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(54) A METHOD FOR PRECIPITATING ARSENIC FROM A SOLUTION

(57) The present invention relation to an electrochemical process for precipitating arsenic from a liquid formulation containing one or more of As(III) and As(V) ions or a mixture thereof, in the form of crystalline scorodite $FeAsO_4.2H_2O$ particles, wherein the process comprises the steps of (i) supplying the formulation to a catholyte in a cathode compartment of an electrochemical cell equipped with a cathode comprising a gas diffusion electrode with a porous electrochemically active material, and adjusting the pH of the thus obtained catholyte to a value of between 0 and 2.0, which cathode compartment further contains a source of Fe ions in an amount which is such that the molar ratio in the catholyte of Fe ions to As ions is minimum 4.0 ; (iii) supplying an O_2 containing oxidant gas to the gas diffusion electrode ; (iv) applying a potential to the cathode which is such as to cause reduction of the O_2 contained in the oxidant gas to one or more of the corresponding peroxide, OH^-, ionic and/or radical reactive oxygen containing species and (v) recovering precipitated, crystalline scorodite.

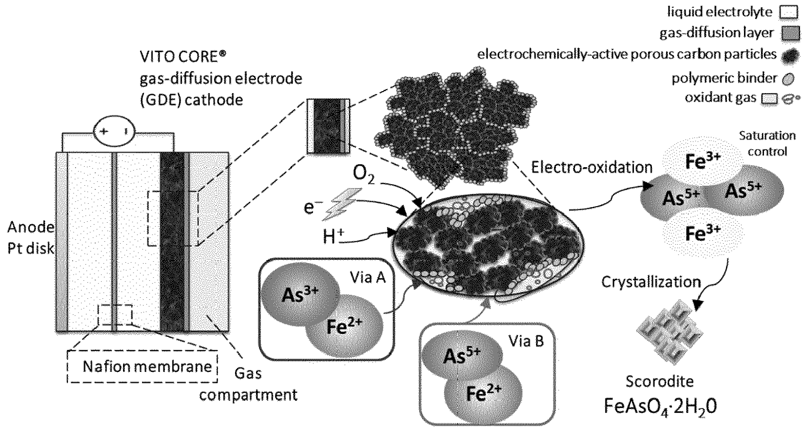

Fig. 1

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Description

[0001] The present invention relates to a method for precipitating arsenic ions from a formulation containing such ions.

Background of the invention.

[0002] Non-ferrous base metal ores, such as those of copper and zinc, are frequently associated to chalcophile elements, such as arsenic and antimony. During smelting, arsenic-containing materials accumulate in high volumes, as a result of which the product obtained is barely marketable due to the inherent toxicity of arsenic [T. Fujita, R. Taguchi, M. Abumiya, M. Matsumoto, E. Shibata and T. Nakamura, Hydrometallurgy, 2008, 90, 92-102]. In fact, arsenic is one of the most problematic impurities in the extractive metallurgical industry due to its extended incidence in mined minerals [P. Gonzalez Contreras, J. Weijma and C. J. N. Buisman, Adv. Mater. Res., 2009, 71-73, 629-632.], and arsenic is one of the most toxic inorganic pollutants [A. Murciego, E. Alvarez-Ayuso, E. Pellitero, M. Rodriguez, A. Garcia-Sanchez, A. Tamayo, J. Rubio, F. Rubio and J. Rubin, J. Hazard. Mater., 2011, 186, 590-601].

[0003] The best available processes for arsenic removal consist of two steps : 1) oxidation of the trivalent arsenic species into the pentavalent state which is a less toxic form of arsenic, and 2) immobilization into stable arsenic residues, for example by precipitation by lime neutralization, sulfide precipitation, co-precipitation of arsenic with ferric ions, or pyrometallurgical treatment to produce a stable residue with calcium and iron salts) [A. M. Nazari, R. Radzinski and A. Ghahreman, Hydrometallurgy, 2017, 174, 258-281]. Most arsenic removal treatments are achieved through ion exchange and sorption, membrane processing, oxidation/chemical precipitation, and coagulation/ coprecipitation [Vu, KB., Kaminski, MD., Nuñez, L. 2003. Review of arsenic removal technologies for Contaminated groundwaters. Chemical Engineering Division. Argonne National Laboratory Report ANL-CMT-03/2. Argonne IL, U.S.A.].

[0004] The immobilization process of choice depends both on the species and amount of arsenic present. However, the disposal and storage of arsenic-containing compounds is not entirely safe, as they easily undergo physical and chemical changes with time, resulting in arsenic releases into the environment. As an example, arsenic sulfide is not stable at pH ≤ 4, whereas calcium arsenate is not effective to completely remove arsenic as pH decreases [X. B. Min, Y. P. Liao, L. Y. Chai, Z. H. Yang, S. Xiong, L. Liu and Q. Z. Li, Trans. Nonferrous Met. Soc. China (English Ed., 2015, 25, 1298-1306]. The precipitation by ferric iron technologies requires a high iron consumption with respect to arsenic, i.e. Fe/As > 4, and large amounts of waste material are produced [Paktunc, J. Dutrizac and V. Gertsman, Geochim. Cosmochim. Acta, 2008, 72, 2649-2672]. Solid-solid separation of arsenical ferrihydrite is extremely inefficient. This gelatinous material contains no more than 6 wt% arsenic, with a maximum solid content of 20-25 %wt.

[0005] Removal of As by electro-coagulation (EC) has been described as well and typically consists on the addition of a flocculating agent which is generated by electro-oxidation of a sacrificial anode, generally made up of iron or aluminium. After the formation of metal (M^{n+}) coagulants (e.g. metallic iron hydrolyzed to polymeric iron or metallic aluminium to aluminium oxyhydroxides) by oxidation of the "sacrificial anode", destabilization of As^{y+} ions takes place leading to a particulate suspension. The emulsion is broken and the destabilized phases aggregate to form flocs. At the cathode, the formation of hydrogen gas and hydroxide ions occurs [Gomes, JAG., at al. 2007. Arsenic removal by electrocoagulation using combined Al-Fe electrode system and characterization of products. J Hazardous Materials B139:220-231; Xu, et al. 2010. Removal of arsenite by simultaneous electro-oxidation and electro-coagulation process Journal of Hazardous Materials 184:472-476]. Coagulation happens when the metal cations combine with the negative particles carried out by electrophoretic transport.

