in the absence of chloride ions.
Sulphur impregnated activated carbons remove mercury from aqueous solution via a complexation mechanism. Removal occurs via complexation between sulphur containing functional groups and $\text{Hg}^{2+}$ and/or $\text{Hg}_2^{2+}$ leading to the formation of new compounds on the surface or in the meso- and macropores of the activated carbon. Reactions between sulphur containing functional groups and neutral mercury species such as $\text{HgCl}_2$ and $\text{Hg(OH)}_2$ can also occur. The reaction between neutral mercury species and surface sulphur groups is proposed by Anoop Krishnan and Anirudhan (2002). These authors base these proposed reactions on Pearson theory (Pearson, 1988). Pearson theory states that during acid-base reactions, hard acids prefer to co-ordinate with hard bases and soft acids with soft bases. Neutral molecules such as $\text{Hg(OH)}_2$ are softer acids than metal cations and according to Pearson theory, the interaction of neutral mercury species with sulphur groups (soft bases) is likely to be favoured in the pH range 4–6.

Neutral mercury compounds, such as $\text{HgCl}_2$ and $\text{Hg(OH)}_2$, can also be removed from aqueous solution by being captured in the pores of activated carbons. This removal mechanism was recently proposed by Anoop Krishnan and Anirudhan (2002). The aforementioned authors used this mechanism to explain the increased removal efficiency that occurred at pH $> 6$ in their study on mercury removal from aqueous solution using an activated carbon prepared from bagasse pith.

1.5.1.2 Physical aspects of mercury removal

The mechanism of mercury sorption by activated carbon involves a number of physical steps. According to Mohan et al (2001) the three consecutive physical steps in the adsorption of an inorganic species by a porous adsorbent are:

1. Transport of the adsorbate to the external surface of the adsorbent (film diffusion)
2. Transport of the adsorbate within the pores of the adsorbent except for a small amount of adsorption that occurs on the external surface (particle diffusion)

3. Adsorption of the adsorbate on the exterior surface of the adsorbent

The third step mentioned above is usually very rapid, and hence does not represent the rate-determining step (Helfferich, 1962). For the other two steps in the overall transport, three distinct cases can occur:

**Case 1**: Rate of external transport < Rate of internal transport (rate is governed by film diffusion)

**Case 2**: Rate of external transport > Rate of internal transport (rate is governed by particle diffusion)

**Case 3**: external transport ≈ internal transport (rapid transport of ions to the boundary may not be possible, leading to the formation of a liquid film with a concentration gradient surrounding the sorbent particles).

The effect of particle diffusion on the sorption of mercury by activated carbon was demonstrated in a study by Cox *et al* (2000). The authors studied the effect of pore size on mercury sorption by testing the removal efficiency of an activated carbon in wet and dry form. Approximately 30% more mercury was sorbed on the wet form. This was attributed to the dried sample undergoing shrinkage and compaction forming narrower pores restricting the diffusion of mercury (II) ions.
1.5.1.3 Studies conducted on the removal of mercury from aqueous solution using activated carbon

A number of studies have been conducted on the removal of mercury from aqueous solution using activated carbon. The majority of studies that have been conducted have used simple aqueous solutions (usually prepared by dissolving HgCl₂ in water); hence there have been very few studies published in the open literature on mercury removal from actual industrial process waters. The major results of studies that are relevant to Bayer process water conditions are discussed in the following paragraphs.

Ekinci et al (2002) investigated the removal of mercury from a simple solution of HgCl₂ in water (20 mg/L) using activated carbon prepared from Turkish coals, apricot stones and furfural. The activated carbons used were prepared by pyrolysis (750°C) in the presence of water vapour. The authors investigated the effect of pH on mercury removal between pH 1 and 8. Mercury removal increased with increasing pH, with ~40% removal occurring at pH 1, ~83% at pH 4 and ~100% at pH 8. Ekinci et al (2002) suggest that the high extent of adsorption at high pH is due to mercuric hydroxide (an amphoteric metal hydroxide) being readily adsorbed on both the weakly acidic and basic surface oxides present in the activated carbon used. Very low desorption (using boiling water) of mercury occurred, with a maximum recovery of mercury of 4% for the activated carbon derived from furfural and 2% for the other activated carbons. This was due to only a small portion of mercury (II) being physically adsorbed with the majority being chemically adsorbed, and hence more difficult to desorb.

Cox et al (2000) studied the removal of mercury from simple aqueous solutions, prepared using HgCl₂ (95 - 500 mg/L), using an activated carbon prepared from flax shive. The activated carbon was prepared from flax shive by dehydration using sulphuric acid. Cox et al (2000) investigated the effect of initial pH (1.2 – 7) on mercury removal efficiency in terms of
sorption capacity. The findings relating to the effect of pH were similar to those reported by Ekinci et al (2002), where increased removal efficiency occurred with increasing pH. Maximum removal efficiency occurred in the pH range 6-7. Cox et al (2000) investigated the effect of temperature on sorption capacity. Increased removal efficiency occurred with increasing temperature over the temperature range studied (25-45°C). Cox et al (2000) also studied the sorption of mercury using both a continuous and intermittent column. The results of the column studies are shown in Figure 9 (Cox et al, 2000). The intermittent column study involved 4h flow (time taken for breakthrough) followed by 8h rest. The drop in mercury concentration in the eluate that occurs when the column is restarted after a rest period is attributed to slow reduction of mercury (II) to insoluble mercury (I) chloride and elemental mercury during the rest period. This releases ion-exchange sites, which can then react with mercury when the flow is restarted. This type of intermittent flow ensured that maximum (and hence the most cost efficient) sorption capacity was achieved.

![Figure 9 Carbon adsorption column studies](image-url)
Anoop Krishnan and Anirudhan (2002a, 2002b) investigated the removal of mercury (II) from aqueous solutions and chlor-alkali industry effluent by steam activated and sulphurised activated carbons prepared from bagasse pith (a waste product from a sugar mill). The sulphurised activated carbons used were prepared by steam activation at 400°C in the presence of H₂S or SO₂ or a mixture of both gases. In this study, the effect of a number of parameters on removal efficiency from simple aqueous solution (50-1000 mg Hg/L) was investigated. These parameters included pH, temperature, initial mercury concentration, activated carbon particle size and ionic strength. The contact time was four hours. The sulphur activated carbons had higher removal efficiencies than the virgin activated carbon over the pH range studied (2-10). Among the different sulphurised activated carbons used, the one prepared using a mixture of H₂S and SO₂ had the highest removal efficiency (~98% at pH 10). The order of removal efficiency that occurred was as follows; activated carbon prepared with H₂S and SO₂ > activated carbon prepared with SO₂ > activated carbon prepared using H₂S > virgin activated carbon. The same removal efficiency order was also reported to occur for removal of mercury from chlor-alkali process water (1.6 mg Hg/L) at pH 6.

Anoop Krishnan and Anirudhan (2002a) tested the effect of ionic strength on Hg (II) removal from aqueous solution at pH 6 by varying the concentration of NaCl (see Figure 10, Anoop Krishnan and Anirudhan 2002a). After a four hour equilibration time, adsorption of Hg (II) was found to decrease significantly with increasing NaCl concentration. ~95% Hg removal occurred in 0.001M NaCl using the H₂S and SO₂ activated carbon, while ~65% removal occurred using the same activated carbon in 0.5M NaCl. Anoop Krishnan and Anirudhan (2002a) attribute this to changes in mercury activity or in the properties of the electric double layer. They also state that cation competition and modification of mercury speciation from added NaCl are less important than the aforementioned factors.
Huang and Blankenship (1994) investigated the removal of mercury (II) from dilute aqueous solution at 2 and 20 mg/L Hg (prepared using HgO) by 11 different activated carbons. Two of the activated carbons tested, Nuchar SA and Nuchar SN (Westvaco), removed ~100% of mercury over a very wide pH range (2.5 - 11). All of the other nine activated carbons tested had high removal efficiencies (80-90%) at pH 4-5, however all were less efficient at high and low pH. Huang and Blankenship (1994) investigated the kinetics of total Hg (II) removal and Hg (II) removal by reduction/volatilisation at various pH values by Nuchar SA (at a dose of 1g/L). At pH 11, > 90% total removal occurred after 8h using an initial Hg concentration of 2 mg/L. Of this 90% approximately 40% was due to reduction/volatilisation.

Other studies investigating the removal of mercury from aqueous solution using activated carbon are summarised in Table 3. As with most studies, the experiments were conducted at low to neutral pH. The results and findings reported in these studies on the mechanism(s) of mercury removal and the effects of solution and activated carbon parameters are for the most part in good agreement with the studies reviewed in detail in the preceding paragraphs.
<table>
<thead>
<tr>
<th>Solution type</th>
<th>Type(s)/source(s) of activated carbon</th>
<th>Procedure, solution parameters investigated</th>
<th>Comments</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic (HgNO₃ in water)</td>
<td>Derived from fertilizer waste, virgin and sulphurised</td>
<td>Batch tests pH, [Hg], temp, particle size</td>
<td>24 hour contact time used to show a decrease in removal with an increase in pH from 2 – 6 (42 to 22 % adsorption respectively). Remaining results not relevant as the tests were conducted at pH 2.</td>
<td>Mohan et al, 2001</td>
</tr>
<tr>
<td>Synthetic Commercial (Filtrasorb 400)</td>
<td>Batch test Particle size</td>
<td>Higher removal efficiencies reported (in terms of sorption capacity) with decreasing particle size.</td>
<td></td>
<td>McKay et al, 1985</td>
</tr>
<tr>
<td>Synthetic (HgCl₂ in water)</td>
<td>Heat treated and sulphurised commercial activated carbon.</td>
<td>Batch tests pH</td>
<td>Removal at pH 2 and 4 investigated. Significantly higher removal at pH 4. Sulphur treated carbons have higher removal efficiencies (reported in terms of sorption capacity).</td>
<td>Gomez-Serrano et al, 1998</td>
</tr>
<tr>
<td>Synthetic (HgCl₂ in water)</td>
<td>Commercial (Le Carbone G210)</td>
<td>Batch tests None</td>
<td>Mechanism of removal investigated. SEM indicated removal via reduction/precipitation mechanism.</td>
<td>Adams, 1991</td>
</tr>
<tr>
<td>Synthetic (HgCl₂ in water)</td>
<td>Three types of furfural-based carbons: air oxidised, steam activated and steam activation + pyrolised apricot stone tar.</td>
<td>Batch tests pH, Hg concentration, contact time.</td>
<td>Maximum adsorption at pH 2 – 5 after which it plateaus. Steam activated furfural (174 mg/g) showed the greatest adsorption due to the greater number of acidic groups on the carbon surface. Equilibrium approached after 20 minutes contact time.</td>
<td>Budinova et al 2003</td>
</tr>
<tr>
<td>Synthetic (HgCl₂ in water)</td>
<td>Coir pith carbonised using sulphuric acid and ammonium persulphate.</td>
<td>Batch tests pH, Hg concentration, contact time and adsorbent dose.</td>
<td>Adsorption increased from pH 2 – 5 (constant to pH 11) as Hg (OH)₂ was favoured over HgCl₂. Adsorption capacity of 154 Hg mg/g carbon achieved which was greater than that of other activated carbons. Coir pith requires approximately 0.3 times the contact time required for other activated carbons tested.</td>
<td>Namasivayam and Kadirvelu, 1999</td>
</tr>
<tr>
<td>Solution type</td>
<td>Type(s)/source(s) of activated carbon</td>
<td>Procedure, solution parameters investigated</td>
<td>Comments</td>
<td>Reference</td>
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<td>----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>Synthetic (\text{HgCl}_2) in water)</td>
<td>Mersorb sulphur impregnated activated carbon</td>
<td>Batch tests pH, Hg concentration, contact time and adsorbent dose.</td>
<td>Up to 120 mg/g Hg adsorption in 10 mg/L. 99% removal at pH 10 with 24 hour contact time. 20 – 40 minutes contact time recommended for industrial use although adsorption increases after 24 hours. Improved bed life achieved by placing a second carbon bed upstream on the Hg removal bed.</td>
<td>Nucon International, 1997</td>
</tr>
<tr>
<td>Synthetic (\text{HgCl}_2) in water)</td>
<td>Pyrolysed wastepaper</td>
<td>Batch tests pH, Hg concentration, contact time.</td>
<td>Mercury adsorption at pH 11 was 43.3 mg/g after 24 hours contact time with a 100 mg/L Hg concentration. The maximum capacity was 153.8 mg/g at mercury concentrations &gt;150 mg/L.</td>
<td>Aoyama et al, 2001</td>
</tr>
<tr>
<td>Pharmaceutica l wastewater containing 60% thimerosal (organic mercury) and 40% Hg (II).</td>
<td>Commercial (Calgon F-400)</td>
<td>Pilot evaluation at pH 8.3.</td>
<td>Small column experiment: 60 minutes contact time. Breakthrough after 100 hours operation. Pilot experiment: 99.8% removal efficiency at 60 minutes contact time. 0.6% breakthrough after 120 hours operation. Operational cost estimate US$0.11 per gallon.</td>
<td>Cyr et al, 2002</td>
</tr>
</tbody>
</table>
1.5.2 Miscellaneous chemicals / materials

1.5.2.1 Silica-based materials

A number of studies have been conducted in recent years on the removal of mercury from aqueous solution using a variety of silica-based materials. A list comprising some of these materials is given in Table 4. Most of the silica-based materials that have been studied consist of silica (in various forms) coated with a compound(s) capable of reacting with mercury. Silica is one of the most preferred solid supports due to its good stability, wide scales of porous volume, specific surface area and available sizes.

<table>
<thead>
<tr>
<th>Table 4 Silica based materials used to remove mercury from aqueous solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrapyrazolic macrocycles bound to silica gel (Radi et al, 2000)</td>
</tr>
<tr>
<td>Silica-polyamine composite materials (Fisher et al, 2000)</td>
</tr>
<tr>
<td>Thiol functionalised mesoporous silica molecular sieves (Mercier and Pinnavai, 1998)</td>
</tr>
<tr>
<td>Amorphous silica (Bonnissil-Gissinger et al, 1999)</td>
</tr>
<tr>
<td>Thiol-functionalised mesoporous silica microspheres (Bibby and Mercier, 2002)</td>
</tr>
<tr>
<td>Poly (ethylenimine) coated onto silica gel (Delacour et al, 1999)</td>
</tr>
<tr>
<td>Silica gel-immobilised-dithioacetal derivatives (Mahmoud and Gohar, 2000)</td>
</tr>
<tr>
<td>Functionalised monolayers on mesoporous supports (Feng et al, 1997)</td>
</tr>
</tbody>
</table>

A summary of some of the studies conducted on the removal of mercury using silica-based materials are given in Table 5. Although the majority of studies conducted on silica-based materials involve the binding of compounds, such as sulphur based functional groups that have a strong affinity for mercury, free silica is also capable of sorbing mercury in aqueous solution. According to Bonnissel-Gissinger et al (1999), amorphous silica adsorbs mercury (II) in aqueous solution via a surface complexation mechanism. This study proposes that this mechanism involves the formation of a monodentate surface complex $\equiv$Si—OHg$^+$ and of
ternary surface complexes with OH surface groups, ≡Si—OHgOH and ≡Si—OHgCl, when chlorides are present. The aforementioned surface complexes were characterised using X-ray photoelectron spectroscopy.

Feng et al (1997) developed functional organic monolayers on ordered mesoporous supports (FMMS). Thiol groups were introduced as the terminal groups of the organic monolayers. A solution with a mercury concentration of 6.35 mg/L mercury at pH 9 was contacted with FMMS at various dose rates for two hours at room temperature with agitation. The resulting mercury concentration ranged between 0.006 and 0.0007 mg/L respectively and the observed mercury loadings on this material ranged between 110 and 340 mg mercury per gram of material (11 and 34% w/w respectively). It was stated that the small pore size should prevent bacteria from solubilising the bound mercury to form methyl mercury and, as such, the materials should have long term disposal stability.

Most of the research conducted on mercury removal using silica-based materials is quite recent and covers a wide variety of silica-based materials in the developmental stage. Reported tests have been conducted under similar test conditions and researchers have not investigated mercury removal from complex synthetic solutions or industrial process waters, particularly solutions at high pH, hence it is difficult to predict if these types of materials would be suitable for removing mercury from Bayer waters.
<table>
<thead>
<tr>
<th>Solution</th>
<th>Silica based material</th>
<th>Procedure, solution parameters investigated</th>
<th>Summary of results</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg (II) in water (1.3 g/L)</td>
<td>Tetrapyrazolic Macrocycles bound to silica gel</td>
<td>Batch tests. 8 different metals tested</td>
<td>Removal efficiency expressed as yield of complexation (calculated as µmole of Hg per µmole tetrapyrazolic compound). Of the 8 metals tested, yield of mercury complexation was highest.</td>
<td>(Radi et al, 2000)</td>
</tr>
<tr>
<td>Tap water spiked with HgCl₂ (6µg/L)</td>
<td>Poly (ethylene imine)/carboxylic acid group/thiol group bound to silica gel</td>
<td>Column tests. None</td>
<td>&gt;80% removal after passing 600 gallons through test column</td>
<td>(Fisher et al, 2000)</td>
</tr>
<tr>
<td>Hg (NO₃) in water (0-35 mg/L)</td>
<td>3-mercaptopropyltrimethoxysilane bound to 3 different silica molecular sieves</td>
<td>Batch tests. None</td>
<td>Removal efficiency expressed in terms of sorption capacity. Hg (II) ions reportedly access all of the complexing thiol groups in one of the materials tested (i.e., Hg/S=1.0).</td>
<td>(Mercier and Pinnavai, 1998)</td>
</tr>
<tr>
<td>Hg (NO₃) in water (2.49mg/L)</td>
<td>Pyrogenic silica (Aerosil 200 from Degussa)</td>
<td>Batch tests pH, [Cl]</td>
<td>Removal increases with increasing pH, ~90% removal at pH 8.5 (no Cl) and ~80% removal at pH 8.5 (0.7 mg/L Cl).</td>
<td>(Bonnissil-Gissinger et al, 1999)</td>
</tr>
<tr>
<td>Hg (NO₃) in water (0-140 mg/L)</td>
<td>3-mercaptopropyltrimethoxysilane bound to mesoporous silica microspheres</td>
<td>Batch tests [Hg]</td>
<td>Sorption reported in terms of capacity. Capacity increases with increasing amount of bound thiol.</td>
<td>(Bibby and Mercier 2002)</td>
</tr>
<tr>
<td>HgCl₂ in water (50-700mg/L)</td>
<td>Poly (ethylenimine) bound to silica gel</td>
<td>Batch and column tests pH, [Hg]</td>
<td>8 different silica-polymer type materials tested. Maximum removal (in terms of capacity) at pH 6 (pH 2-7.5 investigated).</td>
<td>(Delacour, et al 1999)</td>
</tr>
<tr>
<td>Sea water and tap water spiked with mercury (1-10 ng/L)</td>
<td>Dithioacetal derivatives bound to silica gel</td>
<td>Batch tests pH, [Hg], 11 different metals tested</td>
<td>5 different silica-thiocetal materials tested. 90-100% Hg removal from 10 ng/L spiked seawater and tap water. Removal increased with increasing pH over range tested (1-6).</td>
<td>(Delacour, et al 1999)</td>
</tr>
<tr>
<td>Synthetic wastewater containing 6.35 mg/L Hg</td>
<td>Functional organic monolayers on ordered mesoporous supports (FMMS)</td>
<td>Batch tests at pH 3, 7 and 9.</td>
<td>~99% mercury removal (0.0007 - 6.35 mg/L mg/L) at pH 9 following 2 hours contact at room temperature.</td>
<td>(Feng et al, 1997)</td>
</tr>
</tbody>
</table>
1.5.2.2 Waste tyre rubber

Several studies have been conducted on the removal of toxic heavy metals, including mercury, from aqueous solution using waste tyre rubber (Griffith, 1997; Gunasekara et al, 2000; Knocke and Hemphill, 1981; Rowley et al, 1984; Tharin, 1974).

The main constituents of vulcanised rubber are butadiene and styrene polymerised to hold sulphur and carbon black. Sulphur and carbon black (which is very similar to activated carbon (Snoeyink, 1967)) have a high affinity for mercury. The high affinity for mercury of sulphur and carbon black and the low cost of waste tyre rubber, led to waste tyre rubber being considered as a plausible mercury removal material.

Removal of mercury from aqueous solution by waste tyre rubber was first studied by Tharin (1974) who showed that vulcanised rubber removed mercury in almost any physical or chemical form over a wide range of concentrations, temperature and pH values. Since the initial study by Tharin (1974), there have been further investigations using waste tyre rubber (Griffith, 1975; Gunasekara et al, 2000; Knocke and Hemphill, 1981; Rowley et al, 1984). Gunasekara et al (2000) reported that the waste tyre rubber tested was capable of completely sorbing mercury from water for mercury concentrations below 4 mg/L, under the reaction conditions used (batch tests, 1 g waste tyre rubber, 100 mL water, pH not given). The adsorption kinetics were quite slow, however, with only 40 - 50% mercury removed from solution after 3 days contact time.

Knocke and Hemphill (1981) also investigated the removal of mercury from aqueous solution using waste tyre rubber. They found solution pH had a significant effect on the sorption capacity of waste tyre rubber. Mercury sorption decreased significantly at high (>7) and low (<6) pH (see Figure 11, Knocke and Hemphill, 1981). Knocke and Hemphill (1981) did not offer an explanation for the trend observed. According to Gunasekara et al (2000) similar
trends with varying pH have been reported by other authors. These authors however also offer no explanation.

