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Industria y Comercio

SUPERINTENDENCIA

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
INVENTARIO

SOLICITUD
PATENTE DE INVENCION

EXPEDIENTE N°

09-79285

TITULO: METODO Y APARATO PARA
REMOVER ARSENICO DE UNA SOLUCION

CLASIFICACION INTERNACIONAL: _____

SOLICITANTE: MOLYCORP MINERALS, LLC

DOMICILIO: California, Estados Unidos

APODERADO: DARIO CARDENAS NAVAS

BOGOTÁ, D.C. _____

PETITORIO



SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 09-079285-00000-0000

Fecha: 2009-07-30 12:19:21 Dep. 2020 NUECREACION
Tra. 11 PATENTEIYII Eve: 378 FASENACIONALI
Act. 411 PRESENTACION Folios: 110

FORMULARIO UNICO DE SOLICITUD DE PATENTE PCT ENTRADA EN FASE NACIONAL

①

SOLICITUD DE:

☒ X

Patente de Invención

☐

Patente de Modelo de Utilidad

☒ X

Capítulo I

☐

Capítulo II

②

SOLICITANTE

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IDENTIFICACION

☐ NIT

☐ NIT

☐ Otro

☒ Otro

Cuál
Número

③

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IDENTIFICACION

☒ X

NIT

☐ NIT

☐ Otro

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Número 17066629 TP 1250
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④

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4. Estadounidense

⑤ PCT (86)

Solicitud Internacional No. PCT/US2007/087976

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⑥ Título(54): MÉTODO Y APARATO PARA REMOVER ARSÉNICO DE UNA SOLUCIÓN

⑦ Clasificación Internacional (51): C02F 1/58

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(33)País de Origen

(32)Fecha

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Estados Unidos

28.12.06

60/882, 401

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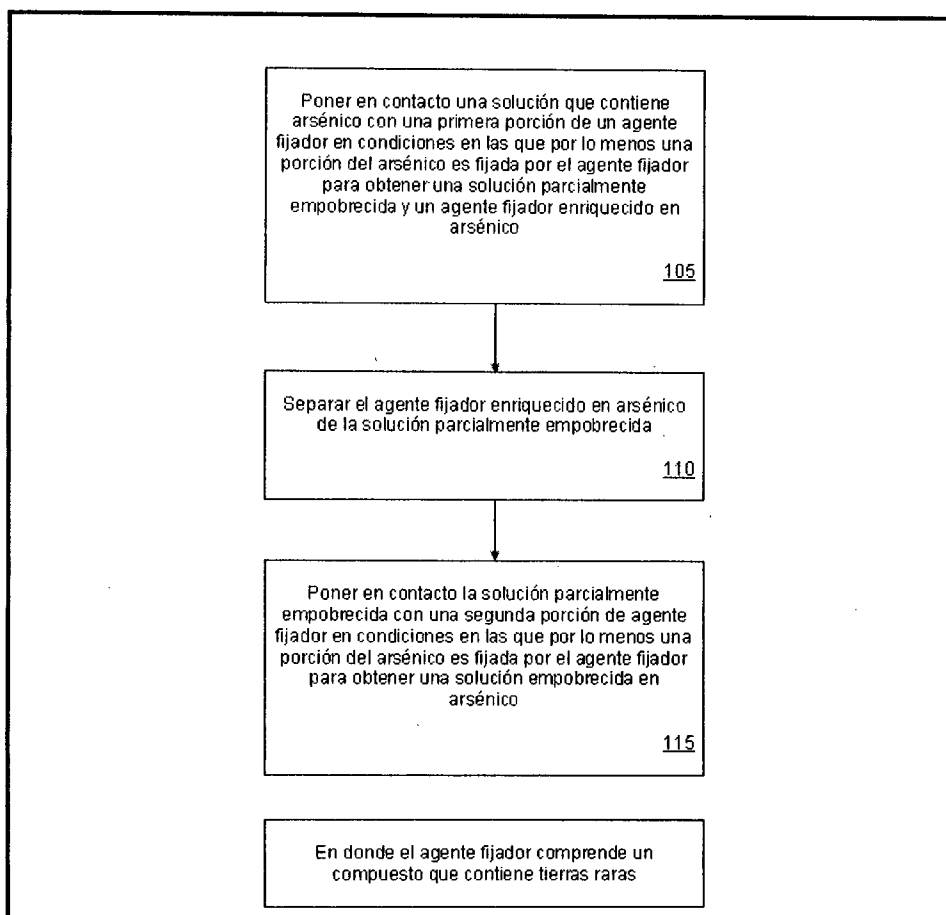
Fecha

24.07.2009

10 ANEXOS

- ☒ Comprobante de pago de la tasa de presentación de la solicitud.
- ☐ Documento que acredita la existencia y representación legal cuando el solicitante sea persona jurídica.
- ☐ Poderes, si fuere el caso.
- ☐ Documento de cesión del inventor al solicitante o a su causante.
- ☒ Traducción de la solicitud internacional al castellano (Resumen, Resumen, descripción, reivindicaciones, dibujos)
- ☐ Copia del examen preliminar internacional efectuado por la Autoridad Internacional de Examen Preliminar (IPEA)
- ☐ Traducción del examen preliminar internacional efectuado por la IPEA.
- ☐ De ser el caso, copia del contrato de acceso.
- ☐ De ser el caso, documento que acredite la licencia o autorización de uso de conocimientos tradicionales de las comunidades indígenas.
- ☐ De ser el caso, certificado de depósito del material biológico.
- ☒ Arte final 12x12.
- ☐ De ser el caso, información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante, relacionadas parcial o totalmente con la invención de esta solicitud.
- ☒ De ser el caso, modificaciones efectuadas a la solicitud internacional.
- ☐ Otros

11 FIGURA CARACTERISTICA



12 Solicito la Concesión de la patente

NOMBRE: **DARIO CARDENAS NAVAS**

FIRMA:

C.C. 17066629 BTA TP.

1250 LHC
C.S.J.

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 09-079285- -00000-0000

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176009-2

RECIBO OFICIAL DE CAJA : 09 - 54,255

FECHA : JULIO 24 DE 2009

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	Vr. PAGO
CARDENAS Y CARDENAS P.I.	CONSIGNACION	BANCO DE BOGOTA	062754387	111851143	24/07/2009	8,905,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01	SOLICITUDES	
		1 TRAMITES DE SOL. DE PATENTE DE IN	540,000.00
		TOTAL :	540,000.00

SON: QUINIENTOS CUARENTA MIL PESOS

CARDENAS Y CARDENAS

RESPONSABLE :

ABOGADOS

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

ESTA CERTIFICACION DE EXCEDENTE DE PAGO SOLO PODRA SER UTILIZADA
COMO PARTE DE LA CANCELACION DE UNA TARIFA VIGENTE Y NO PODRA SER
SUSTITUIDA POR NINGUN RECIBO.

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 09-079285- -00000-0000

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Tra. 11 PATENTEIYII Eve: 378 FASENACIONALI
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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

CERTIFICACION DE EXCEDENTE : 09 - 54,257
FECHA : JULIO 24 DE 2009

*** CONSIGNACION ***

DEPOSITANTE	TIPU PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CARDENAS Y CARDENAS P.I.	CONSIGNACION	BANCO DE BOGOTA	062754387	111851143	24/07/2009	8,905,000.00

*** CONCEPTO ***

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-04	OTROS SERVICIOS DE PROPIEDAD I	
		99 OTROS SERVICIOS ADMINISTRATIVOS	500,000.00
		TOTAL :	\$ 500,000.00

SUN: QUINIENTOS MIL PESOS

CARDENAS Y CARDENAS

RESPONSABLE :

ABOGADOS

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____



SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

DIVISION DE NUEVAS CREACIONES

TARJETA ARCHIVO PROPIETARIOS

Industria y Comercio

SUPERINTENDENCIA

PATENTE DE INVENCION ☐ PCT ☒ MODELO DE UTILIDAD ☐ DISEÑO INDUSTRIAL ☐

(21) N° de solicitud:

(22) Fecha de solicitud:

(51) Clasificación Internacional:

(71) Solicitante(s) **Molycorp Minerals, LLC**

(72) Inventor(es) **John L. Burba; Carl R. Hassler; C. Brock O'Kelley; Charles F. Whitehead.**

(74) Apoderado: **DARIO CARDENAS NAVAS**

(30) Prioridad	(31) No. Prioridad	(32) Fecha	(33) País
	60/882, 401	28.12.2006	Estados Unidos

(85) Fecha inicio fase nacional:

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(86) Datos relativos a la presentación de la solicitud PCT

Fecha: **10.07.2008**

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N° publicación: **WO 2008/082961 A1**

No. de solicitud **PCT/US2007/087976**

(54) Título: **MÉTODO Y APARATO PARA REMOVER ARSÉNICO DE UNA SOLUCIÓN**

Industria y Comercio

SUPERINTENDENCIA

DIVISION DE NUEVAS CREACIONES

TARJETA ARCHIVO TEMATICO

PATENTE DE INVENCION

PCT ☒ X

MODELO DE UTILIDAD

DISEÑO INDUSTRIAL

(21) N° de solicitud:

(22) Fecha de solicitud:

(51) Clasificación Internacional:

(71) Solicitante(s) **Molycorp Minerals, LLC**

(72) Inventor(es) **John L. Burba; Carl R. Hassler; C. Brock O'Kelley; Charles F. Whitehead.**

(74) Apoderado: **DARIO CARDENAS NAVAS**

(30) Prioridad

(31) No. Prioridad

32)

Fecha

(33) Pais

60/882, 401

28.12.2006 Estados Unidos

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Fecha de presentación de la solicitud: 18.12.2007

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Fecha: 10.07.2008

No. Publicación **WO 2008/082961 A1**

(54) Título: **MÉTODO Y APARATO PARA REMOVER ARSÉNICO DE UNA SOLUCIÓN**

(57) Resumen. Un método y aparato para separar arsénico de una solución acuosa que contiene arsénico. El método incluye los pasos de poner en contacto una solución que contiene arsénico con una primera porción de agente fijador para remover por lo menos una porción del arsénico. Un agente fijador enriquecido en arsénico se separa de la solución y la solución parcialmente empobrecida se pone en contacto con una segunda porción del agente fijador. El agente fijador puede incluir un compuesto insoluble de alta área superficial que contiene uno o más de cerio, lantano o praseodimio. Luego de la remoción del arsénico, la solución empobrecida en arsénico se puede procesar adicionalmente para separar un metal recuperable a través de refinación de metales. El agente fijador enriquecido en arsénico se puede filtrar para recuperar y reciclar un filtrado hacia la solución para su tratamiento adicional, así como también se puede utilizar un agente fijador parcialmente saturado para remover arsénico de una solución fresca. Se puede formar una solución que contiene arsénico a partir de sólidos que contienen arsénico tales como suelos contaminados, subproductos industriales y materiales de desecho.

Poner en contacto una solución que contiene arsénico con una primera porción de un agente fijador en condiciones en las que por lo menos una porción del arsénico en dicha solución se separa para obtener una solución parcialmente empobrecida y un agente fijador enriquecido en arsénico.

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Separar el agente fijador enriquecido en arsénico de la solución parcialmente empobrecida.

112

Poner en contacto la solución parcialmente empobrecida con una segunda porción de agente fijador en condiciones en las que por lo menos una porción del arsénico se separa para obtener una solución empobrecida en arsénico.

113

En donde el agente fijador comprende un compuesto que contiene tierras raras.

(21) N° de solicitud:		(51) Int Cl:	
22) Fecha de solicitud:		(71) Solicitante(s) Molycorp Minerals, LLC	
(30) Prioridad	(31) No. Prioridad 60/882, 401	(32) Fecha 28.12.2006	(33) País Estados Unidos
		(72) Inventor(es) John L. Burba; Carl R. Hassler; C. Brock O'Kelley; Charles F. Whitehead.	
		(74) Apoderado: DARIO CARDENAS NAVAS	
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Fecha de presentación de la solicitud: 18.12.2007		N° publicación: WO 2008/082961 A1	
No. de solicitud PCT/US2007/037976			
(54) Título: MÉTODO Y APARATO PARA REMOVER ARSÉNICO DE UNA SOLUCIÓN			

Resumen: Un método y aparato para separar arsénico de una solución acuosa que contiene arsénico. El método incluye los pasos de poner en contacto una solución que contiene arsénico con una primera porción de agente fijador para remover por lo menos una porción del arsénico. Un agente fijador enriquecido en arsénico se separa de la solución y la solución parcialmente empobrecida se pone en contacto con una segunda porción del agente fijador. El agente fijador puede incluir un compuesto insoluble de alta área superficial que contiene uno o más de cerio, lantano o praseodimio. Luego de la remoción del arsénico, la solución empobrecida en arsénico se puede procesar adicionalmente para separar un metal recuperable a través de refinación de metales. El agente fijador enriquecido en arsénico se puede filtrar para recuperar y reciclar un filtrado hacia la solución para su tratamiento adicional, así como también se puede utilizar un agente fijador parcialmente saturado para remover arsénico de una solución fresca. Se puede formar una solución que contiene arsénico a partir de sólidos que contienen arsénico tales como suelos contaminados, subproductos industriales y materiales de desecho.

ABSTRACT OF THE INVENTION

A method and apparatus for separating arsenic from an aqueous solution containing arsenic. The method includes the steps of contacting an arsenic-containing
5 solution with a first portion of fixing agent to remove at least a portion of the arsenic. An arsenic-laden fixing agent is separated from the solution and the partially depleted solution is contacted with a second portion of fixing agent. The fixing agent can include a high surface area insoluble compound containing one or more of cerium, lanthanum, or praseodymium. Following removal of the arsenic, the arsenic-depleted solution can be
10 further processed to separate a recoverable metal through metal refining. The arsenic-laden fixing agent can be filtered to recover and recycle a filtrate to the solution for additional treatment, as well as using a partially saturated fixing agent to remove arsenic from fresh solution. An arsenic-containing solution can be formed from arsenic-containing solids such as contaminated soils, industrial byproducts and waste materials.

METHOD AND APPARATUS FOR REMOVING ARSENIC FROM A SOLUTION

FIELD OF THE INVENTION

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This invention relates generally to the removal of toxic metals from an aqueous solution, and specifically, to the removal of arsenic from aqueous solutions, such as industrial process streams, effluents, solutions prepared from byproducts and waste materials, and drinking water.

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BACKGROUND OF THE INVENTION

The presence of arsenic in waters, soils and waste materials may originate from or have been concentrated through geochemical reactions, mining and smelting operations, the land-filling of industrial wastes, the disposal of chemical agents, as well as past agricultural uses of arsenic-containing pesticides. Because the presence of high levels of arsenic may have carcinogenic and other deleterious effects on living organisms and because humans are primarily exposed to arsenic through drinking water, the U.S. Environmental Protection Agency (EPA) and the World Health Organization have set the maximum contaminant level (MCL) for arsenic in drinking water at 10 parts per billion (ppb). As a result, a problem facing industries such as mining, metal refining, steel manufacturing and power generation is the reduction or removal of arsenic from process streams, effluents and byproducts.

Arsenic occurs in the inorganic form in aquatic environments primarily the result of dissolution of solid phase arsenic such as arsenolite (As_2O_3), arsenic anhydride As_2O_5 and realgar (AsS_2). Arsenic occurs in water in four oxidation or valence states, i.e., -3, 0, +3, and +5. Under normal conditions arsenic is found dissolved in aqueous or aquatic systems in the +3 and +5 oxidation states, usually in the form of arsenite (AsO_2^{-1}) and arsenate (AsO_4^{-3}). The effective removal of arsenic by coagulation techniques requires the arsenic to be in the arsenate form. Arsenite, in which the arsenic exists in the +3 oxidation state, is only partially removed by adsorption and coagulation techniques

because its main form, arsenious acid (HAsO_2), is a weak acid and remains un-ionized at pH levels between 5 and 8 when adsorption is most effective.

Various technologies have been used to remove arsenic from aqueous systems. Examples of such techniques include adsorption on high surface area materials, such as alumina, activated carbon, lanthanum oxide and cerium dioxide, ion exchange with anion exchange resins, precipitation and electrodialysis. In the case of solid or semi-solid waste materials and byproducts containing arsenic, attempts have been made to solidify or stabilize the arsenic in situ to prevent migration into surrounding soils or groundwater. However, because such stabilization procedures tend to be quite costly, and in some cases are unproven, there is a need for alternate method and techniques for handling arsenic in such materials.

SUMMARY OF THE INVENTION

In one embodiment, the present invention provides a method for separating arsenic from an arsenic-containing solution. The method includes the steps of contacting an arsenic-containing solution with a first portion of fixing agent under conditions in which at least a portion of the arsenic is fixed by the fixing agent to yield a partially-depleted solution and an arsenic-laden fixing agent. The fixing agent comprises a rare earth-containing compound. The rare-earth containing compound can include one or more of cerium, lanthanum, or praseodymium. More specifically, the rare-earth containing compound can comprise a cerium-containing compound derived from cerium carbonate. In other embodiments, the rare earth-containing compound comprises cerium dioxide. The first portion of fixing agent can be substantially free of arsenic prior to contacting the arsenic-containing solution or can be partially-saturated with arsenic. When partially-saturated, the fixing agent can comprise between about 0.1 mg and about 80 mg of arsenic per gram of fixing agent.

The method includes the steps of separating the arsenic-laden fixing agent from the partially-depleted solution and contacting the partially-depleted solution with a second portion of fixing agent under conditions in which at least a portion of the arsenic is fixed by the fixing agent to yield an arsenic-depleted solution. When the step of

contacting the partially-depleted solution with the second portion of fixing agent yields a partially-saturated fixing agent, the method can optionally include separating the partially-saturated fixing agent from the arsenic-depleted solution. In such an embodiment, the method optionally include the steps of contacting the partially-saturated
5 fixing agent with a fresh portion of an arsenic-containing solution under conditions in which at least a portion of the arsenic is fixed by the partially-saturated fixing agent to give a second partially-depleted solution and an arsenic-laden fixing agent, and separating the second partially-depleted solution from the arsenic-laden fixing agent. Such a method can also optionally include the step of contacting the second partially-
10 depleted solution with a third portion of fixing agent under conditions in which at least a portion of the arsenic is fixed by the fixing agent to give an arsenic-depleted solution.