[0006] WO2013173914 discloses a method of producing scorodite at atmospheric pressure and at a temperature of about 85°C, wherein to a mixture supersaturated with dissolved arsenic ions, further comprising dissolved copper ions an iron source is added. The iron source may either be particulate pyrite and particulate chalcopyrite. An oxygen-containing gas is supplied so as to maintain an operating potential of the leach solution between 470 and 600 mV versus Ag/AgCl sufficient to oxidize the iron source to provide at least 1 mole of dissolved ferric ions per mole of dissolved arsenic ions, and selectively precipitating the dissolved ferric ions with the dissolved arsenic ions from the leach solution as scorodite. The pH of the solution is maintained below 2.

[0007] The present invention seeks to provide an alternative method for the removal of arsenic ions from a formulation containing such ions independently of the arsenic ion oxidation state, which shows a high selectivity towards the formation of scorodite.

[0008] This is achieved according to the present invention with a method showing the technical features of the characterizing portion of the first claim.

[0009] Thereto the present invention relates to electrochemical process for precipitating arsenic from a liquid medium containing one or more of As(III) and As(V) ions or a mixture thereof, in the form of crystalline scorodite FeAsO4.2H2O particles, wherein the process comprises the steps of

(i) supplying the liquid medium to a catholyte in a cathode compartment of an electrochemical cell equipped with a

cathode comprising a gas diffusion electrode with a porous electrochemically active material, and adjusting the pH of the thus obtained catholyte to a value of between 0 and 2.0, which cathode compartment further contains a source of Fe ions in an amount which is such that the molar ratio in the catholyte of Fe ions to As ions is minimum 4.0 ;
(ii) supplying an O2 containing oxidant gas to the gas diffusion electrode,
(iii) applying a potential to the cathode which is such as to cause reduction of the O2 contained in the oxidant gas to one or more of the corresponding peroxide, OH-, ionic and/or radical reactive oxygen containing species,
(iv) and recovering precipitated, crystalline scorodite.

[0010] The process of the present invention is suitable for use with many types of arsenic containing formulations, including solid particles, solutions containing dissolved arsenic (III) and/or (V), or dispersions containing arsenic particles. The solution or dispersion may be mainly water based or it may contain one or more organic solvents, as often is the case when use is made of industrial waste products.

[0011] The present invention provides a process with which As ions may be precipitated from an aresenic formulation in the form of crystalline scorodite particles ($FeAsO_4 \cdot 2H_2O$), which show a minimal risk to dissolution in water that would be associated with leaching of As ions back into the solution. Indeed, FeAsO4·2H2O, in its amorphous form is rather unstable in aqueous environment, whereas its crystalline form (scorodite) it is suitable for arsenic stabilization and storage under acidic to neutral pH conditions as it shows a minimum risk to dissolution or leaching in these conditions. Thus, the immobilization of arsenic into scorodite is the preferred alternative, given that it is the safest arsenic-containing material because of its low solubility, high stability and compact structure. Besides, a higher arsenic removal capacity and lower demand for iron can be achieved using scorodite precipitation over other types of co-precipitation with ferric iron technologies.

[0012] The present invention is suitable for use with liquid formulations or formulations which may exclusively contain As(V), or As(III) or a mixture thereof in any desired ratio, as any As(III) present may be oxidized to As(V) in the conditions prevailing in the process of this invention. Moreover, usually the content of As(V) and As(III) will be determined by the origin of the formulation, often industrial waste or leached industrial wase. Similarly, the nature of the Fe ion source is not critical to the invention as any metallic Fe or Fe ions present may be oxidized to Fe(III) in the conditions prevailing in the cathode compartment. Otherwise elemental Fe may be dissolved anodically to Fe(II) or Fe(III) as the source of iron.

[0013] A pH range suitable for carrying out the process of this invention is preferably between 0 and 2.0. Within this pH range, any trivalent arsenic present may be oxidized to the pentavalent state, as a result of which the method of the present invention is suitable for use with As sources that may contain either As in the trivalent state, in the pentavalent state or a mixture hereof. Further, by maintaining the acidity at a lower level, precipitation of the arsenic ions as scorodite may be achieved, provided that sufficient Fe(III) ions are available. Above a pH of 2.0 the risk increases to the formation of unwanted side products, which may show an insufficient stability in solution and give rise to the release of As ions upon storage. At a pH of 2 or less, the As ions contained in the formulation to be processed may be kept in solution. Generally speaking, the lower the pH is maintained, the better arsenic may be held in solution, as long as highly oxidizing conditions are not supplied.

[0014] The present invention shows higher arsenic removal capacity and lower demand for iron over other co-precipitation methods employing ferric iron technologies. Scorodite is classically formed hydrothermally at a temperature over 150°C. The hydrothermal formation of scorodite by routing iron- and arsenic-containing solutions directly into an autoclave is, however, a costly solution.

[0015] The process of the present invention may be carried out in one single step, in one single reactor, at atmospheric pressure and moderate temperature of between 25 and 95 °C, which presents an advantage over hydrothermal methods which require a prior oxidation of As(III) into As(V), and are typically carried out by acid pressure oxidation above 150°C and oxygen overpressures of up to 2000 kPa [Demopoulos, G.P., D.J. Droppert, and G. Van Weert, Precipitation of crystalline scorodite (FeAsO4·2H2O) from chloride solutions. Hydrometallurgy, 1995. 38(3): p. 245-261; Dutrizac, J.E. and J.L. Jambor, The synthesis of crystalline scorodite, FeAsO4·2H2O. Hydrometallurgy, 1988. 19(3): p. 377-384; Filippou, D. and G.P. Demopoulos, Arsenic immobilization by controlled scorodite precipitation. JOM, 1997. 49(12): p. 52-58; Riveros, P.A. and J.E. Dutrizac, A Review of Arsenic Practices. European Metallurgical Conference, 2001. 2:373-394].

[0016] In further preferred embodiments, the process of this invention may be carried out in a catholyte the temperature of which is maintained between 35 and 85°C, more preferably between 40 and 75°C, most preferably between 50 and 70°C.