Although waste tyre rubber is a relatively inexpensive material for removing mercury from aqueous solution, it would most likely not be suitable for treating alumina refinery process waters because of its poor performance in alkaline conditions.
1.5.2.3 Precipitation

Precipitation using various chemicals or chelating agents is often used to remove heavy metals such as mercury from industrial process waters. Precipitation is often used in conjunction with subsequent removal technologies such as filtration, gravity settling or dissolved air flotation (Patterson, 1985). Sulphides or sulphur containing chemical reagents are clearly the most frequently investigated agents because of the strong affinity mercury has for sulphur functional groups and the low solubility of Hg-S compounds. Patterson (1985) reports that mercury removal via magnesium sulphide addition is capable of producing discharge concentrations of 10 – 100 µg/L from a feed concentration of 10 mg/L without any additional treatment. The author makes the general claim, however, that removal efficiency decreases significantly above pH 9. This is possibly due to the formation of the soluble complex HgS\(_2\)\(^2-\) at high pH and in the presence of excess sulphide (Paquette and Helz, 1997).\(^3\)

In addition to the instability of Hg-S compounds in high pH environments, the effects of anaerobic microbial activity in lake beds are unknown and immobilised mercury may revert to soluble mercury through oxidation of the sulphide in the lake beds, potentially producing toxic methyl mercury as a result of anaerobic activity of sulphide reduction bacteria. A precipitation process using sulphur compounds is not recommended for removal of mercury from Bayer waters with pH values greater than 9.

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\(^3\) The solubility of HgS is discussed in detail in section 3.2.3.1.
1.5.2.4 **Chelating and complexing agents**

Due to the strong affinity for mercury, most chelating or complexing compounds contain sulphur functional groups. Matlock *et al* (2002) investigated the removal of mercury from aqueous solution using trimercaptotriazine, thio-Red potassium/sodium thiocarbonate and sodium dimethylthiocarbamate. Matlock *et al* (2002) reported that the three compounds tested were unable to reduce the concentration of mercury (initial [Hg] = 50.00 mg/L) to meet EPA discharge standards (0.2 mg/L). The authors also stated that the compounds tested displayed high leaching rates and in some cases decomposed to produce toxic substances. An example of a case where a sulphur containing compound, sodium thiocarbamate, decomposed into toxic secondary products occurred in Indiana, USA. In this case Guide Corporation (an auto parts manufacturer) accidentally released over 1.5 million gallons of wastewater containing traces of sodium thiocarbamate into the city’s wastewater system. This water was then discharged into local state waters where apparently the sodium thiocarbamate decomposed into toxic secondary compounds killing 117 tonnes of fish over a 50 mile stretch.

Matlock *et al* (2001) also recently investigated the removal of mercury from aqueous solution using a sulphur compound that they designed and synthesised: 1,3-benzene diamidoethanethiol (BDETH₂). The authors reported that this compound was capable of reducing a 50 mg/L mercury solution at pH 6 to 0.02 mg/L (99.97% mercury removal) and that the ‘BDETH₂ ligand promises to provide the required long-term stability, which will be determined in future leaching studies’.

Recently, there have been a number of patents lodged on the removal of heavy metals, including mercury, from aqueous solution using sulphur based precipitating / chelating agents (*Atwood et al*, 2002; *Houlachi et al*, 2000; *Malito*, 2002; *Mashima et al*, 1988). This indicates
that there have been several confidential studies conducted on the removal of mercury from aqueous solution using sulphur based precipitating/chelating agents. For example, Atwood et al (2002) recently patented a number of novel sulphur containing ligands for binding heavy metals.

The most relevant study to Bayer process water conditions was a patent lodged by Malito (2002). The patent described the removal of heavy metals including mercury by addition of dithiocarbamate to form a complex that was removed following settling. The specific interest in this patent was its design for application in Bayer process liquor. There was no indication as to whether it had been tested using Bayer process water streams, but its application was confined to oxidised mercury only (S. Ghotsis, S, [Nalco] 2004, Pers. Comm. 24 February), possibly making it unsuitable for use in Bayer water streams because of the highly reducing environment from which they originate.

An issue that is raised with the immobilisation and removal of mercury from condensate streams within a refinery using precipitation by sulphur functional groups is that it would require a second treatment stage to remove the sludge component. Malito (2002) states a 45-minute settling time is required to deposit the complexed mercury. The sludge would then require environmentally responsible disposal. Because of the complexity associated with settling and removal stages and the need to dispose of the sludge, this reagent was not considered suitable for treating digestion condensate.
1.5.2.5 Coagulation

Coagulants such as aluminium sulphate (alum), iron salts and lime have been used to coagulate mercury from process waters. According to Patterson (1985), coagulation using alum followed by filtration achieved greater than 90% mercury removal from acidic process waters. Similarly, iron coagulation followed by filtration achieved up to 98% removal at pH 6. Lime coagulation followed by filtration at pH 11.5 was the only reference found at an alkaline pH, however only 70% mercury removal was achieved. Coagulation does not appear applicable to treating high pH Bayer refinery waters for mercury, particularly due to the requirement of a filtration stage and sludge removal stage following coagulation.

1.5.2.6 Fly ash

According to Kapoor and Viraraghavan (1992), fly ash has been effective in the removal of colour (Gupta et al., 1990), organic impurities (Johnson et al., 1965) and removal of heavy metals (Gangoli et al., 1975; Kapoor and Viraraghavan, 1992; Panday et al., 1985; Yadava et al., 1987) including mercury (II) (Kapoor and Viraraghavan, 1992; Sen and De, 1985). The optimum pH for mercury removal was between 3.5 and 4.5 (Sen and De, 1985) and 5.0 – 5.5 (Kapoor and Viraraghavan, 1992) where almost 98% mercury was removed. The further investigation of mercury removal using fly ash is not recommended because the pH of condensate is outside the effective range for fly ash.

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4 Fly ash is the mineral based residue from the combustion of coal. It is finely divided with particle sizes ranging from 0.5 to 100 µm and a surface area in the range of (1 to 6 m² g⁻¹). Fly ash is composed mainly of silica (SiO₂), alumina (Al₂O₃) and iron oxides (Fe₂O₃) with minor unburnt carbon, calcium, magnesium, sulphur, sodium and potassium compounds. The relatively high surface area and unburnt carbon content makes fly ash a candidate material for use in removing impurities from wastewater.
1.5.2.7 Biomass

The biomass category covers a wide range of natural products including animal and plant derived materials. Many waste biomass products have relatively high surface areas and are potentially less expensive than activated carbon or other materials / treatments. Often surface modification of the biomass material is required to prevent the leaching of organic compounds into solution or to activate the surface by coating it with a functional group with a high affinity for mercury. The results of these studies are summarised into Table 6.

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Comments</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymerised acrylamide onto banana stalk</td>
<td>99.3% from a solution containing 50 mg/L Hg at pH 6 - 9</td>
<td>Shibi and Anirudhan, 2002</td>
</tr>
<tr>
<td>Introduction of polyethylenimine into porous cellulose carriers</td>
<td>100% at pH 6 - 7, 90% at pH 8</td>
<td>Navarro et al, 1996</td>
</tr>
<tr>
<td>Pretreated <em>hardwickia binata</em> bark with formaldehyde in an acidic medium</td>
<td>Adsorption increased with increasing pH with 9.58 mg Hg/g bark achieved at pH = 12. At an initial solution pH = 12 the precipitation of mercuric hydroxide reduced the pH to 10</td>
<td>Deshkar et al, 1990</td>
</tr>
</tbody>
</table>

Although lab-scale studies on some of these materials appear encouraging, adequate and consistent supply of such materials and the ability to modify the material surfaces would prove prohibitive for an industrial scale application.
1.5.2.8 Lignites and coals

Coals can act as low cost mercury adsorbents, particularly because of their high carbon content and relatively high sulphur contents (up to 10% sulphur by mass). Lakatos et al (1999) compared oxidised and non-oxidised coal with activated carbons and ion exchange resins for mercury removal from solutions at pH 5. Uptakes for lignites and an oxidised coal were similar to that of commercially available activated carbons and ion exchange resins (> 90% removal). Up to 30% Hg (w/w) was achieved. The tests were not carried out at pH > 5; however the uptake of mercury did increase as the solution pH approached 5. Adsorption kinetics for the coals was relatively slow with the adsorption uptake levelling out at two hours contact time. In each case the commercially available sorbent materials approached maximum mercury uptakes sooner than the coals.

Viraraghavan and Kapoor (1995) investigated the use of peat for mercury removal from a near neutral process water spiked to achieve 1 mg/L Hg. A pH range of 2 to 9 was studied but it was observed that the peat did not achieve significant adsorption above a pH of 2.

The addition of lignin derivatives (humic and fulvic acids) to mercury contaminated water and soils were investigated by Zhuang and Walsh (2002). Lignin derivatives possessing oxygen-containing functional groups such as phenolic, alcoholic and enolic structures were dissolved into two contaminated wastewaters at pH = 9.2 and 11.6. The lignin derivatives formed a stable colloid with the mercury and the colloids were subsequently coagulated with ferric chloride and settled leaving an effluent with a mercury concentration less than 1 µg/L. The ferric sludge that was produced was not leachable based on USEPA Toxicity Leaching Characteristic Procedure (TCLP) testing.

Bayer liquors contain natural lignin derivatives and fine iron oxides. Such species are ubiquitous within a Bayer circuit and could be added to condensate to encourage mercury
removal; however the need for filtration and sludge removal following the formation of the ferric sludge adds complexity to this process that would be undesirable to a refinery operation.

### 1.5.2.9 Clays and other minerals

Due to the relatively high cost of activated carbon, research is continually being conducted to find cheaper sorbent alternatives. This often includes the modification of material structures and/or surfaces with functional groups to enhance adsorption efficiency.

Crandallite substances have been used to immobilise radioactive fission products and toxic heavy metals. Monteagudo et al (2003) synthesised a Ca/Sr-crandallite type structure (Ca_{0.5}Sr_{0.5}Al_{3}(OH)_6(HPO_4)(PO_4)) and investigated the exchange of Hg (II) for Sr^{2+} and Ca^{2+}. It was found that mercury was selectively bound in preference to strontium and calcium and was immobilised into the crystal network. The initial ion exchange was rapid with maximum adsorption being approached at 30 seconds contact time. The mercury loading into the crandallite was related to the Hg(II) concentration in solution, for example 100 mg Hg adsorbed per g (10% w/w) crandallite from a 120 mg/L solution whereas 18 mg Hg(II) adsorbed per gram of crandallite (2% w/w) from a 20 mg/L solution. The experiments were conducted at pH = 3.5 and subsequent mercury recovery experiments showed that mercury is released from crandallite at pH < 2.5. It is not known how effective the ion exchange would be at high pH values.

Manohar et al (2002) modified natural clay (>90% kaolinite) with 2-mercaptobenzimidazole (MBI) and tested the parameters of sorbate concentration, pH, adsorbent dose, sorbent particle size, ionic strength and temperature against mercury removal. In tests conducted at pH = 6 it was shown that 250 mg of the MBI-clay removed 100 mg/L Hg(II) from 50 mL of solution compared to 1500 mg required for the unmodified clay at pH = 6. It was also demonstrated
that for Hg (II) concentrations ≤ 50 mg/L, the adsorption capacity was approached after approximately 60 minutes contact time. The adsorption capacity depended on the initial solution concentration. For example, after 60 minutes contact time 7.5 mg Hg per gram of clay was adsorbed from a 25 mg/L solution of Hg(II) whereas 22 mg Hg was adsorbed per gram of clay from a 50 mg/L solution. Maximum adsorption onto the MBI-clay occurred between pH 4 and 8. Soft acids such as Hg(OH)₂ are expected to have a high affinity for the soft base functional groups associated with MBI between pH 4 and 8. It is not known what would occur at higher pH values. Compared to the unmodified clay, the modified clay absorbed 80% more mercury over a limited pH range of 4 to 6.

It is not recommended that functionalised clays be further tested because of the high pH of condensate and the requirement to pre-treat the clay to facilitate consistent supply on an industrial scale.

### 1.5.3 Ion exchange

The majority of ion exchange based removal processes involve forming negatively charged \( \text{HgCl}_3^- \) complexes and subsequent removal of this species by an anionic resin. These removal processes are therefore more suited to plants with process waters containing high background chloride levels. In process waters where the background chloride level is not high, cation exchange resins have been effective in removing the mercuric ion. The best technology reported in a review by Patterson (1985) was using a Mtylon-T resin producing effluents at 1 – 5 \( \mu \text{g/L} \) Hg from an influent feed concentration of 25 mg/L using a two-stage column system at slightly acidic pH (Patterson, 1985). Monteagudo and Ortiz (2000) tested a Dowrex XZS-1 resin in the acidic pH range and reduced an influent feed at 90 mg/L to an effluent concentration of 34 \( \mu \text{g/L} \). More relevant tests were conducted at pH 11 using an Ajinomoto
resin, which reduced the feed concentration of 1800 µg/L to 990 µg/L (Patterson, 1985). Ritter and Bibler (1992) conducted pilot trials using Duolite™ GT-73 for removing mercury from complex wastewaters from a waste processing facility. The solution entered the ion exchange facility at pH 12 with an influent concentration ranging from 0.2 to 70 mg/L and was reduced to 1 to 5 µg/L. The nominated capacity of the resin (30 g Hg/L resin) was not achieved, however and it was postulated that oxidation of the thiol groups, heavy organics (mg/L levels) fouling or blocking pores and/or channelling may have contributed to the reduced capacity. The resin was suitable for disposal as it was not classed as a toxic waste by the USEPA. A cubic meter of this resin costs US$17 000 and as only 2% of the nominated capacity was reached this material would most likely not be cost-effective due to large material and operating costs associated with frequent changeovers. Based on the three column volumes per hour that was required in this study, and with condensate flow rates typically ranging from 200 to 490 kL/hour, columns of approximately 60 to 150 cubic meters in volume would be required if this material was used. The large vessels required, in addition to the material costs associated with resin purchases, would be prohibitive in an industrial context.

Liquid ion exchange mercury removal processes have been studied by Larson and Wiencek (1992, 1994) over a wide pH range. Several liquid ion exchangers were characterised as a function of pH, mercury concentration, chloride concentration and ion exchanger concentration. An anionic exchanger, Aliquot 336, was claimed to have good extraction efficiencies up to pH 10 in the presence of halide ions. Above a pH of 10.5 mercury precipitates as the hydroxide and is thus not suitable to ion exchange. Liquid ion exchangers also require a stripping stage to remove the mercury from the organic phase into a strong acid. This transfers the mercury to another solution phase and therefore does not immobilise the mercury into a form suitable for safe disposal. Liquid ion exchange does not appear suitable for treating Bayer process waters.
1.5.4 Cementation and reduction

Reduction of mercury ions to elemental mercury can be achieved using other metals higher in the electromotive series. The advantage of cementation processes is that resultant mercury metal can be directly separated via gravity or filtration. Metals such as zinc, aluminium and tin have been used to study mercury reduction (Biester et al, 2000; Moeller, 2003; Ku et al, 2002; Patterson, 1985).

Ku et al (2002) investigated the use of zinc to reduce mercury and claimed that cementation was more favourable in acidic solutions with a peak performance at pH = 4. Biester et al (2000) used a mossy tin filter to reduce Hg(II) to Hg(0) in solutions between pH 5.5 and 6.5. To prevent mercury metal from dissolving into solution as the Sn:Hg amalgam, an air sparging step was incorporated to volatilise the elemental mercury from solution. A major disadvantage highlighted from this process was the release of tin from the filter and formation of tin hydroxides at levels above legal limits.

In alkaline solutions, the formation of metal hydroxide complexes reduce the effectiveness of cementation processes. Cementation is therefore unsuited to Bayer process waters streams.

1.5.5 Filtration

Effective filtration of mercury from solution requires chemical pre-treatment to produce a complex large enough to filter. Barron-Zambrano et al (2002) investigated a complexation – ultrafiltration process using polyethylenimine (PEI) as a complexing agent. PEI has a molecular weight between 40 – 50 kDa and was filtered using a 15 kDa molecular weight cut-off mineral membrane. At pH values between 6 and 10 (pH = 10 was the maximum value
tested), 100% retention was demonstrated for solution containing chloride ions, whereas in the absence of chloride ions 95% removal was possible. The authors proposed a process with two ultrafiltration steps: the first to concentrate the complexed mercury to produce a purified stream and the second step at pH 3 – 4 to separate the mercury from the polymer to recycle the polymer. The requirement to recycle the polymer involves the transfer of mercury to another stream at low pH rather than complete removal or immobilisation of the mercury and, as such, this process is therefore not suitable for treatment of condensate.

Broom et al (1994) assessed a pilot-scale process designed to clean a variety of heavy metals from toxic waste dump effluents to ng/L levels. The process involved:

- The addition of lime to raise the pH to 11 – 12 and sulphide to complex the heavy metals in a reaction tank
- Settling of the metal precipitates using an 18 hour retention time
- Crossflow microfiltration of the settling tank supernatant

The initial process, sand filtration of the settling tank supernatant with sodium sulphide, was used to polish the discharge solution. Discharge levels of 230 ng/L Cd and 150 ng/L Hg were achieved but were regarded by the authors as being too high. The installation of a microfiltration stage to treat the settling tank discharge reduced the Cd and Hg to 40 and 80 ng/L respectively, meeting required discharge level guidelines. This microfiltration process developed by Broom et al (1994) may be suited to the treatment of high pH process water streams, however, factors that make such an option unattractive include:

- Discharge levels of mercury demonstrated by the technology were greater that the concentration of mercury in condensate
- The requirement for a multi-stage process, adding complexity
• The concentrated mercury in the settling tank and in the microfiltration discharge will require disposal in a form that meets municipal waste disposal standards.

• It is also not known whether the organics present in condensate would cause premature fouling of the microfiltration membrane.

• The installation of microfiltration to clarify the settling tank discharge is more expensive than other clarification processes (Broom et al, 1994).

It is not recommended that complexation and microfiltration be further investigated to treat mercury in condensate.

1.5.6 Air sparging

Mercury (0) has a low solubility in water (56.17 – 63.90 µg/L at 25 °C, Lide, 1979; Sanemasa 1975 and Waite et al 2002) and, according to Henry’s Law, is potentially easily volatilised into the vapour phase by gas sparging techniques (Bloom and Turner, 2004; Looney et al, 2003). Because of the high pH and reducing nature of refinery process water streams (Mullett et al, 2003), elemental mercury is possibly the thermodynamically favoured species (Pourbaix, 1973). Sparging of mercury (0) from Bayer process water streams may therefore be a practical option, however such a process will require a second mitigation stage to remove the mercury from the vapour phase.

Chemical reduction followed by air stripping has been examined by Looney et al (2003) and Bloom and Turner (2004). Looney et al used a stannous chloride reduction technique to convert Hg (II) to the elemental form in ground waters containing 138 ng/L Hg. Approximately 94% mercury removal was observed at 22.8 °C using a gas / water volume ratio of 20:1. The authors found that the mercury removal was most likely controlled by the
air sparging rather than the rate of chemical reduction and recommended that a commercially available sulphur impregnated activated carbon be employed for the vapour phase removal process. Bloom and Turner (2004) investigated removal of mercury from four client supplied caustic soda samples. The mercury concentration in a particular treated solution was reduced from 2.6 mg/L to 0.1 mg/L (96%) using a combination of UV reduction and 30 minutes of air sparging at 130 °C. Nine times greater removal was observed at 130 °C compared to at 100 °C, although it was not clear whether the higher temperature facilitated a higher chemical reduction rate or higher mercury volatilisation rate.

Based on the reducing nature of condensate and the possibility that elemental mercury could be the predominant mercury species, air stripping could be a suitable process option.

1.6 Summary

Bayer refinery digestion condensate is chemically unique owing to its high pH and the chemically reducing environment in which it is formed. Few references in the open literature are relevant to remediation of process water streams similar to condensate. To determine the most suitable processes to pursue via experimentation, a chemical and physical property analysis of condensate is required. Ideal processes for treating condensate would be elegant, single-stage processes requiring no material disposal and leave no residual chemicals in solution that may detrimentally affect downstream refinery operations. Following the findings of the literature review, three potential processes have been selected for investigation for the removal of mercury from Bayer condensate. These are:

1. adsorption onto activated carbon or other suitable substrates

2. sparging mercury into a gas stream
3. complexation or amalgamation onto modified silica substrates using noble metals or sulphur functional groups as impregnates

1.7 Project objectives

The vast majority of research and industrial mercury mitigation initiatives have been concerned with the removal of mercury (II) from acidic to neutral pH waters (Amyot et al., 1994; Amyot et al., 1997; Lalonde et al., 2001; Mason et al., 1994; Vandal et al., 1991; Yamamoto, 1996) because it is the thermodynamically favoured state in most applications. Although unproven, it is likely that mercury exists as mercury (0) in condensate because of the chemically reducing environment from which it is formed. Elemental mercury is only slightly soluble in pure water at room temperature (56.17 – 63.90 µg/L at 25 °C; Lide, 1979; Sanemasa, 1975; Waite et al., 2002), and the solubility is further reduced in high ionic strength solutions (54.9 µg/L at 25 °C, Sanemasa, 1975). Its solubility depends primarily on solute concentration, temperature and the concentration of mercury vapour above the water according to Henry’s law (Sanemasa, 1975). This holds for solutions with temperatures above 5 °C, as below this point the vapour phase begins to condense (Sanemasa, 1975).

