(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) **Title:** REMOVAL OF ARSENIC FROM FLUE-GAS

(57) **Abstract:** The divulged invention concerns a process for the removal of arsenic oxides in process exhaust gases, comprising the step of passing the exhaust gases through a supported ionic liquid phase bed, characterized in that the ionic liquid comprises one or more cations from the list consisting of substituted phosphonium, ammonium, imidazolium, pyrrolidinium, and pyridinium, and one or more anions from the list consisting of chloride, bromide, and carboxylate. Compared to a bed of active carbon, the ionic liquid soaked active carbon bed according to the invention allows for an estimated doubling of the arsenic adsorption capacity of the bed, while also considerably enhancing the kinetics of adsorption.

Removal of arsenic from flue-gas

The present invention concerns a gas cleaning process, specially adapted for the removal of traces of arsenic oxides in exhaust gases, in particular in off-gases from metallurgical smelting
5   processes or coal burning processes.

Arsenic is present in many minerals, concentrates, and recycled metal-bearing materials. Arsenic and many arsenic compounds are also relatively volatile at high temperature. Consequently, most metallurgical operations produce arsenic bearing gases, in particular when
10   pyrometallurgical processes are applied. Examples are burning of coal, or the recovery of metals such as copper and lead, using smelting processes. Emissions from furnaces and converters can cause health problems in the work place and/or result in elevated levels of toxic pollutants such as lead and arsenic in the immediate vicinity of the smelter.

15   According to known processes, the major part of the arsenic in gas streams can be recovered by condensation, filtration, or adsorption on active carbon.

Condensation and filtration allow for arsenic abatement down to about 0.2 to 0.8 mg/Nm^3 in the gas phase. Hydrated lime Ca(OH)2 can be injected in the gas, thereby not only serving as
20   condensation surface, but also adsorbing the arsenic by forming a Ca - As precipitate. A further reduction of arsenic down to 0.05 mg/Nm^3 is then typically obtainable.

A more complete elimination of arsenic is however desired in view of the eco-toxicity of this metal and of its compounds. Moreover, typical industrial operations involve the continuous
25   release of huge volumes of gases, thus exacerbating the environmental issue.

A known process for the further reduction of arsenic is passing the gas through a bed of active carbon.

30   It has been recognized that the effectiveness of arsenic adsorption on active carbon decreases with increasing temperature. The gas stream has therefore to be cooled down to well below 100 °C. Unfortunately, the adsorption kinetics at this temperature are rather slow. A sufficient contacting time between active carbon and gas can only be achieved by using a voluminous bed, which therefore needs to contain a large quantity of active carbon. This results in bulky and
35   expensive equipment. The active carbon is moreover not effectively utilized, as it never gets saturated in arsenic during its normal operational life.

It is the aim of the present divulgation to propose a scheme to solve the above problems, in particular to accelerate the adsorption kinetics of arsenic compared to active carbon, while allowing for the abatement of arsenic down to less than 0.01 mg/Nm^3. This scheme makes use of a bed of SILP (Supported Ionic Liquid Phase), i.e. a porous carrier typically prepared by

5   soaking a carrier phase in a selected ionic liquid.

Processes for the capture of metals or their oxides using supported ionic liquid phases have been described before. They are however not optimized for the elimination of arsenic.

10   US20140001100 discloses a process for the capture of elemental mercury from a hydrocarbon fluid using ionic liquids. Suitable ionic liquids comprise an organic cation, a metal cation, and an anion. The ionic liquid is believed to perform a dual function. First, the metal cation part of the ionic liquid oxidizes the mercury. The oxidized mercury, being destabilized in its organic environment, is then efficiently captured in the ionic liquid.

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US200701 23660 similarly concerns a process for the capture of gaseous forms of elemental or oxidized mercury, but also of lead, zinc and cadmium. Use is made of a combination of a ligand and of an ionic liquid. Oxidizing agents are added when elemental species need to be captured.

