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Removal of mercury from an alumina refinery aqueous stream

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Abstract

Digestion condensate is formed as a by-product of the alumina refinery digestion process. The solution exhibits a high pH and is chemically reducing, containing many volatile species such as water, volatile organics, ammonia, and mercury. Because digestion condensate is chemically unique, an innovative approach was required to investigate mercury removal. The mercury capacity and adsorption kinetics were investigated using a number of materials including gold, silver and sulphur impregnated silica and a silver impregnated carbon. The results were compared to commercial sorbents, including extruded and powdered virgin activated carbons and a sulphur impregnated mineral. Nano-gold supported on silica (88% removal under batch conditions) and 95% removal under flow conditions) and powdered activated carbon (91% under batch conditions and 98% removal under flow conditions) were the most effective materials investigated. The silver and sulphur impregnated materials were unstable in digestion condensate under the test conditions used.

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1. Introduction

During the alumina refinery digestion process, bauxite is mixed with recycled caustic liquor (Bayer liquor) and pumped into autoclaves, where it is commonly heated by the direct injection of superheated steam. The organics that dissolve from the bauxite into the liquor phase are readily oxidised and the digestion process is therefore chemically reducing. The gaseous phase above the digestion process typically includes gases such as hydrogen, nitrogen, methane, ammonia [1], water [1] and some volatile organic carbons (VOCs) [2], with the balance being nitrogen. Mercury, originating from sulphide minerals such as pyrite within the bauxite, is also most likely reduced during digestion and the digestion gases can be saturated with respect to mercury vapour according to Henry's law [3–5]. This has also been observed in condensate waters produced from kilns used to distil HgS in the mercury mining industry [6].

Following the required digestion contact time, the heated slurry is cooled in a series of flash vessels and the evolved

0304-3894/\$ - see front matter © 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat.2006.10.041 steam is condensed inside heat exchangers to recover heat back to the digestion process. The vapour within the heat exchangers is flashed and cooled to produce a predominantly aqueous phase known as digestion condensate (condensate). This solution contains a number of species such as ammonia, mercury and organic compounds that either co-condense or are dissolved in the condensate. In addition to the aforementioned species caustic mist carried over from digestion vapours also dissolves into the condensate to produce a solution with a relatively high pH.

A significant amount of research has been conducted on the removal of mercury from aqueous streams [7–11]; however, most research has focussed on the removal of relatively high concentrations of oxidised mercury (>10 mg/L) from synthetic solutions [12–16]. Due to increasing environmental awareness and increasingly stricter regulations on acceptable levels of mercury emissions, there is greater interest in removing mercury from streams containing relatively low concentrations of mercury (<100 ppb) [17–19]. Condensate typically contains only 20 μ g/L mercury [20]; however, the removal of mercury from this stream is of interest due the high volumes of condensate produced within alumina refineries, which are typically greater than 200 kL/h.

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Condensate is a chemically reducing solution with a high pH, contains low levels of mercury and also exhibits high temperatures (\sim 95 °C) and high flow rates (<200 kL/h). Very little scientific literature describes mercury removal from water streams produced within an industrial refinery environment and, in particular, possessing similar physical and chemical characteristics to that of condensate. As a result, the main aim of this study was to investigate mercury removal from condensate using various types of novel materials and to compare the adsorption kinetics and mercury capacity of these experimental materials to commercially available sorbents, including activated carbon, which remains an industry standard for mercury removal. Because there is the potential for mercury to exist in condensate as both elemental and oxidised forms, the materials tested in this study were also selected for their capability to capture mercury in the two oxidation states.