Where the arsenic-depleted solution comprises a recoverable metal, the method can optionally include the step of separating the recoverable metal from the arsenic-depleted solution. The recoverable metal can include a metal from Group IA, Group IIA,
15 Group VIII, and the transition metals. The recoverable metal can be separated from the arsenic-depleted solution by combining the arsenic-depleted solution with a process stream in a metal refining process, precipitating the recoverable metal from the arsenic-depleted solution and/or electrolyzing the arsenic-depleted solution. The metal refining process can include electrolyzing the arsenic-depleted solution. When the recoverable
20 metal is in solution, the fixing agent is preferably an insoluble compound that does not react with the recoverable metal to form an insoluble product.

The pH of the arsenic-containing solution can be less than about 7 when the arsenic-containing solution is contacted with the first portion of fixing agent. More specifically, the pH of the arsenic-containing solution can be less than about 4, and still
25 more specifically, the pH of the arsenic-containing solution can be less than about 3 when the arsenic-containing solution is contacted with the first portion of fixing agent. In other embodiments, the pH of the arsenic-containing solution can be more than about 7 when the arsenic-containing solution is contacted with the first portion of fixing agent. More specifically, the pH of the arsenic-containing solution can be more than about 9, and still
30 more specifically, the pH of the arsenic-containing solution can be more than about 10 when the arsenic-containing solution is contacted with the first portion of fixing agent.

The method can also optionally include the step of forming the arsenic-containing solution by contacting an arsenic-bearing material with a leaching agent comprising one or more of an inorganic salt, an inorganic acid, an organic acid and an alkaline agent. When the leaching agent includes an alkaline agent, the alkaline agent can include
5 sodium hydroxide. The arsenic-containing solution can comprise more than about 1000 ppm sulfate when the arsenic-containing solution is contacted with the first portion of fixing agent.

In another embodiment, the present invention provides an apparatus for separating arsenic from an arsenic-containing solution. The apparatus includes a first contact zone
10 adapted to receive an arsenic-containing solution. The first contact zone has a fixing agent for contacting the arsenic-containing solution and fixing at least a portion of the arsenic to yield a partially-depleted solution. The fixing agent comprises a rare earth-containing compound. The rare-earth containing compound can include one or more of cerium, lanthanum, or praseodymium. More specifically, the rare-earth containing
15 compound can comprise a cerium-containing compound derived from cerium carbonate. In other embodiments, the rare earth-containing compound comprises cerium dioxide.

A second contact zone is also included that is adapted to receive the partially-depleted solution, and which has a fixing agent for contacting the partially-depleted solution and fixing at least a portion of the arsenic to yield an arsenic-depleted solution.
20 The apparatus further includes a first separator disposed intermediate the first contact zone and the second contact zone for separating fixing agent from the partially-depleted solution.

The apparatus can optionally include a second separator connected to the second contact zone for separating the arsenic-depleted solution from fixing agent. When
25 present, the second separator can include an outlet for providing fluid communication with the first contact zone for directing a partially saturated fixing agent to the first contact zone.

The apparatus can also optionally include a filtration unit operably connected to the first separator for receiving the arsenic-laden fixing agent and producing a filtrate.
30 When present, the filtration unit can include an outlet for providing fluid communication with the first contact zone for directing the filtrate to the first contact zone.

The apparatus can optionally include a metal recovery unit for separating a recoverable metal from the arsenic-depleted solution. The metal recovery unit can comprise one or more of a precipitation vessel and/or an electrolyzer.

5

BRIEF DESCRIPTION OF THE DRAWINGS

The invention may be understood by reference to the following description taken in conjunction with the accompanying drawings.

Figure 1 is a flow chart representation of a method of the present invention.

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Figure 2 is a schematic view of an apparatus of the present invention.

While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof have been shown by way of example in the drawings and are herein described in detail. It should be understood, however, that the description herein of specific embodiments is not intended to limit the invention to the particular forms disclosed, but on the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the appended claims.

15

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

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Illustrative embodiments of the invention are described below. In the interest of clarity, not all features of an actual embodiment are described in this specification. It will of course be appreciated that in the development of any such actual embodiment, numerous implementation-specific decisions must be made to achieve the developers' specific goals, such as compliance with system-related and business-related constraints, which will vary from one implementation to another. Moreover it will be appreciated that such a development effort might be complex and time-consuming, but would nevertheless be a routine undertaking for those of ordinary skill in the art having the benefit of this disclosure.

25

It will be understood that the method and apparatus disclosed herein can be used to treat any aqueous solution that contains undesirable amounts of arsenic. Examples of

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such solutions include, among others, well water, surface waters, such as water from lakes, ponds and wetlands, agricultural waters, industrial process streams, wastewater and effluents from industrial processes, solutions formed from industrial waste and byproducts and geothermal fluids. The arsenic-containing solution can also contain other
5 inorganic contaminants, such as selenium, cadmium, lead, mercury, chromium, nickel, copper and cobalt, and certain organic contaminants. A method and apparatus of the present invention can remove arsenic from such solutions even when elevated concentrations of such inorganic contaminants are present. More specifically, arsenic is effectively removed from solutions comprising more than about 1000 ppm sulfate.

10 Generally, a method and apparatus of the present invention can be used to treat any aqueous solution containing more than about 20 ppb arsenic and is effective for treating solutions containing more than about 1000 ppb arsenic. Moreover, the method and apparatus is effective in decreasing such arsenic levels to an amount less than about 20 ppb, in some cases less than about 10 ppb, in others less than about 5 ppb and in still
15 others less than about 2 ppb.

It has been determined that the adsorption capacity of certain fixing agents for removing arsenic from aqueous solutions is at least in part dependent on the concentration of arsenic in those solutions. More specifically, it has been determined that for a given quantity of fixing agent that comprises a rare earth-containing compound, a
20 greater quantity of arsenic can be removed from solution by contacting the solution with two or more portions of the fixing agent and separating the arsenic-laden fixing agent from the solution between such contacting steps than if the solution were treated with that quantity of fixing agent in a single contact stage. Moreover, the method can be used to effectively remove arsenic from such solutions over a wide range of pH levels, and at
25 extreme pH values, eliminating the need to alter and/or maintain the pH of the solution within a narrow range.

In one aspect of the present invention, a method is provided for separating arsenic from an arsenic-containing solution. The method includes the step of contacting an arsenic-containing solution with a first portion of fixing agent comprising a rare earth-
30 containing compound under conditions in which at least a portion of the arsenic is fixed by the fixing agent to yield a partially-depleted solution and an arsenic-laden fixing

agent. The arsenic-laden fixing agent is separated from the partially-depleted solution, and the partially-depleted solution is contacted with a second portion of fixing agent under conditions in which at least a portion of the arsenic is fixed by the fixing agent to yield an arsenic-depleted solution.

5 The arsenic-containing solution is contacted with the first portion of fixing agent in a tank, container or other vessel suitable for holding such solutions and materials. The solution is at a temperature and pressure, usually ambient conditions, such that the solution remains in the liquid state, although elevated temperature and pressure conditions may be used. The tank may optionally include a mixer or other means for
10 promoting agitation and contact between the arsenic-containing solution and the fixing agent. Non-limiting examples of suitable vessels are described in U.S. Patent No. 6,383,395, which description is incorporated herein by reference. An apparatus of the present invention comprises a first contact zone and a second contact zone with a separator disposed therebetween. The first contact zone and the second contact zone can
15 be housed within a common vessel or reactor, or may be housed separately.

 The fixing agent can be any rare earth-containing compound that is effective at fixing arsenic in solution through precipitation, adsorption, ion exchange or other mechanism. The fixing agent can be soluble, slightly soluble or insoluble in the aqueous solution. In some embodiments, the fixing agent has a relatively high surface area of at
20 least about 70 m²/g, and in some cases more than about 80 m²/g, and in still other cases more than 90 m²/g.

 The fixing agent can include one or more of the rare earths including lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium erbium, thulium, ytterbium and lutetium. Specific
25 examples of such materials that have been described as being capable of removing arsenic from aqueous solutions include trivalent lanthanum compounds (U.S. Patent No. 4,046,687), soluble lanthanide metal salts (U.S. Patent No. 4,566,975), lanthanum oxide (U.S. Patent No. 5,603,838), lanthanum chloride (U.S. Patent No. 6,197,201), mixtures of lanthanum oxide and one or more other rare earth oxides (U.S. Patent No. 6,800,204),
30 cerium oxides (U.S. Patent No. 6,862,825); mesoporous molecular sieves impregnated with lanthanum (U.S. Patent Application Publication No. 20040050795), and

polyacrylonitrile impregnated with lanthanide or other rare earth metals (U.S. Patent Application Publication No. 20050051492). It should be understood that such rare earth-containing fixing agents may be obtained from any source known to those skilled in the art.

5 In some embodiments, the rare-earth containing compound can comprise one or more of cerium, lanthanum, or praseodymium. Where the fixing agent comprises a compound containing cerium, the fixing agent can be derived from cerium carbonate. More specifically, such a fixing agent can be prepared by thermally decomposing a cerium carbonate or cerium oxalate in a furnace in the presence of air. When the fixing
10 agent comprises cerium dioxide, it is generally preferred to use solid particles of cerium dioxide, which are insoluble in water and relatively attrition resistant. Water-soluble cerium compounds such as ceric ammonium nitrate, ceric ammonium sulfate, ceric sulfate, and ceric nitrate can also be used as the fixing agent, particularly where the concentration of arsenic in solution is high.

15 The fixing agent comprising the rare earth-containing compound can be present the first portion of fixing agent that is contacted with the arsenic-containing solution, the second portion of fixing agent that is contacted with a partially depleted solution or in each of the first, second and any additional portions of the fixing agent. The first portion of fixing agent can be substantially free of arsenic prior to contacting the arsenic-
20 containing solution or the first portion can be partially-saturated with arsenic. When partially-saturated, the fixing agent can comprise between about 0.1 mg and about 80 mg of arsenic per gram of fixing agent.

 Optionally, a fixing agent that does not contain a rare earth compound can also be used in the methods and apparatus of the present invention. Such optional fixing agents
25 can include any solid, liquid or gel that is effective at fixing arsenic in solution through precipitation, adsorption, ion exchange or some other mechanism. These optional fixing agents can be soluble, slightly soluble or insoluble in the aqueous solution. Optional fixing agents can include particulate solids that contain cations in the +3 oxidation state that react with the arsenate in solution to form insoluble arsenate compounds. Examples
30 of such solids include alumina, gamma-alumina, activated alumina, acidified alumina such as alumina treated with hydrochloric acid, metal oxides containing labile anions

such as aluminum oxychloride, crystalline alumino-silicates such as zeolites, amorphous silica-alumina, ion exchange resins, clays such as montmorillonite, ferric salts, porous ceramics. Optional fixing agents can also include calcium salts such as calcium chloride, calcium hydroxide, and calcium carbonate, and iron salts such as ferric salts, ferrous salts, or a combination thereof. Examples of iron-based salts include chlorides, sulfates, nitrates, acetates, carbonates, iodides, ammonium sulfates, ammonium chlorides, hydroxides, oxides, fluorides, bromides, and perchlorates. Where the iron salt is a ferrous salt, a source of hydroxyl ions may also be required to promote the co-precipitation of the iron salt and arsenic. Such a process and materials are described in more detail in U.S. Patent No. 6,177,015, issued Jan. 23, 2001 to Blakey et al. Other optional fixing agents are known in the art and may be used in combination with the rare earth-containing fixing agents described herein. Further, it should be understood that such optional fixing agents may be obtained from any source known to those skilled in the art.

Particulate solids such as insoluble fixing agents and insoluble arsenic-containing compounds are separated from the various solutions described herein for further processing. Any liquid-solids separation technique, such as filtration, gravity settling, centrifuging, hydrocycloning or the like can be used to remove such particulate solids. An optional flocculant, coagulant or thickener can also be added to the solution before the particulate solids are removed. Such agents are useful for achieving a desired particle size and improving the settling properties of the arsenic-laden fixing agent. Examples of inorganic coagulants include ferric sulfate, ferric chloride, ferrous sulfate, aluminum sulfate, sodium aluminate, polyaluminum chloride, aluminum trichloride among others. Organic polymeric coagulants and flocculants can also be used, such as polyacrylamides (cationic, nonionic, and anionic), EPI-DMA's (epichlorohydrin-dimethylamines), DADMAC's (polydiallyldimethyl-ammonium chlorides), dicyandiamide/formaldehyde polymers, dicyandiamide/amine polymers, natural guar, etc.

In one embodiment, an arsenic-laden fixing agent is separated from a partially depleted solution in a first separator. The arsenic laden fixing agent is then directed to a filtration unit that is connected to the separator where the fixing agent is further filtered to produce a filtrate and arsenic-laden solids. The solids are directed out of the filtration unit for appropriate disposal or further handling. The filtration unit has an outlet in fluid

communication with a second contact zone for recycling the filtrate to the second contact zone where it is combined with the partially-depleted solution and contacted with fresh fixing agent.

5 In another embodiment, a mixture of an arsenic-depleted solution and a partially saturated fixing agent are directed out of a second contact zone and into a second separator for separating the solution from the fixing agent. The arsenic-depleted solution is directed out of the separator for use, disposal or additional processing. The separator has an outlet in fluid communication with the first contact zone for directing a slurry of the partially-saturated fixing agent to the first contact zone where it contacts in-coming
10 fresh arsenic-containing solution.

The rare earth-containing fixing agents of the present invention are particularly advantageous in their ability to remove arsenic from solution over a wide range of pH values and at extreme pH values. The pH of the arsenic-containing solution can be less than about 7 when the arsenic-containing solution is contacted with the first portion of
15 fixing agent. More specifically, the pH of the arsenic-containing solution can be less than about 4, and still more specifically, the pH of the arsenic-containing solution can be less than about 3 when the arsenic-containing solution is contacted with the first portion of fixing agent. In other embodiments, the pH of the arsenic-containing solution can be more than about 7 when the arsenic-containing solution is contacted with the first portion
20 of fixing agent. More specifically, the pH of the arsenic-containing solution can be more than about 9, and still more specifically, the pH of the arsenic-containing solution can be more than about 10 when the arsenic-containing solution is contacted with the first portion of fixing agent.

To the extent that it is desirable to adjust or control the pH, an optional acid
25 and/or alkaline addition may be added to the solution as is well known in the art. Acid addition can include the addition of a mineral acid such as hydrochloric or sulfuric acid. Alkaline addition can include the addition of sodium hydroxide, sodium carbonate, calcium hydroxide, ammonium hydroxide and the like.

When the arsenic-containing solution includes a recoverable metal, the method
30 can optionally include the step of separating the recoverable metal from the arsenic-depleted solution in a metal recovery unit connected to the second contact zone. As used

herein, recoverable metal can include virtually any metal of interest, but specifically includes metals from Group IA, Group IIA, Group VIII, and the transition metals. Where the recoverable metal is in solution in the arsenic containing solution, the fixing agent is preferably an insoluble compound that selectively adsorbs arsenic from the solution and
5 does not react or reacts only weakly with the recoverable metal to form an insoluble product. The recoverable metal can be separated from the arsenic-depleted solution by combining the arsenic-depleted solution with a process stream in a metal refining process. In some embodiments, the arsenic-depleted solution can be electrolyzed to separate the recoverable metal from solution. By way of example, the removal of
10 contaminants to form a solution for separating various metals through electrorefining processes is described in detail in U.S. Patent No. 6,569,224 issued May 27, 2003 to Kerfoot et al. In other embodiments, the recoverable metal can be precipitated from the arsenic-depleted solution in a precipitation vessel connected to the second contact zone.

When the step of contacting the partially-depleted solution with the second
15 portion of fixing agent yields a partially-saturated fixing agent, the method can optionally include separating the partially-saturated fixing agent from the arsenic-depleted solution. In such an embodiment, the method can further include the steps of contacting the partially-saturated fixing agent with a fresh portion of an arsenic-containing solution under conditions in which at least a portion of the arsenic is fixed by the partially-
20 saturated fixing agent to give a second partially-depleted solution and an arsenic-laden fixing agent. The second partially-depleted solution is separated from the arsenic-laden fixing agent. Such a method can also optionally include the step of contacting the second partially-depleted solution with a third portion of fixing agent under conditions in which at least a portion of the arsenic is fixed by the fixing agent to give an arsenic-depleted
25 solution.

Arsenic can be extracted from solids such as contaminated soils, industrial byproducts and waste materials by leaching or extraction to release the arsenic from such solids. As a result, the method can also optionally include the step of forming the arsenic-containing solution by contacting an arsenic-bearing material with an arsenic
30 extraction agent comprising one or more of an inorganic salt, an inorganic acid, an organic acid and an alkaline agent. Specific examples of inorganic salt arsenic extraction

agents include potassium salts such as potassium phosphate, potassium chloride, potassium nitrate, potassium sulfate, sodium perchlorate and the like. Examples of inorganic acids that may be used to extract arsenic from solids include sulfuric acid, nitric acid, phosphoric acid, hydrochloric acid, perchloric acid and mixtures thereof. Organic acid extractants can include citric acid, acetic acids and the like. Alkaline agents can include sodium hydroxide among others. The arsenic-bearing material is contacted with an extraction agent in a tank, container or other vessel suitable for holding such solutions and materials. Pumps, mixers or other suitable means may be included for promoting agitation and contact between the extraction agent and the arsenic-bearing materials. A more detailed description of arsenic extraction agents and their use may be had by reference to M. Jang et al., "Remediation Of Arsenic-Contaminated Solids And Washing Effluents", *Chemosphere*, 60, pp 344-354, (2005); M. G. M. Alam et al., "Chemical Extraction of Arsenic from Contaminated Soil", *J. Environ Sci Health A Tox Hazard Subst Environ Eng.*, 41 (4), pp 631-643 (2006); and S.R. Al-Abed et al., "Arsenic Release From Iron Rich Mineral Processing Waste; Influence of pH and Redox Potential", *Chemosphere*, 66, pp 775-782 (2007).

DETAILED DESCRIPTION OF THE FIGURES

Figure 1 is a flow chart representation of method 100. Method 100 includes step 105 of contacting an arsenic-containing solution with a first portion of fixing agent under conditions in which at least a portion of the arsenic is fixed by the fixing agent to yield a partially-depleted solution and an arsenic-laden fixing agent. In step 110, the arsenic-laden fixing agent is separated from the partially-depleted solution. In step 115, the partially-depleted solution is contacted with a second portion of fixing agent under conditions in which at least a portion of the arsenic is fixed by the fixing agent to yield an arsenic-depleted solution. The fixing agent comprises a rare earth-containing compound.