[0017] In a preferred embodiment, the electrochemical potential to which the gas-diffusion cathode is subjected, is a reducing potential relative to a reference electrode, preferably below the thermodynamic pH-potential equilibrium region of stability of the oxidant gas in water, more preferably below the region of thermodynamic stability of water but preferably not within the region of thermodynamic stability of hydrogen. This way the risk to the occurrence of water electrolysis to form hydrogen may be minimized. The inventors have observed that subjecting the cathode to an electrochemical potential which is chosen such that it is capable of causing reduction of an oxidant gas supplied to it, permits to induce a redox transformation in the catholyte. This redox transformation involves on the one hand a reduction of the oxidant gas, and may on the other hand cause oxidation of any As(III) contained in the catholyte to As(V) required to form crystalline scorodite, and the oxidation of Fe(0) or Fe(II) to Fe(III). Oxidation of the Fe species present to Fe(III), ensures a high efficiency of the electrochemical process. The electrochemical potential or range of electrochemical potentials at which reduction of the oxidant gas may occur, is well known to the skilled person. Without wanting to be bound by this theory, the inventors assume that reduction of the oxidant gas not only takes place at the cathode surface, but also in the catholyte and may give rise to the formation of one or more peroxide, ionic and/or radical species, usually polyatomic species in the catholyte. It is assumed that in the catholyte a local environment or local reaction front is formed with a high concentration of such species where crystalline scorodite formation takes place. Supersaturation of the local environment with such species may occur. A characteristic pH and redox potential may locally develop, which are different from that of the remainder of the solution and at the external electrode surface.

[0018] In a preferred embodiment, the arsenic formulation supplied to the catholyte is a water based solution containing one or more of As(III) and As(V) ions dissolved therein, as these represent frequently occurring industrial waste products or leachates thereof. It is a particular advantage of the present invention that As ions may be converted into crystalline scorodite, independently of their oxidation state, i.e. 3+ or 5+, without requiring oxidation of As(III) to As(V) in advance of the process of this invention, as any As(III) present may be oxidized to As(V) in the conditions prevailing in the process of this invention. In the process of this invention, trivalent arsenic can be oxidized to pentavalent arsenic with a yield of 99% or more with low operation and equipment costs.

[0019] In a further preferred embodiment the process of this invention is carried out in such a way that the concentration of As ions in the catholyte is at least 0.005 mole/l, preferably at least 0.01 mole/l. The concentration of As ions in the catholyte is preferably maximum 0.5 mole/l, preferably maximum 0.30 mole/l. The afore-mentioned concentration ranges permit simultaneously achieving maximum scorodite yield and minimal risk to clogging of the cathode, while ensuring formation of the desired crystalline scorodite. Below a concentration of 0.005 mole/l, in particular below 0.01 mole/l, the formation of crystalline scorodite cannot be guaranteed, and side products may form which do not show the stability of scorodite. At concentrations above 0.30 mole/l the risk to clogging of the electrode with solid scorodite particles increases.

[0020] In a still further preferred embodiment, the concentration of Fe ions in the catholyte may vary between 0.05 and 1.50 mole/l, preferably between 0.05 and 1.40 mole/l. At concentrations above 1.50 mole/l, in particular above 1.40 mole/l the risk to clogging of the electrode with scorodite and the risk to cathodic reduction of Fe(III) to Fe(II) increases.

[0021] Fe ions may be supplied to the cathode chamber in various ways. As an example, the arsenic formulation may contain one or more dissolved iron ions which will often be the case when use is made of industrial waste, i.e. Fe(II) and/or Fe(III). In a preferred embodiment, the concentration of Fe(III) in the catholyte is minimized, as it may adversely affect the yield of crystalline scorodite and involve formation of unwanted side products with a lower stability towards As ion leaching.

[0022] In another example as a source of iron ions a formulation is used, preferably an aqueous formulation containing an Fe(II) salt dissolved therein. Suitable iron salts include those which show a good water solubility, for example $FeSO_4$, $FeCl_2$,$Fe(NO_3)_2$. Depending on the nature of the Fe(II) salt, crystalline scorodite particles with a varying particle geometry may be obtained. Geometries typically vary from triangular to spherical etc. Preferably however use is made of $FeSO_4$, as this is the most frequent form occurring in industrial waste streams. Furthermore it has been found that smaller anions result in scorodite reaction products with higher crystallinity. Fe may however also be supplied as metallic Fe, as it may be oxidized in the cathode chamber. Therefore, according to still another example a solid Fe object is positioned in the anode chamber or supplied thereto, for example an Fe plate which is positioned facing the gas diffusion electrode in the anodic compartment. Under the conditions prevailing in the anolyte, metallic iron will be oxidized and dissolved in the aqueous anolyte thereby forming dissolved Fe^{2+} and Fe^{3+} ions.

[0023] Although the method of this invention is preferably carried out in a water based catholyte, the catholyte may also contain one or more organic solvents, in particular when use is made of formulations which originate from industrial process streams and which contain one or more organic solvents.

[0024] The oxidant gas used in the process of this invention may consist of pure O_2 or a mixture of O_2 with one or more other gases, which are preferably inert to the electrochemical reaction. Preferably however use is made of pure O_2, as a high oxidizing power provided by pure O_2 supports the formation of crystalline scorodite $FeAsO_4.2H_2O$, and minimizes the risk to forming unwanted side products. With pure oxygen is meant oxygen gas in a purity as generally commercially available. O_2 is an essential element of the oxidation process, it is a source for production of OH^- and H_2O_2 in the catholyte, along with other reactive peroxide species or intermediates, for example peroxide radicals and others, which are assumed to intervene in the formation of crystalline scorodite. In case use is made of a mixture of O_2 with one or more other gases, examples of inert gases suitable for use with this invention include N_2, or a noble gas, more particularly Ar. Oxidant gases particularly suitable for use with this invention include those capable of forming oxidant mono-atomic radicals and/or oxidant polyatomic radicals. When using a mixture of gases (e.g., O_2 and N_2) the skilled person will be capable of adjusting the molar fraction of the oxidant gas in such a way that it is sufficiently high to enable precipitation of crystalline scorodite. Thereby, preferably the O_2 mole fraction in the O_2 containing oxidant gas is at least 0.15, more preferably at least 0.020, although most preferably the O_2 mole fraction in the O_2 containing oxidant gas may be as high as 1, to ensure that an electrolyte redox potential may be achieved in the catholyte which favours crystalline scorodite formation. Low O_2 partial pressures may limit the extent of reaction and give rise to the formation of less stable products.

[0025] In the presence of the oxidant gas a local environment may be created in the catholyte with extreme pH and redox conditions, which are different from those found in the bulk of the catholyte.