2. Experimental

2.1. Materials

The following carbons were used as received unless otherwise stated: extruded virgin activated carbon - RB4 (Norit), silver impregnated granular activated carbon - RB 0.8 AG 1 (Norit), powdered activated carbon - AZO (Norit) and powdered activated carbon - D10 (Norit). The impregnated mineral material (IM) was used as received. Nano-gold and nano-silver impregnated silica were prepared using the method of Zhu et al. [21]. The following chemicals were used as received for the aforementioned preparations: chloroauric acid, HAuCl₄·3H₂O (Aldrich), silver nitrate, AgNO₃, [3-2-(aminoethylamino) propyltrimethoxy silane], H₂NCH₂CH₂NHCH₂CH₂CH₂Si(OCH₃)₃ (Aldrich), cetryltrimethyl bromide (CTAB) (Aldrich), tetraethylorthosilicate (TEOS) (Aldrich), potassium hydroxide, KOH (Fluka). Two different reduction methods were used to prepare two different gold impregnated silica's: (1) hydrogen reduction at 200 °C for 1 h and (2) hydrothermal treatment at 90 °C for 24 h. The silver impregnated silica was prepared using reduction method 1. Thiol SAMMS was prepared using a method very similar to that described by Feng et al. [22]. The MCM-41 used in the preparation of thiol SAMMS was prepared using the method of Katiyar et al. [23]. The following chemicals were used as received to prepare the thiol SAMMS; colloidal silica, tetramethylammonium hydroxide, CTAB, ammonium hydroxide, mercaptopropyltrimethoxysilane, methanol and iso-propyl alcohol.

Digestion condensates were obtained from two alumina refineries in Western Australia (Kwinana and Wagerup).

2.2. Methods

2.2.1. Adjustment of Hg concentration and Eh

The mercury concentration in digestion condensates from different alumina refineries can vary significantly [20], due mainly to differing bauxite mineralogy, while the mercury concentration in digestion condensate at individual refineries can also vary from day to day due to dilution from other streams and operational variations within the digestion process [20]. Due to these variations in concentration, it was decided to pre-treat condensate samples prior to testing to ensure similar initial mercury concentrations in all samples at a concentration that was high enough to allow good analytical sensitivity. The pre-treatment method involved reducing the collected condensate's Eh (redox potential) to <-50 mV (versus SHE) by passing a stream of hydrogen through the condensate (to ensure a similar Eh to that encountered under refinery conditions). This was then followed by passing a stream of mercury saturated nitrogen above a batch of condensate (5-15 L) for at least 24 h to ensure a relatively high and consistent initial mercury concentration. The mercury concentration in the condensates used prior to pre-treatment was 2-10 ppb. Mercury concentration after pre-treatment was typically in the range of 15–35 ppb. According to Clever et al. [24] the solubility of elemental mercury in water at room temperature is 60.8 ± 2.4 ppb. The aforementioned value was derived from data obtained in six independent studies [4,25–29]. Based on the reported solubility of elemental mercury in water and the concentration range used in this study the mercury present in condensate is predominantly in a soluble form.

2.2.2. Eh/pH measurements of condensate

Digestion condensate was sampled from the refinery at $95 \,^{\circ}$ C and allowed to cool to ambient temperature in polyte-traflouroethylene (PTFE) sealed borosilicate bottles with no headspace. The sample remained in this condition until measurement.

2.2.3. Batch tests

Batch tests were conducted using two methods:

- (1) Culture tubes rotated (end over end) in a water bath.
- (2) Stirring (flea) in round bottom flasks. Centrifugation was used to separate the materials from condensate prior to collection of aqueous samples for analysis.

2.2.4. Flow tests

A schematic diagram of the up-flow column apparatus used is given in Fig. 1. Filtration tests were conducted as follows: A pre-weighed portion of material to be tested was placed inside a filter unit. Condensate was forced through the unit using a syringe and plunger.

2.2.5. Analytical measurements and materials characterisation

The following instruments were used for analytical measurements and/or characterisation of the materials investigated:

TPS WP-80D meter/data logger, IJ44 BNC connector double junction "A" glass tip pH electrode, TPS combination platinum IJ Ag/AgCl redox probe – Eh and pH measurements, Agilent Technologies 4500 inductively coupled plasma-mass spectrometer (ICP-MS) – Hg, Si, Au and Ag analysis, OI-Analytical 1010 total carbon analyser – total organic carbon analysis; Micromeritics ASAP 2000 surface area analyser – surface area and average pore



Fig. 1. Schematic diagram of up-flow column apparatus.

size measurements; Bruker Advanced D8 X-ray diffractometer – X-ray diffraction patterns; FEI Quanta 400 FEG scanning electron microscope (SEM) – EDS traces, FEI VG310F X-ray photoelectron spectrometer – identification of surface elements.

Ammonia concentration was determined using a colorimetric method [30].

A detailed description of the method used for quantitative mercury analysis is given elsewhere [1]. The uncertainty for individual mercury measurements was calculated to be $\pm 1.5\%$. Mercury measurements of selected replicate samples had a precision of $\pm 5\%$.