Figure 2 is a schematic representation of apparatus 200. Apparatus 200 receives an arsenic-containing solution from a source 201 and directs it to a first contact zone within mixing tank 205. Tank 205 may optionally receive fresh fixing agent from a source 203 and a partially saturated fixing agent through line 229. The arsenic-

containing solution is contacted with the fixing agent in tank 205. Tank 205 may optionally include a mixer (not shown) within the tank to promote agitation and contact between the arsenic-containing solution and the fixing agent. In this first contact zone, at least a portion of the arsenic is fixed to yield a partially-depleted solution and an arsenic-laden fixing agent.

As illustrated, both the solution and fixing agent are transferred via line 209 to separator 210 where the partially-depleted solution is separated from the arsenic-laden fixing agent. Separator 210 has an overflow outlet that directs the partially-depleted solution through line 211 to tank 215. The fixing agent is directed through an outlet to filter 213. Within filter 213, the fixing agent is filtered to yield a filtrate and arsenic-laden solids. The filtrate is routed through line 219 to tank 215 where it is recombined with the partially-depleted solution from separator 210. The arsenic-laden solids produced from the fixing agent in filter 213 are directed out through line 225.

The partially depleted solution and filtrate are combined in tank 215 and contacted with fresh fixing agent from source 207. Tank 215 may optionally include a mixer (not shown) within the tank to promote agitation and contact between the partially-depleted solution and the fixing agent. In this second contact zone, at least a portion of the arsenic is fixed to yield an arsenic-depleted solution. As illustrated, the arsenic-depleted solution and fixing agent are transferred via line 221 to separator 227 wherein the arsenic-depleted solution is separated from the fixing agent. The fixing agent in separator 227 is partially saturated with arsenic and may be recycled to first contact zone within tank 205 for contacting fresh arsenic-containing solution from source 201. The arsenic-depleted solution separated from the fixing agent in separator 227 is directed out of apparatus 200 through line 223.

Example 1: Single treatment of caustic As-containing mining waste solution

These experiments were conducted to determine the surface loading: volume ratio necessary to treat the caustic As-containing solution. The caustic As-containing solution consisted of 5-7 g/L As (III), 20 g/L Na_2CO_3 , 4 g/L Sulfate, 4 mg/L Ni, and 1 mg/L Cu.

The pH of the solution was approximately 10.5. The fixing agent used in these

experiments was a high surface area ceria, prepared by thermally decomposing cerium carbonate to CeO₂ at 300° C in a muffle furnace with adequate exposure to air.

Single treatment experiments were run using 200 mL of caustic As-containing solution at approximately 75° C and adding between 3-20g of the thermally decomposed cerium carbonate. Under test conditions, the ceria surface became saturated at a loading of 80 mg(As)/g(Ce). When more than 10g of ceria was added, the arsenic concentration dropped below 0.2% and the surface was no longer able to be loaded to the saturation capacity.

Results are provided in Table 1. Observations collected over the course of two hours suggest that the system rapidly reaches a steady state, particularly when the surface becomes saturated with arsenic.

Table 1

Mass ceria (g)	As(ppm) 30min	As(ppm) 1hr	As(ppm) 2hr	Capacity (mg/g)
3.0	4600	4600	4700	80
5.0	3900	3500	3800	76
7.0	3000	3000	2900	80
10	1700	1700	1600	82
15	544	521	549	70
20	133	118	112	57

Example 2: Two-stage counter-current treatment of caustic As-containing solution

A caustic As-containing solution was prepared by adding 10 g NaAsO₂, 20 g Na₂CO₃, 1 mL of 1000 ppm copper nitrate standard, 0.4 mL of 10,000 ppm nickel nitrate standard to 800 mL DI water. The caustic As-containing solution was then diluted to a full liter and the pH was titrated down to 10.5 using concentrated HCl. With the addition of the nickel sulfate and copper sulfate, a majority of nickel and copper precipitated out, due to the high pH of the caustic solution. The resulting caustic As-containing solution consisted of 5 g/L As (III), 20 g/L Na₂CO₃, 300 µg/L Ni, and 300 µg/L Cu. The fixing agent was again a high surface area ceria prepared by thermally decomposing cerium carbonate to CeO₂ at 300° C in a muffle furnace with adequate exposure to air.

The two stage counter-current procedure was carried as follows:

Cycle 1/Stage 1: 12 g of 300 thermally decomposed cerium carbonate was added to 200 mL of the caustic As-containing solution maintained at a temperature of 70-80°C.

The suspension was filtered on Watman paper, the arsenic-laden ceria was discarded, and the supernatant solution was moved to Cycle 1/Stage 2.

5 Cycle 1/Stage 2: The supernatant solution from Cycle 1/Stage 1 was re-treated with 12 g of fresh ceria. The twice-treated solution was filtered and the ceria was collected and transferred to Cycle 2/Stage 1.

Cycle 2/Stage 1: The ceria collected from Cycle 1/Stage 2 was added to 200 mL of fresh caustic As-containing solution. The suspension was filtered, the arsenic-saturated ceria was discarded, and the supernatant solution was advanced to Cycle 2/Stage 2.

10 Cycle 2/Stage 2: The supernatant solution from Cycle 2/Stage 1 was re-treated with 12g of fresh ceria. The twice-treated solution was filtered and the ceria was collected and transferred to Cycle 3/Stage 1.

Cycle 3/Stage 1: The ceria collected from Cycle 2/Stage 2 was added to 200 mL of fresh caustic As-containing solution. The suspension was filtered, the arsenic-saturated ceria was discarded, and the supernatant solution was advanced to Cycle 3/Stage 2.

15 Cycle 3/Stage 2: The supernatant solution filtered in Cycle 3/Stage 1 was re-treated with 12g of fresh ceria.

Results from this two-stage counter current treatment are shown in Table 2.

Capacity (C) takes into account the amount of arsenic adsorbed to the surface in stage 2 of the previous cycle. In all cases, the twice treated solutions had an arsenic
20 concentration of less than about 10 ppm. The two-stage counter current procedure effectively lowered arsenic concentrations 99.86% using 12g of ceria at each stage. The observations collected over two hours support the conclusion that the adsorption kinetics are favorable, especially when the ceria surface becomes saturated with arsenic. The capacity of ceria observed in Cycle 2/Stage 1, taking into account the arsenic already
25 adsorbed in Cycle 1/Stage 2, is comparable to the saturation capacity established from the single treatment experiments. However, relative to the single treatment tests as exemplified by Example 1, the final concentration of arsenic remaining in solution in the two-stage counter current experiment is roughly two orders of magnitude lower for the same mass of ceria.

Table 2

Time (hrs)	As(ppm)	C (mg/g)	As(ppm)	C (mg/g)
<i>Cycle 1</i>	<i>Stage 1</i>		<i>Stage 2</i>	
0.5	1070	77	0.11	18
1	1010	78	0.1	17
2	1040	78	0.1	17
<i>Cycle 2</i>	<i>Stage 1</i>		<i>Stage 2</i>	
0.5	2300	74	2.71	38
1	2250	74	2.07	37
2	2250	75	2	37
<i>Cycle 3</i>	<i>Stage 1</i>		<i>Stage 2</i>	
0.5	2890	85	8.5	48
1	2850	85	6.9	47
2	3000	82	6.5	50

Example 3: Two-stage counter-current treatment of acidic As-containing solution

The two-stage counter-current treatment procedure used in Example 2 was also applied to an acidic As-containing solution containing 35 ppm As(III). The acidic solution was prepared by adding 18.72 mL of 5770 ppm As (III), 1074.3 g Nickel (II) Sulfate, 250 g NaCl, 0.63 g cobalt (II) sulfate, 6 mL of 1000 ppm lead nitrate standard, and 1.5 mL of 1000 ppm copper nitrate standard to 2 L of deionized water. The solution was then diluted to 3 L, to give a pH of approximately 2.

The acidic As-containing solution was then treated with thermally decomposed cerium carbonate using the two stage counter-current procedure. The process treated a liter of the acidic As-containing solution with 0.8 g of ceria. Some dissolution of the cerium fixing agent was observed and measured along with the arsenic concentration of the treated solutions. The results are provided in Table 3. In all cases, the twice treated solutions had an arsenic concentration of less than about 5 ppm.

Table 3

Time (hrs)	As(ppm)	Ce (ppm)	As(ppm)	Ce (ppm)
<i>Cycle 1</i>	<i>Stage 1</i>		<i>Stage 2</i>	
0.5	15.1	5.0	0.6	9.9
1	11.7	7.4	0.3	10.6
2	9.5	8.8	0.2	10.2
<i>Cycle 2</i>	<i>Stage 1</i>		<i>Stage 2</i>	
0.5	22.3	6.1	2.4	10.2
1	19.2	7.3	1.4	10.8
2	18.7	8.7	1.0	10.8
<i>Cycle 3</i>	<i>Stage 1</i>		<i>Stage 2</i>	
0.5	25.5	5.6	4.9	9.3
1	24.2	7.3	3.5	10.0
2	24.0	8.2	2.6	10.4

5 The particular embodiments disclosed above are illustrative only, as the invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. It is therefore evident that the particular embodiments disclosed above may be altered or modified and all such variations are considered within the scope and spirit of the invention. Accordingly, the protection sought herein is as set forth in the

10 claims below.

WHAT IS CLAIMED IS:

1. A method for separating arsenic from an arsenic-containing solution, the method comprising the steps of:
 - 5 contacting an arsenic-containing solution with a first portion of fixing agent under conditions in which at least a portion of the arsenic is fixed by the fixing agent to yield a partially-depleted solution and an arsenic-laden fixing agent, wherein the fixing agent comprises a rare earth-containing compound;
 - 10 separating the arsenic-laden fixing agent from the partially-depleted solution; and
 - contacting the partially-depleted solution with a second portion of fixing agent under conditions in which at least a portion of the arsenic is fixed by the fixing agent to yield an arsenic-depleted solution.
- 15 2. The method of claim 1, wherein the arsenic-depleted solution comprises a recoverable metal from Group IA, Group IIA, Group VIII and the transition metals.
- 20 3. The method of claim 2, further comprising the step of combining the arsenic-depleted solution with a process stream in a metal refining process to separate the recoverable metal.
4. The method of claim 2, further comprising precipitating the recoverable metal from the arsenic-depleted solution.
- 25 5. The method of claim 2, further comprising electrolyzing the arsenic-depleted solution to separate the recoverable metal.
- 30 6. The method of claim 1, wherein the step of contacting the partially-depleted solution with the second portion of fixing agent yields a partially-saturated fixing agent, the method further comprising the step of:

separating the partially-saturated fixing agent from the arsenic-depleted solution.

7. The method of claim 6, further comprising:
- 5 contacting the partially-saturated fixing agent with a fresh portion of an arsenic-containing solution under conditions in which at least a portion of the arsenic is fixed by the partially-saturated fixing agent to give a second partially-depleted solution and an arsenic-laden fixing agent; and
- 10 separating the second partially-depleted solution from the arsenic-laden fixing agent.
8. The method of claim 7, further comprising contacting the second partially-depleted solution with a third portion of fixing agent under conditions in which at least a portion of the arsenic is fixed by the fixing agent to give an arsenic-depleted
- 15 solution.
9. The method of claim 2, wherein the recoverable metal is in solution and the fixing agent comprises an insoluble compound that does not react with the recoverable metal to form an insoluble product.
- 20
10. The method of claim 1, wherein the rare earth-containing compound comprises one or more of cerium, lanthanum, or praseodymium.
11. The method of claim 10, wherein the rare earth-containing compound comprises a
- 25 cerium-containing compound derived from cerium carbonate.
12. The method of claim 10, wherein the rare earth-containing compound comprises cerium dioxide.

13. The method of claim 1, wherein the arsenic-containing solution has a pH of less than about 7 when the arsenic-containing solution is contacted with the first portion of fixing agent.
- 5 14. The method of claim 13, wherein the arsenic-containing solution has a pH of less than about 4 when the arsenic-containing solution is contacted with the first portion of fixing agent.
- 10 15. The method of claim 14, wherein the arsenic-containing solution has a pH of less than about 3 when the arsenic-containing solution is contacted with the first portion of fixing agent.
- 15 16. The method of claim 1, wherein the arsenic-containing solution has a pH of more than about 7 when the arsenic-containing solution is contacted with the first portion of fixing agent.
- 20 17. The method of claim 16, wherein the arsenic-containing solution has a pH of more than about 9 when the arsenic-containing solution is contacted with the first portion of fixing agent.
- 25 18. The method of claim 17, wherein the arsenic-containing solution has a pH of more than about 10 when the arsenic-containing solution is contacted with the first portion of fixing agent.
- 30 19. The method of claim 1, wherein the arsenic-containing solution comprises more than about 1000 ppm sulfate when the arsenic-containing solution is contacted with the first portion of fixing agent.
20. The method of claim 1, further comprising the step of forming the arsenic-containing solution by contacting an arsenic-bearing material with a leaching agent

comprising one or more of an inorganic salt, an inorganic acid, an organic acid and an alkaline agent.

- 5
21. The method of claim 20, wherein the alkaline agent comprises sodium hydroxide.
22. The method of claim 1, wherein the arsenic-depleted solution comprises arsenic in an amount of less than about 20 ppm.
- 10
23. The method of claim 1, wherein the first portion of fixing agent is substantially free of arsenic prior to contacting the arsenic-containing solution.
24. The method of claim 1, wherein the first portion of fixing agent is at least partially-saturated with arsenic.
- 15
25. The method of claim 24, wherein the fixing agent partially-saturated with arsenic comprises between about 0.1 mg and about 80 mg of arsenic per gram of fixing agent.
- 20
26. An apparatus for separating arsenic from an arsenic-containing solution, the apparatus comprising:
- 25
- a first contact zone adapted to receive an arsenic-containing solution, the first contact zone having fixing agent for contacting the arsenic-containing solution and fixing at least a portion of the arsenic to yield a partially-depleted solution, wherein the fixing agent comprises a rare earth-containing compound;
- 30
- a second contact zone adapted to receive the partially-depleted solution, the second contact zone having fixing agent for contacting the partially-depleted solution and fixing at least a portion of the arsenic to yield an arsenic-depleted solution; and
- a first separator disposed intermediate the first contact zone and the second contact zone for separating fixing agent from the partially-depleted solution.

27. The apparatus of claim 26, wherein the rare earth-containing compound comprises one or more of cerium, lanthanum, or praseodymium.
- 5 28. The apparatus of claim 27, wherein the rare earth-containing compound comprises a cerium-containing compound derived from cerium carbonate.
29. The apparatus of claim 27, wherein the rare earth-containing compound comprises cerium dioxide.
- 10 30. The apparatus of claim 26 further comprising a second separator connected to the second contact zone for separating the arsenic-depleted solution from fixing agent.
- 15 31. The apparatus of claim 30, wherein the second separator comprises an outlet for providing fluid communication with the first contact zone for directing a partially saturated fixing agent to the first contact zone.
- 20 32. The apparatus of claim 26, further comprising a filtration unit operable connected to the first separator for receiving the arsenic-laden fixing agent and producing a filtrate.
- 25 33. The apparatus of claim 32, wherein the filtration unit comprises an outlet for providing fluid communication with the first contact zone for directing the filtrate to the first contact zone.
- 30 34. The apparatus of claim 26, further comprising a metal recovery unit connected to the second contact zone for separating a recoverable metal from the arsenic-depleted solution.
35. The apparatus of claim 34, wherein the metal recovery unit comprises one or more of a precipitation vessel and an electrolyzer.