20   A process is hereby divulged for the removal of arsenic oxides in process exhaust gases, comprising the step of passing the exhaust gases through a supported ionic liquid phase bed, characterized in that the ionic liquid comprises one or more cations from the list consisting of substituted phosphonium, ammonium, imidazolium, pyrrolidinium, and pyridinium, and one or more anions from the list consisting of chloride, bromide, and carboxylate.

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By process exhaust gases are meant gases from metallurgical smelting processes or from other burning processes.

Preferably, the substituted phosphonium cation is according to formula $[P_m no_p]^+$, and the

30   substituted ammonium cation is according to formula $[N_m no_p]^+$, wherein the substituents are hydrocarbon chains containing m, n, o, and p carbon atoms each, with the proviso that m+n+o+p > 10 when the anion is a halide, and m+n+o+p < 30 when the anion is a carboxylate.

The hydrocarbon chains substituents of the cation are preferably unbranched and saturated.

35   The anions are preferably unbranched, unsaturated monocarboxylates, containing 1 to 8 carbon atoms.

The most preferred ionic liquid is [P6 6 6 14] Cl. This product is commercially available as CYPHOS® IL 101 .

The process is most suitable for removing arsenic oxides comprising As_2O_3 and/or As_2O_5.

Preferably, the supported ionic liquid phase comprises a support phase from the list consisting of alumina, silica, and activated carbon. A support phase having a BET of more than 50 m^2/g is desired. A weight ratio of support phase to ionic liquid weight between 3 : 1 and 50 : 1 is most suitable.

The advantages are of the disclosed process and corresponding equipment are:
- the volume of the adsorption bed can be reduced;
- the cleaning apparatus itself can be more compact;
- the pressure drop across the adsorption bed can be reduced.

The investment can therefore be lower than when using active carbon, and the running costs decreased.

Such a SILP may also adsorbs elements other than arsenic which may also be present in the gas phase, such as Zn, Hg, Cd, Pb, Sb, and Se, dependent upon the precise ionic liquid selected. For example, the ionic liquid identified as trihexyl-tetradecyl-phosphonium chloride [P6 6 6 14] Cl lends itself well for the capture of As, but also of Pb, Cu, Cd, Se and Zn. There is also clear evidence for the uptake of Sb and Se when using 1-butyl-3-methylimidazolium acetate [C_4Ciim] [C1 CO2]. These ionic liquids were tested using an active carbon substrate.

The supporting substrate should be highly porous and should be wetted by the envisaged ionic liquid. Typical candidates are silica, alumina, titanium oxide, zirconium oxides, activated carbon, porous polymers, zeolites, and metal-organic frameworks.

When targeting the adsorption of arsenic, ionic liquids susceptible to dissolve significant amounts of it are clearly preferred.

When the arsenic-contaminated exhaust gases originate from a metallurgical smelting process, the spent SILP can be directly recycled to that process. A capture mechanism ahead of the SILP adsorption step is then needed to avoid the accumulation of the metals captured by the SILP. The recycled SILP could even be considered as a valuable reaction agent. This would be the case, e.g. when dealing with an active carbon substrate and a pyrometallurgical process

needing a reducing agent. Similarly, silica or alumina substrates could usefully be recycled to a process needing fluxing for the formation of a slag.

In a first example, the increase in capacity of the SILP is demonstrated.

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For the preparation of activated carbon-based SILP, activated carbon WS 490 from Chemviron Carbon® is used. One part by weight of the ionic liquid is dissolved in nine volume parts of methanol. The solution is added to nine part by weight of activated carbon and left overnight to ensure complete adsorption. The solvent is removed in three steps: 1.5 h at 45 °C and

10   300 mbar, 1.5 h at 65 °C and 300 mbar, and 1.5 h at 65 °C and 250 mbar.