3. Results and discussion

3.1. Digestion condensate—characteristics, composition and mercury speciation

As no information was available in the open literature on the chemical and physical characteristics, composition and the species of mercury present in condensate, various tests were conducted to obtain the aforementioned information to assist in the selection of materials to study. The results of the analyses conducted to determine some of the chemical and physical characteristics and composition of the digestion condensates used in this study are presented in Table 1.

A search of the literature on methods for speciation of mercury in aqueous solution at mercury concentrations similar to those encountered in digestion condensate revealed that it is ideal to speciate mercury in solutions that may contain volatile mercury (such as digestion condensate) within hours of collection by purging the mercury onto appropriate trapping media [31]. As no similar proven procedure was available for speciating mercury in a complex industrial wastewater such as digestion condensate, and because the development and validation of such a procedure would be a research study in its own right, it was decided to determine the predominant mercury species in digestion condensate using an indirect method-Eh and pH measurements and Pourbiax (stability) diagrams. The results of these measurements and the Pourbaix diagram generated are given in Fig. 2. Based on the data obtained, the predominant species of mercury in digestion condensate is elemental mercury. From Fig. 2 it can be seen however, that the co-ordinates for condensate on the Pourbaix diagram place the predicted mercury species very close to the stability boundary for Hg(II)/Hg(0). Although a small increase in Eh would position the coordinates in the region where Hg(II)was the thermodynamically stable species, the oxidation of elemental mercury is relatively slow unless strong oxidants [32], UV light and dissolved organic matter [33-36], or chloride ions

Table 1

Characteristics/composition of Bayer digestion condensates from two alumina refineries in Western Australia

Parameter	Concentration
COD (mg/L) Total Organics as C (mg/L) Ammonia (mg/L as N)	$ \begin{array}{c} 210-230 \\ 60^{a}, 35^{b} \\ 100^{a}, 50^{b} \\ 0c^{a}, 02^{b} \end{array} $
pH	90,95 11.0 ^a , 10.1 ^b

^a Condensate from Kwinana refinery.

^b Condensate from Wagerup refinery.





Fig. 2. Eh and pH measurements for digestion condensate overlaid onto a Pourbaix diagram with stability fields re-calculated for $20 \mu g/L$ mercury.

[37] are present. These agents and/or chemical species are not likely to be present in condensate within the refinery process. As a result, a small ingress of oxygen during a mercury removal process would be unlikely to effect a change in the mercury oxidation state.

3.2. Materials characterisation

Characterisation data for the materials investigated is given in Table 2. The size of the gold and silver nano-particles in the Au–Si and Ag–Si materials were calculated using the X-ray diffraction patterns of the respective materials and the Scherrer diffraction formula [38]. The S wt.% of the thiol SAMMS was calculated based on the assumption used by Feng et al. [22] that 5×10^{18} molecules of MPTMS can occupy one square meter if a dense monolayer is formed. EDS traces confirmed the presence of sulphur in the thiol SAMMs (Fig. 3) and IM material (Fig. 4). EDS traces also confirmed the presence of Au and Ag in the Au–Si and Ag–Si materials, respectively. XPS analysis confirmed the presence of Sn in the IM material.

3.3. Mercury removal—batch tests

Mercury removal from condensate using each of the materials listed in Table 2 was first investigated using batch tests. The results of these tests are given in Table 3. The order of mercury removal using a material concentration of 0.2 g/L was Au–Si (Au nano-particles $\sim 2.4 \text{ nm}$) > PACD > PACA > Au–Si (Au nano-particles $\sim 18.7 \text{ nm}$) > Ag–C > Ag–Si > TS > VACN >



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Fig. 4. EDS trace of impregnated mineral material.

AS>Blank 3>MCM-41>Blank 2>Blank 1. The high extent of removal obtained using the Au-Si materials indicates that mercury in condensate is predominantly present as Hg(0) (supporting the prediction based on Eh and pH measurements discussed earlier) as the high extent of removal using these materials is most likely due to the well known formation of amalgamations or chemisorption between Hg and Au [39,40]. Due to the low concentration of Hg used in this study it was not possible to confirm amalgam formation or chemisorption by X-ray diffraction analysis as this technique is not sufficiently sensitive to detect the extremely low degree of amalgamation or chemisorption that could potentially form. Of the virgin carbons tested (PACD, PACA and VACN), the powdered forms were clearly more effective than the particulate form. This is most likely due to better solid-solution contact and possibly also due to the powdered forms having larger average pore sizes, which are more suited to mercury adsorption (refer to Table 2) [41]. The other noble metal impregnated materials investigated, Ag-Si and Ag-C, were both capable of similar moderately high mercury removal (~70%), offering further support that the mercury in condensate is predominantly Hg(0) as removal was most likely due to well known