At neutral pH, oxygen partial pressures greater than 10^{-20} atm can create a solution Eh in which Hg (II) is thermodynamically favoured over Hg (0) (Pourbaix, 1973), however the oxidation of Hg (0) is relatively slow without the presence of stronger oxidants such as hydroxy radicals or peroxide; UV light or ligands, such as hydroxide, nitrate, sulphite and halides (Nelson et al., 2004). In alkaline conditions other oxidation reactions can occur which generally require the presence of dissolved organic matter and ultraviolet light (Cooper et al., 1994; Scholtz et al., 2002; Schroeder et al., 1992; Turner, 1989). Bayer storage lakes frequently contain dissolved organic matter and are exposed to sunlight, therefore the possibility of Hg (0) oxidation to Hg (II) exists. Mercury (II) is significantly more soluble
than mercury (0). For example at 20 °C, the concentration of \( \text{HgCl}_2 = 69,000 \text{ mg/L} \) and \( \text{HgO} = 53 \text{ mg/L} \) (Lide, 1979; Weast, 2005). Therefore, capturing mercury while in its elemental state would prevent the build up to enhanced steady state mercury (II) concentrations in process waters and marine and aquatic environments. The objectives of this study are therefore to:

- Determine the specific chemical and physical characteristics of condensate solution to enable reasonable predictions to be made as to the thermodynamically stable mercury phase(s).

- Use this information to highlight some candidate processes suitable to pursue through experimentation. Such processes would:
  - Target the appropriate mercury oxidation state(s)
  - Demonstrate a high mercury removal efficiency and good kinetics
  - Be stable in alkaline environments

- Conduct experiments on candidate processes

- Conduct capital and operating cost estimates for favourable options

- Make recommendations for treatment options
2 MERCURY SPECIATION AND ANALYSES

2.1 Introduction

In order to select and investigate processes for removing a particular compound or element from a process water or waste water, it is important to have an understanding of the compound chemistry and the chemistry of the solution from which it is to be removed. This information is also important from a health and safety perspective, as different species can have significantly different toxicity ratings. Alumina refinery digestion condensates are generally similar in terms of their physical properties and chemical matrices, but may differ in the concentration of chemical components. Table 2 (see page 12) summarises general analytical data for digestion condensates and also gives some specific data taken from spot analyses of Alcoa’s Wagerup and Kwinana refineries.

Another important requirement when studying the removal of a compound or element is having access to a sound analytical method for measuring the concentration of the compound or element of interest. As stated previously, there have been no reported studies in the available literature on either the chemistry of mercury in alumina refinery condensates (or the chemistry of alumina refinery condensates in general) or on methods for measuring the concentration of mercury in alumina refinery condensates (or solutions of similar chemistry). Due to the lack of information in the aforementioned areas the main aims of the research undertaken in this chapter were as follows:

- To review analytical methods for accurately measuring relatively low (µg/L) quantities of mercury in aqueous solutions and to develop a routine analytical procedure for measuring mercury in alumina refinery process waters.
To investigate the conditions/chemistry of condensate at the point it is produced during the alumina refining process and to determine the mercury species most likely present in condensate.

2.2 Review of analytical techniques for mercury determination

Clevenger et al (1997) conducted a detailed review of the analysis of trace levels of mercury. This review describes a number of available methods and includes a table summarising the applications, limits of detection (LOD) and precision of various analytical methods. The techniques relevant to analysing condensate solutions are summarised below. In the context of this project on the removal of mercury from alumina refinery waters, methods suitable for analysing mercury in aqueous samples will ideally be relatively simple (minimal sample preparation and analysis time) and have detection limits below 1 µg/L. The specifications for the techniques deemed most appropriate for this project are shown in Table 7.

Table 7 Best reported LODs for various mercury analysis techniques

<table>
<thead>
<tr>
<th>Method</th>
<th>LOD</th>
<th>%RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>CV-AAS</td>
<td>0.02 µg/L</td>
<td>2%</td>
</tr>
<tr>
<td>CV-AFS</td>
<td>0.1 ng/L</td>
<td>5%</td>
</tr>
<tr>
<td>ICP-AFS</td>
<td>40 ng/L</td>
<td>N/A</td>
</tr>
<tr>
<td>ETA-AAS</td>
<td>0.1 ng/L</td>
<td>2.7%</td>
</tr>
<tr>
<td>XRFS</td>
<td>60 ng/L</td>
<td>N/A</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>0.08 ng/L</td>
<td>2.7%</td>
</tr>
</tbody>
</table>

Flame Atomic Absorption Spectroscopy (F-AAS) does not have the same sensitivity as flameless techniques, such as cold vapour AAS (CV-AAS). The detection limits for F-AAS are typically 25 mg/L. A precision of 2.9% was achieved by using a gold-coated dual tube atom trap to reduce mercury volatility but the method was not as sensitive as CV-AAS.
Improved detection limits (1 - 5 mg/L) were demonstrated using atomic fluorescence spectrometry (F-AFS) (Clevenger et al., 1997).

Cold vapour AAS allows direct determination of mercury without the need for atomisation. In this technique ionic mercury is reduced in solution and purged out using a carrier gas. Reductants involved in this process include stannous chloride and stannous sulphate. Organomercurial compounds can be oxidised by hot acid and UV irradiation to release the mercury. For solutions containing low concentrations of mercury, the mercury can be pre-concentrated onto noble metals, particularly gold, which are heated to release the mercury back into the carrier gas en route to the detector.

Cold vapour atomic fluorescence spectrometry (CV-AFS) is increasingly becoming more popular than CV-AAS. CV-AFS has a larger dynamic linear range, lower detection limits and less interference than CV-AAS. For example, a LOD of 0.04 µg/L with a precision of 2 – 3% has been reported (Clevenger et al., 1997). In 2000, the US EPA proposed AFS Method 1631 for the analysis of mercury in water (Cai, 2000).

Inductively coupled plasma AFS (ICP-AFS) can achieve an LOD of 200 ppt during multi-element detection and 40 ppt in single element detection (Cai, 2000). ICP atomic emission spectrometry (ICP-AES) is capable of analysing mercury in aqueous samples with a detection limit of 1.3 µg/L with an RSD of 2.8% (Clevenger et al., 1997).

An electrothermal atomisation technique measured trace levels of mercury in drinking water using uncoated graphite furnace cuvettes ((ETA)-AAS) (Clevenger et al., 1997). The method had a reported detection limit of 0.6 µg/L and agreed well with USEPA reference standard values.

The mercury in lead battery plant effluents was measured using X-ray fluorescence spectroscopy (XRFS) following the drying of slurries prior to analysis (Clevenger et al.,
Good reproducibility at µg/L levels was achieved. A preconcentration step using a mixture of carbamites lowered the detection limit to 60 ppt (Clevenger et al., 1997).

Inductively coupled plasma ionisation coupled with mass spectrometry (ICP-MS) has been popular for the analysis of trace metals because of its superior selectivity and detection limits. Measurement of mercury by ICP-MS can however suffer from matrix and memory effects associated with the physical adsorption of mercury to components within the sample transfer part of the instrument. This mercury desorbs and reports to the detector during subsequent analyses, affecting accuracy and precision. ICP-MS analysis of mercury using direct injection nebulisation was shown to have a detection limit as low as 30 ppt for drinking water samples (Clevenger et al., 1997). Rose et al. (2001) compared CV AAS and ICP-MS for mercury analysis during a series of proficiency tests for the Food Analysis Performance Assessment Scheme on behalf of the United Kingdom Ministry of Agriculture, Fisheries and Food. ICP outperformed AAS in the majority of tests.

Stripping voltammetry analysis of mercury potentially has a lower LOD than ICP-MS or AAS (0.2-20 ng/L, Barek, et al (2001)). These methods are generally used for research, however, and are not practical for the analysis of multiple samples where very low detection limits are not required.

Based on the mercury analytical methods reviewed and the equipment available at RMIT University and Alcoa’s R&D labs in WA it was decided to develop a method for measuring mercury in alumina refinery process waters using ICP-MS.
2.3 Development of analytical method for mercury determination in condensates

There were three requirements associated with the research:

- The instrumental methods developed had to be capable for analysing solutions with the complex matrices of alumina refinery condensates.

- The method also had to be capable of detecting mercury at low levels (µg/L).

- The third research component was to develop a sample preparation technique that allowed samples to remain stable prior to being batched up for analysis.

It was decided to develop a method for measuring mercury in condensate using ICP-MS (Agilent Technologies model 4500). This decision was based on the availability of this instrument at RMIT University and a review of instruments that can be used to measure low levels of mercury in aqueous solutions. The first stage of the method development involved investigation of current ICP-MS methods for measuring mercury in aqueous solutions. A method published in a technical paper by Bakowska (2000) was obtained and it was decided to use this method as the basis for developing a method for measuring mercury in alumina refinery process waters. Key aspects of the method developed by Bakowska (2000) are summarised below:
Sample preparation

Samples may be analysed directly by pneumatic nebulization without acid digestion if the samples have been properly preserved with acid and have a turbidity of < 1 NTU at the time of analysis.

Memory effects

In acidic solution, mercury has a tendency to be retained on the injector tip of the torch and in the spray chamber. This leads to memory interferences (commonly referred to as memory effects) as the analyte signal is enhanced due to contribution from a previous high concentration sample. Memory effects lead to the use of long washout times between samples. This can be reduced by off-line addition of gold to samples, which presumably forms an amalgam with mercury allowing it to be effectively washed from the system.

Reagents and standards

Good quality reagents must be used and mercury standards prepared daily. It is recommended that Terbium be used as an internal standard. EPA Method 200.8 specifies the maximum concentration of the calibration standard to be 5 µg/L.

Method testing and development

It was decided to investigate the measurement of mercury in condensate samples using a method very similar to Bakowska (2000). A summary of this method is given below:

- Dilute and acidify sample (1% v/v HNO₃)
- Calibration standards range 0-5 µg/L
- Add gold off-line to samples and standards (100 µg/L)
• Terbium (50 µg/L) internal standard

• Analyse samples within 2 hours of preparation

• Instrument conditions:
  
  o Aux. Gas flow rate – 1.0 L/min

  o Carrier gas flow rate – 1.18 L/min

  o RF Power – 1350 W

  o Nebuliser – cross flow

  o Spray chamber - glass, double pass

  o Spray chamber temperature – 2 °C

  o Sample uptake rate – 0.4 mL/min

  o Sampler cone - Nickel

  o Sampling depth – 9 mm
2.3.1 Memory effect

The first aspect of this method that was investigated was the possibility of memory effects. This was investigated by comparing the Hg concentration values obtained when samples and standards were analysed with and without washout periods in between (washout’s were performed using a 5% nitric acid solution). The only pre-treatment performed on condensate samples prior to analysis was the standard acidification (1% HNO₃) which is usually used for ICP-MS samples. To assist in the assessment of memory effects, another alumina refinery water, with a more complex organic and inorganic matrix (seal water⁵), was used. The project was initially to involve investigating mercury removal from seal water in addition to condensate, however due to time restrictions and level of priority, seal water was not investigated further.

The results of these tests showed that significant memory effects occurred for seal water. These samples required very long washout periods (~30 min) after analysis to ensure subsequent samples were not biased. No significant memory effects were observed for the standards. Based on the aforementioned findings it was decided to make the following alterations to the Bakowska (2000) method to try and reduce/eliminate the long washout periods required for very high concentration samples:

- Increase gold concentration from 100 µg/L to 160 µg/L

- Reduce mercury concentration analysis range from 0-5 µg/L to 0 - 0.8 µg/L

- Do not analyse proceeding sample until [Hg] in blank (0 µg/L standard) is below 0.02 µg/L

⁵ Seal water is a very low flow stream that contains consistently high concentrations of mercury (up to 400 µg/L).
The results obtained using the altered conditions showed that the washout periods were reduced considerably to ~10 minutes. This washout period was considered acceptable and no further alterations to reduce memory effects were investigated.

### 2.3.2 Accuracy

In order to evaluate accuracy it was necessary to obtain accurate mercury data using another method/technique for comparison. The data used for comparison was obtained by McGuinness (2003) at Alcoa World Alumina’s R&D laboratories in WA, using a Nippon Mercury Analyser. The same sample pre-treatment/analysis conditions as used for investigation of memory effects was used for ICP-MS analysis. The data obtained by ICP-MS using the method developed for this project and the Nippon Mercury Analyser is presented in Table 8. The results from the two instruments compared well at approximately 17 µg/L, however there appeared to be a low bias for ICP-MS in the lower concentration samples. The ICP-MS method was regarded as being capable of analysing mercury concentrations similar to those typically found in condensate solution (20 µg/L, Table 2, see page 12).

<table>
<thead>
<tr>
<th>Sample</th>
<th>ICP-MS</th>
<th>Nippon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seal water (µg/L Hg)</td>
<td>17.3, 17.7</td>
<td>17.2, 17.3, 17.5, 16.9</td>
</tr>
<tr>
<td>Condensate (µg/L Hg)</td>
<td>1.2, 1.3, 1.4</td>
<td>2.0, 1.8</td>
</tr>
</tbody>
</table>
2.3.3 The effect of sample storage and pre-treatment

It was envisaged that samples from mercury removal experiments would require some form of pre-treatment and storage. As a result, the following storage conditions and pre-treatment methods were investigated:

- Effect of acidification prior to storage
- Effect of filtration
- Effect of storage time

The effect of the type of container used for storage was not investigated as previous studies had shown that glass is the most suitable material for storage. Some refinery process waters can contain organics that precipitate upon acidification, potentially trapping mercury, and that these compounds adhere to plastic and Teflon (L McGuiness, [Alcoa World Alumina] 2003, pers. comm., 21 March).

Based on the results presented in Table 9, filtration, acidification and storing samples for up to 4 days in glass culture tubes with minimal headspace does not appear to have any significant effect on mercury analysis.

**Table 9 Mercury preservation investigation**

<table>
<thead>
<tr>
<th>Age of sample</th>
<th>Preservation method</th>
<th>Mercury concentration (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condensate - 4 days</td>
<td>Filter - acidify (20 mL sample + 5mL concentrated HCl) - store in culture tube, minimal head space</td>
<td>1.99</td>
</tr>
<tr>
<td>Condensate - 4 days</td>
<td>Filter - no acid - store in culture tube, minimal head space</td>
<td>1.95</td>
</tr>
<tr>
<td>Condensate - 4 days</td>
<td>No Filtration - acidify – store in culture tube, minimal head space</td>
<td>2.54</td>
</tr>
<tr>
<td>Condensate - 4 days</td>
<td>No filtration – no acidification – store in culture tube, minimal head space</td>
<td>1.85</td>
</tr>
<tr>
<td>Condensate - 3 hours</td>
<td>No filtration – acidification</td>
<td>1.81</td>
</tr>
<tr>
<td>Condensate - 3 hours</td>
<td>Filtration - acidification</td>
<td>1.95</td>
</tr>
</tbody>
</table>
### 2.3.4 The sample storage method developed for the project

Samples and standards were prepared within 2-3 hours of analysis as follows:

- Transfer amount required (acidified sample or standard) into 50 mL volumetric flask
- Add 1 mL 50:50 (vol) concentrated nitric acid : milli-Q water
- Add ~20 mL milli-Q water
- Add 2 mL 4000 µg/L Au standard
- Add 1 mL 4000 µg/L Tb standard
- Make up to 50 mL with milli-Q water

An experimental error of ± 1.5 % is associated with sampling, sample preparation and sample preservation.

### 2.4 Investigation of mercury speciation in condensate

Although all Bayer refineries operate using the chemistry developed by Karl Bayer, the specific operating conditions of each is determined to a large degree by the composition of the bauxite from which alumina is extracted. Process waters, particularly condensate, that are derived from the digestion processes in Bayer refineries world wide are generally similar in terms of chemistry because the digestion process is alkaline and chemically reducing. The solutions produced will be affected by the digest temperature and the types and concentration of organics within the bauxite. Similarly, the mercury concentration within these solutions will be influenced by the mercury concentration in the bauxite feed. Despite subtle chemical
differences between such process waters from specific refineries, all will be chemically reducing and will potentially contain mercury in the same oxidation state(s).

Western Australian bauxite is sourced from the Darling Scarp near Perth and contains aluminium hydroxide mostly in the form of gibbsite. The Alcoa refineries in Western Australia at Kwinana, Pinjarra and Wagerup (see Figure 12) source their bauxite from mines within close proximity along the Darling Scarp. The bauxite is therefore very similar in terms of its mineralogical and organic composition and as such the refineries operate using a similar digestion temperature of approximately 145 °C. The solutions tested in this study were sourced from the Kwinana refinery, a suitable surrogate for digestion condensate from all three Alcoa refineries.

![Location of Alcoa World Alumina's refinery operations within Western Australia](image)

**Figure 12** Location of Alcoa World Alumina’s refinery operations within Western Australia

Complex analytical techniques, such as separation of species by gas chromatography followed by microwave induced plasma atomic emission spectrometry; flameless atomic absorption spectrometry; mass spectrometry or inductively coupled plasma mass spectrometry (Emteborg, 1996, Qian, 2001) exist to speciate mercury in solution. These analyses, however, are confined to specialised laboratories and such speciation could not be conducted within the
RMIT or Alcoa laboratories. In addition, it is the experience of those involved in such analyses that it would be highly probable that transport and storage of samples would affect the integrity of the samples prior to analysis due to speciation changes during transit (N. Bloom [Frontier Geosciences] 2003, pers.comm., 10 September). For this reason it was decided to determine the predominant species of mercury in condensate using an indirect method that involved measuring the Eh and pH of fresh condensate solutions using suitable monitoring equipment. From these results, the mercury phase was predicted by comparing the monitoring results with thermodynamic data displayed on a Pourbaix diagram.

Digestion condensate was sampled from the Kwinana refinery at 95 °C and allowed to cool to ambient temperature in Polytetrafluoroethylene (PTFE) sealed borosilicate bottles with no headspace. The sample remained in this condition until measurement. The measurement was conducted using the equipment listed in Table 10. The Eh/pH measurements are plotted on a modified Pourbaix diagram (see Figure 13) on which the boundary separation lines have been re-calculated for a solution containing 20 µg/L Hg, the typical condensate Hg concentration (see Table 2, page 12). To demonstrate the effect of mercury concentration on the positioning of the stability fields, an extra line (in red), denoted (11' 20 mg/L), has been calculated for a concentration of 20 mg/L Hg.
Table 10  Equipment used for measurement and logging

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Make/model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meter/data logger</td>
<td>Dual channel TPS WP-80D</td>
</tr>
<tr>
<td>Temperature probe</td>
<td>TPS pH-mV-temperature</td>
</tr>
<tr>
<td>Software</td>
<td>TPS WP series software</td>
</tr>
<tr>
<td>pH electrode</td>
<td>IJ44 BNC connector double junction &quot;A&quot; glass tip</td>
</tr>
<tr>
<td>Redox probe</td>
<td>TPS combination platinum IJ Ag/Ag Cl</td>
</tr>
</tbody>
</table>

Figure 13  Eh and pH measurements for Kwinana digestion condensate overlaid onto a Pourbaix diagram with stability fields re-calculated for 20 µg/L mercury

Note: The line in red (11’ 20 mg/L) has been calculated for a concentration of 20 mg/L Hg to demonstrate the effect of mercury concentration on mercury speciation.
The major observation from the diagram, based on a simple water system, was that the Eh and pH for condensate solution places it very close to the phase separation line between Hg (0) and Hg(OH)_2. Hg (0) is predicted as the thermodynamically favoured state, however, according to Pourbaix (1976), if the solution was in contact with greater than 10⁻²⁰ atm of oxygen, this stability will become tenuous because a solution Eh, in which Hg(II) is the thermodynamically favoured state, will be created. Because the Eh and pH conditions measured for condensate were close to the Hg (0) and Hg (II) phase separation lines, purging experiments were conducted using air and other gases (see Figures 14 and 15) to determine how contact with these gases would affect the Eh/pH conditions and therefore predicted oxidation states for mercury under those conditions.

The tests were conducted using Kwinana digestion condensate samples, which were collected at a discharge temperature of 90 °C and again stored into PTFE sealed Borosilicate bottles. The bottles were cooled to ambient temperature using ice en route to the laboratory to allow the measurements to be conducted within the temperature range defined by the measurement equipment and to avoid loss of volatiles. Care was taken to ensure no headspace was present in the sample jar to minimise dissolution of oxygen into the condensate and loss of Hg (0) to the headspace. Similarly, any transfer of condensate between containers in preparation for the data logging was done under a flow of nitrogen.

During each test the Eh, pH and temperature of two condensate sub-samples were logged simultaneously at intervals of 20 seconds or 8 minutes depending on the rate of change of Eh and/or pH. Magnetic stirrer bars were placed into the sample jars, situated on magnetic stirrers for solution agitation. The headspace of one sample jar was purged with nitrogen gas and sealed with Parafilm® to act as a control. The second jar was also covered with Parafilm® but not perfectly sealed to allow the chosen purge gas, nitrogen, air or carbon dioxide to ventilate.

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6 Kwinana condensate is very similar to Wagerup digestion condensate because it is produced under almost identical digestion conditions and is sourced from bauxite mined from the same region of the Darling Scarp in Western Australia and therefore possesses a similar organic and mineral composition.
AR grade nitrogen and carbon dioxide from BOC gases were used. Laboratory instrument air produced from a compressor was used.