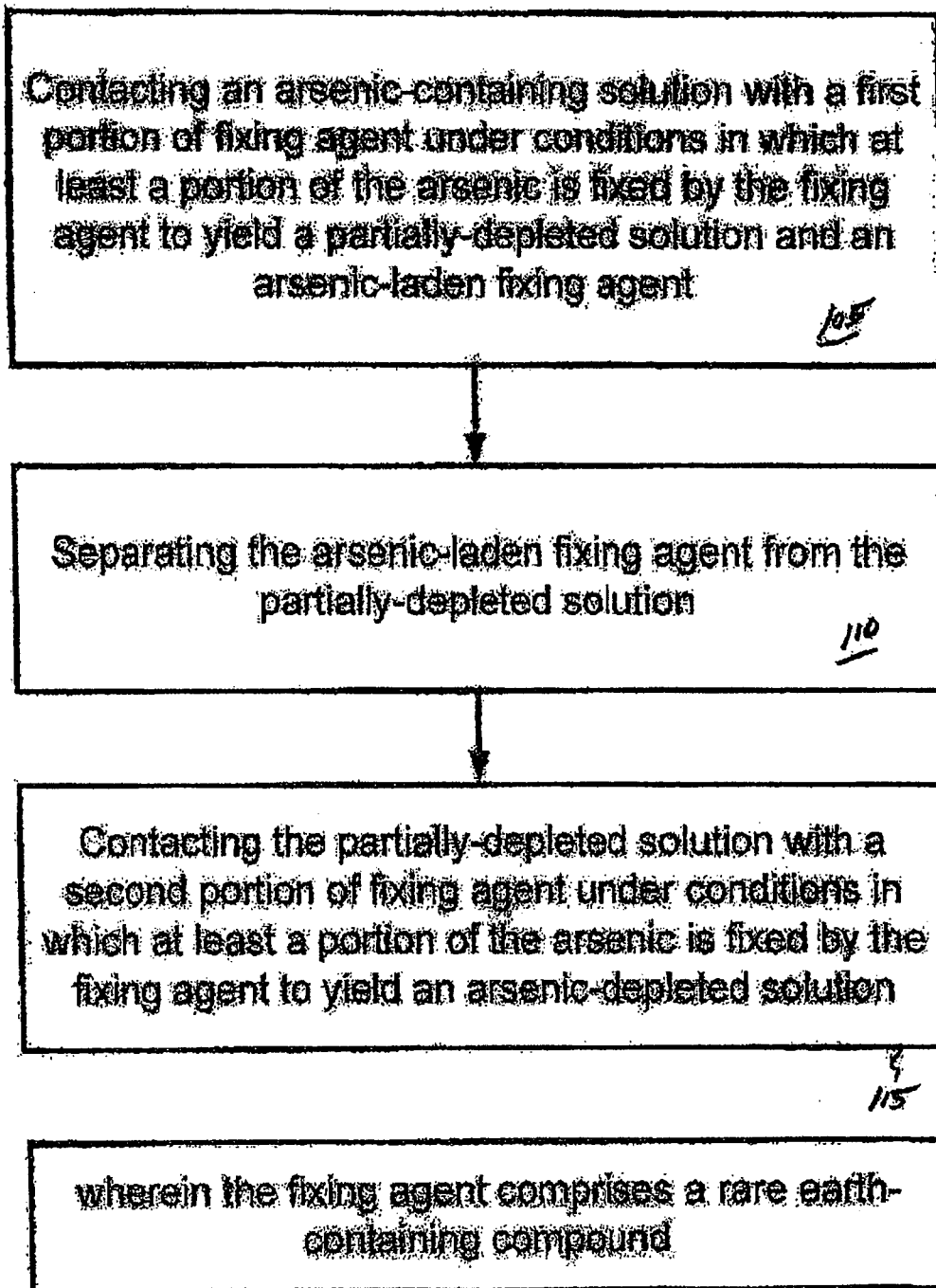


Figure 1

1/2

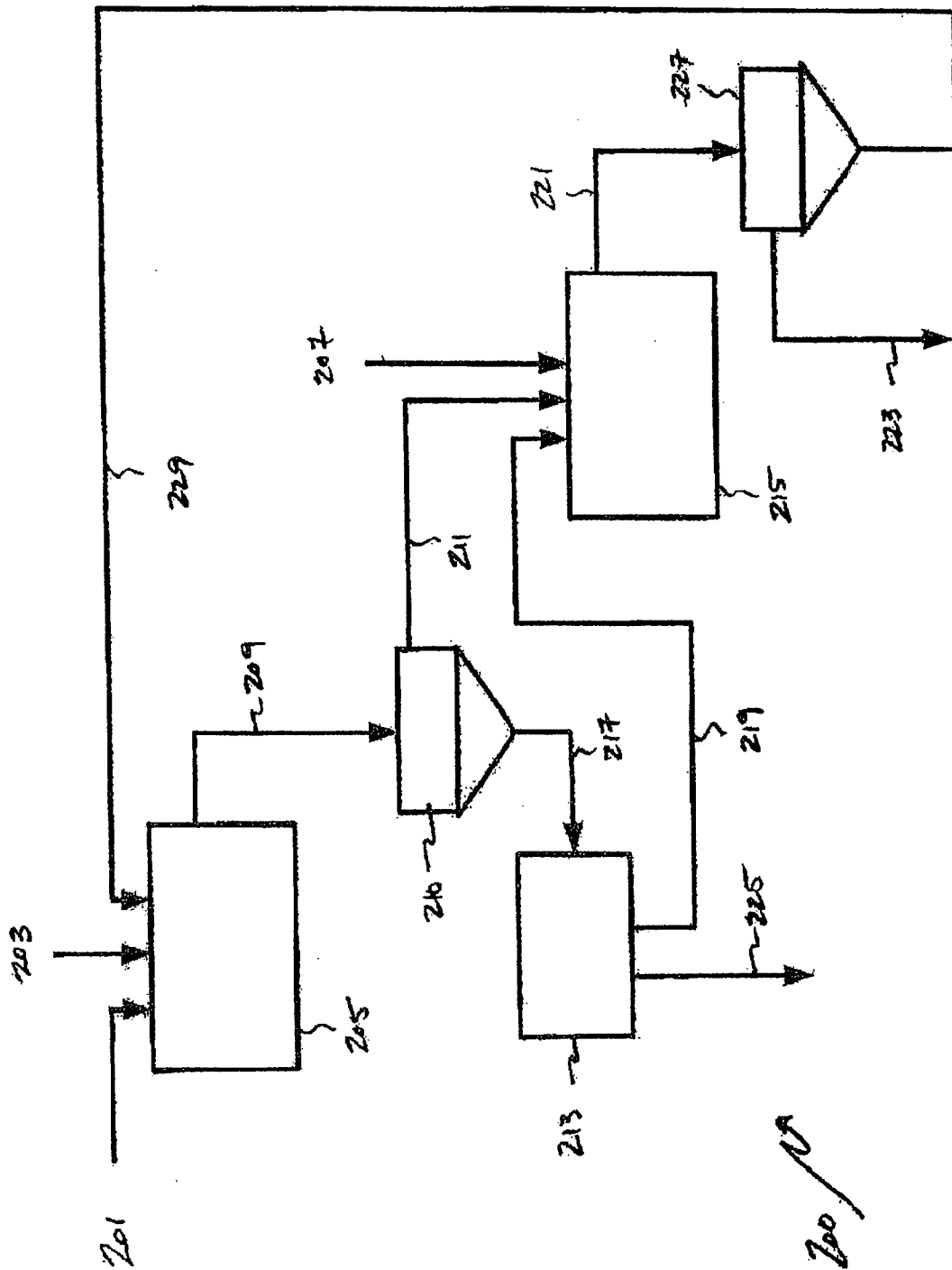


Figure 2

2/2

RESUMEN

Un método y aparato para separar arsénico de una solución acuosa que contiene arsénico. El método incluye los pasos de poner en contacto una solución que contiene arsénico con una primera porción de agente fijador para remover por lo menos una porción del arsénico. Un agente fijador enriquecido en arsénico se separa de la solución y la solución parcialmente empobrecida se pone en contacto con una segunda porción del agente fijador. El agente fijador puede incluir un compuesto insoluble de alta área superficial que contiene uno o más de cerio, lantano o praseodimio. Luego de la remoción del arsénico, la solución empobrecida en arsénico se puede procesar adicionalmente para separar un metal recuperable a través de refinación de metales. El agente fijador enriquecido en arsénico se puede filtrar para recuperar y reciclar un filtrado hacia la solución para su tratamiento adicional, así como también se puede utilizar un agente fijador parcialmente saturado para remover arsénico de una solución fresca. Se puede formar una solución que contiene arsénico a partir de sólidos que contienen arsénico tales como suelos contaminados, subproductos industriales y materiales de desecho.

(HAsO_2), es un ácido débil y permanece sin ionizarse a niveles de pH de entre 5 y 8 cuando la adsorción es más efectiva.

Se han utilizado varias tecnologías para remover arsénico de sistemas acuosos. Entre los ejemplos de dichas tecnologías, se incluyen adsorción en
5 materiales de alta área superficial, tales como alúmina, carbón activado, óxido de lantano y dióxido de cerio, intercambio iónico con resinas de intercambio aniónico, precipitación y electrodiálisis. En el caso de materiales sólidos o semisólidos, se han realizado esfuerzos para solidificar o estabilizar el arsénico in situ de modo de prevenir la migración hacia suelos circundantes o aguas subterráneas. Sin
10 embargo, en razón de que dichos procedimientos de estabilización tienden a ser muy costosos, y en algunos casos no han sido probados, existe la necesidad de métodos y técnicas alternativos para manejar el arsénico en dichos materiales.

RESUMEN DE LA INVENCION

15

En una modalidad, la presente invención proporciona un método para separar el arsénico de una solución que contiene arsénico. El método incluye los pasos de poner en contacto una solución que contiene arsénico con una primera porción de un agente fijador en condiciones en las que por lo menos una porción
20 del arsénico es fijada por el agente fijador para obtener una solución parcialmente empobrecida y un agente fijador enriquecido en arsénico. El agente fijador comprende un compuesto que contiene tierras raras. El compuesto que contiene tierras raras puede incluir uno o más de cerio, lantano o praseodimio. Más específicamente, el compuesto que contiene tierras raras puede comprender un
25 compuesto que contiene cerio obtenido de carbonato de cerio. En otras modalidades, el compuesto que contiene tierras raras comprende dióxido de cerio. La primera porción del agente fijador puede encontrarse sustancialmente libre de arsénico antes de ponerse en contacto con la solución que contiene arsénico o puede encontrarse parcialmente saturada con arsénico. Cuando se encuentra
30 parcialmente saturada, el agente fijador puede comprender entre alrededor de 0.1 mg y alrededor de 80 mg de arsénico por gramo de agente fijador.

El método incluye los pasos de separar el agente fijador enriquecido en arsénico de la solución parcialmente empobrecida y poner en contacto la solución
35 parcialmente empobrecida con una segunda porción de agente fijador en condiciones en las cuales por lo menos una porción del arsénico es fijada por el agente fijador para obtener una solución empobrecida en arsénico. Cuando del paso de poner en contacto la solución parcialmente empobrecida con la segunda porción de agente fijador se obtiene un agente fijador parcialmente saturado, el

método puede opcionalmente incluir el separar el agente fijador parcialmente saturado de la solución empobrecida en arsénico. En dicha modalidad, el método puede opcionalmente incluir los pasos de poner en contacto el agente fijador parcialmente saturado con una porción fresca de una solución que contiene arsénico en condiciones en las que por lo menos una porción del arsénico es fijada por el agente fijador parcialmente saturado para dar una segunda solución parcialmente empobrecida y un agente fijador enriquecido en arsénico, y separar la segunda solución parcialmente empobrecida del agente fijador enriquecido en arsénico. Dicho método puede también opcionalmente incluir el paso de poner en contacto la segunda solución parcialmente empobrecida con una tercera porción de agente fijador en condiciones en las que por lo menos una porción del arsénico es fijada por el agente fijador para dar una solución empobrecida en arsénico.

En los casos en los que la solución empobrecida en arsénico comprende un metal recuperable, el método puede opcionalmente incluir el paso de separar el metal recuperable de la solución empobrecida en arsénico. El metal recuperable puede incluir un metal del Grupo IA, Grupo IIA, Grupo VIII y los metales de transición. El metal recuperable se puede separar de la solución empobrecida en arsénico combinando la solución empobrecida en arsénico con una corriente de proceso en un proceso de refinación de metales, precipitando el metal recuperable de la solución empobrecida en arsénico y/o electrolizando la solución empobrecida en arsénico. El proceso de refinación de metales puede incluir el electrolizar la solución empobrecida en arsénico. Cuando el metal recuperable se encuentra en solución, el agente fijador es preferiblemente un compuesto insoluble que no reacciona con el metal recuperable para formar un producto insoluble.

El pH de la solución que contiene arsénico puede ser de menos de alrededor de 7 cuando la solución que contiene arsénico se pone en contacto con la primera porción del agente fijador. Más específicamente, el pH de la solución que contiene arsénico puede ser de menos de alrededor de 4, y aún más específicamente, el pH de la solución que contiene arsénico puede ser de menos de alrededor de 3 cuando la solución que contiene arsénico se pone en contacto con la primera porción del agente fijador. En otras modalidades, el pH de la solución que contiene arsénico puede ser de más de alrededor de 7 cuando la solución que contiene arsénico se pone en contacto con la primera porción del agente fijador. Más específicamente, el pH de la solución que contiene arsénico puede ser de más de alrededor de 9, y aún más específicamente, el pH de la solución que contiene arsénico puede ser de más de alrededor de 10 cuando la solución que contiene arsénico se pone en contacto con la primera porción del agente fijador.

El método puede opcionalmente incluir el paso de formar una solución que contiene arsénico poniendo en contacto un material portador de arsénico con un agente lixivador que comprende uno(a) o más de una sal inorgánica, un ácido inorgánico, un ácido orgánico y un agente alcalino. Cuando el agente lixivador incluye un agente alcalino, el agente alcalino puede incluir hidróxido de sodio. La solución que contiene arsénico puede comprender más de alrededor de 1000 ppm de sulfato cuando la solución que contiene arsénico se pone en contacto con la primera porción del agente fijador.

En otra modalidad, la presente invención proporciona un aparato para separar el arsénico de una solución que contiene arsénico. El aparato incluye una primera zona de contacto adaptada para recibir una solución que contiene arsénico. La primera zona de contacto tiene un agente fijador para ponerse en contacto con la solución que contiene arsénico y fijar por lo menos una porción del arsénico para obtener una solución parcialmente empobrecida. El agente fijador comprende un compuesto que contiene tierras raras. El compuesto que contiene tierras raras puede incluir uno o más de cerio, lantano o praseodimio. Más específicamente, el compuesto que contiene tierras raras puede comprender un compuesto que contiene cerio obtenido de carbonato de cerio. En otras modalidades, el compuesto que contiene tierras raras comprende dióxido de cerio.

Se incluye también una segunda zona de contacto que se encuentra adaptada para recibir la solución parcialmente empobrecida, y la cual tiene un agente fijador para ponerse en contacto con la solución parcialmente empobrecida y fijar por lo menos una porción del arsénico para producir una solución empobrecida en arsénico. El aparato además incluye un primer separador dispuesto entre la primera zona de contacto y la segunda zona de contacto para separar el agente fijador de la solución parcialmente empobrecida.

El aparato puede opcionalmente incluir un segundo separador conectado a la segunda zona de contacto para separar la solución empobrecida en arsénico del agente fijador. Cuando se encuentra presente, el segundo separador puede incluir una salida para proveer una comunicación fluida con la primera zona de contacto para dirigir un agente fijador parcialmente saturado a la primera zona de contacto.

El aparato puede también opcionalmente incluir una unidad filtradora conectada de forma operable al primer separador para recibir el agente fijador enriquecido en arsénico y obtener un filtrado. Cuando se encuentra presente, la unidad filtradora puede incluir una salida para proveer una comunicación fluida con la primera zona de contacto para dirigir el filtrado a la primera zona de contacto.

El aparato puede opcionalmente incluir una unidad de recuperación de metales para separar un metal recuperable de la solución empobrecida en arsénico. La unidad de recuperación de metales puede comprender un recipiente de precipitación o un electrolizador o ambos.

5

BREVE DESCRIPCIÓN DE LAS FIGURAS

Se puede comprender la invención por referencia a la descripción siguiente en conjunción con las figuras adjuntas.

10 La Figura 1 es una representación en diagrama de flujo de un método de la presente invención.

La Figura 2 es una vista esquemática de un aparato de la presente invención.

15 Si bien la invención es susceptible de varias modificaciones y formas alternativas, se han mostrado modalidades específicas de la misma a manera de ejemplo en las figuras y se describen aquí en detalle. Se debe entender, no obstante, que la descripción de modalidades específicas no pretende limitar la invención a las formas particulares divulgadas, sino al contrario, la intención es cubrir todas las modificaciones, equivalentes y alternativas que se encuentren
20 dentro del espíritu y ámbito de la invención como se define en las reivindicaciones adjuntas.

DESCRIPCIÓN DETALLADA DE LAS MODALIDADES PREFERIDAS

25 A continuación se describen modalidades ilustrativas de la invención. Para mayor claridad, no se describen en esta descripción todas las características de una modalidad concreta. Se apreciará por supuesto que en el desarrollo de cada modalidad concreta, se deben realizar varias decisiones específicas de implementación para alcanzar los objetivos específicos de quien la desarrolla, tales como el cumplimiento de restricciones relacionadas con el sistema o con
30 motivos comerciales, que variarán de una implementación a otra. Más todavía, se apreciará que dicho esfuerzo de desarrollo será complejo y demandará tiempo, pero será sin embargo una tarea rutinaria para una persona versada en la materia que tenga el beneficio de esta divulgación.

35 Se entenderá que el método y aparato que se describen aquí pueden utilizarse para tratar cualquier solución acuosa que contiene cantidades indeseables de arsénico. Entre los ejemplos de dichas soluciones, se incluyen, entre otros, agua de pozo, aguas superficiales, tales como agua de lagos,

estanques y pantanales, aguas agrícolas, corrientes de procesos industriales, aguas residuales y efluentes de procesos industriales, y soluciones formadas de desechos y subproductos industriales. La solución que contiene arsénico puede contener otros contaminantes inorgánicos, tales como selenio, cadmio, plomo, mercurio, cromo, níquel, cobre y cobalto, y ciertos contaminantes orgánicos. Un método y aparato de la presente invención pueden remover arsénico de dichas soluciones incluso cuando se encuentran presentes concentraciones elevadas de dichos contaminantes inorgánicos. Más específicamente, se puede remover efectivamente el arsénico de soluciones que comprenden más de alrededor de 1000 ppm de sulfatos.

Generalmente, se pueden utilizar un método y aparato de la presente invención para tratar cualquier solución acuosa que contiene más de alrededor de 20 ppb de arsénico y son efectivos para tratar soluciones que contienen más de alrededor de 1000 ppb. Además, el método y aparato son efectivos para reducir dichos niveles de arsénico a una cantidad de menos de 20 ppb, en algunos casos de menos de alrededor de 10 ppb, en otros casos de menos de alrededor de 5 ppb, e incluso en otros casos de menos de alrededor de 2 ppb.

Se ha determinado que la capacidad de adsorción de ciertos agentes fijadores para remover arsénico de soluciones acuosas es por lo menos en parte dependiente de la concentración de arsénico en dichas soluciones. Más específicamente, se ha determinado que para una cantidad dada de agente fijador que comprende un compuesto que contiene tierras raras, se puede remover una cantidad mayor de arsénico de la solución poniendo en contacto la solución con una o más porciones del agente fijador y separando el agente fijador enriquecido en arsénico de la solución entre dichos pasos de contacto, que si la solución fuese tratada con esa cantidad de agente fijador en una sola etapa de contacto. Además, se puede utilizar el método para remover efectivamente arsénico de dichas soluciones en un amplio rango de niveles de pH, y a valores extremos de pH, eliminando la necesidad de alterar y/o mantener el pH de la solución dentro de un estrecho rango.

En un aspecto de la presente invención, se proporciona un método para separar el arsénico de una solución que contiene arsénico. El método incluye el paso de poner en contacto una solución que contiene arsénico con una primera porción de agente fijador que comprende un compuesto que contiene tierras raras en condiciones en las que por lo menos una porción del arsénico es fijada por el agente fijador para obtener una solución parcialmente empobrecida y un agente fijador enriquecido en arsénico. El agente fijador enriquecido en arsénico se separa de la solución parcialmente empobrecida, y la solución parcialmente

empobrecida se pone en contacto con una segunda porción de agente fijador en condiciones en las que por lo menos una porción del arsénico es fijada por el agente fijador para obtener una solución empobrecida en arsénico.