Table 2			
Characterisation of	data for	materials	investigated

Material	Surface area (m ² /g)	Average pore diameter (Å)	Other
Virgin activated carbon (VACN)	1173	17.3	0.5–1.4 mm particles ^a
Ag-impregnated carbon (Ag-C)	1194	19.0	0.8 mm diameter particles ^b , 0.1 wt.% Ag ^b
Impregnated mineral (IM)	NA ^c	NA ^c	\sim 2 mm vermiculite flakes, Sn on surface confirmed by XPS,
			S on surface confirmed by SEM-EDX
Powdered activated carbon AZO (PACA)	701	30.2	$PSD - D90 < 37 \ \mu m^b$
Powdered activated carbon D10 (PACD)	639	24.9	$PSD-D90 < 140 \ \mu m^{b}$
Au-silica (Au-Si)	174	30.7	\sim 2.5 wt.% Au, fine powder, average size of nano-particles
			using H ₂ reduction method \sim 2.4 nm, average size of
Ag silica (Ag Si)	14	72.2	~ 2.5 wt % Ag fine powder, average size of papo particles
Ag-sinca (Ag-51)	14	12.2	$\sim 5.6 \mathrm{nm}$
Thiol SAMMS (TS)	854 ^d	NA ^c	Fine powder, ~xx wt.% S
MCM-41	854	~35	Fine powder

^a Supplied as \sim 3 mm diameter extruded particles, crushed and dry sieved to obtain 0.5–1.4 mm size fraction.

^b Data from manufacturer data sheets.

^c Accurate surface area measurement could not be obtained due to sulphur evaporating during pre-treatment required for surface area analysis.

^d Surface area prior to impregnation.

formation of amalgams or chemisorption between Hg and Ag. The thiol SAMMS material, which according to Feng et al. [22] is capable of removing both Hg(0) and Hg(II) species, was capable of moderately high mercury removal (\sim 70%). It was visibly apparent that the method used to separate the materials from condensate (centrifugation) was not completely effective for the thiol SAMMS as this material contained extremely fine particles. The aqueous sample from the 1.0 g/L test was therefore filtered through a 0.45 µm membrane and re-analysed to determine the effect of removing the fine particles. The mercury removal

Table 3 Batch test results ($T = 22 \degree C$, t = 24 h)

Material Material concentration (g/L)		Mercury removal (%)
Blank 1 ^a		3.9
Blank 2 ^b		17.4
Blank 3 ^c		24.5
VACN ^a	0.2	47.8
Ag–C ^a	0.2	74.4
AS ^a	0.2	34.3
PACA ^b	0.2	81.5
PACD ^b	0.2	83.2
Au–Si ^b	0.2	75.8 ^d , 83.3 ^e
Ag-Si ^c	0.2	69.7
TS ^b	0.2	68.9
MCM-41 ^b	0.2	14.9
VACN ^a	2.0	50.7
Ag–C ^a	2.0	83.7
IM ^a	2.0	53.7
PACA ^b	1.0	91.2
PACD ^b	1.0	89.0
Au–Si ^b	1.0	75.0, 88.4
Ag-Si ^c	1.0	88.4
TS ^b	1.0	73.6
MCM-41 ^b	1.0	25.6

^a Initial Hg concentration = 20.3 ppb.

^b Initial Hg concentration = 36.3 ppb.

^c Initial Hg concentration = 63.1 ppb.

^d Au nano-particles ~18.7 nm.

^e Au nano-particles ~2.4 nm.

measured after filtration was significantly higher at 95.6% cf. to 73.6% due to the fines not reporting to analysis (mercury removal in filtered blank solution was 24.5% cf. to 17.4%). The two worst performing materials were the IM and MCM-41. The poor performance of the MCM-41 was expected as this material contained no impregnated functional groups that react with mercury. The poor performance of the IM material was however, unexpected as this material contained tin and impregnated sulphur, which are both known to interact strongly with mercury. This result could have been due to poor mixing of this material in the 0.2 g/L test (significant portion floated in round bottom flask) and/or the impregnated sulphur or tin being unstable in condensate. The significantly higher mercury removal obtained using the IM in the 2.0 g/L test, where more suitable mixing conditions for this material were used (end-over-end rotation), suggested that the poor mixing did influence mercury removal in the 0.2 g/L test.