[0026] The rate with which the O_2 containing oxidant gas may be supplied to the cathode chamber is preferably variable. In a preferred embodiment a supply rate with which the oxidant gas is supplied ranges between 5.0 and 300.0 ml/min, preferably between 5.0 and 250.0 ml/min, more preferably between 5.0 and 150.0 ml/min.

[0027] The inventors have observed that in the course of the reaction, the pH of the catholyte may gradually progresses towards alkalinity. To maintain the pH within the desired range of 0 - 2.0, a buffer may be added. Usually a strong acid will be used, for example H_2SO_4, or HNO_3. In a preferred embodiment, at the start of the process of this invention, the pH of the catholyte is adjusted to 2. However, typical waste streams or leachates thereof would already provide this condition as they usually comprise concentrated amounts of H_2SO_4.

[0028] If so desired, a supporting electrolyte may be supplied to the catholyte, although in general this will not be necessary in the process of this invention. The presence of the supporting electrolyte will permit to maintain the ionic conductivity of the catholyte at a sufficiently high level in the course of the reaction. Maintaining of the conductivity at a sufficiently high level may be of particular importance when the process of this invention is operated in a continuous manner and the risk to a varying conductivity in the course of the process may be minimised.

[0029] A current density over the cathode is preferably maintained of between 10.0 and 1000.0 A/m^2, preferably of between 10.0 and 500.0 A/m^2, to ensure a sufficiently high rate of generation of reactive oxidative species in the catholyte.

[0030] In the process of this invention, usually the working potential of the cathode is set at a value between -50.0 and -750 mV vs. Ag/AgCl, preferably at a value between -100.0 and -650 mV, more preferably between -250 and -500 mV. In general, more negative potentials approaching respectively -750 mV, - 650 mV or - 500mV are expected to increase the reaction rate. However hydrogen evolution reaction could be a competing process, reducing the current efficiency.

[0031] The present invention is further elucidated in the examples below, and in the enclosed figures which relate to the examples.

Figure 1 shows a schematic gas-diffusion electrocrystallization (GDEx) immobilization of arsenic as scorodite.

Figure 2 shows gas-diffusion electrocrystallization (GDEx) immobilization of arsenic into scorodite in batch and continuous mode.

Figure 3a shows chronoamperometry test at -0.15V_{SHE} using As(III) and Fe (II) as precursors at 50°C and 70°C (experiments 1 and 2, Table 2). Fig. 3b shows chronoamperometry test at -0.15V_{SHE} using As (V) and Fe (II) as precursors at 50°C and 70°C (experiments 3 and 4, Table 2).

Figure 4 presents the XRD patterns from the solid scorodite collected from experiments 1 to 4 (Table 2). All patterns are consistent with highly crystalline and pure scorodite. Indeed, by quantitative analysis based on these XRD patterns, the scorodite obtained in all these cases was 100% pure.

Figure 5 shows SEM images at 5 μm of scorodite products using different precursors and temperature of synthesis.

[0032] As a working electrode, 10 cm^2 of VITO CORE® multi-layered carbon-based gas-diffusion cathodes were used to enable the GDEx process. The multi-layered electrodes consist of a current collector made of stainless steel gauze including a wire diameter 100 μm and mesh 44 (316L, Solana, Belgium), a hydrophilic active layer (activated carbon base embedded in a porous polymeric matrix), and a hydrophobic gas-diffusion outer layer of polytetrafluoroethylene (Teflon® PTFE 6N, Dupont), and fluorinated ethylene propylene resin (Teflon® FEP 8000, Dupont), employed to fabricate the VITO CORE® as polymer binder for both the active layer and the gas-diffusion layer. The composition of the active layer was 20% PTFE and 80% of activated carbon. Norit®SXIG (878 m^2 g^{-1}, Norit Americas Inc., USA) was employed as the active carbon source. The manufacturing method for the working electrode was cold-rolling. The counter electrode (anode) consisted of a 10 cm^2 of platinum/iridium (97%/3%) sheet, laser-welded to a titanium plate current collector. The anode and cathode compartments were separated by a proton exchange membrane (Nafion® separator N117, Ion power, Germany). An acid pretreatment procedure of Nafion® was carried out in order to enhance the ionic conductivity of the membrane by 3 wt% H_2O_2, 50 wt% HNO_3 and 0,5 M H_2SO_4.

[0033] A 3M KCl saturated Ag/AgCl reference electrode (+200 mV vs. SHE) (REF321, Radiometer Analytical, Hach, USA) was inserted in proximity to the working electrode, via an external connector chamber, filled with 3 M KCl. A long cotton thread (e.g., 30 cm, packed within the external connector chamber) verged the reference and the working electrodes, through a small channel, with the purpose of establishing a microchannel enabling a continuous capillary-suction of electrolyte. The thread was not treated, since due to its manufacturing process the wax layer that naturally covers cotton fibres is removed, making it more polar and hydrophilic due to exposure of the fibrous structure of cellulose, rich in hydroxyl (OH-) group. All potentials here reported are referred versus the Standard Hydrogen Electrode (SHE).

[0034] To assess the suitability of arsenic removal and its immobilization into scorodite a novel GDEx process was employed as described in Figure 1. For the purpose of this investigation, GDEx was operated chronoamperometrically at a constant polarization potential of -0.15 V_{SHE} using a multichannel potentiostat (VMP-3, Bio-Logic SAS, France).

[0035] All experiments were performed in batch mode with recirculation. The catholyte recirculated at 35 mL min^{-1} around the active layer cathode compartment, where electrocrystallization occurred. The flow rate for the anolyte was also 35 mL min^{-1}. The total liquid volume, anolyte and catholyte respectively, was 250 mL which was continuously stirred in a recirculation bottle (i.e., a borosilicate glass bottle) at a rotation rate of 450 rpm using a polygonal, PTFE-coated rotating magnetic stirring bar. Pure oxygen was fed through the cathodic gas compartment at a flow rate of 200 mL min^{-1}. A mass gas flow meter and controller (GF40 Bronkhorst hi-tech B.V, Netherlands) was set in place. An overpressure of 15 mbarg over a water column was applied at the gas exhaust.