The results of the condensate purging experiments are shown in Figures 14 and 15. The equations for the individual phase separation lines are shown on the graphs. It was observed that condensate was very poorly buffered in terms of Eh and the thermodynamically stable phase of mercury was initially elemental, but a very small oxygen addition, such as that associated with nitrogen addition via unforseen seal leaks etc, shifted the predicted favoured oxidation state of mercury from Hg(0) towards Hg(II) (see Figure 15). Where air was purged through the solution, the Eh increased further into the Hg(II) stability region. It was also observed that the purging volatilised the ammonia present in the condensate (see Table 2, page 12), caused a drop in solution pH. For the 18-hour data, nitrogen purging removed 49% of the initial ammonia content (ammonia measured as N\textsuperscript{7}), whereas air purging removed 33%. Maintaining a nitrogen headspace removed no ammonia from solution.

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\textsuperscript{7} The concentration of ammonia is determined by reacting the solution with hypochlorite in slightly alkaline solution (pH between 8 and 11.5) to form monochloramine. In the presence of phenol, sodium nitroprusside and excess hypochlorite, indophenol (an intensely blue coloured compound) is formed. The ammonia concentration is determined colorimetrically at 630 nm against standards made from 0 to 36 ppt in deionised water (Lachat Instruments, 1994)
Chemistry changes of treated condensate solutions overlayed onto stability fields diagram for mercury at 0.00002 g/L Hg.

Legend:
Condensate held with a nitrogen headspace for 18 hours
Condensate held with a nitrogen headspace for 48 minutes
Condensate purged for 18 hours with air
Condensate purged for 48 minutes with air

Figure 14 Changes in Eh and pH for condensate following gas sparging of air and nitrogen overlaid onto an Eh/pH diagram re-calculated for 20 µg/L mercury at 1 Atm and 20 °C.

Figure 15 Changes in Eh and pH for condensate following gas sparging of air and nitrogen overlaid onto an Eh/pH diagram re-calculated for 20 µg/L mercury at 1 Atm and 20 °C. Area expanded to show greater detail.
At ambient temperature, an increase in solution Eh occurred due to oxygen addition to the condensate. As a result Hg (II) became thermodynamically favoured over Hg (0), although the final solution Eh was not positioned far above the Hg(II)/Hg(0) phase separation line, particularly at pH 10 (see Figure 15). Because the Eh and pH conditions for mercury in condensate are so close to the Hg(0) / Hg(II) phase boundary, it may be possible that both forms of mercury co-exist in condensate within the refinery, however, in the refinery process condensate typically exists at 90 °C. Oxygen solubility at this temperature is only 2.8 mg/L, compared to 8.32 mg/L at 25 °C. Because oxygen is less soluble at higher temperatures, the solution Eh would be less affected by oxygen in the vapour phase, leading to lower rates of mercury oxidation. In addition, oxidation of elemental mercury is quite slow unless strong oxidants (Nelson et al, 2004), UV light and dissolved organic matter (Cooper et al, 1994; Scholtz et al, 2002; Schroeder et al, 1992; Turner, 1989) or chloride ions (de Magalhaes and Tubino, 1995) are present. These agents and/or chemical species are not likely to be present in condensate within the refinery process and, as such, it is expected that conversion of Hg(0) to Hg(II) would be quite slow.

Once condensate is deposited within a lake body, the solution chemistry alters. The oxygen concentration, due to the ambient temperature within the lake and exposure to air, increases. In addition, the presence of sunlight, organic matter and possibly hydroxy radicals, could facilitate the formation of Hg(II) (Cooper et al, 1994; Scholtz et al, 2002; Schroeder et al, 1992; Turner, 1989). Because Hg(II) is far more soluble than Hg(0) (Lide, 1979; Weast, 2005), the concentration of mercury in the lake could significantly increase and, in addition, anaerobic bioactivity within an anoxic water body could readily convert Hg(II) to methyl mercury, which is highly toxic and accumulates one million times in concentration as it moves up the food chain. It is preferable to remove Hg(0) from condensate prior to oxidation occurring in a lake environment.
Elemental mercury is volatile and, as such, may be sparged from the solution under appropriate conditions, presenting a mercury removal opportunity. Although it is unlikely that oxidation would be rapid enough to form Hg(II) if air was used as the sparging gas, further sparging experiments were conducted using carbon dioxide gas because it prevents oxidation and because of its availability from refinery combustion stacks. When carbon dioxide was sparged into the solution, the pH dropped significantly due to the dissolution of the gas and removal of ammonia (see Figure 16). Carbon dioxide caused the pH of the solution to reduce, but did not affect Eh, allowing the predicted Hg state to remain as elemental. Combustion stack gases may be a viable sparging source for a removal process, however the engineering logistics associated with plumbing stack gases to a column would be complex.

![Chemistry changes of treated condensate solutions overlayed onto stability fields diagram for mercury at 0.00002 g/L Hg](image)

**Figure 16** Changes in Eh and pH for condensate following gas sparging of carbon dioxide and nitrogen overlaid onto an Eh/pH diagram re-calculated for 20 µg/L mercury at 1 Atm and 20 °C
2.5 Conclusions

The following conclusions were drawn from the research described in this chapter:

- ICP-MS is a capable method for analysing mercury in alumina refinery waste waters.
- Acidified seal water and condensate samples can be stored in glass with no significant loss of mercury.
- Based on Eh and pH measurements elemental mercury is the thermodynamically favoured phase, however the positions of these conditions on a Pourbaix diagram are very close to the phase separation line between Hg(0) and Hg(OH)₂.
- The oxidation of elemental mercury is relatively slow without the presence of other agents (Canela and Jardim, 1997; Mroczek, 2000 and Nelson et al, 2004) and, as such, it is expected that Hg(0) would be relatively stable in condensate within plant operations.
- Exposure to excess oxygen and other agents in a lake environment may make mercury in condensate more susceptible to oxidation.
- Because the Eh and pH conditions for mercury in condensate are so close to the Hg(0) / Hg(II) phase boundary, it may be possible that both forms of mercury co-exist.
3 MERCURY REMOVAL USING COMMERCIALy AVAILABLE ADSORBENTS

3.1 Introduction

Based on the literature reviewed in section 1.5, it is clear that a number of different activated carbon varieties are capable of removing mercury from simple aqueous solutions. Unfortunately there is limited literature on the removal of mercury from complex aqueous solutions that exist in “real” process waters, particularly those with high alkalinity and relatively high organic concentrations. It is therefore difficult to predict with any confidence whether activated carbon would be capable of efficiently removing mercury from alumina refinery process waters. Although there is no indication that a high pH would hinder removal by carbon, the organics content (Leeder, 2002; Leeder, 2004a; Leeder 2004b) of condensate could have an adverse effect on mercury removal (see Table 2, page 12) as it is possible that organics could compete with mercury for removal sites.

Although mercury can exist in the environment in three oxidation states (0, 1 and 2), the vast majority of academic and industrial research has been concerned with the removal of Hg(II) (Amyot et al, 1994; Amyot et al, 1997; Lalonde, et al., 2001; Mason et al, 1994; Vandal et al, 1991; Yamamoto, 1996) because of its prevalence in wastewaters and the environment. A variety of activated carbon types, including chemically impregnated carbons, have been investigated and developed for removal of Hg(II), whereas little research has been published on activated carbon adsorption of Hg(0), the mercury state likely to be prevalent in condensate based on the results described in section 2.4.

The main aim of the research undertaken in this chapter was to investigate mercury removal from condensate using various types and forms of activated carbon and another commercially available sorbent (impregnated mineral). These materials were chosen for two main reasons.
Firstly, virgin activated carbon is an industry standard for use in mercury removal and the ability of amended carbons and other materials to remove mercury can be directly compared with virgin activated carbon under the specific conditions employed during the tests. Secondly, each of these materials is expected to be capable of removing both elemental and oxidised mercury.

The specific aims of the research undertaken in this chapter were as follows:

1. Investigate sorption of the dissolved elemental mercury presumably present in condensate using various sorbents
2. Gain an understanding of the impact of other dissolved species on adsorption of mercury
3. Investigate the stability of various sorbents in alumina refinery condensate

3.2 Experimental

3.2.1 Materials

The following materials were used as received unless stated otherwise: virgin activated carbon (Norit RB4), sulphur activated carbon (Norit RBHG4), sulphur activated carbon (Envirotrol Hg Free), silver activated carbon (Norit 0.8 Ag), powdered activated carbon (Norit AZO), powdered activated carbon (Norit D10), a proprietary impregnated mineral (PIM). Characteristics of these materials are discussed in section 3.3.1.

3.2.2 Batch test procedures

Batch tests were conducted using two different procedures. The first procedure involved mixing using a rotating water bath at ambient temperature in which various masses of carbon
were added to 23 mL condensate solution in 25 mL culture tubes and rotated end-over-end for
the prescribed time. The tests were conducted at ambient temperature. The second procedure
involved mixing a pre-determined amount of carbon in 500 mL of condensate using a
magnetic stirrer and stirrer bar in a 500 mL round bottom flask. These tests were also
conducted at room temperature.

3.2.3 Up-flow column tests – apparatus and procedure

Up-flow column testing was conducted using the experimental set-up shown in Figures 17
and 18. Two glass columns were constructed with a glass frit at the base and a removable
ground glass joint at the top to allow the sorbent materials to be inserted. The columns were
either used in parallel, to run two simultaneous tests, or in series (see Figure 18) to double the
effective retention time for a single test. Solutions were pumped up through the columns from
the base via a peristaltic pump operated by an overhead laboratory stirrer. Solutions were run
at the flow rate necessary to produce the required empty bed contact time (EBCT). The coarse
flow rate was controlled by adjusting the speed of the overhead stirrer used to operate the
peristaltic pump and by adjusting the bypass valve, which directs excess flow back to the feed
vessel. Fine control was made by adjusting a flow control valve at the base of the flow meter.
Figure 17 Schematic diagram of up-flow column testing apparatus

Figure 18 Up flow column apparatus set up in series formation
3.2.4 Sampling from fixed bed columns

Blanks – Blank samples were collected from a tap inserted between the outlet of the flow meter and the column entry point for one of the column units (tap is not visible in Figure 18). These blank samples were taken to monitor the possible effects of the plastic tubing, pumping action of the peristaltic pump and the increase in feed reservoir headspace that occurs during testing.

Samples – Prior to collection of the samples the column was isolated by turning off the tap at the top of the column (to avoid backflow of solution). The solution was then allowed to pass through the tap from which the sample was required for 5-10 minutes, before sample collection.

3.2.5 Powdered activated carbon filter aid tests – apparatus and procedure

The powdered activated carbons (a 50:50 volume mixture of Norit AZO and Norit D10) were tested using a Buchner funnel, side-arm flask and vacuum line. The carbon bed was formed in the Buchner funnel on top of a Whatman No. 1 filter paper, and pre-determined portions of condensate were sucked through the carbon bed using vacuum. Blank tests were also conducted using only a Whatman No. 1 filter paper. The bed volume was established to provide a specific residence time. Details of the PACs used in these tests are given in Table 11. Both PACs were used as supplied by the manufacturer.
3.2.6 Sample collection / preservation

Duplicate samples were collected in all tests. The first duplicate was collected in an A Grade 20 mL volumetric flask and transferred to a 25 mL culture tube, followed by the addition of 5 mL concentrated hydrochloric acid (HCl, AR Grade). The second duplicate sample was collected in a 25 mL culture tube and centrifuged at 1000 rpm for 1 minute. 20 mL of this sample was then transferred to another culture tube followed by addition of 5 mL concentrated HCl.

3.2.7 Standards and Reagents

Mercury calibration standards (0.0, 0.2, 0.4, 0.8 μg/L) were prepared from a fresh 20 μg/L Hg solution. The 20 μg/L Hg solution was prepared from a fresh 2000 μg/L Hg solution, which was prepared using a 1000 mg/L mercury standard solution (BDH Chemicals).

4000 μg/L Tb internal standard solution was prepared from a 0.985 g/L Terbium nitrate stock solution prepared using terbium nitrate pentahydrate (99.9% Aldrich).

4000 μg/L Au solution was prepared from a 1000 mg/L Au standard solution (Spectrosol APS Chemicals).

Milli-Q water was used for all dilutions.
3.2.8 Methods

3.2.8.1 ICP-MS Analysis

Mercury analysis was conducted using an Agilent Technologies 4500 ICP-MS as described in Chapter 2.

3.2.8.2 ICP-OES Analysis

Trace metals concentration were determined using a Perkin-Elmer, Optima 3000 inductively coupled plasma atomic emission spectrometer (ICP-AES). All samples were diluted (milli-Q water) and acidified (concentrated hydrochloric acid) prior to analysis. The detailed method is described by Eyer and Leavy (1997).

3.2.8.3 Chloride and sulphate analysis

Capillary electrophoresis (CE) was used to determine chloride (Cl\(^-\)) and sulphate (SO\(_4^{2-}\)) concentration. Electrophoresis is a technique where charged ions or molecules in an electrolyte are separated by differential migration under an applied electric field. The detailed method is described by Mullett and Houghton (1999).
Organic carbon concentration was determined quantitatively using a 1010 Total Organic Carbon Analyser (O-I Analytical). Samples were diluted (milli-Q water) and acidified with diluted orthophosphoric acid solution (conc. orthophosphoric acid, AR, BDH Chemicals) prior to analysis. The organic carbon concentration is then determined as follows:

1. The instrument is calibrated using a series of organic carbon standards prepared from potassium hydrogen phthalate (Aldrich) and milli-Q water.

2. Samples are then automatically injected into the instrument reaction chamber where they are reacted with further acid (5% w/v ortho phosphoric acid) to convert any remaining inorganic carbon (CO$_3^{2-}$) to carbon dioxide, which is then removed by a stream of nitrogen (instrument grade).

3. The remaining organic carbon is then oxidised to CO$_2$ using sodium persulphate (200g/L) and UV light.

4. The CO$_2$ liberated is then detected using an IR detector, and used to evaluate the amount of organic carbon in the original sample.
3.2.8.5  **BET specific surface area**

Surface area and pore size distribution data were obtained using a Micromeritics ASAP 2000 surface area analyser. Samples were pre-treated by heating under vacuum at 250°C overnight. A 40 second equilibration interval was used for all sample analyses.

3.2.8.6  **Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Analysis (EDS)**

The images and Energy Dispersive Spectroscopy (EDS) analyses were obtained using an FEI Quanta 400 FEG scanning electron microscope (SEM). This "field emission" instrument also features low vacuum (LV) operation that prevents charging on the sample during analysis. Images were obtained using Secondary Electron (SE) imaging that highlights topography in the sample. EDS data were obtained using spot or area analyses. The modern EDS detector and pulse processor, combined with the field emission source, provide higher x-ray count rates and improved element detection compared to earlier instruments.

3.2.8.7  **Mixed acid digest followed by ICP-OES for sulphur determination in solids**

Sulphur in the impregnated mineral (PIM) was determined by dissolving the material in an acid mixture containing concentrated HCl, HClO₄, HNO₃ and HF. The aqueous samples were then pre-oxidised using potassium dichromate to convert the sulphides present to sulphates. The acid digest was conducted at room temperature for 1 hour. The resulting solution was diluted accordingly and the sulphur content analysed by ICP-OES.
3.2.9 Pre-treatment of solution – adjustment of Eh and mercury concentration.

To ensure that experiments were conducted under conditions that would most accurately represent the condensate solutions present in a refinery environment, it was necessary to adjust the condensate prior to experimentation. The two key aspects of condensate which were expected to change between the time of collection and testing were mercury concentration and solution Eh. The mercury concentration in condensate was not expected to be stable due to mercury being predominantly present in the volatile elemental form and stored samples have the potential to lose mercury over time. For this reason it is necessary to measure the mercury concentration of the test solutions prior to experimentation and if necessary, increase the concentration to ~20 µg/L (a concentration typically encountered in digestion condensate) to enable good sensitivity in the tests. Conducting experiments at elemental mercury concentrations typically encountered in digestion condensate is also beneficial from a process evaluation viewpoint as it is important to understand the performance of a process under likely operating conditions.

Oxygen addition to condensate undoubtedly occurs during sampling and transport, leading to an increase in solution Eh. This could result in conversion of the pre-existing elemental mercury to mercury (II). In order to return the condensate to its original Eh state, it was required that solution Eh also be measured prior to experimentation and adjustments to lower the Eh made if necessary.

At 25 °C the solubility of elemental mercury in water is 0.064 mg/L, which occurs when the vapour phase concentration is in equilibrium with the solution phase concentration (Lide, 1979; Sanemasa, 1975; Waite et al, 2002). Mercury concentrations in Alcoa’s alumina refinery condensates vary from 4 µg/L – 35 µg/L (see Table 2, page 12). Although concentrations of ~35 µg/L have been measured, typical concentrations are in the vicinity of 20 µg/L (Armanios et al, 2001; Armanios et al, 2002a; Armanios et al, 2002b; McGuiness,
Since 20 µg/L has been measured as a typical mercury concentration for condensate, it was the target concentration for the test work. In addition, a concentration of 20 µg/L provides good analytical sensitivity for determining the effectiveness of various processes.

A number of different procedures were attempted to produce reasonably large quantities (~20 L) of low Eh condensate at approximately 20 µg/L mercury for use in tests. These procedures included:

1) Bubbling hydrogen gas through condensate (to lower solution Eh) followed by addition of liquid elemental mercury, which was left to dissolve and reach close to saturation

2) Bubbling hydrogen through condensate followed by addition of mercury (II) chloride solution, which would be reduced due to the low redox potential to mercury (0)

3) Bubbling hydrogen through condensate followed by passing a stream of nitrogen gas saturated with elemental mercury vapour into the headspace of a container containing the reduced condensate sample.

Of the procedures described above none were able to generate ~20 L of low Eh solution with a suitable mercury concentration in a reasonable amount of time (< 3 days).

Procedure 3 described above was, however, successful when a lower volume of condensate (~12 L) was used. This procedure was therefore adopted for preparation of the solutions for testing.
3.3 Results and Discussion – Treatment of condensate

3.3.1 Characterisation of materials investigated

The characteristics of the materials tested in this chapter are shown in Table 11. SEM micrographs of each material are shown in Figures 19 – 24. The impregnated mineral (PIM) is the proprietary product of a company and the “impregnation” process was not volunteered by the manufacturers. XPS analysis was conducted to detect a possible impregnate (see Figure 28) in this material. The XPS method is highly surface specific due to the short range of the photoelectrons that are excited from the solid. This analysis can only be regarded as a relative indication of surface elemental composition as no elemental calibrations were made. In addition volatile compounds and elements such as sulphur are not stable under the high vacuum conditions used. Tin, which is a known amalgamating agent for mercury, (Biester, et al, 2000) was detected in trace levels by XPS, however because of the low levels it is unlikely that tin was the main impregnate to assist mercury removal. A mixed acid digest followed by sulphur analysis showed that the impregnated mineral did contain sulphur (4.7% S w/w.). In addition, an Energy Dispersive X-Ray Analysis (EDS) was conducted on the impregnated mineral at low vacuum confirming the presence of sulphur (see Figure 27). EDS was also used to identify sulphur crystals which were visible on SEMs of the material surface and in the edge structures of silica based conglomerates (see Figure 29).
### Table 11 Characteristics of adsorbents

<table>
<thead>
<tr>
<th>Material</th>
<th>Source company</th>
<th>Design use</th>
<th>Pre-treatment</th>
<th>Surface area (m²/g)</th>
<th>Average pore diameter (Å)</th>
<th>Particle size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Norit virgin activated carbon (VACN)</td>
<td>Norit Pte Ltd, Singapore</td>
<td>Air – purification of odours. Precursor to SACN.</td>
<td>Steam activation, extrudation</td>
<td>1,015²</td>
<td>16.0</td>
<td>Extruded &gt;3.35 mm</td>
</tr>
<tr>
<td>Norit silver impregnated activated carbon (AgACN)</td>
<td>Norit Pte Ltd, Singapore</td>
<td>Purification and sterilisation of water.</td>
<td>Steam activation, extrudation 0.1% Ag impregnation⁹</td>
<td>1250¹⁰</td>
<td>19.0</td>
<td>Extrudate (0.8 mm diameter)</td>
</tr>
<tr>
<td>Norit sulphur impregnated activated carbon (SACN)</td>
<td>Norit Pte Ltd, Singapore</td>
<td>Mercury removal from vapours</td>
<td>Steam activation, extrudation min 10% S impregnation</td>
<td>~880¹¹</td>
<td>16.3</td>
<td>Extruded &gt;3.35 mm</td>
</tr>
<tr>
<td>Envirotrol sulphur impregnated activated carbon (SACE)</td>
<td>Envirotrol carbon purchased from Envirotrol Inc, PA, USA</td>
<td>Mercury removal from vapours and waters.</td>
<td>Steam activation, extrudation 13% S (as S₂) impregnation</td>
<td>1,000¹²</td>
<td>21.3</td>
<td>Granular ~2.5 mm</td>
</tr>
<tr>
<td>Norit AZO activated carbon (PACNA)</td>
<td>Norit Pte Ltd, Singapore</td>
<td>Removal; of inorganics, particularly mercury from caustic soda</td>
<td>Steam activation</td>
<td>700¹³</td>
<td>30.4</td>
<td>Powder, D₉₀ &lt;37 µm</td>
</tr>
<tr>
<td>Norit D10 activated carbon (PACND)</td>
<td>Norit Pte Ltd, Singapore</td>
<td>Removal of odorous organics from water</td>
<td>Steam activation</td>
<td>639¹⁴</td>
<td>24.9</td>
<td>Powder, D₉₀ &lt;140 µm</td>
</tr>
<tr>
<td>Impregnated mineral (PIM)</td>
<td>N/A</td>
<td>Mercury removal from vapours and waters.</td>
<td>Not available on data sheet¹⁵. Base material vermiculite.</td>
<td>59.5¹⁶</td>
<td>N/A</td>
<td>~3 mm flakes</td>
</tr>
</tbody>
</table>

---

² Data from Norit data sheet.
⁹ Data from Norit data sheet. XPS analysis confirmed silver on surface present exclusively as silver metal (Ag⁰).
¹⁰ Total = 1250 (manufacturer data sheet), 1194 (BET analysis). External = 360 (BET analysis).
¹¹ Measured BET surface area is an approximation. A significant amount of sulphur evolved from the sample during sample pre-treatment.
¹² (min. pre- S impregnation)
¹³ Data from Norit data sheet.
¹⁴ Data from Norit data sheet.
¹⁵ XPS suggests possible impregnation with tin, however sulphur also present.
¹⁶ BET analysis
Figure 19  SEM micrograph of VACN

Figure 20  SEM micrograph of AgACN
Figure 21. SEM micrograph of SACN

Figure 22. SEM micrograph of SACE
Figure 23 SEM micrograph of PACNA

Figure 24 SEM micrograph of PACND
Figure 25 SEM micrograph of PIM. Sulphur crystals on surface
(Courtesy of Dr Alex Badalyan, University of South Australia)

Figure 26 SEM micrograph of PIM Sulphur crystals on surface
Figure 27 EDS trace of PIM showing relatively high sulphur peak

Figure 28 XPS trace of PIM showing the presence of tin
3.3.2 Removal of mercury from condensate using different sorbents

Four sorbent materials were assessed for their capacity to adsorb mercury from condensate (see Table 11). The sorbents were:

- An extruded virgin carbon (VACN, industry standard)
- A granular sulphur impregnated carbon (SACE)
- An extruded silver impregnated carbon (AgACN)
- A proprietary impregnated mineral (PIM), a sulphur impregnated vermiculite. The AgACN and PIM materials were used as supplied (refer to Table 11).
The VACN and SACE carbons were pre-treated (crushed and dry sieved) to obtain a smaller particle size similar to the AgACN to ensure a more accurate comparison between these materials.