Using this method, batches of SILP are produced using ionic liquids $[P_{6\ 6\ 6\ 14}]$ Cl and [C4Ci im] $[C_1CO_2]$.

15   The BET is measured to characterize the specific surface of the obtained SILP material. From this analysis, the pore volume and the pore size is determined using BJH analysis. These determinations are performed using nitrogen for the untreated activated carbon (AC) as well as for the above-prepared SILP samples. This is reported in Table 1.

20   Table 1: BET results for untreated activated carbon (AC) and for SILPs

Material	Pore volume ($cm^3 g^{-1}$)	Pore area ($m^2 g^{-1}$)
AC (uncoated)	0.78	1191.8
AC with 10 wt.% $[P_{6\ 6\ 6\ 14}]$ Cl	0.63	1021.4
AC with 10 wt.% $[C_4C_1im]$ $[C_1CO_2]$	0.68	1088.7

The pore size of all three materials are also recorded. In all three materials pore diameters smaller than 40 **A** are dominant. This demonstrates the persistence of the pore structure after coating of the activated carbon with the ionic liquids. However, the fraction of these small pores

25   is slightly reduced after coating. It is therefore assumed that the ionic liquid covers the inner pores of the activated carbon.

Ionic liquids are selected according to their capacity to dissolve AS2O3. This list is reported in Table 2, along with the saturation limit as function of temperature.

Table 2: As_2O_3 solubility in selected ionic liquids

Ionic liquid	50 °C		70 °C		80 °C	
	wt.%	mol%	wt.%	mol%	wt.%	mol%
$[P_{2228}]$ Cl	-	-	-	-	4.94	6.55
$[P_{4444}]$ Cl	-	-	-	-	5.95	8.61
$[P_{4446}]$ Cl	1.13	1.82	3.50	5.58	5.43	8.56
$[P_{4448}]$ Cl	--	--	-	--	3.86	6.65
$[P_{66614}]$ Cl	1.63	4.17	3.02	7.55	9.13	20.8
$[P_{88810}]$ Cl	0.68	1.85	-	-	7.10	17.4
$[P_{88818}]$ Cl	2.31	2.31	-	-	28.4	28.4
$[N_{8881}]$ Cl	1.54	3.08	-	-	6.24	12.0
$[P_{22214}]$ $[HCO_2]$	8.08	9.77	11.5	24.12	14. 8	29.0
$[P_{4444}]$ $[HCO_2]$	5.88	11.9	14.9	16.71	18.3	20.4
$[P_{2228}]$ $[C_1CO_2]$	21.5	28.7	23.2	30.72	23.3	30.7
$[P_{22214}]$ $[C_1CO_2]$	7.03	12.5	10.6	18.38	13.9	25.4
$[C_2C_1im]$ $[C_1CO_2]$	18.2	16.1	25.7	22.94	26.8	26.8
$[C_4C_1im]$ $[C_1CO_2]$	12.2	12.2	28.4	28.48	34.7	35.6
$[C_8C_1im]$ $[C_1CO_2]$	11.9	14.8	19.6	23.87	19.6	23.9

It can be derived from Table 1 that the coating layer of the selected ionic liquids is capable of adsorbing about 10 kg of As_2O_3 per tonne of SILP. Assuming that the active carbon substrate will also contribute to the capacity of adsorption, the total capacity of the SILP can be estimated to be double the capacity of the active carbon alone. This increase of capacity is a first advantage of soaking the active carbon in a selected ionic liquid.

In a second example, the enhanced adsorption kinetics is shown.

In a first step, two adsorption columns are prepared, one filled with un-soaked activated carbon to be used as a reference, the filled other with activated carbon soaked in $[P_{66614}]$ Cl as described in Example 1. Each column comprises a small amount of glass wool at the bottom, followed by a steel mesh and 10 g of adsorption material. Two additional layers of adsorption material are added, each separated by a steel mesh. Each layer has an average height of 1.63 cm. A steel mesh and glass wool is added on the top layer so as to stabilize the adsorption bed. The internal diameter of the column is about 4.2 cm.