La solución que contiene arsénico se pone en contacto con la primera
5 porción del agente fijador en un tanque, contenedor u otro recipiente adecuado para mantener dichas soluciones y materiales. La solución se encuentra a una temperatura y presión, usualmente condiciones ambientales, tales que la solución permanece en el estado líquido, sin perjuicio de que también se pueden utilizar temperatura y presión elevadas. El tanque puede opcionalmente incluir un agitador
10 u otros medios para promover la agitación y el contacto entre la solución que contiene arsénico y el agente fijador. Ejemplos no limitativos de recipientes adecuados se describen en la patente de los Estados Unidos No. 6,383,395, cuya descripción se incorpora aquí por referencia. Un aparato de la presente invención comprende una primera zona de contacto y una segunda zona de contacto con un
15 separador dispuesto entre ellas. La primera zona de contacto y la segunda zona de contacto pueden albergarse dentro de un recipiente o reactor común, o pueden albergarse de forma separada.

El agente fijador puede ser cualquier compuesto que contiene tierras raras que es efectivo para fijar arsénico en solución mediante precipitación, adsorción,
20 intercambio iónico u otro mecanismo. El agente fijador puede ser soluble, poco soluble o insoluble en solución acuosa. En algunas modalidades, el agente fijador tiene un área superficial relativamente alta de por lo menos alrededor de $70 \text{ m}^2/\text{g}$, y en algunos casos más de alrededor de $80 \text{ m}^2/\text{g}$, e incluso en otros casos más de $90 \text{ m}^2/\text{g}$.

El agente fijador puede incluir una o más tierras raras incluyendo lantano, cerio, praseodimio, neodimio, prometio, samario, europio, gadolinio, terbio, disprosio, holmio, erbio, tulio, iterbio y lutecio. Ejemplos específicos de dichos materiales que se han descrito como capaces de remover arsénico de soluciones acuosas incluyen compuestos de lantano trivalente (patente de los Estados Unidos
30 No. 4,046,687), sales solubles de metal lantánido (patente de los Estados Unidos No. 4,566,975), óxido de lantano (patente de los Estados Unidos No. 5,603,838), cloruro de lantano (patente de los Estados Unidos No. 6,197,201), mezclas de óxido de lantano y uno o más óxidos de otras tierras raras (patente de los Estados Unidos No. 6,800,204), óxidos de cerio (patente de los Estados Unidos No.
35 6,862,825); tamices moleculares mesoporosos impregnados con lantano (solicitud de patente de los Estados Unidos No. 20040050795) y poliacrilonitrilo impregnado con metales lantánidos o u otros metales de tierras raras (solicitud de patente de los Estados Unidos No. 20050051492). Se debe también entender que se pueden

obtener dichos agentes fijadores que contienen tierras raras de cualquier fuente conocida para las personas versadas en la materia.

En algunas modalidades, el compuesto que contiene tierras raras puede comprender uno o más de cerio, lantano o praseodimio. En los casos en los que el agente fijador comprende un compuesto que contiene cerio, el agente fijador puede obtenerse de carbonato de cerio. Más específicamente, se puede preparar dicho agente fijador descomponiendo térmicamente un carbonato de cerio u oxalato de cerio en un horno en presencia de aire. Cuando el agente fijador comprende dióxido de cerio, se prefiere generalmente utilizar partículas sólidas de dióxido de cerio, las cuales son insolubles en agua y relativamente resistentes al desgaste. Se pueden también utilizar compuestos de cerio solubles en agua tales como nitrato de amonio cérico, sulfato de amonio cérico, sulfato cérico y nitrato cérico como el agente fijador, especialmente en los casos en los que la concentración de arsénico en solución es alta.

El agente fijador que comprende el compuesto que contiene tierras raras puede encontrarse presente en la primera porción de agente fijador que se pone en contacto con la solución que contiene arsénico, en la segunda porción de agente fijador que se pone en contacto con la solución parcialmente empobrecida o en la primera porción, la segunda porción y cualesquiera porciones adicionales de agente fijador. La primera porción del agente fijador puede encontrarse sustancialmente libre de arsénico antes de ponerse en contacto con la solución que contiene arsénico o la primera porción puede encontrarse parcialmente saturada con arsénico. Cuando se encuentra parcialmente saturada, el agente fijador puede comprender entre alrededor de 0.1 mg y alrededor de 80 mg de arsénico por gramo de agente fijador.

Opcionalmente, en los métodos y aparatos de la presente invención, se puede utilizar también un agente fijador que no contiene un compuesto de tierras raras. Dichos agentes fijadores opcionales pueden incluir cualquier sólido, líquido o gel que es efectivo para fijar arsénico en solución mediante precipitación, adsorción, intercambio iónico o algún otro mecanismo. Estos agentes fijadores opcionales pueden ser solubles, poco solubles o insolubles en solución acuosa. Los agentes fijadores opcionales pueden incluir sólidos particulados que contienen cationes en el estado de oxidación +3 que reaccionan con el arsenato en solución para formar compuestos insolubles de arsenato. Entre los ejemplos de dichos sólidos, se incluyen alúmina, alúmina gamma, alúmina activada, alúmina acidificada como la alúmina tratada con ácido clorhídrico, óxidos metálicos que contienen aniones lábiles tales como oxiclورو de aluminio, aluminosilicatos cristalinos como zeolitas, sílice alúmina amorfa, resinas de intercambio iónico,

arcillas como montmorillonita, sales férricas, cerámicas porosas. Los agentes fijadores opcionales pueden también incluir sales cálcicas como cloruro de calcio, hidróxido de calcio y carbonato de calcio, y sales de hierro como sales férricas, sales ferrosas o una combinación de las mismas. Entre los ejemplos de sales a

5 base de hierro, se incluyen cloruros, sulfatos, nitratos, acetatos, carbonatos, yoduros, sulfatos de amonio, cloruros de amonio, hidróxidos, óxidos, fluoruros, bromuros y percloratos. En los casos en los que la sal de hierro es una sal ferrosa, se puede requerir también de una fuente de iones hidroxilo para promover la co-precipitación de la sal de hierro y el arsénico. Dichos proceso y materiales se

10 describen con más detalle en la patente de los Estados Unidos No. 6,177,015, otorgada el 23 de enero de 2001 a Blakey et al. Se conocen en la técnica otros agentes fijadores opcionales y se pueden utilizar en combinación con los agentes fijadores que contienen tierras raras aquí descritos. Además, se debe entender que se pueden obtener dichos agentes fijadores opcionales de cualquier fuente

15 conocida para las personas versadas en la materia.

Los sólidos particulados tales como agentes fijadores insolubles y compuestos insolubles que contienen arsénico se pueden separar de las varias soluciones descritas aquí para su posterior procesamiento. Se puede utilizar cualquier técnica de separación de líquidos-sólidos, como filtración, sedimentación

20 por gravedad, centrifugación, hidrociclado o similares para remover dichos sólidos particulados. Se puede también añadir un floculante, coagulante o espesador adicional a la solución antes de que se remuevan los sólidos particulados. Dichos agentes son útiles para alcanzar un tamaño de partícula deseado y mejorar las propiedades de sedimentación del agente fijador

25 enriquecido en arsénico. Entre los ejemplos de coagulantes inorgánicos, se incluyen sulfato férrico, cloruro férrico, sulfato ferroso, sulfato de aluminio, aluminato de sodio, cloruro de polialuminio, tricloruro de aluminio, entre otros. También se pueden utilizar coagulantes y floculantes poliméricos orgánicos, tales como poliacrilamidas (catiónicas, no iónicas y aniónicas), EPI-DMA's

30 (epiclorhidrina- dimetilaminas), DADMAC's (cloruros de polidialildimetilamonio), polímeros de dicianidamida/formaldehído, polímeros de dicianidamida/amina, guar natural, etc.

En una modalidad, un agente fijador enriquecido en arsénico se separa de una solución parcialmente empobrecida en un primer separador. El agente fijador

35 enriquecido en arsénico entonces se dirige hacia una unidad filtradora que se encuentra conectada al separador donde el agente fijador se filtra para obtener un filtrado y sólidos enriquecidos en arsénico. Los sólidos se dirigen hacia fuera de la unidad de filtración para su disposición apropiada o manejo posterior. La unidad

filtradora tiene una salida en comunicación fluida con una segunda zona de contacto para reciclar el filtrado hacia la segunda zona de contacto donde se combina con la solución parcialmente empobrecida y se pone en contacto con agente fijador fresco.

5 En otra modalidad, una mezcla de una solución empobrecida en arsénico y un agente fijador parcialmente saturado se dirige fuera de una segunda zona de contacto y hacia un segundo separador para separar la solución del agente fijador. La solución empobrecida en arsénico se dirige fuera del separador para su utilización, disposición o procesamiento adicional. El separador tiene una salida en
10 comunicación fluida con la primera zona de contacto para dirigir una pasta del agente fijador parcialmente saturado hacia la primera zona de contacto donde se pone en contacto con una solución que contiene arsénico entrante y fresca.

Los agentes fijadores que contienen tierras raras de la presente invención son particularmente ventajosos por su habilidad para remover arsénico de una
15 solución en un amplio rango de valores de pH y a valores extremos de pH. El pH de la solución que contiene arsénico puede ser de menos de alrededor de 7 cuando la solución que contiene arsénico se pone en contacto con la primera porción del agente fijador. Más específicamente, el pH de la solución que contiene arsénico puede ser de menos de alrededor de 4, y aún más específicamente, el
20 pH de la solución que contiene arsénico puede ser de menos de alrededor de 3 cuando la solución que contiene arsénico se pone en contacto con la primera porción del agente fijador. En otras modalidades, el pH de la solución que contiene arsénico puede ser de más de alrededor de 7 cuando la solución que contiene arsénico se pone en contacto con la primera porción del agente fijador. Más
25 específicamente, el pH de la solución que contiene arsénico puede ser de más de alrededor de 9, y aún más específicamente, el pH de la solución que contiene arsénico puede ser de más de alrededor de 10 cuando la solución que contiene arsénico se pone en contacto con la primera porción del agente fijador.

En la medida en que es deseable ajustar o controlar el pH, se puede añadir
30 una adición ácida y/o alcalina opcional a la solución como es bien conocido en la materia. La adición ácida puede incluir la adición de un ácido mineral como ácido clorhídrico o sulfúrico. La adición alcalina puede incluir la adición de hidróxido de sodio, carbonato de sodio, hidróxido de calcio, hidróxido de amonio y similares.

Cuando la solución que contiene arsénico incluye un metal recuperable, el
35 método puede opcionalmente incluir el paso de separar el metal recuperable de la solución empobrecida en arsénico en una unidad de recuperación de metales conectada a la segunda zona de contacto. En la forma en que se utiliza aquí, el metal recuperable puede incluir casi cualquier metal de interés, pero

específicamente incluye metales del Grupo IA, Grupo IIA, Grupo VIII y los metales de transición. En los casos en los que el metal recuperable se encuentra en solución en la solución que contiene arsénico, el agente fijador es preferiblemente un compuesto insoluble que selectivamente adsorbe arsénico de la solución y no reacciona o reacciona sólo débilmente con el metal recuperable para formar un producto insoluble. El metal recuperable se puede separar de la solución empobrecida en arsénico combinando la solución empobrecida en arsénico con una corriente de proceso en un proceso de refinación de metales. En algunas modalidades, la solución empobrecida en arsénico se puede electrolizar para separar el metal recuperable de la solución. A manera de ejemplo, la remoción de contaminantes para formar una solución para separar varios metales a través de procesos de electrorrefinación se describe en detalle en la patente de los Estados Unidos No. 6,569,224 otorgada el 27 de mayo de 2003 a Kerfoot et al. En otras modalidades, el metal recuperable se puede precipitar de la solución empobrecida en arsénico en un recipiente de precipitación conectado a la segunda zona de contacto.

Cuando del paso de poner en contacto la solución parcialmente empobrecida con la segunda porción de agente fijador se obtiene un agente fijador parcialmente saturado, el método puede opcionalmente incluir separar el agente fijador parcialmente saturado de la solución empobrecida en arsénico. En dicha modalidad, el método puede además incluir los pasos de poner en contacto el agente fijador parcialmente saturado con una porción fresca de una solución que contiene arsénico en condiciones en las que por lo menos una porción del arsénico es fijada por el agente fijador parcialmente saturado para dar una segunda solución parcialmente empobrecida y un agente fijador enriquecido en arsénico. La segunda solución parcialmente empobrecida se separa del agente fijador enriquecido en arsénico. Dicho método puede también opcionalmente incluir el paso de poner en contacto la segunda solución parcialmente empobrecida con una tercera porción de agente fijador en condiciones en las que por lo menos una porción del arsénico es fijada por el agente fijador para dar una solución empobrecida en arsénico.

El arsénico se puede extraer de sólidos tales como suelos contaminados, subproductos industriales y materiales de desecho mediante lixiviación o extracción para liberar el arsénico de dichos sólidos. Como resultado, el método puede también opcionalmente incluir el paso de formar la solución que contiene arsénico poniendo en contacto un material portador de arsénico con un agente extractor de arsénico que comprende uno(a) o más de una sal inorgánica, un ácido inorgánico, un ácido orgánico y un agente alcalino. Entre los ejemplos

específicos de sales inorgánicas como agentes extractores, se incluyen sales de potasio, tales como fosfato de potasio, cloruro de potasio, nitrato de potasio y sulfato de potasio, perclorato de sodio y similares. Entre los ejemplos de ácidos inorgánicos que se pueden utilizar para extraer el arsénico de sólidos, se incluyen

5 ácido sulfúrico, ácido nítrico, ácido fosfórico, ácido clorhídrico, ácido perclórico y mezclas de los mismos. Los ácidos orgánicos como extractantes pueden incluir ácido cítrico, ácidos acéticos y similares. El material portador de arsénico se pone en contacto con el agente extractor en un tanque, contenedor u otro recipiente adecuado para mantener dichas soluciones y materiales. Se pueden incluir

10 bombas, agitadores u otros medios adecuados para promover la agitación y contacto entre el agente extractor y los materiales portadores de arsénico. Se puede tener una descripción más detallada de los agentes extractores de arsénico y su utilización mediante referencia a M. Jang et al., "Remediation Of Arsenic-Contaminated Solids And Washing Effluents", *Chemosphere*, 60, pp. 344-354,

15 (2005); M. G. M. Alam et al., "Chemical Extraction of Arsenic from Contaminated Soil", *J. Environ Sci Health A Tox Hazard Subsidi Environ Eng.*, 41 (4), pp. 631 -643 (2006); y S.R. Al-Abed et al., "Arsenic Release From Iron Rich Mineral Processing Waste; Influence of pH and Redox Potential", *Chemosphere*, 66, pp. 775-782 (2007).

20

DESCRIPCIÓN DETALLADA DE LAS FIGURAS

La Figura 1 es una representación en diagrama de flujo del método 100. El método 100 incluye el paso 105 de poner en contacto la solución que contiene

25 arsénico con una primera porción de agente fijador en condiciones en las que por lo menos una porción del arsénico es fijada por el agente fijador para obtener una solución parcialmente empobrecida y un agente fijador enriquecido en arsénico. En el paso 110, el agente fijador enriquecido en arsénico se separa de la solución parcialmente empobrecida. En el paso 115, la solución parcialmente empobrecida

30 se pone en contacto con una segunda porción de agente fijador para obtener una solución empobrecida en arsénico. El agente fijador comprende un compuesto que contiene tierras raras.

La Figura 2 es una representación esquemática del aparato 200. El aparato 200 recibe una solución que contiene arsénico de una fuente 201 y la dirige hacia

35 una primera zona de contacto al interior del tanque de mezcla 205. El tanque 205 puede opcionalmente recibir agente fijador fresco de una fuente 203 y un agente fijador parcialmente saturado a través de la vía 229. La solución que contiene arsénico se pone en contacto con el agente fijador en el tanque 205. El tanque 205

puede opcionalmente incluir un agitador (no mostrado) en el interior del tanque para promover la agitación y el contacto entre la solución que contiene arsénico y el agente fijador. En esta primera zona de contacto, por lo menos una porción del arsénico es fijada para obtener una solución parcialmente empobrecida y un agente fijador enriquecido en arsénico.

Como se ilustra, tanto la solución como el agente fijador se transfieren mediante la vía 209 hacia el separador 210 donde la solución parcialmente empobrecida se separa del agente fijador enriquecido en arsénico. El separador 210 tiene una salida de desbordamiento (*overflow*) que dirige la solución parcialmente empobrecida mediante la vía 211 hacia el tanque 215. El agente fijador se dirige a través de una salida hacia el filtro 213. Dentro del filtro 213, el agente fijador se filtra para obtener un filtrado y sólidos enriquecidos en arsénico. El filtrado se encamina a través de la vía 219 hacia el tanque 215 donde se recombina con la solución parcialmente empobrecida proveniente del separador 210. Los sólidos enriquecidos en arsénico obtenidos a partir del agente fijador en el filtro 213 se dirigen hacia fuera mediante la vía 225.

La solución parcialmente empobrecida y el filtrado se combinan en el tanque 215 y se ponen en contacto con agente fijador fresco de la fuente 207. El tanque 215 puede opcionalmente incluir un agitador (no mostrado) en el interior del tanque para promover la agitación y el contacto entre la solución parcialmente empobrecida y el agente fijador. En esta segunda zona de contacto, por lo menos una porción del arsénico es fijada para obtener una solución empobrecida en arsénico. Como se ilustra, la solución empobrecida en arsénico y el agente fijador se transfieren mediante la vía 221 hacia el separador 227 donde la solución empobrecida en arsénico se separa del agente fijador. El agente fijador en el separador 227 se encuentra parcialmente saturado con arsénico y puede reciclarse hacia la primera zona de contacto al interior del tanque 215 para ponerse en contacto con una solución fresca que contiene arsénico proveniente de la fuente 201. La solución empobrecida en arsénico separada del agente fijador en el separador 227 se dirige hacia fuera del aparato 200 mediante la vía 223.