3.3.2.1 Batch tests

The four adsorbents (VACN, SACE, AgACN and PIM) were tested at two dosages; 0.2 and 2.0 g/L. The higher dose samples were agitated end-over-end in 25 mL culture tubes, while the lower dose samples were mixed (using a magnetic stirrer) in a round bottom flask with a volume of 500 mL to facilitate a more accurate weighing of the sample and to improve the sensitivity of the test. The amount of mercury adsorbed was reported as a percentage of the mass of the sorbent and the removal from solution was reported as a percentage of the start concentration.

The results of the batch tests are given in Table 12. All sorbents were capable of removing a significant amount of mercury under the testing conditions used. The AgACN clearly removed the highest amount of mercury under both sets of testing conditions (83.7 and 74.4% respectively).
Table 12 Batch test results
Conditions: T= 22°C, particle size VACN and SACE = 0.5 – 1.4 mm, AgACN = 0.8 mm, Impregnated mineral = 3 mm.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Sorbent concentration (g/L)</th>
<th>Ratio of sorbent concentration (g/L) to mercury concentration (g/L).</th>
<th>% Mercury removal*</th>
<th>Mercury adsorbed (% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (blank)</td>
<td>N/A</td>
<td>N/A</td>
<td>3.9</td>
<td>N/A</td>
</tr>
<tr>
<td>VACN‡</td>
<td>0.2</td>
<td>10,256</td>
<td>47.8</td>
<td>0.005</td>
</tr>
<tr>
<td>AgACN‡</td>
<td>0.2</td>
<td>10,256</td>
<td>74.4</td>
<td>0.008</td>
</tr>
<tr>
<td>PIM‡</td>
<td>0.2</td>
<td>10,256</td>
<td>34.3</td>
<td>0.004</td>
</tr>
<tr>
<td>SACE‡</td>
<td>0.2</td>
<td>10,256</td>
<td>56.7</td>
<td>0.006</td>
</tr>
<tr>
<td>VACN+</td>
<td>2.0</td>
<td>102,564</td>
<td>50.7</td>
<td>0.0005</td>
</tr>
<tr>
<td>AgACN+</td>
<td>2.0</td>
<td>102,564</td>
<td>83.7</td>
<td>0.0009</td>
</tr>
<tr>
<td>PIM+</td>
<td>2.0</td>
<td>102,564</td>
<td>53.7</td>
<td>0.0005</td>
</tr>
<tr>
<td>SACE++</td>
<td>2.0</td>
<td>102,564</td>
<td>80.8</td>
<td>0.0008</td>
</tr>
</tbody>
</table>

*Initial mercury concentration = 20.3 µg/L
‡Tests conducted in culture tubes – mixed end over end
§Tests conducted in round bottom flasks - mixed with stirrer flea.

At the higher doses, the PIM performed similarly to VACN, while the SACE performed similarly to the AgACN. The poor performance of PIM may have been due to the poor mixing that was observed in the round bottom flask due to the flakey nature of the silicate mineral (vermiculite) causing it to partially float. From the results presented in Table 12, it is evident that decreased mercury loading occurred with an increased material loading for all of the sorbents tested. This implies that a physical adsorption process is occurring whereby the degree of adsorption is a function of mercury concentration in solution. A higher solution concentration exerts a higher driving force to physically adsorb the mercury (Anoop Krishnan and Anirudhan, 2002b). This observation also suggests that for the impregnated sorbents, physical adsorption is the major process occurring and that chemisorption which is expected to occur for the sulphur and silver impregnated materials is limited. Mechanisms of sorption for the materials tested are detailed in section 3.2.2.5.
Based on the reasonably promising results in terms of % mercury removal obtained in the batch tests it was decided to investigate mercury removal from condensate in more detail using the up-flow column apparatus described in section 3.1.

### 3.3.2.2 Up-flow column screening tests for mercury removal

Prior to conducting detailed up-flow column experiments using the sulphur impregnated carbons (SACE and SACN) in fixed bed columns, screening tests were conducted with these materials to investigate their stability. These tests were conducted due to sulphur being susceptible to dissolution under alkaline conditions. It was possible that the stability of the two sulphur impregnated carbons may differ because Envirotrol, the manufacturers of SACE, claim that the sulphur is impregnated purely as the sulphur dimer, which is unique for sulphur impregnated carbons. The mercury concentration of the condensate used in the initial up-flow column screening tests was only 2 µg/L as the condensate used in these tests was not altered as discussed in section 3.2.8. The low mercury concentration in the condensate used, however, would not prevent an assessment of the stability of the carbons in condensate.

Complete mercury removal occurred using SACE and SACN over the entire testing period (15 bed volumes) using a residence time of 28 minutes, however significant reductions in treated condensate pH occurred. The pH of condensate treated with SACE dropped from 10.7 to 2.7 after 2 bed volumes were treated and returned to 6.1 after 15 bed volumes were treated. The significant drop in pH was assumed to be most likely due to sulphur dissolution, which is discussed further in section 3.3.2.5.
Further column tests were conducted using a condensate solution with enhanced mercury concentration and Eh/pH matched to resemble in-situ refinery condensate (Section 3.2.8). These tests were conducted to assess mercury removal from condensate using VACN, AgACN and PIM. The results of the quantitative column tests are shown in Figures 30 - 32. After approximately 40 bed volumes the VACN appeared to reach saturation compared to approximately 60 bed volumes for the PIM. Over the entire period of the test (170 bed volumes) the AgACN consistently removed greater than 80% of the influent mercury using each of the four residence times studied (2.5, 5.0, 7.5 and 10.0 min). Unlike AgACN, residence time had a significant effect on the extent of mercury removal using PIM, with increasing mercury removal occurring with increasing residence time up to ~70 bed volumes. There was a distinct improvement between 2.5 and 5 minutes residence time. The relatively high mercury removal observed using the Ag impregnated carbon compared to the virgin activated carbon is most likely due to mercury removal via amalgamation between the impregnated silver(0) and elemental mercury. Mechanisms of mercury removal are discussed in detail in section 3.3.2.5.
Figure 30  Mercury concentration at different residence times versus bed volumes for condensate passed through a column of VACN

Figure 31  Mercury concentration at different residence times versus bed volumes for condensate passed through a column of AgACN
3.3.2.4 Up-flow column tests – TOC removal

The removal of TOC from condensate in the up-flow column tests was also investigated. Although TOC is present in relatively low quantities (<50 mg/L), it was possible that TOC may compete with mercury for active sites. The results for each of the sorbents studied are presented in Figures 33 - 35. Of the sorbents studied the carbon materials removed the TOC consistently over the 170 bed volumes of condensate passed through the bed. There was no evidence that the carbons were reaching saturation levels for TOC. The AgACN clearly removed the most TOC (~60-70%) under the testing conditions used. VACN also removed a significant amount of TOC (30-50%), while the PIM did not remove any TOC, as expected from a silicate-based material. Residence time and bed volumes had very little effect on the extent of TOC removal observed using the silver impregnated carbon and virgin activated carbon.
Figure 33  TOC concentration at different residence times versus bed volumes for mercury saturated condensate passed through a column of VACN.

Figure 34  TOC concentration at different residence times versus bed volumes for mercury saturated condensate passed through a column of AgACN.
3.3.2.5 Discussion of mechanisms of mercury removal from condensate

The results of the adsorption tests brought about an understanding of the likely removal mechanisms for each carbon type. Each sorbent type used in the tests possessed particular characteristics that distinguished it from the others as a candidate material for a mercury removal process. These characteristics included different impregnation materials such as sulphur or silver, different base materials such as carbon or mineral and different particle sizes and pore structures. As a result, the materials were expected to adsorb mercury via a number of different mechanisms including physical adsorption, chemisorption and amalgamation. It was important to understand the adsorption mechanism utilised by each material to determine the amount of mercury that was expected to be removed, and therefore assess the effectiveness of the material.
3.3.2.5.1 Virgin activated carbon

Virgin activated carbon (VAC) adsorbs elemental mercury via a physical adsorption process and was therefore expected to be controlled by the driving force associated with the mercury concentration in solution (Anoop Krishnan and Anirudhan, 2002b; Budinova et al, 2003). Budinova et al (2003) developed Langmuir isotherms for mercury adsorption onto a range of VACs. The authors determined that for a solution containing up to 100 mg/L Hg(II), that the mercury capacity ranged from 0.07 to 17%, depending on the carbon used (Budinova et al, 2003).

The lowest initial concentration for which the carbon loading was determined by Anoop Krishnan and Anirudhan (2002b) was 2 mg/L, approximately 100 times the concentration used in this study. At this initial mercury concentration the mercury capacity for the different carbons ranged from 3.5 to 10 % (w/w). More relevant to this study was work conducted by Huang and Blankenship 1994 who conducted adsorption studies on three carbon types at concentrations as low as 500 µg/L. Figure 36 shows data extrapolated from Huang and Blankenship (1994) using the carbon that exhibited the highest mercury loading. Assuming a linear relationship in the data ($R^2 = 0.999$), the predicted capacity for a carbon exposed to 20 µg/L mercury at pH 11 can be extrapolated according to equation 3.1. This predicts a mercury capacity of 0.08% (w/w). Assuming that the extrapolation is valid for comparing the adsorptions observed in this study, the mercury loading onto the VAC was not approached during the batch tests. This suggests that the mercury adsorption was impeded.
VACN was contacted with 20.3 µg/L mercury at two carbon concentrations; 0.2 and 2.0 g/L. The two carbon concentrations demonstrated similar mercury removal for the VAC (48% removal at 0.2 g/L cf 51% removal at 2 g/L) implying that the removal process was controlled by the driving force associated by the mercury concentration in solution. This is typical of a physical adsorption process.

The influence of solution concentration was also reflected in the observed mercury loadings onto the VAC (0.005% w/w for 0.2 g/L carbon and 0.0005% w/w for 2.0 g/L carbon) where the driving force was more dominant than available surface area. These mercury loadings did not approach the loading extrapolated from Huang and Blankenship (1994) of 0.08% (w/w) for 10 µg/L mercury. It must be noted that Huang and Blankenship (1994) used Hg(II) in their experiments and it is difficult to predict that Hg(0) would adsorb at the same rate or

Mercury loading (% w/w) = 0.7382 x [Hg] (µg/L) - 1.1132

3.1
demonstrate a similar capacity. A summary of potential reasons for the relatively low mercury loadings observed are:

- Competition for active sites from organics in solution (see Table 2, page 12 and Figure 33)

- The concentration of mercury in solution was too low to effectively provide enough driving force to demonstrate a higher mercury loading.

- The form in which mercury is present in condensate is not readily removed due to one or more of the following reasons:
  
  - (1) Hg(0) is present in solution predominantly as “microballs” that are too large to be removed via pore capture using the carbons studied

  - (2) Potential Hg(II) species such as Hg(OH)$_2$\textsuperscript{17} and Hg (organic) are too large to be removed via pore inclusion

  - (3) Hg(0) and Hg(II) species present do not readily adsorb on the surfaces of the carbons tested under the conditions used.

Because of the low mercury capacity observed when testing the VAC, further tests to develop a granular VAC process option are not recommended.

\textsuperscript{17} Molecular size approximately 0.7 nm based on atomic radii.
3.3.2.5.2 Sulphur activated carbon

The pH measurements taken from treated condensate from the up-flow column screening tests indicated that the sulphur activated carbons were not stable in condensate (no pH changes occurred for condensate treated with the virgin or silver impregnated carbons). The dissolution of sulphur in alkaline solution is described in Equations 3.2 and 3.3. The instability of SACN in condensate was verified by an analysis of the elevated sulphate concentration in the solution elutriated from the column containing SACN. The sulphate analysed in the condensate treated using SACN increased from 0.07 to 0.26 g/L.

\[ S + 2OH^- \rightarrow S^{2-} + H_2O + \frac{1}{2}O_2 \]  \hspace{1cm} (3.2)

\[ S^{2-} + 2O_2 \rightarrow SO_4^{2-} \]  \hspace{1cm} (3.3)

\[ S^{2-} + HgS \rightarrow [HgS_2]^{2-} \]  \hspace{1cm} (3.4)

Once sulphide ions were in solution, mercury may have formed the compound HgS, however in the presence of hydroxide ions and excess sulphide ions, the highly soluble [HgS_2]^{2-} complex may have formed (Greenwood and Earnshaw, 2002; Paquette and Helz, 1997) according to Equation 3.4. As a result of the sulphur dissolution, the SACs effectively behaved the same as the VAC, reaching a maximum mercury loading of 0.006% w/w (see Table 12), implying that the adsorption process was physical, rather than chemical.
3.3.2.5.3 Silver impregnated carbon

Silver is a known amalgamating agent for mercury metal and carbon is known to adsorb Hg(II). As such, AgACs may offer enhanced mercury removal compared to a virgin activated carbon by amalgamating and/or chemisorbing Hg(0) and by adsorbing Hg(II). This would be relevant if it was found that condensate contains a mixture of Hg(0) and Hg(II). The AgACN material demonstrated the highest mercury loading of the batch tested materials (0.008% w/w), however the mercury capacity for the AgACN was not approached due to breakthrough not being achieved. The higher loading observed for the AgACN could not be entirely attributed to the presence of the silver. The AgACN had the highest surface area of all the carbons tested (see Table 11) which, according to Anoop Krishnan et al (2002b) and Mohan et al (2001), would contribute to enhanced mercury capacity.

Although the AgACN demonstrated a superior mercury removal efficiency and slightly higher Hg loading than the other carbons tested, the magnitude of each would not warrant further consideration for use in a mercury removal process. In addition, the relatively high adsorption of TOC may detrimentally affect the long term efficiency of the adsorption process. The tests do, however, indicate that mercury amalgamation or chemisorption onto suitable metals is a potential removal opportunity and further testing to demonstrate this process is recommended.

3.3.2.5.4 Impregnated mineral material

Like the SACs, it is possible that sulphur was removed from the impregnated mineral material during contact with the condensate. An SEM and EDS analysis was conducted on a subsample of PIM used in the column tests. Figure 37 shows the surface of used PIM without the visible sulphur crystals observed in the unused PIM (see Figure 25). The EDS analysis of the material surface (see Figure 38) showed a reduced sulphur peak, although a significant
amount of sulphur was still detected. A mixed acid digest analysis of the start material and the PIM material used in the column tests described in section 3.3.2.2 indicated that sulphur had been removed from the material. The sulphur concentrations for the materials were 4.72% and 2.10% (w/w) respectively. PIM does not appear to have the resilience required for a mercury removal process in alkaline solution due to sulphur losses.

Figure 37 PIM SEM image following contact with condensate in a fixed bed column. No sulphur crystals are present at the surface or on the structural edges.
3.3.3 Removal of mercury from condensate using a mixture of powdered activated carbon

The adsorption loading of mercury onto microporous granulated activated carbons, regardless of impregnation, was lower than desirable, which was most likely due to (see Table 12) the inability of mercury species present in the condensate to diffuse into the micropores. Anoop Krishnan and Anirudhan (2002b) report that mercury primarily adsorbs to the outer surface of the carbon and therefore by increasing the mesoporosity and macroporosity, enhanced mercury capture would result. For this reason, mercury removal from condensate was also investigated using a mixture of two powdered activated carbons (PACs), AZO and D10, which have larger pore sizes than the GACs tested (see Table 11 and 13). The AZO and D10 were mixed and used as a filter bed. The D10 is sacrificial in that it acts to remove low molecular weight organics while the AZO, possessing the highest average pore diameter, is specifically designed for removing mercury from caustic soda. In addition to the larger
average pore size contributing to better mercury adsorption, the larger pore size should also reduce potential pore blockage from condensate solutes, which may have reduced the effectiveness of the GACs.

### Table 13 PAC characteristics

<table>
<thead>
<tr>
<th>PAC trade name</th>
<th>Surface area</th>
<th>Particle size distribution*</th>
<th>Average pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Norit AZO</td>
<td>Total = 700 (manufacturer data sheet), 1030 (BET – his study) External = 451 (BET – this study)</td>
<td>D₁₀ – 3 µm D₅₀ – 30 µm D₉₀ – 140 µm</td>
<td>30.41</td>
</tr>
<tr>
<td>Norit D10</td>
<td>Total = 600 (manufacturer data sheet), 865 (BET – this study) External = 333 (BET – this study)</td>
<td>&gt; 37 µm &gt; 53 µm &gt; 74 µm &gt; 106 µm &gt; 150 µm &gt; 250 µm</td>
<td>24.54</td>
</tr>
</tbody>
</table>

*Data obtained from Norit Datasheets.

### 3.3.3.1 PAC batch test results

Batch tests were conducted in which two doses of each (0.2 and 1 g/L) PAC type were agitated in 23 mL condensate in 25 mL culture tubes at ambient temperature for 24 hours. The results are shown in Table 14. The maximum loading achieved during the tests was 0.013% (w/w) for the 0.2 g/L carbon dose. This mercury loading was approximately double that achieved by the granular activated carbons but still less than the value of 0.08% (w/w) extrapolated from data produced by Huang and Blankenship (1994) (Chapter 1.1.5.2). This relatively low mercury loading may have been due to a low driving force associated with the initial mercury concentration or be indicative of TOC in solution competing with mercury for adsorption sites. This is discussed in section 3.3.3.3.
Although the removal efficiency was high in the test using 1 g/L of D10 (89%), the measured efficiency was further improved by filtering the post-test solution through a 0.45 µm membrane\(^\text{18}\) (see Table 14). This suggests two scenarios:

- Some of the non-adsorbed mercury may be in the form of micro balls (Bloom and Turner, 2004), which are too large for pore capture but are retained by the 0.45 µm filter membrane

- Some fine PAC containing mercury was not settled during centrifugation but was retained by the 0.45 µm membrane.

### Table 14 PAC batch test results

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Sorbent concentration (g/L)</th>
<th>Final mercury concentration (µg/L)</th>
<th>% Mercury removal*</th>
<th>Mercury adsorbed (% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>N/A</td>
<td>30</td>
<td>17.4</td>
<td>N/A</td>
</tr>
<tr>
<td>AZO</td>
<td>0.2</td>
<td>6.7</td>
<td>81.5</td>
<td>0.013</td>
</tr>
<tr>
<td>D10</td>
<td>0.2</td>
<td>11.6</td>
<td>68</td>
<td>0.011</td>
</tr>
<tr>
<td>AZO</td>
<td>1</td>
<td>3.2</td>
<td>91.2</td>
<td>0.003</td>
</tr>
<tr>
<td>D10*</td>
<td>1</td>
<td>4</td>
<td>89</td>
<td>0.003</td>
</tr>
<tr>
<td>D10</td>
<td>1</td>
<td>0</td>
<td>100</td>
<td>0.004</td>
</tr>
</tbody>
</table>

Initial mercury concentration = 36.3 µg/L
Solution filtered using an 0.45 µm syringe filter prior to analysis.