In a second step, AS2O3 bearing gas is fed to the columns. To this end, a side stream is sampled from the off-gases produced by a lead blast furnace. After a first dust filter, the gas is divided into three parallel streams. One stream is directly passed through to a cascade of washing bottles for the analysis of the inlet concentrations. The analysis of the AS2O3 in the washing bottles allows for the determination of the input concentration. The other two are passed through the respective adsorption columns. Each column outlet is individually connected to a separate cascade of washing bottles. Each cascade is followed by a drying column and a pump where the gas flow rate is adjusted to 3 L/min for each stream. The temperature of the gas entering the columns is about 140 °C. The experiment is conducted for 48 h.

As summarized in Table 3, it is observed that the output arsenic concentration is reduced by a factor of 3 when ionic liquid soaked active carbon is utilized instead of un-soaked active carbon. As the operating conditions are identical, and as the levels are far below saturation effects, it is believed that the ionic liquid provides for accelerated adsorption kinetics. This is a second advantage of soaking the active carbon in a selected ionic liquid. This advantage prevails even when substrates other than activated carbon are used, such as silica or alumina.

Table 3: Arsenic adsorption and yield

Column	Input concentration mg/Nm3	Output concentration mg/Nm3	Capture yield (%)
None (pass through)	0.45	0.45	0.
AC (un-soaked)	0.45	0.0059	98.7
AC with 10 wt.% $[Pe e_{6\ 14}] Cl$	0.45	0.0013	99.7

Claims

1.   Process for the removal of AS2O3 and/or AS2O5 in process exhaust gases, comprising the step of passing the exhaust gases through a supported ionic liquid phase bed, characterized in that the ionic liquid comprises one or more cations from the list consisting of substituted phosphonium, ammonium, imidazolium, pyrrolidinium, and pyridinium, and one or more anions from the list consisting of chloride, bromide, and carboxylate.

2.   Process according to claim 1, wherein the substituted phosphonium cation is according to formula $[P_m no_p]^+$, and the substituted ammonium cation is according to formula $[N_m no_p]^+$, wherein the substituents are hydrocarbon chains containing m, n, o, and p carbon atoms each, with the proviso that m+n+o+p > 10 when the anion is a halide, and m+n+o+p < 30 when the anion is a carboxylate.

3.   Process according to claims 1 or 2, characterized in that the carboxylate is an unbranched, unsaturated monocarboxylate, containing 1 to 8 carbon atoms.

4.   Process according to any one of claims 1 to 3, wherein the supported ionic liquid phase comprises a support phase from the list consisting of alumina, silica, and activated carbon.

5.   Process according to claim 4, whereby the support phase has a BET of more than 50 m^2/g.

6.   Process according to any one of claims 1 to 5, whereby the weight ratio of support phase to ionic liquid weight ratio is between 3 : 1 and 50 : 1.

7.   Process according to claim 6, wherein the process exhaust are off-gases from a metallurgical smelting process, characterized in that the supported ionic liquid phase is recycled to that process.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01D53/64
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01D   F23J   B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal , WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 2016/271559 A1 (CORCORAN ROBERT C [US] ET AL) 22 September 2016 (2016-09-22) paragraphs [0015], [0016], [0021] - [0023], [0026], [0027], [0029], [0123]; examples 1,2 -----	1-7
A	FR 3 009 204 A1 (IFP ENERGIES NOUVELLES [FR]) 6 February 2015 (2015-02-06) page 1, lines 1-7 page 6, line 27 - page 7, line 27 page 12, lines 12-28 -----	1-7
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[X] Further documents are listed in the continuation of Box C.   [X] See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
1 February 2018	09/02/2018

Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Howe, Patrick

C(Continuation).	DOCUMENTS CONSIDERED TO BE RELEVANT	

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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