From the data given in Table 3 it can be seen that material concentration did not have a significant effect on mercury removal for the concentrations studied. The only exception was for the IM material, where the difference was most likely due to the different batch test procedures used as discussed in the previous paragraph.

3.3.1. Mercury removal—up-flow column and filtration tests

Mercury removal using the materials listed in Table 2 was also investigated using various flow-based procedures. The materials in particulate form (VACN, Ag–C, IM) were investigated using an up-flow column apparatus (Fig. 2) and the materials in powder form (PACD, PACN, Au–Si, thiol SAMMS, MCM-41) were investigated using the filtration procedure described in Section 2. The materials in powder form were investigated using a filtration procedure as the fittings in the up-flow column apparatus were not strong enough to cope with the significant pressure drop across the powdered material beds. Due to the high pressure drop attributable to the small particle sizes of these materials,



Fig. 5. Mercury concentration at different residence times vs. bed volumes for mercury saturated condensate passed through a column of VACN. Bed porosity = 0.11.



Fig. 6. Mercury concentration at different residence times vs. bed volumes for mercury saturated condensate passed through a column of Ag–C. Bed porosity = 0.14.

the use of these materials on an industrial scale would also only most likely be viable if they were used as filtration aids and not in packed columns.

The results of the flow-based tests for the particulate materials (VACN, Ag–C, IM) are presented in Figs. 5–7. Of the three particulate materials tested, the Ag–C was clearly the most effective at removing mercury from condensate, achieving almost complete mercury removal for each of the residence times investigated over the total number of bed volumes tested. The VACN and IM also were capable of significant mercury removal; however, the extent of removal dropped significantly after ~50 bed



Fig. 7. Mercury concentration at different residence times vs. bed volumes for mercury saturated condensate passed through a column of IM. Bed porosity = 0.88.



Fig. 8. % TOC removal vs. bed volumes for various residence times (see legend) for up-flow column test using Ag–C.

volumes. The mercury removal trend for the particulate materials in the up-flow column tests was consistent with that observed in the batch tests. The high extent of removal obtained using the Ag–C compared to the VACN of similar particle size, surface area and average pore size, indicated that Hg–Ag amalgamation or chemisorption was the main mechanism of mercury removal. The poor performance of the VACN after a low number of bed volumes was thought to be most likely due to either a lack of capture sites for mercury(0) or blockage or competition for these sites by the organic compounds present in condensate.

Figs. 8 and 9 show the extent of organic carbon removal that occurred during testing of the Ag–C and VACN materials. To investigate the effect of the organic compounds (and other inorganic species) present in condensate on mercury removal the VACN was tested using pH 11 milli-Q water containing \sim 35 ppb mercury(0). VACN was able to completely remove mercury from the aforementioned solution, indicating that the poor mercury removal results observed with condensate were most likely due to the interference by the organic compounds (or inorganic species) present in condensate. The relatively poor performance of the IM material was probably due to either a deficiency in the amount of impregnated sulphur available to react with the mercury(0) and/or the impregnated sulphur was unstable under the test conditions used. The stability of this material is discussed in detail in the next section. As would be expected



Fig. 9. % TOC removal vs. bed volumes for various residence times (see legend) for up-flow column test using VACN.



Fig. 10. % mercury removal from condensate for materials in powder form using a flow based (flitration) procedure. Residence time = 6 s, bed volumes treated = 50, initial Hg concentration = 55.7 ppb.

for a mineral-based sorbent, the IM did not remove TOC from condensate.

Based on the results obtained from the up-flow column tests, the Ag impregnated carbon was clearly the most suitable material for removing mercury from digestion condensate. The optimum conditions for removing >95% mercury using this material are: (1) passing digestion condensate through the material bed using an upward flow and (2) using a residence time of 5 min or more.

The results of the first series of flow (filter) tests conducted using the materials in powder form are presented in Fig. 10. Under the conditions used the Au–Si and the powdered activated carbons clearly removed the highest amount of mercury from condensate. The TS also removed a high amount of mercury (~80%), while the Ag–Si material removed the lowest amount of mercury. A significant amount of mercury was also removed during the blank test. This was most likely due to a combination of: (1) the high extent of mercury supersaturation in the batch of condensate used; (2) the testing procedure used which could have led to mercury being purged from condensate; (3) mercury adhering to the plastic plunger and/or filtration unit, which has been previously reported to occur [42].