### 3.3.3.2 PAC filter bed results

The mercury removal results for the tests using the PAC filter bed are presented in Figures 39 and 40. The PACs were able to completely remove mercury from condensate over the entire number of bed volumes studied for each of the residence times investigated. This high removal efficiency was achieved with very fast residence times of 6.3 and 13 seconds. Time limitations did not enable the tests to continue beyond 250 bed volumes, at which point no imminent breakthrough was apparent.

---

\(^\text{18}\) It has been demonstrated that the membranes do not remove mercury from solution (Section 2.3.4).
The PACs have higher average pore diameter (see Table 11) compared to the virgin granular activated carbon. The superior adsorption demonstrated by the PACs implies that the mercury is adsorbing to the external surface of the carbon or within the larger pores, and is consistent with the findings of Anoop Krishnan and Anirudhan (2002b) who reported that mercury primarily adsorbs to the outer surface of the carbon and increasing the mesoporosity and macroporosity would result in enhanced mercury capture.

**Figure 39** Mercury concentration versus bed volumes for mercury saturated condensate passed through a filter bed of carbon (50% v/v Norit Azo and 50% v/v Norit D10). Residence time = ~29 sec

**Figure 40** Mercury concentration versus bed volumes for mercury saturated condensate passed through a filter bed of carbon (50% v/v Norit Azo and 50% v/v Norit D10) using different residence times
The relatively efficient mercury removal obtained using the PACs compared to the granular activated carbons is most likely due to:

- Larger average pore size and greater external surface area.

- Small particle size of carbons (improved solid solution contact leading to good mercury sorption kinetics).

- Two different types of carbon being used in combination. D10 preferentially removes organics that may have otherwise block the pores of the AZO, which is specifically designed for mercury removal.

### 3.3.3.3 Effect of TOC on PACs

The adsorption of condensate TOC onto a combination of the two PACs during the filtration tests is presented in Figure 41. The PAC mixture removed a significant amount of TOC (~70%) over the total number of bed volumes used for each of the residence times investigated. This removal of TOC may eventually impede the mercury removal efficiency of the PACs, however this was not demonstrated after 250 bed volumes of condensate were filtered. It may be possible that the TOC is penetrating the micropores and mesopores of the carbon allowing the mercury to adsorb to the surface and macropores of the carbon. In addition, it was not determined whether the D10 was preferentially removing TOC, as it is designed to do, to enable the AZO to adsorb the mercury unimpeded.
Figure 41 TOC concentration versus bed volumes for mercury saturated condensate passed through a bed of a mixture of powdered activated carbon (50% Norit AZO and 50% Norit D10) using different residence time.

3.3.3.4 PAC tests conclusions

The PACs did not reach the mercury loading expected for the mercury concentrations used in the tests (based on data extrapolated from Blankenship, 1994). This was possibly due to potential fouling from organics, however, the low contact time associated with the filtration process and 100% mercury removal efficiencies demonstrated for the PACs justifies further investigation as a potential process to treat digestion condensate.

3.3.4 Conclusions

The significant parameters affecting removal of dissolved elemental mercury were determined to be the adsorbent particle size, carbon pore size and solution residence times.

There was negligible difference in the dissolved elemental mercury adsorbed to the SIACs compared to the VAC. It was determined that the most likely reason for this was sulphur
dissolution from the SIACs into the alkali solution. Sulphur dissolution was also observed from the impregnated silicate material, reducing its potential capacity.

The nominal expected mercury loadings for each respective carbon based on manufacturers specifications and literature findings were not approached during any of the 24 hour batch tests. The mercury loadings for PAC were significantly greater than for the GACs and the PACs also demonstrated the greatest mercury removal efficiency of the carbons tested. The high mercury removal efficiency of the PAC, in addition to the short residence time during filtration, justifies further investigation as a process option.

It is difficult to compare the two types of materials, PACs and GACs, in terms of performance due to differences external surface area and the type of process involving each carbon, i.e. filtration and fixed bed column adsorption respectively. It was possible, however, to determine that mercury preferably adsorbs to the external surface of the carbon or within the larger pores associated with the PACs.

Mercury removal efficiency was potentially hindered by the presence of mercury micro balls as well as TOC adsorption. TOC does not adsorb to PIM and as such it will not reduce its in-service life, however sulphur losses from the mineral reduce its suitability for process use.
4 GAS SPARGING

4.1 Introduction

Gas sparging has been effectively used to remove elemental mercury from aqueous solution at laboratory scale (Bloom and Turner, 2004; Looney et al, 2003). The theory of this process is readily explained by Henry’s law which states that the amount of a gas that dissolves in a liquid is proportional to the partial pressure of the gas over the liquid, provided no chemical reaction takes place between the liquid and the gas. Henry’s law is shown in Equation 4.1, where $P$ refers to the partial pressure of the vapour, $x$ refers to the mole fraction of the solute (mercury) and $K$ is a constant of proportionality known as Henry’s coefficient.

\[ P = x K \quad (4.1) \]

Henry’s coefficient is the ratio of the concentration of the volatile species in the air over the concentration in water. Mercury (0) has a relatively high Henry’s coefficient (Waite et al, 2002) which means that the vapour pressure above the solution has to be relatively high to induce significant concentrations in the solution phase. Figure 42 shows the Henry’s coefficients for mercury above pure water and the associated solubility. Figure 43 shows the relationships between the partial pressure of mercury and solubility of mercury between 0 and 100°C.
Because of the relatively high Henry's coefficients for mercury, air sparging has been used routinely in analytical techniques to volatilise elemental mercury. For example, mercury sparging is utilised in cold-vapour AAS, a common analytical technique that involves chemical reduction of mercury (II) to mercury (0), which is air sparged to the detector. Under such conditions, detection limits of 0.02 µg/L can be achieved (Rose et al, 2001) due to practically complete mercury volatilisation.
Air sparging has also been used to remove mercury from aqueous process waters and natural waters. Looney *et al* (2003) used stannous chloride reduction of mercury (II) and gas sparging to remove 94% of mercury at 22.8 °C from a groundwater sample, which had an initial mercury concentration of 120 ng/L. Bloom and Turner (2004) investigated removal of mercury from caustic soda by chemically reducing the mercury in solution. The mercury concentration depleted from 2.6 mg/L to 0.1 mg/L (96%) at 130 °C. Nine times greater removal was observed at 130 °C compared to 100 °C, however the authors could not differentiate the effects of mercury volatility or enhanced chemical reduction at the higher temperature.

Based on the results of the Eh and pH investigation of condensate conducted in Section 2.4, which indicated that elemental mercury is the thermodynamically favoured species (Pourbaix, 1976), it is possible that sparging could be a potential method for removing mercury from condensate. Henry’s law predicts a relationship between the partial pressure of mercury above a liquid and the concentration in solution. By reducing the vapour pressure above the solution, the mercury concentration in the headspace is depleted and mercury evasion from the liquid is encouraged. The higher saturated vapour pressure for mercury that is associated with higher temperatures further improves the separation of mercury because of the increased affinity for mercury to report to the vapour phase. Since the temperature of condensate is 95 °C at the point of production, and thus exhibits a high mercury vapour pressure, mercury sparging could be a viable removal process if the mass transfer could be suitably controlled.
4.2 Experimental

4.2.1 Preparation of condensate solution for tests.

The sparging test work was conducted in laboratory facilities at Alcoa’s Kwinana refinery (unless otherwise stated) and, for convenience, the condensate samples were collected from the Kwinana refinery. The laboratory facilities did not enable the solution to be prepared as described in section 3.2.9, which involved reducing the condensate with hydrogen gas and saturating the headspace of a bottle with mercury vapour.

The following sample preparation applies to the preliminary sparging experiments and the phase 1 and 2 sparging tests. Kwinana digestion condensate was collected at 95°C directly into 2.5 L glass Winchester bottles with no headspace. A small bead (approximately 5 g) of liquid mercury was placed into the Winchester, which was then sealed and shaken. This procedure attempted to ensure the mercury concentration was close to the equilibrium solubility of elemental mercury in solution or at least significantly high enough to allow a suitably high sensitivity for detecting a concentration change using ICP-MS analysis.

The sample preparation for the phase 3 sparging experiments was similar to those described above except that the Winchester bottles containing hot condensate plus the liquid mercury bead were placed on a bottle roller for approximately two hours.

4.2.2 Mercury analysis

Mercury was analysed using ICP-MS (Agilent Technologies model 4500) as described in section 2.3.

4.2.3 Preliminary sparging (Phase 1) experiments.

Preliminary sparging tests were conducted to assess whether mercury could be volatilised from condensate solution and hence to determine if more extensive testing under more...
controlled tests would be warranted. The preliminary sparging experiment apparatus used three stainless steel 4 L stirred reactors set up in series (see Figure 44). Nitrogen gas was used to sparge the mercury through the reactors to prevent the potential formation of Hg(II) during the experiment via oxidation. The sparging gas was introduced into the stripping vessel as a single pass of nitrogen gas through a glass frit bubbler.

![Diagram](image)

**Figure 44 Apparatus for preliminary sparging experiments**

The description of the vessels used in the apparatus is as follows:

- **Reactor 1**: 3 L deionised water thermostatically controlled at 90 °C to humidify the dry nitrogen and minimise evaporation of condensate solution from reactor 2.

- **Reactor 2**: 2.75 L condensate thermostatically controlled at 90 °C.

- **Reactor 3**: Iced water used as a coolant for a condenser required to collect evaporated water to account for volume loss and to correct raw concentration data.
The following procedure was used for the preliminary gas sparging experiments: Duplicate start samples were taken from reactor 2 using a syringe and injected into 40 mL glass VOA vials without headspace for mercury analysis. Nitrogen was then purged through the system at 3 L/min\(^9\). Further samples were taken from reactor two at the time intervals shown in Table 15. A water mass balance was calculated to normalise concentration data (Appendix 1).

4.2.4 Phase 2 sparging experiments

Most of the resistance to gas exchange from liquid to vapour lies in the water film (99\%) (Poissant \textit{et al}, 2000). Therefore, increasing the surface area of the air interfacing with the liquid greatly increases the mass transfer of mercury into the vapour phase (Loux, 2000; Loux, 2004). Because of this, the Phase 2 sparging experiments were conducted using an Outokumpu Flash Flotation Machine (see Figure 45) operating at the maximum rotational speed of the machine impellor (1200 rpm). This instrument was used to create the best available mixing of sparging gas with the solution and hence ensure excellent mass transfer conditions. The nitrogen was mixed into the solution from a nitrogen blanket held over the mixing vessel through a vortex produced from the high speed impellor. The nitrogen blanket was maintained over the test solution throughout to prevent oxidation of the elemental mercury. The test vessel (2 L glass beaker) was placed in a water bath, which was maintained at 40 °C.

\[^9\] It was determined during safety analysis of the apparatus that greater flows over pressurised the system, causing seal failures.
Samples were taken from the froth flotation unit at 0, 2 and 5 minutes. Blank tests were run in parallel where the solutions were not subjected to nitrogen sparging. Both Eh and pH were monitored to ensure the thermodynamically favoured state of the mercury remained as Hg(0).

The tests were run at 40 °C due to the following reasons:

- Limitations in the practical use of the laboratory equipment, specifically the froth flotation unit
- To prevent high volume losses associated with moisture evaporation
4.2.5 Phase 3 sparging experiments

The phase 3 sparging experiments were conducted almost identically to the phase 2 experiments described in section 4.2.3. One divergence from the procedure was the addition of 37% formaldehyde (in water) to the condensate to promote the reduction of any oxidised mercury to Hg(0). Bloom and Turner (2004) used an organic reductant to effectively reduce Hg(II) to Hg(0) in caustic soda solution and subsequently sparged out 96% of the mercury. A dose of 0.33 mL of formaldehyde was added to 2.5 L condensate (~4 x 10^5 times molar excess relative to 10 µg/L mercury), in a Winchester bottle. The bottle was rolled at 10 rpm on a bottle roller prior to sparging. Formaldehyde was not added to the condensate used in the blank test.

4.3 Results and discussion

4.3.1 Preliminary (phase 1) sparging tests

Analytical results for the preliminary sparging experiments using the method described in section 4.2.1 are shown in Table 15 and Figure 46. Approximately 220 mL of water evaporated over the 120 minutes test period. It was assumed that this loss was linear at 1.83 mL/min over the time of the experiment and analytical data was corrected for this loss (see Table 15). The rate of Hg removal was greatest between 0 and 20 minutes and levelled out after approximately one hour, at which time 75% of the mercury had volatilised. The mass transfer of mercury to the vapour phase in this test would have been limited by the relatively low nitrogen flow rate (3 L/min) and the introduction of relatively coarse nitrogen bubbles (via a glass frit). Despite these conditions, the concept of mercury volatilisation from solution was proven and the results warranted further investigations using improved mass transfer conditions, such as the introduction of finer bubbles and a higher gas addition rate.
Table 15 *Preliminary tests analytical data*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Purge time (min)</th>
<th>Corrected volume in reactor 2* (mL)</th>
<th>Hg (µg/L)</th>
<th>Mass Hg in reactor 2 (µg)</th>
<th>Hg reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MT0</td>
<td>0</td>
<td>2750</td>
<td>19.1</td>
<td>52.5</td>
<td>0.0</td>
</tr>
<tr>
<td>MT1</td>
<td>10</td>
<td>2686</td>
<td>12.2</td>
<td>32.8</td>
<td>37.6</td>
</tr>
<tr>
<td>MT2</td>
<td>20</td>
<td>2623</td>
<td>7.3</td>
<td>19.1</td>
<td>63.5</td>
</tr>
<tr>
<td>MT3</td>
<td>40</td>
<td>2577</td>
<td>6.5</td>
<td>16.8</td>
<td>68.1</td>
</tr>
<tr>
<td>MT4</td>
<td>60</td>
<td>2532</td>
<td>4.7</td>
<td>11.9</td>
<td>77.3</td>
</tr>
<tr>
<td>MT5</td>
<td>120</td>
<td>2560</td>
<td>5.0</td>
<td>12.8</td>
<td>75.6</td>
</tr>
</tbody>
</table>

* The volume was corrected for evaporative losses.

**Figure 46** *Preliminary mercury sparging results*
4.3.2 Phase 2 sparging experiments

The preliminary phase 1 experiments showed that mercury could be volatilised from solution using a simple apparatus. Due to the resistance to gas exchange from liquid to vapour lies in the water film (99%) (Poissant et al., 2000) the mass transfer of mercury needed to be close to optimal to fully evaluate gas sparging as a removal option. The apparatus used in these experiments was an Outokumpu flash flotation unit (see Figure 45) designed to create micro bubbles for froth flotation. In this apparatus, the high mass transfer conditions are created by nitrogen being drawn into solution by a vortex created from a high agitation impellor rotating at 1200 rpm. The results of these tests are shown in Table 16.

<table>
<thead>
<tr>
<th>Condensate sparging test</th>
<th>Blank run*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (min)</td>
<td>Hg (µg/L)</td>
</tr>
<tr>
<td>0</td>
<td>5.7</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
</tr>
<tr>
<td>5</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Conditions: T= 40 °C, pH = 10.3.
- Equivalent volume, nitrogen headspace and temperature, pH conditions as for the sparging tests without the sparging or mixing process.

It can be seen that under conditions of improved mass transfer, that approximately 80% removal occurs after only two minutes sparging time. This ~80% removal was also measured after 5 minutes sparging time, which indicated that there was a limit to the amount of mercury that could be sparged under these conditions. In the phase 1 experiments, a limit of ~75% removal was observed. The phase 1 conditions had a more favourable temperature, which increased the mercury vapour pressure above the solution, and the phase 2 conditions had more favourable mass transfer conditions due to the larger surface area of air exposed to liquid. During both the phase 1 and 2 experiments, the rate of mercury removal levelled out at
approximately 75 and 80% respectively. The limitations to extraction may be due to the following reasons:

(1) Reaction temperature and mass transfer limitations

A greater temperature and longer sparge time (Phase 1) demonstrated no better mercury removal than a lower temperature with significantly improved mass transfer conditions (Phase 2). In each case, the mercury removal was limited to between 75% and 80%. The main difference observed was the rate of mercury removal. The maximum mercury extraction for the Phase 1 experiment was approached after 60 minutes, compared to only 2 minutes during Phase 2. This implies that mass transfer is a significant parameter in controlling the rate of mercury volatilisation.

(2) A concentration gradient between the liquid and gaseous phase

The concentration gradient between mercury in the liquid phase and the gaseous phase can be significant in determining the rate of mercury evasion from the liquid (Loux, 2000, Loux, 2004). Hence it could be considered that the observed 20% mercury removal limitation is due to the concentration in solution depleting during extraction. The maximum extraction in phase 2 was reached at \(~1 \mu g/L\) mercury. It is known that mercury volatilisation in analytical techniques such as cold vapour AAS detects mercury down to 0.02 \(\mu g/L\) mercury and as such the volatilisation of mercury to the detector must be effectively close to 100%. In addition, Looney et al (2003) used stannous chloride reduction of Hg(II), followed by gas sparging, to remove 94% mercury from a groundwater sample at 22.8 \(^{\circ}\)C down to 7 ng/L. It is unlikely, therefore, that the concentration gradient with \(~1 \mu g/L\) mercury remaining in solution would cause the levelling out of the rate of removal that was observed in these tests.
(3) The presence of oxidised mercury and/or unspargable micro-balls of mercury

The pH and Eh of condensate is generally in a region on a Pourbaix diagram that would predict elemental mercury as the thermodynamically favoured form, however the measured pH and Eh of the start condensate solution used in this test was 10.3 and +600 (mV, SHE) respectively. These conditions predict the presence of the un-spargable Hg(OH)_2 compound (see Figure 15, Pourbaix, 1976). The Eh dropped to +273 mV (SHE) after 5 minutes sparge time, which was very close to the phase separation line between Hg(0) and Hg(II) and, as such, the actual species under these conditions could not be predicted with confidence. Hg(0) and Hg(II) may have been co-present in solution. In support of the possibility of mixed mercury species being present, Bloom and Turner (2004) speciated the mercury in caustic soda samples prior to conducting sparging tests. The mercury speciation was found to be 16% particulate mercury (co-precipitated ionic mercury), 73% ionic mercury and 11% elemental mercury. The presence of ionic mercury in the condensate may have accounted for the 20% of the sample remaining following the sparging. Another possibility is that the solution contained un-spargable micro-balls of mercury caused by agglomeration of elemental mercury in solution (Bloom and Turner, 2004).

Of the possible reasons for the observed ~80% removal limitation, the most likely reasons for the remaining ~20% mercury following sparging was the presence of Hg(II) or Hg(0) microballs in the condensate. The phase 3 tests were designed to determine if the limiting extraction by sparging was due to the presence of oxidised mercury by facilitating a chemical reduction of Hg(II) to Hg(0).
4.3.3 Phase 3 sparging experiments

The possibility that a proportion of the mercury in condensate existed as Hg(II) was investigated by conducting sparging tests on condensate containing a reducing agent to convert any Hg(II) present to the more spargable elemental form. Stannous chloride and organic gases, including acetylene, have been used to effectively reduce Hg(II) to Hg(0) in caustic soda solutions to facilitate the removal of 96% of the mercury through sparging (Bloom and Turner, 2004). The use of a highly flammable gas as a combined sparging gas and reductant was regarded as too hazardous to attempt in a laboratory environment and as such alternative reductants were considered. Stannous chloride was considered as it reacts with mercuric hydroxide according to equation 4.1.

\[
\text{Hg (OH)}_2^0 + \text{Sn}^{2+} \rightarrow \text{Hg}^0 + 2(\text{OH})^- + \text{Sn}^{4+} \quad 4.1
\]

\[
2\text{OH}^- + \text{Sn}^{2+} \rightarrow \text{Sn(OH)}_2 \quad (\text{Ksp} = 5.45 \times 10^{-27}) \quad 4.2
\]

There was concern that insoluble stannous hydroxide (Lide, 1979) may precipitate in the condensate according to Equation 4.2, reducing the pH of the solution and therefore significantly changing the redox chemistry. In addition, the formation of a precipitate may cause the removal of mercury from solution as a co-precipitant or adsorbed species would confound the sparging results. It was therefore decided to use an alternative reductant.

Formaldehyde was selected as the most appropriate reductant because it naturally exists in condensate solution in trace levels of 0.2 – 0.4 mg/L (Leeder, 2002) and has been used previously as a reductant for converting Hg(II) to Hg(0) in caustic soda solution (Nealon and Harrowfield, 2002). The initial concentration of formaldehyde in the condensate used in tests...
was unknown so additional formaldehyde was added to the condensate solution in a $4 \times 10^5$ times molar excess (0.11 g/L) relative to 10 µg/L Hg. The results of the test are shown in Table 17.

| Table 17 Phase 3 condensate sparging test results |
|----------------|----------------|----------------|----------------|----------------|
|                | Condensate sparging test | Blank run*     |
| Time (min) | Hg (µg/L) | Hg removal (%) | Eh (SHE) (mV) | Hg (µg/L) | Hg removal (%) | Eh (SHE) (mV) |
| 0          | 23.7      | 3.6            | 200           | 24.6      | 0              | 200           |
| 2          | 1.7       | 93             | 236           |           |                |               |
| 5          | 6.9       | 71             | 234           | 25.4      | -3             | 212           |

Conditions: T= 40 °C, pH = 10.4.
* Equivalent volume, nitrogen headspace and temperature, pH conditions as for the sparging tests without the sparging or mixing process.