Ejemplo 1: Tratamiento único de solución cáustica de desecho minero con contenido de arsénico

Estos experimentos se llevaron a cabo para determinar la carga superficial: cociente volumétrico necesario para tratar la solución cáustica con contenido de arsénico. La solución cáustica con contenido de arsénico consistió de 5-7 g/L de As (III), 20 g/L de Na₂CO₃, 4 g/L de sulfato, 4 mg/L de Ni y 1 mg/L de Cu. El pH de

la solución era de aproximadamente 10.5. El agente fijador utilizado en estos experimentos fue dióxido de cerio (ceria) de una alta área superficial, preparado mediante la descomposición térmica de carbonato de cerio a CeO_2 a 300 °C en un horno de mufla con adecuada exposición al aire.

- 5 Se realizaron experimentos de tratamiento único utilizando 200 mL de solución cáustica con contenido de arsénico a aproximadamente 75 °C y añadiendo entre 3-20 g del carbonato de cerio térmicamente descompuesto. Bajo las condiciones de prueba, la superficie del dióxido de cerio se saturó a una carga de 80 mg(As)/g(Ce). Cuando se añadieron más de 10 g de dióxido de cerio, la
- 10 concentración de arsénico cayó por debajo de 0.2% y la superficie ya no fue capaz de ser cargada hasta la capacidad de saturación.

Los resultados se proporcionan en la Tabla 1. Las observaciones recogidas en el curso de dos horas sugieren que el sistema rápidamente alcanza un estado fijo, especialmente cuando la superficie se satura con arsénico.

Tabla 1

Ceria masa (g)	As(ppm) 30 min	As(ppm) 1 hr	As(ppm) 2 hr	Capacidad (mg/g)
3.0	4600	4600	4700	80
5.0	3900	3500	3800	76
7.0	3000	3000	2900	80
10	1700	1700	1600	82
15	544	521	549	70
20	133	118	112	57

Ejemplo 2: Tratamiento de dos fases en contracorriente de solución cáustica con contenido de arsénico

5

Se preparó una solución cáustica con contenido de arsénico añadiendo 10 g de NaAsO₂, 20 g de Na₂CO₃, 1 mL de nitrato de cobre estándar 1 000 ppm, 0.4 mL de nitrato de níquel estándar 10 000 ppm a 800 mL de agua DI. La solución cáustica con contenido de arsénico se diluyó entonces a un litro completo y el pH se tituló a 10.5 utilizando HCl concentrado. Con la adición del sulfato de níquel y del sulfato de cobre, la mayoría del níquel y el cobre precipitaron, debido al alto pH de la solución cáustica. La solución que contiene arsénico que se obtuvo consistió de 5 g/L de As (III), 20 g/L de Na₂CO₃, 300 µg/L de Ni y 300 µg /L de Cu. El agente fijador fue nuevamente dióxido de cerio de alta área superficial preparado por descomposición térmica de carbonato de cerio a CeO₂ a 300 °C en un horno de mufla con adecuada exposición al aire.

10

15

El procedimiento de dos fases en contracorriente se llevó a cabo de la siguiente manera:

Ciclo 1/Fase 1: 12 g de 300 de carbonato de cerio térmicamente descompuesto se añadieron a 200 mL de la solución cáustica con contenido de arsénico mantenida a una temperatura de 70-80 °C.

20

La suspensión se filtró en papel Watman, el dióxido de cerio enriquecido en arsénico se desechó, y la solución sobrenadante pasó al Ciclo 1/Fase 2.

Ciclo 1/Fase 2: La solución sobrenadante del Ciclo 1/Fase 1 se trató nuevamente con 12 g de dióxido de cerio fresco. La solución dos veces tratada se filtró y el dióxido de cerio se recogió y transfirió al Ciclo 2/Fase 1.

25

Ciclo 2/Fase 1: El dióxido de cerio recogido en el Ciclo1/Fase 2 se añadió a 200 mL de solución cáustica fresca con contenido de arsénico. La suspensión se filtró, el dióxido de cerio saturado de arsénico se desechó, y la solución sobrenadante avanzó hacia el Ciclo 2/Fase 2.

30

Ciclo 2/Fase 2: La solución sobrenadante del Ciclo 2/Fase 1 se trató nuevamente con 12 g de dióxido de cerio fresco. La solución dos veces tratada se filtró y el dióxido de cerio se recogió y transfirió al Ciclo 3/Fase 1.

5 Ciclo 3/Fase 1: El dióxido de cerio recogido en el Ciclo2/Fase 2 se añadió a 200 mL de solución cáustica fresca con contenido de arsénico. La suspensión se filtró, el dióxido de cerio saturado de arsénico se desechó, y la solución sobrenadante avanzó hacia el Ciclo 3/Fase 2.

Ciclo 3/Fase 2: La solución sobrenadante filtrada en el Ciclo 3/Fase 1 se trató nuevamente con 12 g de dióxido de cerio fresco.

10

Los resultados de este tratamiento de dos fases en contracorriente se muestran en la Tabla 2. La capacidad (C) toma en cuenta la cantidad de arsénico adsorbido a la superficie en la fase 2 del ciclo previo. En todos los casos, las soluciones dos veces tratadas tenían una concentración de arsénico de menos de
15 alrededor de 10 ppm. El procedimiento de dos fases en contracorriente efectivamente disminuyó las concentraciones de arsénico un 99.86% utilizando 12 g de dióxido de cerio en cada fase. Las observaciones recogidas en el curso de dos horas sustentan la conclusión de que la cinética de adsorción es favorable, especialmente cuando la superficie del dióxido de cerio se satura de arsénico. La
20 capacidad del dióxido de cerio observada en el Ciclo 2/Fase 1, teniendo en cuenta la cantidad de arsénico ya adsorbida en el Ciclo 1/Fase 2, es comparable a la capacidad de saturación establecida a partir de los experimentos de tratamiento único. Sin embargo, en relación con las pruebas del tratamiento único como se ejemplifican en el Ejemplo 1, la concentración de arsénico remanente en solución
25 en el experimento de dos fases en contracorriente es aproximadamente dos órdenes de magnitud inferior para la misma masa de dióxido de cerio.

Tabla 2

Tiempo (hrs)	As(ppm)	C (mg/g)	As(ppm)	C (mg/g)
Ciclo 1	Fase 1		Fase 2	
0.5	1070	77	0.11	18
1	1010	78	0.1	17
2	1040	78	0.1	17
Ciclo 2	Fase 1		Fase 2	
0.5	2300	74	2.71	38
1	2250	74	2.07	37
2	2250	75	2	37
Ciclo 3	Fase 1		Fase 2	
0.5	2890	85	8.5	48
1	2850	85	6.9	47
2	3000	82	6.5	50

Ejemplo 3: Tratamiento de dos fases en contracorriente de una solución ácida con contenido de arsénico

5

El procedimiento en dos fases en contracorriente utilizado en el Ejemplo 2 se aplicó también a una solución ácida con contenido de arsénico que contenía As (III) 35 ppm. La solución ácida se preparó añadiendo 18.72 mL de As (III) 5770 ppm, 1074.3 g de sulfato de níquel (II), 250 g de NaCl, 0.63 g de sulfato de cobalto (II), 6 mL de nitrato de plomo estándar 1000 ppm y 1.5 ml de nitrato de cobre estándar 1000 ppm a 2 L de agua desionizada. La solución se diluyó entonces a 3 L, para dar un pH de aproximadamente 2.

10

La solución ácida con contenido de arsénico se trató entonces con carbonato de cerio térmicamente descompuesto utilizando el procedimiento de dos fases en contracorriente. El proceso trató un litro de la solución ácida con contenido de arsénico con 0.8 g de dióxido de cerio. Se observó alguna disolución del agente fijador de cerio y se la midió junto con la concentración de arsénico de las soluciones tratadas. Los resultados se suministran en la Tabla 3. En todos los casos, las soluciones dos veces tratadas tuvieron una concentración de arsénico de menos de alrededor de 5 ppm.

15

20

Tabla 3

Tiempo (hrs)	As(ppm)	C (mg/g)	As(ppm)	C (mg/g)
Ciclo 1	Fase 1		Fase 2	
0.5	15.1	5.0	0.6	9.9
1	11.7	7.4	0.3	10.6

2	9.5	8.8	0.2	10.2
Ciclo 2	Fase 1		Fase 2	
0.5	22.3	6.1	2.4	10.2
1	19.2	7.3	1.4	10.8
2	18.7	8.7	1.0	10.8
Ciclo 3	Fase 1		Fase 2	
0.5	25.5	5.6	4.9	9.3
1	24.2	7.3	3.5	10.0
2	24.0	8.2	2.6	10.4

Las modalidades particulares descritas arriba son únicamente ilustrativas, pues la invención puede modificarse y practicarse de maneras diferentes pero equivalentes, evidentes para las personas versadas en la técnica que tengan el beneficio de las presentes enseñanzas. Es más, no se pretende ninguna limitación a los detalles de construcción o diseño aquí mostrados, salvo las que se describen en las reivindicaciones que siguen. Es por lo tanto evidente que se pueden alterar y modificar las modalidades particulares divulgadas arriba y que todas estas variaciones se consideran dentro del ámbito y espíritu de la invención. En consecuencia, la protección que aquí se busca es como consta en las reivindicaciones que siguen.

LO QUE SE REIVINDICA ES:

1. Un método para separar arsénico de una solución que contiene arsénico, donde el método comprende los pasos de:

5 poner en contacto una solución que contiene arsénico con una primera porción de un agente fijador en condiciones en las que por lo menos una porción del arsénico es fijada por el agente fijador para obtener una solución parcialmente empobrecida y un agente fijador enriquecido en arsénico, donde el agente fijador

10 comprende un compuesto que contiene tierras raras; separar el agente fijador enriquecido en arsénico de la solución parcialmente empobrecida; y,

15 poner en contacto la solución parcialmente empobrecida con una segunda porción de agente fijador en condiciones en las que por lo menos una porción del arsénico es fijada por el agente fijador para obtener una solución empobrecida en arsénico.

2. El método de la reivindicación 1, en el que la solución empobrecida en arsénico comprende un metal recuperable del Grupo IA, Grupo IIA, Grupo
- 20 VIII y los metales de transición.

3. El método de la reivindicación 2, que además comprende el paso de combinar la solución empobrecida en arsénico con una corriente de proceso en un proceso de refinación de metales para separar el metal recuperable.
- 25

4. El método de la reivindicación 2, que además comprende precipitar el metal recuperable de la solución empobrecida en arsénico.

5. El método de la reivindicación 2, que además comprende electrolizar la solución empobrecida en arsénico para separar el metal recuperable.
- 30

6. El método de la reivindicación 1, en el que del paso de poner en contacto la solución parcialmente empobrecida con la segunda porción del agente fijador se obtiene un agente fijador parcialmente saturado, donde el método además comprende el paso de:
- 35

separar el agente fijador parcialmente saturado de la solución empobrecida en arsénico.

7. El método de la reivindicación 6, que además comprende:
- 5 poner en contacto el agente fijador parcialmente saturado con una
 porción fresca de una solución que contiene arsénico en
 condiciones en las que por lo menos una porción del arsénico es
 fijada por el agente fijador parcialmente saturado para dar una
 segunda solución parcialmente empobrecida y un agente fijador
 enriquecido en arsénico; y,
10 separar la segunda solución parcialmente empobrecida del agente
 fijador enriquecido en arsénico.
8. El método de la reivindicación 7, que además comprende poner en contacto
15 la segunda solución parcialmente empobrecida con una tercera porción de
 agente fijador en condiciones en las que por lo menos una porción del
 arsénico es fijada por el agente fijador para dar una solución empobrecida
 en arsénico.
9. El método de la reivindicación 2, en el que el metal recuperable se
20 encuentra en solución y el agente fijador comprende un compuesto
 insoluble que no reacciona con el metal recuperable para formar un
 producto insoluble.
10. El método de la reivindicación 1, en el que el compuesto que contiene
25 tierras raras comprende uno o más de cerio, lantano o praseodimio.
11. El método de la reivindicación 10, en el que el compuesto que contiene
 tierras raras comprende un compuesto que contiene cerio obtenido de
 carbonato de cerio.
12. El método de la reivindicación 10, en el que el compuesto que contiene
30 tierras raras comprende dióxido de cerio.
13. El método de la reivindicación 1, en el que la solución que contiene
35 arsénico tiene un pH de menos de alrededor de 7 cuando la solución que
 contiene arsénico se pone en contacto con la primera porción de agente
 fijador.

14. El método de la reivindicación 13, en el que la solución que contiene arsénico tiene un pH de menos de alrededor de 4 cuando la solución que contiene arsénico se pone en contacto con la primera porción de agente fijador.

5

15. El método de la reivindicación 14, en el que la solución que contiene arsénico tiene un pH de menos de alrededor de 3 cuando la solución que contiene arsénico se pone en contacto con la primera porción de agente fijador.

10

16. El método de la reivindicación 1, en el que la solución que contiene arsénico tiene un pH de más de alrededor de 7 cuando la solución que contiene arsénico se pone en contacto con la primera porción de agente fijador.

15

17. El método de la reivindicación 16, en el que la solución que contiene arsénico tiene un pH de más de alrededor de 9 cuando la solución que contiene arsénico se pone en contacto con la primera porción de agente fijador.

20

18. El método de la reivindicación 17, en el que la solución que contiene arsénico tiene un pH de más de alrededor de 10 cuando la solución que contiene arsénico se pone en contacto con la primera porción de agente fijador.

25

19. El método de la reivindicación 1, en el que la solución que contiene arsénico comprende más de alrededor de 1000 ppm de sulfato cuando la solución que contiene arsénico se pone en contacto con la primera porción de agente fijador.

30

20. El método de la reivindicación 1, que además comprende el paso de formar la solución que contiene arsénico poniendo en contacto un material portador de arsénico con un agente lixivador que comprende uno o más de una sal inorgánica, un ácido inorgánico, un ácido orgánico y un agente alcalino.

35

21. El método de la reivindicación 20, en el que el agente alcalino comprende hidróxido de sodio.

22. El método de la reivindicación 1, en el que la solución empobrecida en arsénico comprende arsénico una cantidad de menos de alrededor de 20 ppm.
- 5
23. El método de la reivindicación 1, en el que la primera porción de agente fijador se encuentra sustancialmente libre de arsénico antes de ponerse en contacto con la solución que contiene arsénico.
- 10
24. El método de la reivindicación 1, en el que la primera porción de agente fijador se encuentra por lo menos parcialmente saturada con arsénico.
25. El método de la reivindicación 24, en el que el agente fijador parcialmente saturado con arsénico comprende entre alrededor de 0.1 mg y alrededor de 80 mg de arsénico por gramo de agente fijador.
- 15
26. Un aparato para separar el arsénico de una solución que contiene arsénico, donde el aparato comprende:
- 20
- una primera zona de contacto adaptada para recibir una solución que contiene arsénico, teniendo la primera zona de contacto un agente fijador para ponerse en contacto con la solución que contiene arsénico y fijar por lo menos una porción del arsénico para obtener una solución parcialmente empobrecida, donde el agente fijador comprende un compuesto que contiene tierras raras;
- 25
- una segunda zona de contacto adaptada para recibir la solución parcialmente empobrecida, teniendo la segunda zona de contacto un agente fijador para ponerse en contacto con la solución parcialmente empobrecida y fijar por lo menos porción del arsénico para obtener una solución empobrecida en arsénico; y,
- 30
- un primer separador dispuesto entre la primera zona de contacto y la segunda zona de contacto para separar el agente fijador de la solución parcialmente empobrecida.
- 35
27. El aparato de la reivindicación 26, en el que el compuesto que contiene tierras raras comprende uno o más de cerio, lantano o praseodimio.

- 28. El aparato de la reivindicación 27, en el que el compuesto que contiene tierras raras comprende un compuesto que contiene cerio obtenido de carbonato de cerio.
- 5 29. El aparato de la reivindicación 27, en el que el compuesto que contiene tierras raras comprende dióxido de cerio.
- 30. El aparato de la reivindicación 26, que además comprende un segundo separador conectado a la segunda zona de contacto para separar la
10 solución empobrecida en arsénico del agente fijador.
- 31. El aparato de la reivindicación 30, en el que el segundo separador comprende una salida para proveer comunicación fluida con la primera zona de contacto para dirigir un agente fijador parcialmente saturado hacia
15 la primera zona de contacto.
- 32. El aparato de la reivindicación 26, que además comprende una unidad filtradora conectada de forma operable al primer separador para recibir el agente fijador enriquecido en arsénico y producir un filtrado.
20
- 33. El aparato de la reivindicación 32, en el que la unidad filtradora comprende una salida para proveer comunicación fluida con la primera zona de contacto para dirigir el filtrado hacia la primera zona de contacto.
- 25 34. El aparato de la reivindicación 26, que además comprende una unidad de recuperación de metales conectada a la segunda zona de contacto para separar un metal recuperable de la solución empobrecida en arsénico.
- 30 35. El aparato de la reivindicación 34, en el que la unidad de recuperación de metales comprende un recipiente de precipitación o un electrolizador o ambos.