[0036] The anode recirculation reservoir was filled up with 0.8 M H_2SO_4 solution as anolyte, at pH = 0.0. The cathode recirculation reservoir was filled up with 0.8 M H_2SO_4 containing 20 g L^{-1} of As^{5+} in the form of As_2O_5 99.9% (Alfa Aesar, Thermo Fisher GmbH, Germany) or As^{3+} in the form of As_2O_3 99.9% (Alfa Aesar, Thermo Fisher GmbH, Germany) and 80 g L^{-1} of Fe^{2+} in the form of $FeSO_4 \cdot 7H_2O$ (Sigma Aldrich, >= 99%). Thus, the molar ratio Fe:As was 5.4:1, which is in the characteristic range (>3:1) for the propagation of scorodite through other methods [P. Gonzalez Contreras, J. Weijma and C. J. N. Buisman, Adv. Mater. Res., 2009, 71-73, 629-632; S. Sorlini and F. Gialdini, Water Res., 2010, 44, 5653-5659]. Moreover, precipitation of ferric arsenates with Fe:As ratios of >4 needs most attention because arsenic is otherwise rejected in processing operations [P. Gonzalez Contreras, J. Weijma and C. J. N. Buisman, Adv. Mater. Res., 2009, 71-73, 629-632; D. Paktunc, J. Dutrizac and V. Gertsman, Geochim. Cosmochim. Acta, 2008, 72, 2649-2672]. The anolyte and catholyte recirculation reservoir were placed in an oil bath, which was supported on a heating plate with a temperature control to be raised and maintained at 50 °C and 70 °C. The solutions employed did not contain any parent scorodite. The effect of temperature was assessed, at 50 °C and 70 °C.

[0037] Oxygen provided through the gas chamber of the electrochemical cell, is electrochemically reduced at the active porous carbon layer of the gas-diffusion cathode (Figures 1 and 2). The products of the electrochemical ORR, profusely available at the electrochemical interface, react with the metals ions in solution (e.g. Fe^{2+}, As^{3+}), which are transported to the hydrophilic porous carbon on the cathode, via the flowing aqueous electrolyte. When these metal ions meet the ORR products (or highly reactive intermediaries) supersaturation is reached, resulting in the nucleation of the scorodite. Additive OH- concentration and supersaturation keep ongoing, thus secondary nucleation and crystal growth proceed during the transient period of residence of the primary nuclei formed within the cathodic interface. The resulting precipitate progressively strips out, as a result of the flow and polarization conditions. The warm colloidal suspension was filtrated using a 0.45 μm PTFE filter, at a pressure of 4 bar. The solid precipitated collected was then washed using demineralized water, with the purpose to eliminate most of the remaining sulfuric acid. The leachate was collected separately from the remaining precipitated, which was dried at 60 °C during 18 h to be further analyzed by X-ray diffraction (XRD). The As and Fe content was determined in axial view using inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent, 5100), equipped with a baffled cyclonic spray chamber and a conical nebulizer. The atomic emission lines of 188.979 nm and 259.940 nm were used for arsenic and iron, respectively. 0.45 μm filters (Millipore, USA) were used to filter all liquid samples before ICP analysis.

Product characterization

[0038] The precipitates formed through GDEx were characterized by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). SEM analysis was performed in a FEI Nova NanoSEM 450 instrument, with a resolution of 1 nm for gold on carbon. The samples were mounted on a sticky carbon tab. With a Cressington HR208 a thin layer of about 2.5 nm was sputtered on this stub, which was placed on the SEM where the photomicroscopes were made. EDX was used for elemental analysis, using a Bruker 200 EDX system.

[0039] XRD analysis was obtained with a diffractometer (Empyrean, Malvern Panalytical, United Kingdom) using CuKα radiation (λ=1.5405 Å) with 40 mA-45 kV and a finer step size of 0.013° in the same scan range. Quantitative phase analysis (QPA) by Rietveld refinement method with the HighScore Plus software (Empyrean, Malvern Panalytical, United Kingdom) was carried out for the quantitative analysis of the phase distrubutions (%), using the measured diffraction profile and a calculated profile crystal from the inorganic crystal structure database (ICSD).

[0040] The crystallite size (D) was calculated using Scherrer's equation. This is expressed by equation (1):

$$D = \frac{B\lambda}{\beta_{1/2} cos\theta} \qquad (1)$$

Where B is the Scherrer constant (0.9), λ is the wavelength of the X-ray beam (1.5405 Å), $\beta_{1/2}$ is the full width at half maximum of the diffraction peak and θ is the diffraction angle.

Mass balances and process efficiency

[0041] The yield of arsenic recovered into scorodite formation ($Y_{Sc/As}$, %) was calculated on the basis of the initial amount of arsenic (As_0, g) with respect to the quantitative mass of arsenic in scorodite produced at the end of the experiment (As_{SC}, g), determined from XRD analysis. This is expressed by equation (2):

$$Y_{Sc/As} = \frac{As_{sc}}{As_0} \times 100 \qquad (2)$$

[0042] The current efficiency for precipitation was calculated based on the measured mass in grams of iron and arsenic in scorodite in (g) and the total charge consumed was converted to molar mass using Faraday's law. Using the algebraic sum-of-trapezoids method to integrate the area under the current versus time curve (i-t curve), we determined the total charge consumed in dry products and from there a Charge efficiency was calculated by equation 3:

$$\Delta P = \frac{\int_{t0}^{t} I(t)dt}{F \times b} \qquad (3)$$

where ΔP is the quantitative mass of scorodite (g), I is the total current (in A), t is time (in s), F is Faraday's constant (96 485 C mol^{-1}) and b is the stoichiometric number of electrons in the product.

Arsenic leaching tests

[0043] The samples were analysed according to extraction with Milli-Q water in a liquid/solid ratio of 10 for 24 hours (shaking). The results are summarized in table 1 below. The extraction solution was allowed to settle, then the supernatant was filtrated with a 0.45 μm filter. The extraction solution was measured in 3 different dilutions and on different analytical lines, which all confirmed the data. The As and Fe content was determined in axial view using inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent, 5100).

Table 1.