The addition of excess formaldehyde in the sparged sample did not appear to reduce the solution Eh relative to the blank (no formaldehyde addition) (see Table 17). Despite this, the solution Eh for this test was considerably lower than for the solutions used in the phase 2 tests, which may have been within the natural variation of condensate conditions (see Table 16). The Eh/pH conditions for the phase 3 tests would predict that the mercury is in the elemental form (see Figure 15, Pourbaix, 1976).

The sample representing two minutes of sparging demonstrated a 93% extraction, which would somewhat justify the hypothesis that un-spargable oxidised mercury exists in the condensate and the addition of a reductant facilitates a conversion of Hg(II) to Hg(0), increasing the amount of volatile mercury. However, the sample taken after 5 minutes sparging showed a 70% extraction which was significantly lower than the sample taken after 2 minutes of sparging. Due to the confounding results, it was difficult to determine whether the ~ 20% un-spargable mercury seen in the phase 1 and 2 tests is due to the presence of oxidised mercury or mercury microbeads, both of which are un-spargable (Bloom and Turner, 2004).
4.4 Conclusions

All laboratory results showed that mercury purging from condensate was limited to ~80%. It was determined that the mass transfer of mercury to the vapour phase controlled the rate of removal but did not significantly impact on the amount of mercury removed. There appeared to be a residual ~20% of mercury that could not be sparged from solution. This may be attributable to condensate containing elemental mercury micro balls and/or oxidised mercury, both of which are not amendable to sparging (Bloom and Turner, 2004). An attempt to reduce Hg(II) in solution to assess whether the un-spargable mercury was oxidised mercury was inconclusive.

There were restrictions associated with operating the flash flotation unit at temperatures above 40 °C as this was the maximum temperature that could be thermostatically maintained. Therefore, the benefits associated with combining higher temperatures with high mass transfer could not be determined. In the refining process, condensate exists at 95 °C and this temperature could be well utilised in an industrial sparging technique providing suitable mass transfer conditions were also applied.
5 SORPTION/AMALGAMATION USING NOVEL MATERIALS

5.1 Introduction

As discussed in chapter 1, a range of different types of materials (aside from carbon-based materials) have been used to remove mercury from aqueous solution. Of the materials investigated, silica based materials have clearly been the most widely studied. Most of the silica-based materials that have been studied consist of silica (in various forms) coated with a compound(s) capable of reacting with mercury. Silica is one of the most preferred solid supports due to its good stability, wide scales of porous volume, specific surface area, available sizes and effectiveness in basic solutions.

The majority of studies conducted on silica-based materials involve the binding of compounds, such as sulphur based functional groups that have a strong affinity for mercury. Feng et al (1997), for example, developed functional organic monolayers on ordered mesoporous supports (FMMS). Thiol groups were introduced as the terminal groups of the organic monolayers. A 6.35 mg/L mercury solution at pH 9 was contacted with FMMS for two hours at room temperature with agitation. The FMMS removed up to 99% of the mercury present and mercury loadings on this material ranged between 11% and 34 % mercury (w/w). This test material developed at Pacific Northwest National Laboratory is capable of removing all forms of mercury, has a very high reported mercury capacity (63.5% w/w) based on tests using Hg(II) and is capable of quick mercury uptake.

A mesoporous silica substrate could also be used to support impregnations of noble metals, such as gold or silver. The presence of gold or silver would encourage chemisorption or amalgamation of elemental mercury from solution while the mesoporous silica should provide an adsorption surface for mercury (II) (Bonnissil-Gissinger et al, 1999). Hence, this form of
silica based adsorbent would be suitable for solutions containing mixed oxidation states of mercury.

The main aims of the research detailed in this chapter were: (1) synthesise a variety of silica based materials, (2) investigate removal of mercury from condensate using these materials (3) investigate the stability of these materials. Silica impregnated with thiol groups, gold and silver were selected for investigation based on the findings discussed in the previous paragraphs.

5.2 Experimental

5.2.1 Preparation of materials

5.2.1.1 Carbons

The powdered activated carbons studied in this chapter (Norit AZO and Norit D10) were used as received. The characteristics of these carbons were described earlier in section 3.2.1, Table 11. Refer to Figures 23 and 24 for surface structure information of these carbons.

5.2.1.2 Preparation of gold impregnated high surface area silica

Gold impregnated silica was prepared using the co-assembly method of Zhu et al (2003). Briefly, a gold complex, [Au((CH₃O)₃Si(CH₂)₃NH(CH₂)₂NH₂)₂], was prepared by mixing HAuCl₄.3H₂O and H₂NCH₂CH₂NHCH₂CH₂Si(OMe)₃ in water. The silica support was then prepared in the solution containing the gold complex by adding CTAB, KOH and tetraethyl orthosilicate. This solution was then mixed at room temp for 20 h. The resulting precipitate
was collected by filtration, washed with water and dried for 1 day under vacuum. The dried solid was then reduced using two different procedures:

(I) Hydrothermal treatment at 90°C for 24 h

(II) Hydrogen reduction at 200°C for 1h.

5.2.1.3 Preparation of silver impregnated high surface area silica

This material was prepared using the same procedure as for the gold impregnated silica except AgNO₃ was used in place of HAuCl₄.₃H₂O. The silver impregnated silica was reduced under a flow of 5% Hydrogen in Argon at 200°C for 1h.

5.2.1.4 Preparation of thiol-SAMMS

The silica support, MCM-41, was prepared separately using the method of Katiyar et al (2005). A silica source solution (prepared using colloidal silica, water and tetramethylammonium hydroxide) and a template solution (prepared using cetyltrimethylammonium bromide (CTAB), water and ammonium hydroxide) were prepared. The silica source solution and template solution were then mixed and heated in a Teflon-lined autoclave under autogenous pressure at 100°C for 72 hours. The solids were collected by filtration, washed, dried at ambient temperature, and calcined at 550°C for 10h under airflow. The heating rate was 2°C / min and cooling rate 15°C / min. Before impregnation of the thiol complex the prepared MCM-41 was characterised using XRD and BET surface area analysis. XRD analysis showed a peak at 2θ =2.6° which corresponds to a 100 interplanar spacing of ~35Å and confirmed the material was macroporous.
The thiol containing compound, mercaptopropyltrimethoxysilane (MPTMS) was impregnated into the MCM-41 as follows: MCM-41, water and toluene were mixed for 2 hours at room temp. MPTMS was then added and the mixture was heated to reflux for 6 hours. The water and methanol in the mixture were then distilled off. The mixture was then cooled and the Thiol-SAMMS was collected by filtration and washed with copious amounts of iso-propyl alcohol and allowed to air dry for 3 days.

5.2.2 Analytical methods

5.2.2.1 Gold, silver, silica and mercury analysis

Mercury analyses were conducted according to the method described in Chapter 3.2.8.1 using a 4500 series Agilent Technologies Inductively Coupled Plasma - Mass Spectrometer (ICP-MS). Gold, silver and silicon in aqueous samples were analysed by ICP-MS using a semi-quantitative method.

5.2.2.2 TOC Analysis

Refer to method described in Chapter 3.2.8.4.

5.2.2.3 BET specific surface area

Refer to method described in Chapter 3.2.8.5.
5.2.2.4 Material characterisation

X-ray diffraction was performed using a Bruker Advanced D8 X-ray diffractometer.

Surface area and pore size distribution measurements were performed using a Micromeritics ASAP 2000 Surface Area Analyser.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Analysis (EDS) were conducted according to the method described in Chapter 3.2.8.6.

5.2.3 Pre-treatment of condensate solutions – adjustment of condensate Eh and mercury concentration

Refer to method described in Chapter 3.2.9.

5.2.4 Batch tests procedure

The materials to be tested and condensate were combined in culture tubes, which were rotated end-over-end in a water bath at ambient temperature.

5.2.5 Kinetic tests procedure

A pre-determined volume of the material to be tested was placed on a 0.45 µm nylon filter base inside a re-useable syringe filter unit. A pre-determined amount of condensate was then passed through the filter unit using a pre-determined flow rate.
5.3 Results and discussion

5.3.1 Characterisation of materials

Characterisation data for the materials investigated is given in Table 18. All of the materials investigated were in a similar physical form (all fine powders). ESEM micrographs were taken of the surface of each material to gain information on the respective surface structures. EDS traces were also taken to determine the relative extent of impregnation of the thiol complex in the MCM-41 silica substrate.

Table 18 Characterisation data of materials investigated

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface area (m²/g)</th>
<th>Average pore diameter (Å)</th>
<th>XRD</th>
<th>Particle size distribution</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au-Si</td>
<td>174</td>
<td>30.7</td>
<td>Peaks present at 38°, 44°, 65°</td>
<td>N/A</td>
<td>~2.5 wt% gold. Fine powder.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>and 77.5° (2θ scale) represent Au (111),</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(200), (220) and (311) planes.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag-Si</td>
<td>14</td>
<td>72.2</td>
<td>Peaks present at 38.5° and 45.5°</td>
<td>N/A</td>
<td>~2.5 wt% silver. Fine powder</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(2θ scale) represent Ag (111) and (200) planes.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thiol SAMMS</td>
<td>854</td>
<td>NA</td>
<td>N/A</td>
<td>N/A</td>
<td>Fine powder</td>
</tr>
<tr>
<td>MCM-41</td>
<td>854</td>
<td>~35</td>
<td>Peak at 2.6° (2θ scale) corresponds to a</td>
<td>N/A</td>
<td>Fine powder</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100 interplanar spacing of ~35Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAC – AZO</td>
<td>701</td>
<td>30.2</td>
<td>NA</td>
<td>D₉₀ &lt;37 µm*</td>
<td>Fine powder</td>
</tr>
<tr>
<td>PAC – D10</td>
<td>639</td>
<td>24.9</td>
<td>NA</td>
<td>D₉₀ &lt;140 µm*</td>
<td>Fine powder</td>
</tr>
</tbody>
</table>

*Data obtained from Norit data sheets
† Surface area prior to impregnation of thiol ligand – accurate surface area measurement after impregnation not possible due to sulphur group not being stable under the conditions required to pre-treat the sample for surface area analysis (heating under vacuum).

5.3.1.1 Gold impregnated high surface area silica material.

The Au-Silica materials were prepared using two different reduction methods:

(I) Hydrothermal treatment at 90°C for 24 h

(II) Hydrogen reduction at 200°C for 1h.
The average size of the gold nano-particles in the samples were estimated by the width of the Au (111) peak in the respective XRD patterns using the Scherrer diffraction formula (Klug, 1959). The respective average sizes of gold nano-particles are ~2.4 nm for the Au-Silica prepared using the hydrogen gas reduction method and ~18.7 nm for the Au-Silica prepared using the hydrothermal reduction method (see Figures 47 and 48).

Figure 47 XRD trace of hydrothermal impregnation of gold on the silica substrate
Figure 48  *XRD* trace of hydrogen reduction impregnation of gold on the silica substrate

The surface structure of the untreated silica substrate is shown in Figure 49 and the EDS trace shown in Figure 50. The gold impregnated material, produced by method (II) (Hydrogen reduction at 200°C for 1h) is characterised in Figures 50 and 51. Note the small gold peak in the EDS trace confirming impregnation.
Figure 49 *SEM micrograph of non-impregnated silica substrate*

Figure 50 *EDS trace of non-impregnated silica substrate*
Figure 51 SEM micrograph of gold-impregnated silica substrate

Figure 52 EDS trace of gold-impregnated silica substrate
5.3.1.2 Silver impregnated high surface area silica material.

This material was prepared using the same hydrogen reduction method for creating the gold impregnated silica, the exception being that AgNO₃ was used in place of HAuCl₄·3H₂O. The average size of the silver nano-particles in the Ag-Silica material was calculated using the Scherrer equation (Klug, 1959) to be ~5.6 nm based on the line width of the Ag (111) peak (see Figure 53).

Figure 53 XRD trace of hydrogen reduction impregnation of silver on the silica substrate
The surface structure of the silver impregnated material is shown in Figure 54. The EDS trace in Figure 55 confirms the impregnation.

Figure 54 SEM micrograph of silver-impregnated silica substrate
5.3.1.3 Thiol SAMMS material

The surface structure of the Thiol-SAMMS material is shown in Figure 56. Figure 57 verifies the impregnation by sulphur functional groups.

Figure 55 EDS trace of silver-impregnated silica substrate
Figure 56 *SEM* micrograph of Thio-SAMMS.

Figure 57 *EDS* trace of Thio-SAMMS.
5.4 Results and discussion

5.4.1 Batch test results

5.4.1.1 Mercury removal

The batch tests described in section 5.2.4 were used to evaluate the mercury removal efficiencies of the materials listed in table 18, including Au-Silica materials prepared using both methods (I) and (II). Two PACs (AZO and D10, refer to Chapter 3) were also investigated as a means to compare the results of the novel materials against an industry standard process.

Initial results indicated the following:

- The base silica material, MCM-41, did not remove mercury relative to the blank solution. The loss associated with the blank solution can be explained by mercury volatilisation from the headspace, which was previously saturated with respect to mercury, to air. This was unfortunately unavoidable when conducting the tests.

- The Ag-Si material removed 90% of the mercury from solution.

- The mercury removal efficiency of the Au-Silica materials prepared using methods (I) and (II) varied slightly, with the Au-Si material containing smaller gold particles (2.4 nm, method (II)) removing a greater amount of mercury (90%) than the material produced using method (I) (75%).

- The PAC results (90% removal) were consistent with the results achieved in chapter 3.

- Removal using the Thiol-SAMMS material was only 70%.

The above results, particularly the inconsistency associated with the two Au-Si samples and the low result for the Thiol-SAMMS, warranted further investigation. To assay the solution
for mercury following the tests, it was necessary to separate the solids from the treated condensate. The initial separation method (centrifugation) was not entirely successful as fines were observed in some supernatants. As a result, it was assumed that erroneously high mercury concentrations could have been determined in the solution assays as the fines may have contained mercury that was reported in the analysis. Filtration of the post-test solutions was tested, using a disposable 0.45 mm nylon syringe filter. The effect of filtering samples is also shown in Figure 58. Filtration removed the fines that were apparent after centrifugation of treated samples. As a result, more accurate analytical results were achieved and removal efficiencies of approximately 90% were observed for each material except for the MCM-41 silica substrate, which adsorbed minor amounts of mercury during the tests.

**Figure 58** Percentage mercury removal using various materials

*Conditions: T = 22°C, [material] = 1.0 g/L, [Hg]₀ = 36.3 µg/L, t = 24 h. Samples filtered through 0.45µm nylon filter. Note: [Hg]₀ for Au-Silica (batch 3) and Ag-Silica tests = 63.1 µg/L.*

---

20 Previous studies have shown that nylon filters alone do not remove a significant quantity of mercury from solution.
A further series of batch tests were conducted to determine the effect of combining each of the noble metal impregnated materials with the Thiol SAMMS material to assess if any mercury removal synergies existed. These combinations were investigated based on the hypothesis that different species of mercury could possibly be present in condensate (refer to section 4.1) and that the different materials are known to target the removal of different species of mercury (Au and Ag target elemental mercury, Thiol SAMMS material targets both elemental and ionic mercury (Zhu et al, 2003)). Two concentrations of adsorbents were tested and the filtered and unfiltered results are reported (see Figures 59 and 60).

The combination of silica based materials performed very similarly to the two carbon powders at concentrations of 0.44 and 0.88 g/L. This is consistent with the silica based materials used on their own, and as such it appears that there is no significant benefit in combining thiol-SAMMS and noble metal-based materials.

![Figure 59](image-url)  
*Figure 59* Percentage mercury removal using various materials  
*Conditions: $T = 22^\circ$C, $[\text{material}] = 0.44 \text{ g/L}^\ast$, $[\text{Hg}]_i = 63.1 \ \mu\text{g/L}$, $t = 24 \ \text{h}$. Samples filtered through 0.45μm nylon filter.*  
*For mixtures 50% w/w of each material was used*
Figure 60 Percentage mercury removal using various materials
Conditions: $T = 22^\circ\text{C}$, $[\text{material}] = 0.88 \text{ g/L}$*, $[\text{Hg}]_i = 63.1 \mu\text{g/L}$, $t = 24$ h. Samples filtered through 0.45 µm nylon filter.
*For mixtures 50% w/w of each material was used

5.4.1.2 Stability of materials

The stability of the Au-Si, Ag-Si and Thiol SAMMS materials were investigated to determine whether certain components of these materials were leached into the condensate solution. The liquor samples collected from the batch tests were analysed for relevant constituents. ICP-MS analysis was used to determine Si (semi-quantitative) and Au plus Ag (semi-quantitative) for the noble metal based materials. No method was available for trace analysis of sulphur so the stability of the sulphur in the Thiol SAMMS material was investigated using TOC analysis. This was appropriate as the thiol containing ligand consists of a number of carbon atoms and it was assumed that if the ligand was significantly leached then this could be determined by TOC analysis. The results of the ICP-MS analyses are presented in Tables 19 and 20. It can be seen that there was a significant increase in Si concentration in the condensate samples treated with silica based materials. As these materials consisted of fine particles it is possible that a proportion of this increase was due to very small “undissolved” silica particles not being removed by filtration. Based on the semi-quantitative ICP-MS analysis, approximately
5-7% of the Si in each of the silica based materials investigated was either leached into condensate or could not be removed by centrifugation and filtration (0.45 µm). Further tests would need to be conducted to determine if this Si loss was only an initial occurrence or whether the materials would continue to degrade in contact with condensate.

The semi-quantitative ICP-MS data for Au and Ag indicates that the Ag-Si material leaches Ag into condensate under the test conditions. The quantity of Ag leached is, however, quite small and corresponds to ~5% of the impregnated Ag being leached (based on the assumption that the Ag-Si material is ~2.5% wt Ag), and as for the Si result, further tests would need to be conducted to determine if Ag would continually leach into condensate over time.

From the Au concentration data obtained it is difficult to determine the stability of the Au in the Au-Si material. This is partly due to the need to add the same quantity of gold to all samples prior to analysis for mercury by ICP-MS, reducing the analytical sensitivity for Au. It does appear, however, that Au-Si did not leach a significant amount of gold into condensate under the test conditions.

### Table 19 ICP-MS results on batch tested materials

*Conditions: $T = 22^\circ C$, $[\text{material}] = 1.0 \text{ g/L}$, $t = 24 \text{ h}$. Note - data in tables is for diluted samples and should be used only for comparing samples with blanks.*

<table>
<thead>
<tr>
<th>Material</th>
<th>Au (µg/L)</th>
<th>Si (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (condensate)</td>
<td>81</td>
<td>100</td>
</tr>
<tr>
<td>None (milli-Q H₂O)</td>
<td>59</td>
<td>93</td>
</tr>
<tr>
<td>Au-Si (batch 1)</td>
<td>20 (100)</td>
<td>1,100 (1,200)</td>
</tr>
<tr>
<td>Thiol SAMMS</td>
<td>61 (50)</td>
<td>710 (690)</td>
</tr>
<tr>
<td>MCM-41</td>
<td>83 (71)</td>
<td>1300 (1300)</td>
</tr>
<tr>
<td>PAC-D10</td>
<td>71</td>
<td>100</td>
</tr>
<tr>
<td>PAC-AZO</td>
<td>90</td>
<td>100</td>
</tr>
</tbody>
</table>

Filtered data in parentheses
**Table 20 ICP-MS results on batch tested materials**
*Conditions: T = 22°C, [material] = 0.88 g/L*, t = 24 h. Note – data in tables for diluted samples and should be used only for comparing samples with blanks.*

<table>
<thead>
<tr>
<th>Material</th>
<th>Au (µg/L)</th>
<th>Ag (µg/L)</th>
<th>Si (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (condensate)</td>
<td>110</td>
<td>0.84</td>
<td>130</td>
</tr>
<tr>
<td>None (milli-Q H₂O)</td>
<td>150</td>
<td>0.16</td>
<td>170</td>
</tr>
<tr>
<td>Ag-Si + Thiol SAMMS</td>
<td>150 (120)</td>
<td>2.5† (18)</td>
<td>220† (1500)</td>
</tr>
<tr>
<td>Au-Si + Thiol SAMMS</td>
<td>(150)</td>
<td>(8.9)</td>
<td>(1800)</td>
</tr>
</tbody>
</table>

Filtered data in parentheses
*For mixtures 50% w/w of each material was used
†Values are most likely outliers due to experimental or instrumental error

Based on the TOC results obtained for samples treated with the Thiol SAMMS material (see Table 21), where there was a significant increase in TOC concentration, the ligands binding the thiol groups to the silica substrate do not appear to be stable in condensate. The extent of leaching/decomposition of this material was difficult to determine accurately because the exact percentage by weight of thiol containing ligand in the Thiol SAMMS was unknown. Based on the assumption used by Feng *et al* (1997) that $5 \times 10^{18}$ molecules of the thiol containing ligand can occupy 1 square meter if a dense monolayer is formed, and the surface area of the MCM-41 used to prepare the material (854 m²/g), it can be approximated that the Thiol SAMMS material contained ~23% wt carbon. Using the assumption that the *complete* thiol containing ligand becomes detached from the MCM-41 (i.e. there is no chain scission of the ligand); the extent of leaching in terms of carbon was ~5%. This corresponds to an increase in sulphur concentration in treated condensate of ~ 8.7 mg/L.