1/2

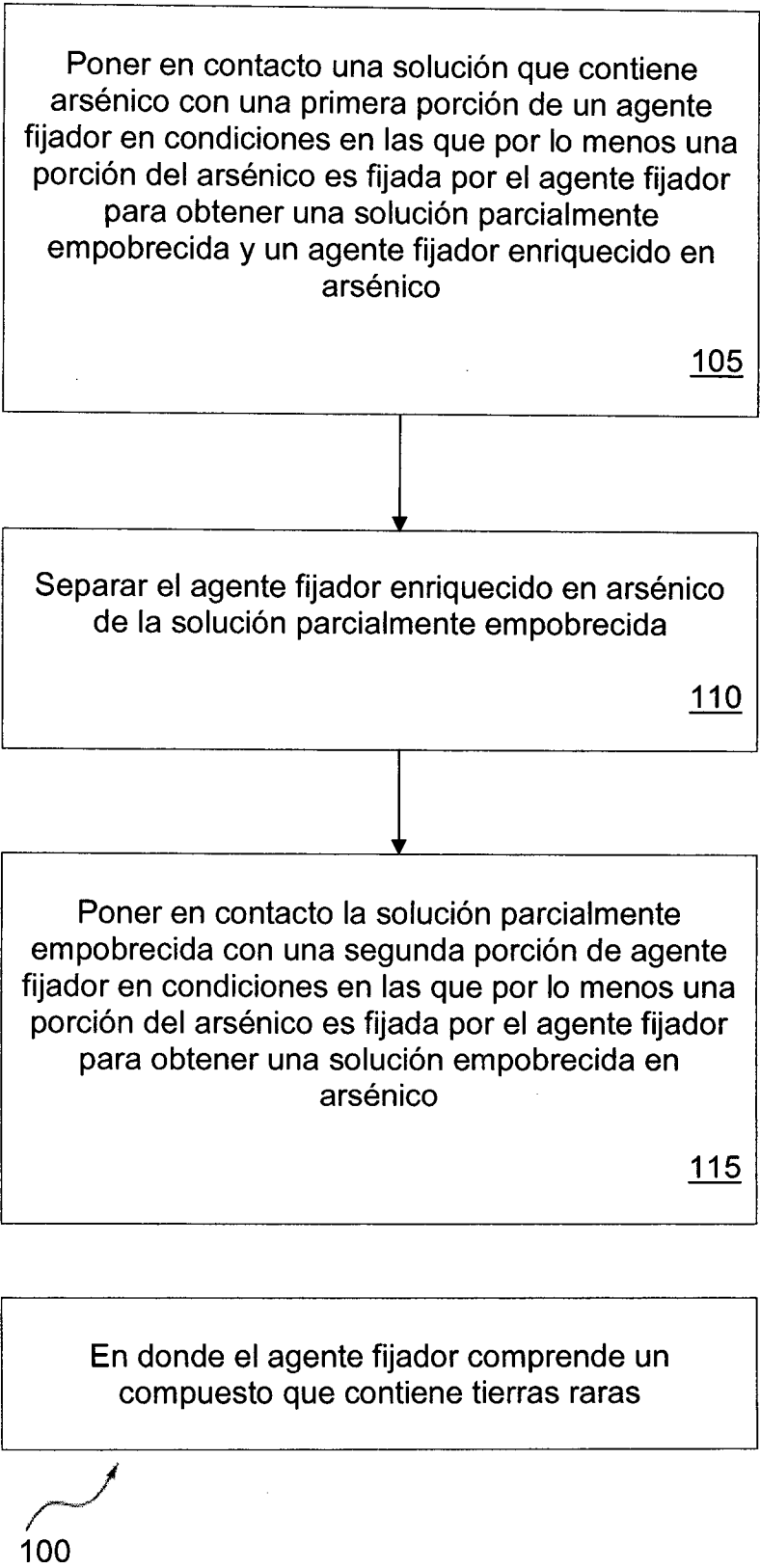


FIG. 1

2/2

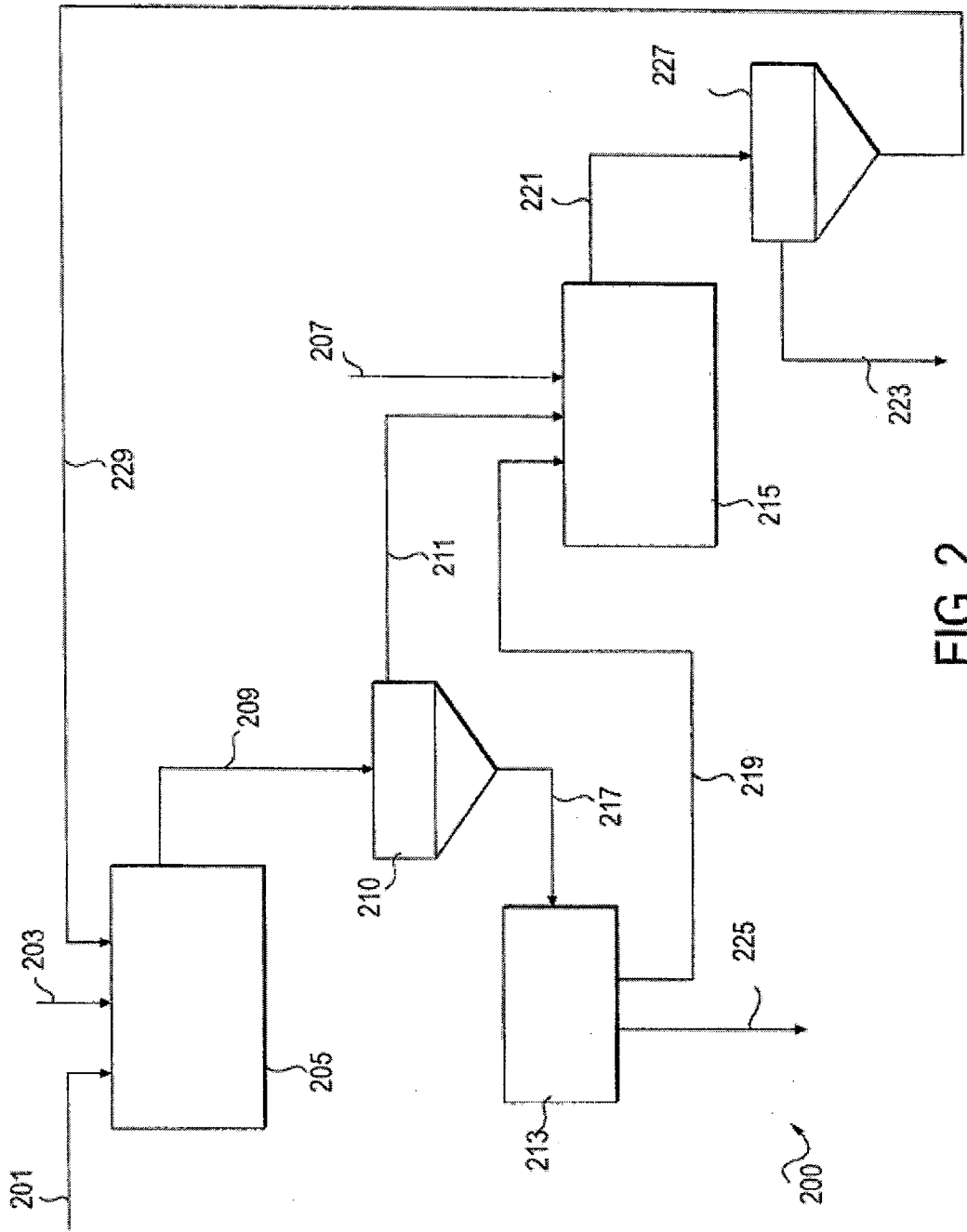


FIG. 2

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 11/958,968	FOR FURTHER ACTION	see Form PCT/ISA/220 as well as, where applicable, item 5 below.
International application No. PCT/US 07/87976	International filing date (day/month/year) 18 December 2007 (18.12.2007)	(Earliest) Priority Date (day/month/year) 28 December 2006 (28.12.2006)
Applicant CHEVERON U.S.A INC.		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 2 sheets.

☐ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the language, the international search was carried out on the basis of:

☒ the international application in the language in which it was filed.

☐ a translation of the international application into _____ which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b)).

b. ☐ This international search report has been established taking into account the rectification of an obvious mistake authorized by or notified to this Authority under Rule 91 (Rule 43.6bis(a)).

c. ☐ With regard to any nucleotide and/or amino acid sequence disclosed in the international application, see Box No. I.

2. ☐ Certain claims were found unsearchable (see Box No. II).

3. ☐ Unity of invention is lacking (see Box No. III).

4. With regard to the title,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the abstract,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. With regard to the drawings,

a. the figure of the drawings to be published with the abstract is Figure No. 1

☒ as suggested by the applicant.

☐ as selected by this Authority, because the applicant failed to suggest a figure.

☐ as selected by this Authority, because this figure better characterizes the invention.

b. ☐ none of the figures is to be published with the abstract.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 07/87976

A. CLASSIFICATION OF SUBJECT MATTER IPC(8) - C02F 1/58 (2008.01) USPC - 210/714; 208/251H 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) USPC: 210/714; 208/251H Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched All Classes (text search - see terms below) Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WEST (PGPB,USPT,USOC,EPAB,JPAB); Google Search Terms: arsenic solution, removal, rare earth, cerium, group VI, group I, group II														
C. DOCUMENTS CONSIDERED TO BE RELEVANT														
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.												
Y	US 4,891,067 A (Rappas et al.) 2 January 1990 (02.01.1990) fig. 3, 7, 8; col 2, ln 47-51; col 5, ln 11-12; col 6, ln 14; col 7, ln 62-64; col 8, ln 8-16; col 9, ln 10-42; col 10, ln 35-44; col 11, ln 52-60; col 12, ln 15-59	1-35												
Y	US 2006/0207945 A1 (Witham et al.) 21 September 2006 (21.09.2006) para [0006]; [0016]-[0017]	1-35												
Y	US 2004/0089841 A1 (Green) 13 May 2004 (13.05.2004) para [0052]-[0053]	5, 35												
Y	US 6,428,705 B1 (Allen et al.) 6 August 2002 (06.08.2002) fig. 1; col 4, ln 12-21; col 5, ln 23-41	32-33												
☐ Further documents are listed in the continuation of Box C. ☐														
<table border="0"><tr><td>* Special categories of cited documents:</td><td>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td></tr><tr><td>"A" document defining the general state of the art which is not considered to be of particular relevance</td><td>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td></tr><tr><td>"E" earlier application or patent but published on or after the international filing date</td><td>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td></tr><tr><td>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td><td>"&" document member of the same patent family</td></tr><tr><td>"O" document referring to an oral disclosure, use, exhibition or other means</td><td></td></tr><tr><td>"P" document published prior to the international filing date but later than the priority date claimed</td><td></td></tr></table>			* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family	"O" document referring to an oral disclosure, use, exhibition or other means		"P" document published prior to the international filing date but later than the priority date claimed	
* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention													
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone													
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art													
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"O" document referring to an oral disclosure, use, exhibition or other means														
"P" document published prior to the international filing date but later than the priority date claimed														
Date of the actual completion of the international search 01 April 2008 (01.04.2008)		Date of mailing of the international search report 30 APR 2008												
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201		Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774												

Form PCT/ISA/210 (second sheet) (April 2007)

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To:
Frank C. Turner
Chevron Corporation, Law Department
Post Office Box 6006
San Ramon, CA 94583-0806

PCT

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43bis.1)

*I ✓ IPm
Art 34 AMD 10-28-08*

Date of mailing
(day/month/year)

30 APR 2008

Applicant's or agent's file reference
11/958,968

FOR FURTHER ACTION

See paragraph 2 below

International application No.
PCT/US 07/87976

International filing date (day/month/year)
18 December 2007 (18.12.2007)

Priority date (day/month/year)
28 December 2006 (28.12.2006)

International Patent Classification (IPC) or both national classification and IPC
IPC(8) - C02F 1/58
USPC - 210/714; 208/251H

Applicant **CHEVRON U.S.A INC.**

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the international application
- ☐ Box No. VIII Certain observations on the international application

2. **FURTHER ACTION**

If a demand for international preliminary examination is made, this opinion will be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1bis(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

3. For further details, see notes to Form PCT/ISA/220.

Name and mailing address of the ISA/US
Mail Stop PCT, Attn: ISA/US
Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450
Facsimile No. 571-273-3201

Date of completion of this opinion
01 April 2008 (01.04.2008)

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-1774

Form PCT/ISA/237 (cover sheet) (April 2007)

Entered 05/22/08

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

International application No.

PCT/US 07/87976

Box No. I Basis of this opinion

1. With regard to the language, this opinion has been established on the basis of:
 - ☒ the international application in the language in which it was filed.
 - ☐ a translation of the international application into _____ which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b)).
2. ☐ This opinion has been established taking into account the rectification of an obvious mistake authorized by or notified to this Authority under Rule 91 (Rule 43bis.1(a))
3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, this opinion has been established on the basis of:
 - a. type of material
 - ☐ a sequence listing
 - ☐ table(s) related to the sequence listing
 - b. format of material
 - ☐ on paper
 - ☐ in electronic form
 - c. time of filing/furnishing
 - ☐ contained in the international application as filed
 - ☐ filed together with the international application in electronic form
 - ☐ furnished subsequently to this Authority for the purposes of search
4. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table(s) relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.
5. Additional comments:

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.

PCT/US 07/87976

Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	1-35	YES
	Claims	None	NO
Inventive step (IS)	Claims	None	YES
	Claims	1-35	NO
Industrial applicability (IA)	Claims	1-35	YES
	Claims	None	NO

2. Citations and explanations:

Claims 1-4, 6-31 and 34 lack an inventive step under PCT Article 33(3) as being obvious over US 4,891,067 A to Rappas et al. (hereinafter 'Rappas') in view of US 2006/0207945 A1 to Witham et al. (hereinafter 'Witham').

Regarding claims 1 and 26, Rappas teaches a method and apparatus for separating arsenic from an arsenic-containing solution (fig. 3), the method comprising the steps of:
contacting an arsenic-containing solution with a first portion of fixing agent (stream 36; fig. 3; col 8, ln 8-16) under conditions in which at least a portion of the arsenic is fixed by the fixing agent to yield a partially-depleted solution (stream 63) and an arsenic-laden fixing agent (stream 54);

separating the arsenic-laden fixing agent from the partially-depleted solution (vessel 53); and
contacting the partially-depleted solution with a second portion of fixing agent (stream 57) under conditions in which at least a portion of the arsenic is fixed by the fixing agent (vessel 61) to yield an arsenic-depleted solution (stream 82).
Rappas does not teach the fixing agent is the same for each step nor does Rappas teach wherein the fixing agent comprises a rare earth-containing compound, but does teach the arsenic is oxidized from the As(III) state to the As(V) state (col 7, ln 62-64). Witham teaches using a rare-earth containing compound for the treatment of solutions containing arsenic that oxidize arsenic in the +3 oxidation state to arsenic in the +5 oxidation state (para [0006]). A skilled artisan would have found it obvious to use the compound taught by Witham in the process taught by Rappas to develop a system with improved arsenic removal properties using the same fixing agent in different steps.

Regarding claim 2, Rappas teaches the arsenic-depleted solution comprises a recoverable metal from Group IA, Group IIA, Group VIII and the transition metals (Fe; stream 90; Bismuth; col 2, ln 30-31; antimony; col 5, ln 12).

Regarding claims 3 and 34, Rappas teaches the step of combining the arsenic-depleted solution with a process stream in a metal refining process to separate the recoverable metal (recycled to a smelter; col 10, ln 41-44).

Regarding claim 4, Rappas teaches precipitating the recoverable metal from the arsenic-depleted solution (col 10, ln 35-44).

Regarding claim 6, Rappas teaches the step of contacting the partially-depleted solution with the second portion of fixing agent yields a partially-saturated fixing agent, the method further comprising the step of:
separating the partially-saturated fixing agent (stream 66; fig. 3; col 9, ln 10-19) from the arsenic-depleted solution (stream 82).

Regarding claim 7, Rappas teaches further:
contacting the partially-saturated fixing agent (stream 66; fig. 3) with a fresh portion of an arsenic containing solution under conditions in which at least a portion of the arsenic is fixed by the partially-saturated fixing agent to give a second partially-depleted solution (stream 58) and an arsenic-laden fixing agent (stream 59); and
separating the second partially-depleted solution from the arsenic-laden fixing agent (vessel 55).

Regarding claim 8, Rappas teaches contacting the second partially-depleted solution (stream 58; figs. 3 and 7) with a third portion of fixing agent (stream 109) under conditions in which at least a portion of the arsenic is fixed by the fixing agent to give an arsenic-depleted solution (stream 110; col 12, ln 15-59).

Regarding claim 9, Rappas teaches a recoverable metal is in solution (antimony; col 5, ln 11-22). Witham teaches the fixing agent comprises an insoluble compound (para [0006] and [0017]); therefore it would have been obvious to a skilled artisan that the recoverable metal is in solution and the fixing agent comprises an insoluble compound that does not react with the recoverable metal to form an insoluble product as the metal and the arsenic need to be separated.

Regarding claims 10 and 27, Witham teaches the rare earth-containing compound comprises one or more of cerium, lanthanum, or praseodymium (para [0016]).

—Please See Continuation Sheet

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

International application No.

PCT/US 07/87976

Supplemental Box

In case the space in any of the preceding boxes is not sufficient.

Continuation of:

Box V. 2. Citations and explanations:

Regarding claims 11 and 28, Witham teaches the rare earth-containing compound comprises a cerium-containing compound derived from cerium carbonate (para [0016]).

Regarding claims 12 and 29, Witham teaches the rare earth-containing compound comprises cerium dioxide (para [0027]).

Regarding claims 13-15, Rappas teaches the arsenic-containing solution has a pH of less than about 7, 4 or 3 when the arsenic-containing solution is contacted with the first portion of fixing agent (col 8, ln 12-16).

Regarding claims 16-18, Rappas does not teach the arsenic-containing solution has a pH of more than about 7, 9 or 10 when the arsenic-containing solution is contacted with the first portion of fixing agent. Rappas does teach a pH of more than about 7, 9 or 10 in the second contacting zone (tank 60; fig. 3) therefore a skilled artisan would have found pH of more than about 7, 9 or 10 for the first zone obvious without undue experimentation.

Regarding claim 19, Rappas teaches the arsenic-containing solution comprises a sulfate (col 2, ln 47-51) and a large weight percent of sulfur in the initial feed (Table II; col 14); therefore a skilled artisan would have found the arsenic solution having more than about 1000 ppm sulfate when the arsenic-containing solution is contacted with the first portion of fixing agent an obvious solution property.

Regarding claim 20, Rappas teaches the step of forming an arsenic-containing solution by contacting an arsenic-bearing material with a leaching agent comprising one or more of an inorganic salt, an inorganic acid, an organic acid and all alkaline agent (caustic leach-1; vessel 61; fig. 3); therefore using a leaching step to form the arsenic solution would have been obvious to a skilled artisan.

Regarding claim 21, Rappas teaches the alkaline agent comprises sodium hydroxide (stream 57).

Regarding claim 22, Rappas teaches the arsenic-depleted solution comprises arsenic in an amount of less than about 20 ppm (col 9, ln 42).

Regarding claim 23, Rappas does not specify the first portion of fixing agent is substantially free of arsenic prior to contacting the arsenic-containing solution, but does teach "predominately sulfuric acid" (col 6, ln 14); therefore a skilled artisan would have found an arsenic free agent an obvious design parameter.

Regarding claim 24, Rappas does not specify the first portion of fixing agent is at least partially saturated with arsenic, but does teach a recycle of NaOH (stream 57; fig. 3) therefore a skilled artisan would have found the presence of arsenic obvious.