	Characterisation of reaction products			
Precursor	As^{3+}	As^{3+}	As^{5+}	As^{5+}
Temperature (°C)	50	70	50	70
End product	Scorodite	Scorodite	Scorodite	Scorodite
Stoichiometry	$FeAsO_4 \cdot 2H_2O$	$FeAsO_4 \cdot 2H_2O$	$FeAsO_4 \cdot 2H_2O$	$FeAsO_4 \cdot 2H_2O$
Purity (%)	100	100	100	100
Crystallite size (nm)	70.68 ± 2.32	108.25 ± 0.57	70.49 ± 5.51	66.34 ± 3.88
Fe leaching from scorodite (mg/kg)	4220	173	5606	34096
Arsenic recovery into scorodite (%)	1,2	3,7	7	24
kWh m^{-3} of scorodite recovered	767	215	204	32

[0044] Four operational conditions were tested, as presented in Table 2, 3 and 4. In order to dissolve the metal precursors, the solution was heated to at least 50 °C. Thus, although the intended Fe/As ratio for all experiments was 4, the Fe/As ratio at the experimentation temperature was determined at the corresponding temperature, before starting the electrochemical experiments.

Table 2 Experimental conditions.

Experiment	Precursor	T (°C)	Total charge consumed (C)	Processing time (h)	Current density (mA cm^{-2})	Charge density (kC cm^{-2} L^{-1})	Fe/As molar ratio
1	As (III), Fe (II)	50	107350	308	10 ± 2	43	5
2	As (III), Fe (II)	70	96713	304	9 ± 3	39	6
3	As (V), Fe (II)	50	77131	53	39 ± 7	31	7
4	As (V), Fe (II)	70	74540	50	41 ± 1	30	9

[0045] A constant potential was imposed and the current response was recorded. The response in current was similar in magnitude for the cases with As(III) (circa -10 mA cm^2), as well as for the cases of As(V) (circa -40 mA cm^2), at the steady state, correspondingly (Figure 3). Charge consumption was relative to the form of As supplied, i.e., lower charge consumption for As(V) than for As(III). Indeed, when As(III) is supplied it first needs to be oxidized to As(V), before precipitating into scorodite. Slightly more charge was required for the systems operating at 50 °C than for those operating at 70 °C. It is inferred that, at lower temperatures, the energy required to form scorodite is supplemented by the excess current when the thermal gradient is insufficient. Figure 3 shows representative current and charge profiles obtained for the different As precursors.

[0046] The mass and energy balances calculated for the examples detailed in Table 2, 3 and 4 are presented in Table 3 below. As the process has not been optimized yet, some arsenic and iron may be left in the catholyte after processing. Also, some arsenic transports through the membrane to the anolyte may have occurred. Both aspects impact on the process efficiency but may be solved. Increasing the amount of reacted arsenic can be solved by increasing the retention time in the electrochemical cell, by fine-tuning the Fe/As ratio, so that less unreacted precursors remain, by using in stead of a cation exchange membrane an anion exchange membrane to minimize migration to the anolyte. Arsenic recovery in the solids produced ranged from 1.2-24%. The highest recovery is achieved when As(V) is employed as precursor, at a temperature of 50 °C. Energy consumption is low, as observed from Table 3, in comparison with what is required to enable competitive processes.

Table 3 Experimental conditions tested

Precursor	As^{3+}	As^{3+}	As^{5+}	As^{5+}
Temperature (°C)	50	70	50	70
Arsenic Influent (g)	5.1	5.6	3	4
Arsenic migrated to anode (g)	1.9	1.6	0.3	0.5
Arsenic unreacted in the catholyte (g)	3.2	3.8	2.6	2.6
Arsenic in Scorodite formed (g)	0.1	0.2	0.2	1
Arsenic recovery in the solid (%)	1.2	3.7	7	24
kWh m^{-3} of stream treated	182	259	244	232
kWh kg^{-1} of scorodite recovered	767	215	204	32

The norm for dangerous waste category determines the limit at 25 mg kg^{-1} of dry matter, therefore the scorodite here produced by GDEx using As (III) as precursor would be considered safe for disposal. i.e., 8.6 mg kg^{-1} of dry matter.

Table 4 Experimental conditions tested.

Precursor	As^{3+}	As^{3+}	As^{5+}	As^{5+}
Temperature (°C)	50	70	50	70
Rate of Fe^{2+} oxidation (mmol/d)	0.33	0.26	1.4	7.8

(continued)

Precursor	As^{3+}	As^{3+}	As^{5+}	As^{5+}
Rate of As^{3+} oxidation (mmol/d)	0.06	0.22		
Current efficiency for precipitation (%)	0.9	1.2	0.8	4.2

[0047] Although the current efficiency for precipitation is low (Table 4), this can be optimized by optimizing the ratio between O_2 reduction and an appropriate Fe/As ratio. Otherwise the rates of iron and arsenic oxidation are competitive with existing routes.

[0048] In the present invention gas diffusion electrocrystallization is revealed as a new route for the safe immobilisation of arsenic through the electricity driven of highly stable scorodite ($FeAsO_4 \cdot 2H_2O$). GDEx successfully produces fully crystalline scorodite in a single-stage reactor, from both As^{3+} and As^{5+} waste streams. Increasing the temperature improves the arsenic recovery rate (24% in the solid) at 70°C, however this does not impact on the purity obtained. Operating at a lower temperature (50°C) than other scorodite technologies is feasible. Scorodite produced by GDEx using As^{3+} as precursor would be considered safe for disposal.

Claims

1. An electrochemical process for precipitating arsenic from a liquid formulation containing one or more of As(III) and As(V) ions or a mixture thereof, in the form of crystalline scorodite $FeAsO_4.2H_2O$ particles, wherein the process comprises the steps of

   (i) supplying the formulation to a catholyte in a cathode compartment of an electrochemical cell equipped with a cathode comprising a gas diffusion electrode with a porous electrochemically active material, and adjusting the pH of the thus obtained catholyte to a value of between 0 and 2.0, which cathode compartment further contains a source of Fe ions in an amount which is such that the molar ratio in the catholyte of Fe ions to As ions is minimum 4.0 ;
   (ii) supplying an O_2 containing oxidant gas to the gas diffusion electrode,
   (iii) applying a potential to the cathode which is such as to cause reduction of the O_2 contained in the oxidant gas to one or more of the corresponding peroxide, OH^-, ionic and/or radical reactive oxygen containing species,
   (iv) and recovering precipitated, crystalline scorodite.

2. An electrochemical process as claimed in claim 1, wherein the concentration of the As ions in the catholyte is at least 0.005 mole/l, preferably at least 0.01 mole/l.