**Table 21 TOC concentration results for batch tested materials**

<table>
<thead>
<tr>
<th>Material</th>
<th>Material Concentration (g/L)</th>
<th>TOC (mg/L)</th>
<th>% TOC (increase(+) or decrease(-))</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>-</td>
<td>35.2</td>
<td>0</td>
</tr>
<tr>
<td>Au-Si (batch 3)</td>
<td>1.0</td>
<td>33.9</td>
<td>- 3.7</td>
</tr>
<tr>
<td>Ag-Si</td>
<td>1.0</td>
<td>34.5</td>
<td>- 2.0</td>
</tr>
<tr>
<td>Thiol SAMMS</td>
<td>1.0</td>
<td>46.6</td>
<td>+32.4</td>
</tr>
<tr>
<td>MCM-41</td>
<td>1.0</td>
<td>34.4</td>
<td>- 2.3</td>
</tr>
<tr>
<td>PAC-D10</td>
<td>1.0</td>
<td>14.3</td>
<td>- 59.4</td>
</tr>
<tr>
<td>PAC-AZO</td>
<td>1.0</td>
<td>13.9</td>
<td>- 60.5</td>
</tr>
<tr>
<td>Ag-Silica + Thiol SAMMS</td>
<td>0.88</td>
<td>40.2</td>
<td>+14.2</td>
</tr>
<tr>
<td>PAC AZO + D10</td>
<td>0.88</td>
<td>13.6</td>
<td>- 61.4</td>
</tr>
</tbody>
</table>
The extent of leaching estimated for the Thiol SAMMS material could have been overestimated due to small particles of this material not being captured during filtration, or underestimated if chain scission of the ligand occurred. In an attempt to corroborate the TOC results that implied ligand detachment or breakdown, it was decided to investigate the amount of sulphur in the Thiol SAMMS using EDS analysis. Figures 57 and 61 show the EDS traces of Thiol-SAMMS unused and used respectively. The reduced sulphur peak, relative to other peaks in the analysis of the used sample, corroborated the sulphur loss indicated by the TOC results. These results are shown in Table 22.

Figure 61 EDS trace of Thiol SAMMS showing reduced sulphur peak
Table 22 Peak ratios for used and unused Thiol-SAMMS

<table>
<thead>
<tr>
<th>Analytes</th>
<th>Peak ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unused Thiol-SAMMS</td>
</tr>
<tr>
<td>S/Si</td>
<td>0.10</td>
</tr>
<tr>
<td>S/O</td>
<td>0.20</td>
</tr>
<tr>
<td>S/C</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Conditions: EDS conducted at 25.0 kV at 10 mm working distance scanning full screen

5.4.2 Kinetic test results

The removal of mercury from condensate was investigated using the filtration procedure described in section 5.2.5 to determine the relative rates of removal for the silica-based materials. Two contact times were compared; 6 and 12 seconds. The results of the first series of kinetic tests, which were conducted using a residence time of six seconds, are presented in Figure 62. From the results presented in Figure 62 it can be seen that both PACs and the Au-Si material removed a high amount of mercury (>85%) under the conditions used. The Thiol SAMMS material was also capable of removing a relatively high amount of mercury (~80%) while the Ag-Si material removed ~60%. The high amount of mercury removed in the blank test (~50%) is most likely due to a combination of loss of mercury through volatilisation, mercury being purged from condensate under the test conditions used and/or adsorption to the plastic syringe filter unit (L McGuiness, [Alcoa World Alumina] 2003, pers. comm., 21 March).
Further kinetic tests were conducted using a longer residence time (12 sec) and a higher number of bed volumes to determine the effect of residence time on the mercury removal efficiencies of the various materials and to investigate the effect of the number of bed volumes used. The results of these tests are presented in Figure 63. The longer residence time did not significantly improve the mercury removal for any of the materials tested. The MCM-41 material did not remove a high amount of mercury, which was expected based on the batch test results. The procedural uncertainty for these tests was not determined, however it could be expected that the small differences in the results associated with the number of bed volumes tested would be within the expected uncertainty levels. This would also explain why the removal efficiency associated with the Ag-Si appeared to improve with increasing bed volumes. Based on this assumption, the number of bed volumes tested had very little effect on mercury removal for the materials, implying that the experiment was not conducted long enough to determine the capacity of the materials under the test conditions and at what stage the removal efficiency would significantly decline.
Figure 63 Kinetic test results
Conditions: $T=22\, ^\circ \text{C}$, residence time = 12 sec, bed volumes (see graph legend), $[\text{Hg}]_i = 47.1\, \mu \text{g/L}$.

5.5 Conclusions

- All silica-based materials demonstrated efficient mercury removal, which occurs quite rapidly (~6 seconds). The efficiency does not significantly decline over 120 bed volumes.

- The novel materials were slightly unstable in condensate under the test conditions. Si was leached from all three novel materials tested.

- TOC and S were leached from the Thiol SAMMS material.

- Ag was leached from the Ag-Si material.

It is recommended that mercury removal using Thiol SAMMS prepared using a supercritical method be investigated. According to a personal communication with G. Fryxell (2004, 12 June) this material is more stable in alkaline conditions and hence, better suited for treating condensate. It was originally planned to include the supercritical prepared Thiol SAMMS.
material in this study however the laboratory that produces this material was unable to produce any for this study in a timely manner.

It is also recommended that any further studies conducted using the Au-Si or Thiol SAMMS material involve investigations on the recycling (regeneration and re-use) of these materials to improve the economic viability of the materials.

In addition, Au and/or thiol containing ligands impregnated on other supports such as polymers that are stable in alkaline solution should be considered for investigation. The lower surface areas of such materials may however lead to reduced capacities and/or removal rates.

### 6 PROCESS RECOMMENDATIONS

#### 6.1 Activated carbon

Activated carbon is regarded as the industry benchmark for mercury removal from process waters and the effectiveness of an alternative removal process is often evaluated by comparing it to an activated carbon application. A variety of activated carbons were tested to assess the carbons as removal options and also to develop a standard by which to compare the other process options investigated.

The activated carbon varieties tested were:

- granular and extrudate virgin activated carbon
- granular and extrudate sulphur impregnated activated carbon
- an extruded silver impregnated activated carbon
- a combination of two powdered virgin activated carbons.
Each carbon type tested exhibited unique surface and chemical properties (see Table 11) that would indicate it as a potential candidate for mercury removal. The results associated with each carbon type are summarised below.

Virgin activated carbon (VAC) adsorbs elemental mercury via a physical adsorption process which is controlled to a large extent by the driving force associated with the mercury concentration in solution (Anoop Krishnan and Anirudhan, 2002b; Budinova et al, 2003). At relatively low concentrations, such as those used in this study, extrapolations from data sourced from Huang and Blankenship (1994) suggest the expected mercury loadings following treatment of condensate would be ~0.08% (w/w). These expected mercury loadings were not approached by the granular activated carbons where a maximum loading of 0.005 (w/w) was observed. It was concluded that the lower than expected mercury loadings were attributable to:

- Competition for active sites from organics in solution (see Table 2, page 12 and Figure 33)
- The form in which mercury is present in condensate (microballs, Hg(OH)_2 and Hg(organic)) is not readily removed under the conditions.

As a result of the lower than expected mercury capture, virgin activated carbon was not recommended as a mercury removal option.

Sulphur impregnated carbons (SIAC) were investigated due to their high mercury capacities. In stoichiometric terms, up to 20% (w/w) have been reported, however Nucon carbon demonstrated a mercury capacity of 0.1 – 1% (w/w) using a sulphur impregnated carbon (Nucon International Inc., 1997). The extra capacity associated with sulphur impregnation was not demonstrated during these tests because a loss of sulphur occurred during contact  

\[21 \text{ Molecular size approximately 0.7 nm based on atomic radii.} \]
with the basic condensate solution (Equations 3.1 – 3.3). As a result, the SIACs demonstrated a similar loading to that of the granular VAC, which were 0.006% and 0.005% (w/w) respectively. It was concluded that due to the loss of sulphur the mechanism driving mercury adsorption onto the SIACs was a physical process. It was hypothesised that the TOC within the solution affected the mercury loading by preferentially adsorbing to active sites. Between 30% – 50% TOC removal occurred in the column tests over a large number of bed volumes (170 BV). During this contact time the TOC removal had not levelled out, indicating that the full effect of preferential adsorption had not been reached and as a result, the mercury adsorption would most likely have continued to decline. Because the SIACs effectively acted as granular VACs, they were not recommended for use in a mercury removal process.

The silver impregnated into the activated carbon (AgACN) is designed to act as a sterilisation reagent. Norit Carbon does not recommend this carbon for mercury removal (C. Cheong, [Norit Carbon] 2003, pers. comm. 29 July) and, as such, the expected mercury capacity for this material is not known. The AgACN was assessed to determine whether amalgamation or chemisorption may be occurring between the silver and dissolved elemental mercury in condensate. Amalgamation/chemisorption may have been demonstrated because the AgACN clearly removed the highest amount of mercury under the batch test conditions (84%). The AgACN also removed the highest amount of TOC of all carbons tested, however if chemisorption or amalgamation is the primary mechanism for mercury removal, preferential adsorption or pore blockage from TOC would not significantly impede the process. AgACN is very expensive and would not be considered for a plant-scale process unless a suitable regeneration technique was also developed.

Following recommendations from Norit carbon (C. Cheong, [Norit Carbon] 2003, pers. comm. 29 July), two powdered virgin activated carbons (PAC) were mixed and used in a filtration arrangement. The PACs efficiently removed mercury during filtration tests with no breakthrough after 250 bed volumes. Breakthrough was not achieved due to time constraints.
within the project preventing an extended test. TOC readily adsorbed to the PACs but no reduction in efficiency was observed as a consequence.

The relatively efficient mercury removal obtained using the PACs is most likely due to:

- Small particle size of carbons (improved solid solution contact leading to good mercury sorption kinetics and also reduced likelihood of channelling)

- Two different types of carbon (D10 preferentially removes organics that may have blocked the pores of AZO or have adsorbed preferentially to the mercury)

- Larger average pore sizes (macropores and mesopores) relative to the other carbons tested.

Although high mercury removal efficiencies were observed, the maximum mercury loading demonstrated for the PACs (0.013% w/w) did not approach the expected loading for VACs (~0.08% w/w) estimated by extrapolating data from Huang and Blankenship (1997). This may have been attributable to fouling from organics.

Despite a lower than desirable mercury loading, the high mercury removal efficiency and very low residence times during filtration (<30 seconds) may warrant that further tests be conducted, particularly to determine the number of bed volumes of condensate that can be passed through the filter before mercury breakthrough occurs.

### 6.1.1 Conclusions

- Virgin granular activated carbons are not recommended because of the lower than expected mercury loading, relatively poor removal efficiencies and high potential for contamination and de-activation from TOC.
• Sulphur impregnated carbons are not recommended due to dissolution of sulphur in basic solutions such as condensate.

• Due to time constraints the filtration tests for the PACs did not achieve mercury breakthrough. To fully assess the potential for PACs, further tests are required. A recommendation is to develop a testing apparatus to enable continuous filtration that would allow in excess of 250 bed volumes to be passed through the filter bed and therefore determine the number of bed volumes of condensate required to achieve mercury breakthrough. Based on the breakthrough data, an economic assessment of a PACs process can be conducted.

• Further evaluation of amalgamation or chemisorption processes for removing mercury from condensate using a high surface area form of a suitable metal such as tin.

6.2 Impregnated mineral material

The sulphur impregnated activated carbons (SACs) were expected to have a superior mercury capacity compared to VACs, however, being typical for carbons, they also have a high affinity for organics which may reduce the removal efficiencies over time. For this reason it was decided to test a non-carbon (mineral) sulphur impregnated material. The material used (PIM) was an impregnated vermiculite. Unfortunately, this material, like the SACs, suffered from sulphur dissolution in the condensate and so is not recommended for further investigation.
6.3 Chemisorption/amalgamation using silica based materials

The silica based materials tested (Au-Si, Ag-Si and Thiol SAMMS) were capable of removing comparably high amounts of mercury from condensate under the batch and kinetic test conditions when compared to the PACs. However there are questions about the stability of both the Thiol-SAMMs and the Ag-Si material in condensate at room temperature. The thiol-SAMMs appeared to lose organic carbon and sulphur from the ligands attached to the silica substrate, although it was difficult to accurately determine the extent of this loss. Similarly, silver appeared to leach into the condensate solution from the Ag-Si material. It could be expected that this lack of stability in condensate would be exacerbated at the condensate operating temperature of 95 °C.

It is recommended that extended testing and evaluation be conducted on the Au-Si material to determine the capacity of the material and long-term stability. Such studies should include regeneration processes to improve the economic viability of the materials.

In addition, it is recommended that Thiol-SAMMS be produced using a supercritical method, which is expected to improve the stability of the material in alkaline solutions. Regeneration tests should also be conducted on the Thiol-SAMMS.

6.4 Gas sparging

Gas sparging was investigated as elemental mercury has a high Henry’s coefficient and because it had been successfully used to remove mercury in previous studies (Bloom and Turner, 2004; Looney et al, 2003.) A consistent extraction efficiency of 80% was achieved without the addition of a chemical reduction stage. The sparging gas used was free of oxygen to prevent changing the chemical conditions to favour non-spargable mercuric hydroxide over
elemental mercury, however the oxidation of elemental mercury in air is relatively slow (Canela and Jardim, 1997; Mroczek, 2000; Nelson et al, 2004) and the use of an oxygen free gas may not be necessary in practise. The impact of oxygen on sparging would need to be determined prior to investing in the development of plant-scale sparging equipment.

Although efficient mercury sparging was demonstrated in laboratory-scale tests, the process merely transferred mercury to a vapour phase. It is recommended that a sparging process also includes a recompression / condensation stage to allow the collected mercury to be collected as a metal. Another recommendation is that steam be used as the sparging gas to maintain a high extraction temperature, facilitating greater removal.

A potential process for the sparging of mercury from condensate is described below. It is schematically represented in Figure 64. The process combines the sparging of mercury at 95 °C in a single-stage packed column with recompression and condensation of mercury in a liquid ring vacuum pump for collection via a gravity fed collection vessel. Although air would be a suitable sparge gas because the oxidation of elemental mercury in air is relatively slow (Canela and Jardim, 1997; Mroczek, 2000; Nelson et al, 2004), low pressure steam is recommended as the sparging gas to sustain a high temperature to further facilitate mercury volatilisation. A heat exchanger will cool the stripped vapour to approximately 30 °C using cooling water drawn from a storage lake.

The suggested process is as follows:

- Sparge using low pressure steam to maintain the low solution Eh required to keep mercury in the zero oxidation state and to keep the sparging temperature as high as possible.
- Introduce the steam to the condensate at 95 °C.
- Maintain a vacuum above the packed bed to decrease the mercury vapour pressure using a vacuum pump positioned downstream.

- The vacuum seal water is sourced from an ambient lake to cool the sparged vapours as much as possible to encourage mercury condensation within the vacuum pump and therefore the collection pot.

- The vapour is compressed in the vacuum pump, encouraging further mercury condensation.

- Condensed mercury is collected in a pot and liquid mercury is regularly collected from the pot.

Data produced during the experimentation was used to develop an estimate of capital and operating expenditure for a steam sparging process. Other data required for a cost estimate is shown in Table 23. The equipment costs and capital estimate are shown in Table 24. The cost
of operating the unit on an annual basis is shown in Table 25. Assuming the condensate in in the feed stream is at 20 µg/L and that 80% sparging efficiency occurs, a mass balance of mercury across the process is shown in Table 26.

<p>| Table 23 Data used for the development of a cost estimate for a steam sparging process |
|-----------------------------------------------|----------------------------------|------------------|------------------|-------------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Condensate flow (kL/h)</th>
<th>Condensate temperature (°C)</th>
<th>Steam flow (tonnes/hour)</th>
<th>Steam temperature (°C)</th>
<th>Packing material</th>
<th>Stripper tower dimensions (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>95</td>
<td>2</td>
<td>110</td>
<td>1” HDPP saddles</td>
<td>H = 8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>D = 2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cooling water temperature (°C)</th>
<th>Nominal pressure drop (Pa)</th>
<th># transfer units</th>
<th>Prefiltration (µm)</th>
<th>Construction material</th>
<th>Packing volume (m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>5</td>
<td>4</td>
<td>5</td>
<td>Mild steel</td>
<td>25</td>
</tr>
</tbody>
</table>

| Table 24 Capital expense estimate |
|-----------------------------------|-----------------|
| Item                              | AUD x 1000 |
| HX                                | 100           |
| Pre-filtration                    | 250           |
| Stripper                          | 400           |
| Piping                            | 400           |
| Electrical                        | 130           |
| Instrumentation / PLC             | 500           |
| Control room                      | 100           |
| Civil                             | 500           |
| Site work and commissioning       | 500           |
| Packing ($1k/m³)                  | 25            |
| Vacuum pump                       | 200           |
| Seal water separation pot         | 50            |
| Mercury collection pot            | 5             |
| **Sub total**                     | **3160**      |
| Eng + project management (20%)    | 632           |
| **Total**                         | **3792**      |
Table 25  *Annual operating expense estimate*

<table>
<thead>
<tr>
<th>Item</th>
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</tr>
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<tbody>
<tr>
<td>Electricity</td>
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<tr>
<td>Filtration cartridges</td>
<td>50</td>
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<tr>
<td>Maintenance</td>
<td>100</td>
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<tr>
<td>Steam production</td>
<td>160</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>510</strong></td>
</tr>
</tbody>
</table>

Table 26  *Mercury mass balance (per year)*

<table>
<thead>
<tr>
<th>Mercury source</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercury into stripper (kg)</td>
<td>43.8</td>
</tr>
<tr>
<td>Mercury to heat exchanger (kg)</td>
<td>35.0</td>
</tr>
<tr>
<td>Mercury in discharge water (kg)</td>
<td>0.4</td>
</tr>
<tr>
<td>Mercury collected in pot (kg)</td>
<td>34.7</td>
</tr>
<tr>
<td><strong>Removal efficiency (%)</strong></td>
<td><strong>79.2</strong></td>
</tr>
</tbody>
</table>

7  **GENERAL SUMMARY**

Bayer refinery digestion condensate is chemically unique because it exhibits high pH and originates from the digestion process, which is chemically reducing. Eh and pH measurements of digestion condensate indicated that elemental mercury was the thermodynamically favoured state present in condensate. Digestion condensate also exists at high temperatures of \(~95\,^\circ\text{C}\) and has high flow rates up to 490 kL/hour. A literature review of mercury removal processes was conducted to determine candidate processes suited to the unique chemical and physical conditions of digestion condensate. Three broad process options were selected for investigation. These were:

- adsorption onto activated carbon

- sparging mercury into a gas stream

- complexation onto modified silica substrates containing sulphur functional groups as impregnates
amalgamation/chemisorption onto modified silica substrates using noble metals as impregnates

A variety of activated carbon types were tested including granular virgin activated carbon (VAC); granular and extrudate sulphur impregnated activated carbon (SIAC); an extruded silver impregnated activated carbon (AgAC) and a combination of two powdered virgin activated carbons (PAC). The adsorption mechanism for both the VAC and the SIACs was physical. The sulphur that was impregnated into the SIAC did not increase the mercury capacity due to dissolution into the condensate solution. The removal efficiency and mercury loading demonstrated by these carbon types was poor and did not justify further investigation.

The PACs demonstrated a superior mercury loading and a higher removal efficiency compared to the VAC and SIACs. Time constraints did not allow the volume of condensate required to reach mercury breakthrough to be determined and it is recommended that further evaluation of these carbons be conducted.

The AgAC demonstrated the highest mercury loading of the granular and extruded carbon types. This may be attributable to amalgamation or chemisorption of elemental mercury onto the silver and it is recommended that mercury removal via amalgamation/chemisorption be investigated using a high surface area form of suitable metals such as silver and tin.

As was the case for the SIACs, the impregnated mineral material suffered from sulphur dissolution in the condensate. This material is therefore not recommended for further investigation.

Each of the silica based materials, except for the gold impregnated silica, demonstrated poor stability in condensate and should not be considered for implementation. Although the gold impregnated silica was stable, and demonstrated effective mercury removal, it would be too expensive to justify for use on an industrial scale without a process for regeneration of the
active gold sites. It did, however, further illustrate the merits of amalgamation as a likely process for mercury removal.

Gas sparging was the most viable opportunity for mercury removal with 80% mercury removal demonstrated. A system involving steam sparging followed by compression and re-condensation of the mercury for collection was costed. It was estimated that the system would cost approximately $4 million dollars to install with annual operating costs of approximately $500 000.
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## 9.1 Water mass balance for mercury sparging experiments - Phase 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Purge time (min)</th>
<th>Hg (µg/L)</th>
<th>TOC (mg/L)</th>
<th>Cumulative sample volume removed (mL)</th>
<th>Calculated volume remaining (mL)</th>
<th>Measured volume remaining (mL)</th>
<th>Volume unaccounted for (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MT0</td>
<td>0</td>
<td>19.1</td>
<td>56</td>
<td>0</td>
<td>2750</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MT1</td>
<td>10</td>
<td>12.2</td>
<td>70</td>
<td>82</td>
<td>2668</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MT2</td>
<td>20</td>
<td>7.3</td>
<td>42</td>
<td>164</td>
<td>2586</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MT3</td>
<td>40</td>
<td>6.5</td>
<td>42</td>
<td>246</td>
<td>2504</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MT4</td>
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<td>4.7</td>
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<td>328</td>
<td>2422</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>5.0</td>
<td>46</td>
<td>410</td>
<td>2340</td>
<td>2200</td>
<td>220</td>
</tr>
<tr>
<td>MT6</td>
<td>distillate</td>
<td>0.5</td>
<td>64</td>
<td>360</td>
<td></td>
<td></td>
<td></td>
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