A second series of tests was conducted using the materials in powder form with a slightly longer residence time and a higher number of bed volumes. The results of these tests are presented in Fig. 11. Again, PAC removed the highest amount of mercury over the number of bed volumes tested. The Au–Si and TS materials were also both capable of a high extent of mercury removal, with the TS material removing significantly more mercury using a longer residence time. Of the impregnated materials,





the Ag–Si again removed the least amount of mercury. The poor performance of the Ag–Si material could possibly have been due to channelling occurring during testing. The likelihood of channelling was supported by the observation that the bed of this material was very dry following testing, compared to the other materials tested. The trend in mercury removal observed for this material (increased removal with increasing bed volumes) also supported that channelling/poor wetting occurred during testing.

Based on the results obtained for the flow (filter) tests the most efficient material for removing mercury from digestion condensate was powdered activated carbon. This material was capable of removing >95% mercury from digestion condensate using a residence time of 6 s.

3.4. Stability of materials

In order for a material to be utilised on an industrial scale it is essential that the material is stable during operation from an efficiency (economic) perspective. In addition, potentially hazardous or toxic species must not leach from the materials from an environmental perspective. The extent of leaching of various components of the silica based materials and the Ag–C were therefore investigated. The concentrations of Si, Au and Ag in condensate treated with the various materials are given in Table 4. The Ag–Si and Ag–C materials both leached Ag under the test conditions used. The extent of Ag leaching was $\sim 5\%$ for the Ag–Si and $\sim 4\%$ for the Ag–C based on semi-quantitative ICP-MS analysis. The Au–Si was stable with respect to gold; however, a significant amount of Si from this material was detected in the filtered sample. The IM material was stable with respect to Si.

As no method was readily available for trace analysis of sulphur, the stability of the sulphur in the thiol SAMMS material was investigated indirectly 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. Based on the TOC results obtained for the condensate treated with the thiol SAMMS material (Table 5), where there was a significant increase in TOC concentration, this material does not appear to have been stable in condensate under the test conditions used. 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

Table 4	
Stability	results

Material	Concentration of leached element (ppb)			
	Au	Ag	Si	
Blank	28	6	3438	
Au–Si	8	6	26,562	
Ag–Si	9	125	3125	
Ag–C	6	38	3125	
IM	5	3	3125	

[Material] = 1.0 g/L; samples filtered through 0.45 μ m membrane.

 Table 5

 TOC concentration results for batch tested materials

Material	TOC (ppm)	% TOC (increase (+) or decrease $(-)$)
None	35.2	0
Au–Si	33.9	-3.7
Ag-Si	34.5	-2.0
Thiol SAMMS	46.6	+32.4
MCM-41	34.4	-2.3
PAC-D10	14.3	-59.4
PAC-AZO	13.9	-60.5

[Material] = 1.0 g/L.

carbon was $\sim 5\%$. This corresponds to an increase in sulphur concentration in treated condensate of $\sim 8.7 \text{ mg/L}$.

The stability of sulphur in the IM material was also evaluated qualitatively by comparing the sulphur peak in the EDS traces of this material before and after use. A significant reduction in the height of this peak in the used sample (relative to other peaks) indicated that the sulphur impregnated in this material was not stable in condensate. The loss of sulphur into the condensate solution could be accounted for by the dissolution of sulphur in the alkaline solution as described in Eq. (1). Some mercury may have formed the compound HgS on the surface of the sorbent; however, once excess sulphide ions were present in solution, the highly soluble $[HgS_2]^{2-}$ complex may have formed [43,44] according to Eq. (2):

$$S + 2OH^{-} \rightarrow S^{2-} + H_2O + \frac{1}{2}O_2$$
 (1)

$$S^{2-} + HgS \rightarrow [HgS_2]^{2-}$$
⁽²⁾

4. Conclusions

Based on Eh/pH measurements and a Pourbaix stability diagram, the predominant mercury species in alumina refinery digestion condensate is mercury(0). A number of materials can be used to remove a significant amount of mercury from condensate containing relatively low levels of mercury. Nano-gold impregnated silica and powdered virgin activated carbon were the most efficient materials used in this study. Ag and S impregnated materials were found to be unstable in condensate.

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