3. An electrochemical process as claimed in claim 1 or 2, wherein the concentration of As ions in the catholyte is maximum 0.50 mole/l, preferably maximum 0.30 mole/l.

4. An electrochemical process as claimed in any of the previous claims, wherein the formulation is a water based solution containing one or more of As(III) and As(V) ions or a mixture thereof, dissolved therein.

5. An electrochemical process as claimed in any of the previous claims, wherein the temperature of the catholyte is maintained between 25 and 95°C, preferably between 35 and 85°C, more preferably between 50 and 70°C.

6. An electrochemical process as claimed in any of the previous claims, wherein the concentration of Fe ions in the catholyte varies between 0.05 and 1.40 mole/l.

7. An electrochemical process as claimed in any of the previous claims, wherein the formulation further contains one or more dissolved iron ions, or wherein as a source of iron ions use is made of a solution containing an iron compound dissolved therein, or of a solid Fe object is positioned in the anode chamber acting as a dissolvable anode, or of solid Fe supplied to the anode chamber which is dissolvable in the anolyte.

8. An electrochemical process as claimed in any of the previous claims, wherein the oxidant gas is an oxygen containing gas, preferably oxygen.

9. A electrochemical process as claimed in any one of the previous claims, wherein the formulation is selected from one or more of an aqueous solution, an organic solvent, a mixture of two or more organic solvents, a mixture of water with one or more organic solvents, but preferably the formulation is water-based.

10. An electrochemical process as claimed in any of the previous claims, wherein a current density over the cathode is maintained of between 10.0 and 1000.0 A/m^2, preferably of between 10.0 and 500.0 A/m^2.

11. An electrochemical process according to any one of the previous claims, wherein the working potential of the cathode is set at a value between -50.0 and -750 mV vs. Ag/AgCl, preferably at a value between -100.0 and -650 mV, more preferably between -250 and -500 mV.

12. Crystalline $FeAsO_4 \cdot 2H_2O$ obtained with the method according to any one of claims 1-11.

13. A method for safe disposal of arsenic, wherein use is made of the method of any one of claims 1-11.

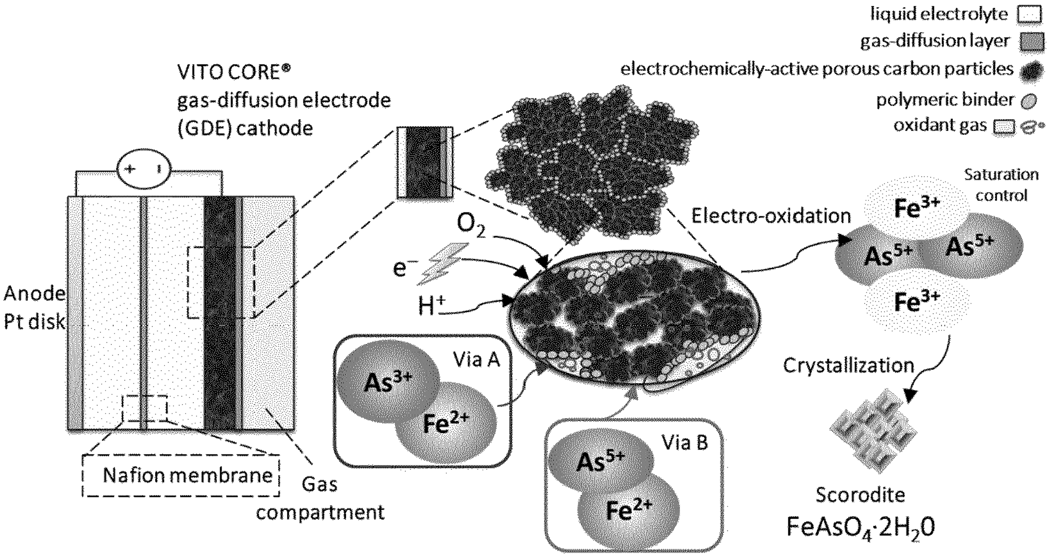
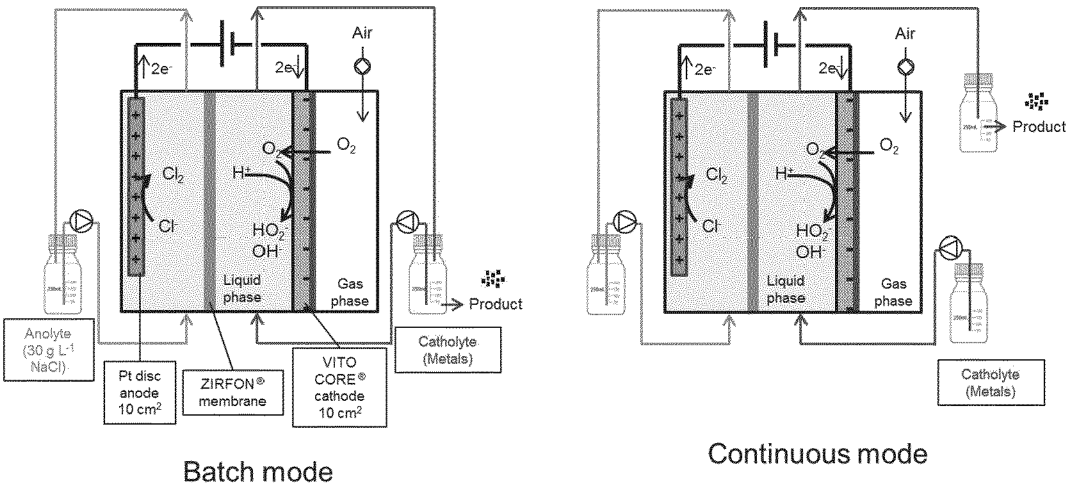


Fig. 1



Batch mode

Continuous mode

Fig. 2

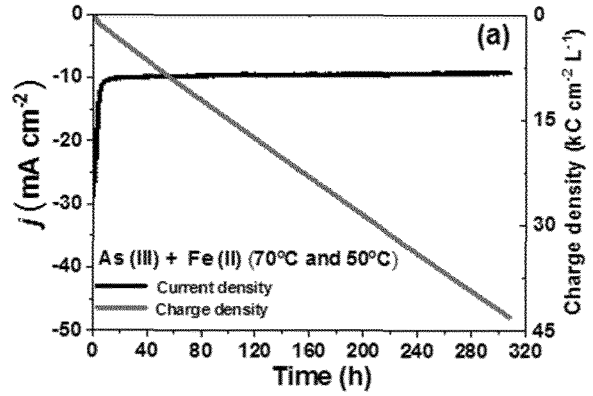


Fig. 3a

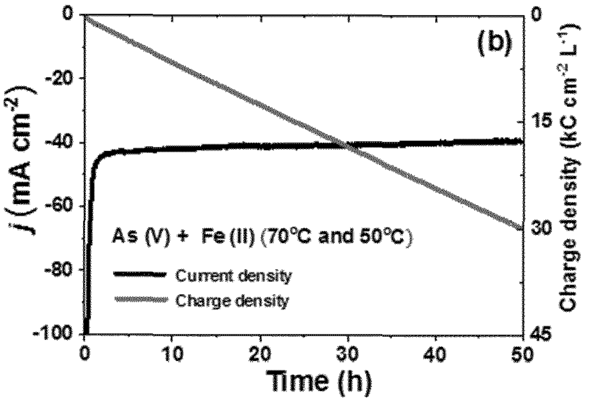


Fig. 3b

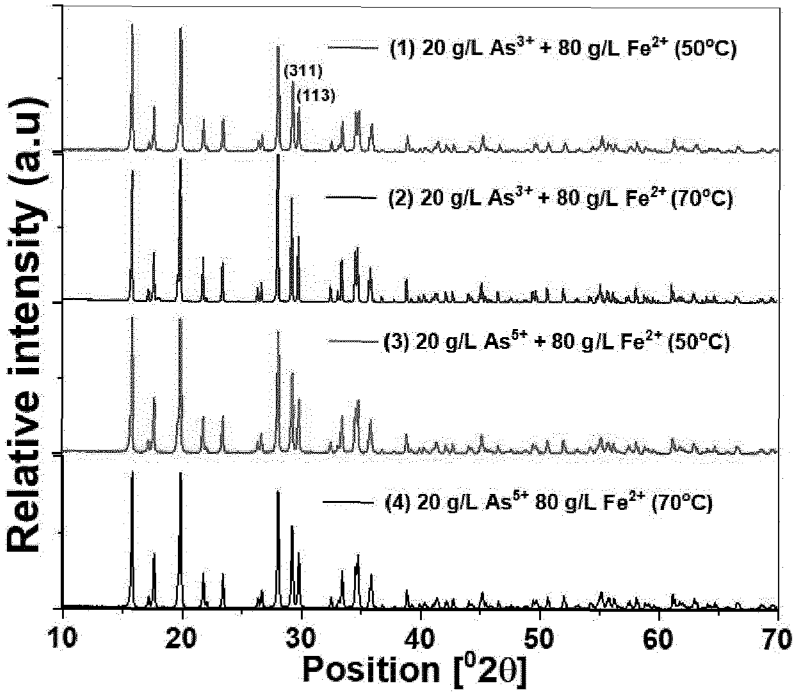


Fig. 4

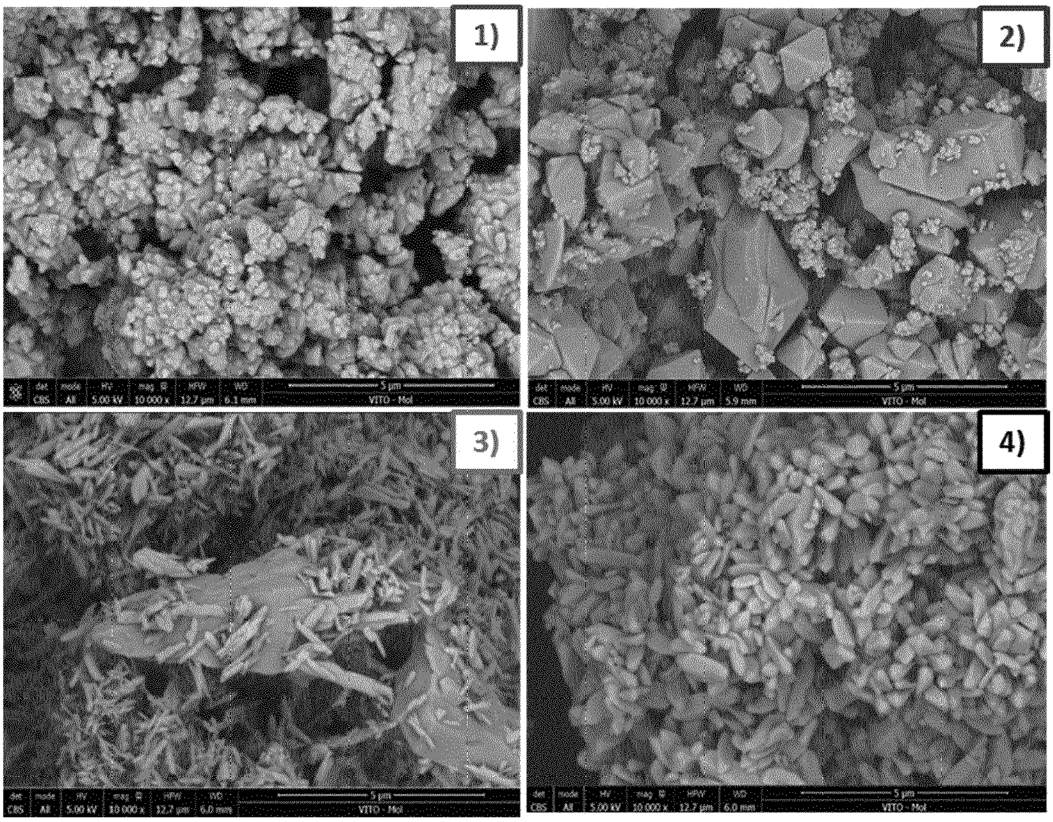

1)
2)
3)
4)
det mode HV mag HFW WD
CBS All 5.00 kV 10 000 x 12.7 µm 6.1 mm
5 µm
VITO - Mol
CBS All 5.00 kV 10 000 x 12.7 µm 5.9 mm
CBS All 5.00 kV 10 000 x 12.7 µm 6.0 mm
CBS All 5.00 kV 10 000 x 12.7 µm 6.0 mm

Fig. 5

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EUROPEAN SEARCH REPORT

Application Number
EP 18 24 8215

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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	13 June 2019	Hammerstein, G

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X : particularly relevant if taken alone
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