Regarding claim 25, Rappas does not teach the fixing agent partially-saturated with arsenic comprises between about 0.1 mg and about 80 mg of arsenic per gram of fixing agent, but a skilled artisan would have found these values obvious without undue experimentation.

Regarding claim 30, Rappas teaches a second separator (vessel 61) connected to the second contact zone for separating the arsenic-depleted solution (stream 82) from fixing agent.

Regarding claim 31, Rappas does not teach the second separator comprises an outlet for providing fluid communication with the first contact zone for directing a partially saturated fixing agent to the first contact zone, but does teach the agent is further contacted with an arsenic solution of higher concentration (vessel 60); therefore a skilled artisan would have found it obvious to direct the agent to the first contact zone.

Claims 5 and 35 lack an inventive step under PCT Article 33(3) as being obvious over Rappas in view of Witham in further view of US 2004/0089841 A1 (Green).

Regarding claims 5 and 35, Rappas does not specify electrolyzing the arsenic-depleted solution to separate the recoverable metal, but does teach an electrolytic cell (cell 38; fig. 3) and teaches that this can be done in any types of solutions (col 11, ln 52-60). Green teaches electrolyzing a solution to separate the recoverable metal (para [0052]-[0053]). A skilled artisan would have found it obvious to combine the method taught by Rappas with the oxidizing agent taught by Witham and the electrolyzing taught by Green to develop a method that electrolyzes the arsenic-depleted solution to separate the recoverable metal.

Claims 32-33 lack an inventive step under PCT Article 33(3) as being obvious over Rappas in view of Witham in further view of US 6,428,705 B1 to Allen et al. (hereinafter 'Allen').

Regarding claim 32, neither Rappas nor Witham teach the use of a filtration unit. Allen teaches an apparatus for the removal of arsenic from solution using (col 4, ln 12-21) comprising a filtration unit (col 5, ln 38-41) that is used after chemical additives such as coagulants and oxidizing agents have been added to the arsenic solution (col 5, ln 23-29). A skilled artisan would have found it obvious to combine the apparatus to remove arsenic taught by Rappas with the oxidizing agent taught by Witham and the post filtering apparatus taught by Allen to develop a system that has a filtration unit operable connected to the first separator for receiving the arsenic-laden fixing agent and producing a filtrate.

Regarding claim 33, Allen teaches the filtration unit comprises an outlet for providing fluid communication with the first contact zone for directing the filtrate to the first contact zone (fig. 1; filtrate 54 to pretreatment area).

Claims 1-35 have industrial applicability as defined by PCT Article 33(4) because the subject matter can be made or used in industry.

NOTES TO FORM PCT/ISA/220 (continued)

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers, claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

"Statement under Article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international application is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments and any accompanying statement, under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the time of filing the amendments (and any statement) with the International Bureau, also file with the International Preliminary Examining Authority a copy of such amendments (and of any statement) and, where required, a translation of such amendments for the procedure before that Authority (see Rules 55.3(a) and 62.2, first sentence). For further information, see the Notes to the demand form (PCT/IPEA/401).

If a demand for international preliminary examination is made, the written opinion of the International Searching Authority will, except in certain cases where the International Preliminary Examining Authority did not act as International Searching Authority and where it has notified the International Bureau under Rule 66.1bis(b), be considered to be a written opinion of the International Preliminary Examining Authority. If a demand is made, the applicant may submit to the International Preliminary Examining Authority a reply to the written opinion together, where appropriate, with amendments before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later (Rule 43bis.1(c)).

Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see the *PCT Applicant's Guide*, Volume II.

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

(19) World Intellectual Property Organization
International Bureau



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10 July 2008 (10.07.2008)

PCT

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60/882,376 28 December 2006 (28.12.2006) US
- (71) Applicant (for all designated States except US):
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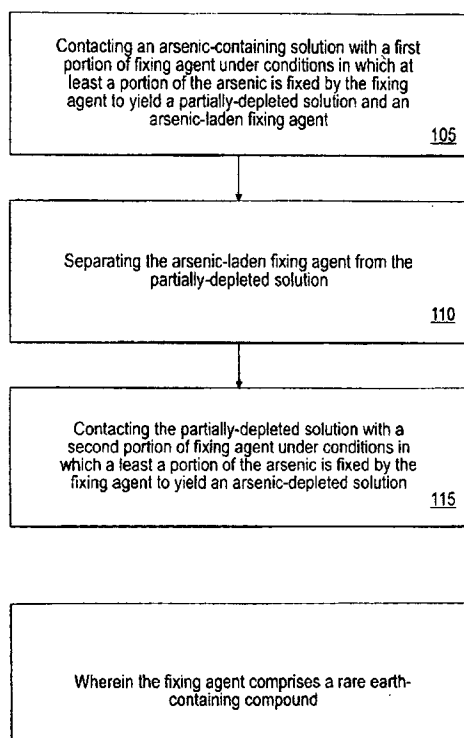
(74) Agents: TURNER, Frank C. et al.; Chevron Corporation,
Law Department, Post Office Box 6006, San Ramon, Cal-
ifornia 94583-0806 (US).

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH,
CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG,
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IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK,
LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW,
MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL,
PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY,
TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA,
ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,

[Continued on next page]

(54) Title: METHOD AND APPARATUS FOR REMOVING ARSENIC FROM A SOLUTION



(57) Abstract: A method and apparatus for separating arsenic from an aqueous solution containing arsenic. The method includes the steps of contacting an arsenic-containing solution with a first portion of fixing agent to remove at least a portion of the arsenic. An arsenic-laden fixing agent is separated from the solution and the partially depleted solution is contacted with a second portion of fixing agent. The fixing agent can include a high surface area insoluble compound containing one or more of cerium, lanthanum, or praseodymium. Following removal of the arsenic, the arsenic-depleted solution can be further processed to separate a recoverable metal through metal refining. The arsenic-laden fixing agent can be filtered to recover and recycle a filtrate to the solution for additional treatment, as well as using a partially saturated fixing agent to remove arsenic from fresh solution. An arsenic-containing solution can be formed from arsenic-containing solids such as contaminated soils, industrial byproducts and waste materials.

WO 2008/082961 A1



GM, KE, LS, MW, MZ, NA, SD, SI, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

METHOD AND APPARATUS FOR REMOVING ARSENIC FROM A SOLUTION

FIELD OF THE INVENTION

5

This invention relates generally to the removal of toxic metals from an aqueous solution, and specifically, to the removal of arsenic from aqueous solutions, such as industrial process streams, effluents, solutions prepared from byproducts and waste materials, and drinking water.

10

BACKGROUND OF THE INVENTION

The presence of arsenic in waters, soils and waste materials may originate from or have been concentrated through geochemical reactions, mining and smelting operations, the land-filling of industrial wastes, the disposal of chemical agents, as well as past agricultural uses of arsenic-containing pesticides. Because the presence of high levels of arsenic may have carcinogenic and other deleterious effects on living organisms and because humans are primarily exposed to arsenic through drinking water, the U.S. Environmental Protection Agency (EPA) and the World Health Organization have set the maximum contaminant level (MCL) for arsenic in drinking water at 10 parts per billion (ppb). As a result, a problem facing industries such as mining, metal refining, steel manufacturing and power generation is the reduction or removal of arsenic from process streams, effluents and byproducts.

Arsenic occurs in the inorganic form in aquatic environments primarily the result of dissolution of solid phase arsenic such as arsenolite (As_2O_3), arsenic anhydride As_2O_5 and realgar (AsS_2). Arsenic occurs in water in four oxidation or valence states, i.e., -3, 0, +3, and +5. Under normal conditions arsenic is found dissolved in aqueous or aquatic systems in the +3 and +5 oxidation states, usually in the form of arsenite (AsO_2^{-1}) and arsenate (AsO_4^{-3}). The effective removal of arsenic by coagulation techniques requires the arsenic to be in the arsenate form. Arsenite, in which the arsenic exists in the +3 oxidation state, is only partially removed by adsorption and coagulation techniques

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because its main form, arsenious acid (HAsO_2), is a weak acid and remains un-ionized at pH levels between 5 and 8 when adsorption is most effective.

Various technologies have been used to remove arsenic from aqueous systems. Examples of such techniques include adsorption on high surface area materials, such as alumina, activated carbon, lanthanum oxide and cerium dioxide, ion exchange with anion exchange resins, precipitation and electrodialysis. In the case of solid or semi-solid waste materials and byproducts containing arsenic, attempts have been made to solidify or stabilize the arsenic in situ to prevent migration into surrounding soils or groundwater. However, because such stabilization procedures tend to be quite costly, and in some cases are unproven, there is a need for alternate method and techniques for handling arsenic in such materials.

SUMMARY OF THE INVENTION

In one embodiment, the present invention provides a method for separating arsenic from an arsenic-containing solution. The method includes the steps of contacting an arsenic-containing solution with a first portion of fixing agent under conditions in which at least a portion of the arsenic is fixed by the fixing agent to yield a partially-depleted solution and an arsenic-laden fixing agent. The fixing agent comprises a rare earth-containing compound. The rare-earth containing compound can include one or more of cerium, lanthanum, or praseodymium. More specifically, the rare-earth containing compound can comprise a cerium-containing compound derived from cerium carbonate. In other embodiments, the rare earth-containing compound comprises cerium dioxide. The first portion of fixing agent can be substantially free of arsenic prior to contacting the arsenic-containing solution or can be partially-saturated with arsenic. When partially-saturated, the fixing agent can comprise between about 0.1 mg and about 80 mg of arsenic per gram of fixing agent.

The method includes the steps of separating the arsenic-laden fixing agent from the partially-depleted solution and contacting the partially-depleted solution with a second portion of fixing agent under conditions in which at least a portion of the arsenic is fixed by the fixing agent to yield an arsenic-depleted solution. When the step of

contacting the partially-depleted solution with the second portion of fixing agent yields a partially-saturated fixing agent, the method can optionally include separating the partially-saturated fixing agent from the arsenic-depleted solution. In such an embodiment, the method optionally include the steps of contacting the partially-saturated
5 fixing agent with a fresh portion of an arsenic-containing solution under conditions in which at least a portion of the arsenic is fixed by the partially-saturated fixing agent to give a second partially-depleted solution and an arsenic-laden fixing agent, and separating the second partially-depleted solution from the arsenic-laden fixing agent. Such a method can also optionally include the step of contacting the second partially-
10 depleted solution with a third portion of fixing agent under conditions in which at least a portion of the arsenic is fixed by the fixing agent to give an arsenic-depleted solution.

Where the arsenic-depleted solution comprises a recoverable metal, the method can optionally include the step of separating the recoverable metal from the arsenic-depleted solution. The recoverable metal can include a metal from Group IA, Group IIA,
15 Group VIII, and the transition metals. The recoverable metal can be separated from the arsenic-depleted solution by combining the arsenic-depleted solution with a process stream in a metal refining process, precipitating the recoverable metal from the arsenic-depleted solution and/or electrolyzing the arsenic-depleted solution. The metal refining process can include electrolyzing the arsenic-depleted solution. When the recoverable
20 metal is in solution, the fixing agent is preferably an insoluble compound that does not react with the recoverable metal to form an insoluble product.

The pH of the arsenic-containing solution can be less than about 7 when the arsenic-containing solution is contacted with the first portion of fixing agent. More specifically, the pH of the arsenic-containing solution can be less than about 4, and still
25 more specifically, the pH of the arsenic-containing solution can be less than about 3 when the arsenic-containing solution is contacted with the first portion of fixing agent. In other embodiments, the pH of the arsenic-containing solution can be more than about 7 when the arsenic-containing solution is contacted with the first portion of fixing agent. More specifically, the pH of the arsenic-containing solution can be more than about 9, and still
30 more specifically, the pH of the arsenic-containing solution can be more than about 10 when the arsenic-containing solution is contacted with the first portion of fixing agent.

The method can also optionally include the step of forming the arsenic-containing solution by contacting an arsenic-bearing material with a leaching agent comprising one or more of an inorganic salt, an inorganic acid, an organic acid and an alkaline agent. When the leaching agent includes an alkaline agent, the alkaline agent can include sodium hydroxide. The arsenic-containing solution can comprise more than about 1000 ppm sulfate when the arsenic-containing solution is contacted with the first portion of fixing agent.

In another embodiment, the present invention provides an apparatus for separating arsenic from an arsenic-containing solution. The apparatus includes a first contact zone adapted to receive an arsenic-containing solution. The first contact zone has a fixing agent for contacting the arsenic-containing solution and fixing at least a portion of the arsenic to yield a partially-depleted solution. The fixing agent comprises a rare earth-containing compound. The rare-earth containing compound can include one or more of cerium, lanthanum, or praseodymium. More specifically, the rare-earth containing compound can comprise a cerium-containing compound derived from cerium carbonate. In other embodiments, the rare earth-containing compound comprises cerium dioxide.

A second contact zone is also included that is adapted to receive the partially-depleted solution, and which has a fixing agent for contacting the partially-depleted solution and fixing at least a portion of the arsenic to yield an arsenic-depleted solution. The apparatus further includes a first separator disposed intermediate the first contact zone and the second contact zone for separating fixing agent from the partially-depleted solution.

The apparatus can optionally include a second separator connected to the second contact zone for separating the arsenic-depleted solution from fixing agent. When present, the second separator can include an outlet for providing fluid communication with the first contact zone for directing a partially saturated fixing agent to the first contact zone.

The apparatus can also optionally include a filtration unit operably connected to the first separator for receiving the arsenic-laden fixing agent and producing a filtrate. When present, the filtration unit can include an outlet for providing fluid communication with the first contact zone for directing the filtrate to the first contact zone.

The apparatus can optionally include a metal recovery unit for separating a recoverable metal from the arsenic-depleted solution. The metal recovery unit can comprise one or more of a precipitation vessel and/or an electrolyzer.

5 **BRIEF DESCRIPTION OF THE DRAWINGS**

The invention may be understood by reference to the following description taken in conjunction with the accompanying drawings.

Figure 1 is a flow chart representation of a method of the present invention.

10 Figure 2 is a schematic view of an apparatus of the present invention.

While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof have been shown by way of example in the drawings and are herein described in detail. It should be understood, however, that the description herein of specific embodiments is not intended to limit the invention to the particular
15 forms disclosed, but on the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the appended claims.

20 **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

Illustrative embodiments of the invention are described below. In the interest of clarity, not all features of an actual embodiment are described in this specification. It will of course be appreciated that in the development of any such actual embodiment, numerous implementation-specific decisions must be made to achieve the developers'
25 specific goals, such as compliance with system-related and business-related constraints, which will vary from one implementation to another. Moreover it will be appreciated that such a development effort might be complex and time-consuming, but would nevertheless be a routine undertaking for those of ordinary skill in the art having the benefit of this disclosure.

30 It will be understood that the method and apparatus disclosed herein can be used to treat any aqueous solution that contains undesirable amounts of arsenic. Examples of

such solutions include, among others, well water, surface waters, such as water from lakes, ponds and wetlands, agricultural waters, industrial process streams, wastewater and effluents from industrial processes, solutions formed from industrial waste and byproducts and geothermal fluids. The arsenic-containing solution can also contain other
5 inorganic contaminants, such as selenium, cadmium, lead, mercury, chromium, nickel, copper and cobalt, and certain organic contaminants. A method and apparatus of the present invention can remove arsenic from such solutions even when elevated concentrations of such inorganic contaminants are present. More specifically, arsenic is effectively removed from solutions comprising more than about 1000 ppm sulfate.

10 Generally, a method and apparatus of the present invention can be used to treat any aqueous solution containing more than about 20 ppb arsenic and is effective for treating solutions containing more than about 1000 ppb arsenic. Moreover, the method and apparatus is effective in decreasing such arsenic levels to an amount less than about 20 ppb, in some cases less than about 10 ppb, in others less than about 5 ppb and in still
15 others less than about 2 ppb.

It has been determined that the adsorption capacity of certain fixing agents for removing arsenic from aqueous solutions is at least in part dependent on the concentration of arsenic in those solutions. More specifically, it has been determined that for a given quantity of fixing agent that comprises a rare earth-containing compound, a
20 greater quantity of arsenic can be removed from solution by contacting the solution with two or more portions of the fixing agent and separating the arsenic-laden fixing agent from the solution between such contacting steps than if the solution were treated with that quantity of fixing agent in a single contact stage. Moreover, the method can be used to effectively remove arsenic from such solutions over a wide range of pH levels, and at
25 extreme pH values, eliminating the need to alter and/or maintain the pH of the solution within a narrow range.

In one aspect of the present invention, a method is provided for separating arsenic from an arsenic-containing solution. The method includes the step of contacting an arsenic-containing solution with a first portion of fixing agent comprising a rare earth-
30 containing compound under conditions in which at least a portion of the arsenic is fixed by the fixing agent to yield a partially-depleted solution and an arsenic-laden fixing

agent. The arsenic-laden fixing agent is separated from the partially-depleted solution, and the partially-depleted solution is contacted with a second portion of fixing agent under conditions in which at least a portion of the arsenic is fixed by the fixing agent to yield an arsenic-depleted solution.

5 The arsenic-containing solution is contacted with the first portion of fixing agent in a tank, container or other vessel suitable for holding such solutions and materials. The solution is at a temperature and pressure, usually ambient conditions, such that the solution remains in the liquid state, although elevated temperature and pressure conditions may be used. The tank may optionally include a mixer or other means for
10 promoting agitation and contact between the arsenic-containing solution and the fixing agent. Non-limiting examples of suitable vessels are described in U.S. Patent No. 6,383,395, which description is incorporated herein by reference. An apparatus of the present invention comprises a first contact zone and a second contact zone with a separator disposed therebetween. The first contact zone and the second contact zone can
15 be housed within a common vessel or reactor, or may be housed separately.

 The fixing agent can be any rare earth-containing compound that is effective at fixing arsenic in solution through precipitation, adsorption, ion exchange or other mechanism. The fixing agent can be soluble, slightly soluble or insoluble in the aqueous solution. In some embodiments, the fixing agent has a relatively high surface area of at
20 least about 70 m²/g, and in some cases more than about 80 m²/g, and in still other cases more than 90 m²/g.

 The fixing agent can include one or more of the rare earths including lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium. Specific
25 examples of such materials that have been described as being capable of removing arsenic from aqueous solutions include trivalent lanthanum compounds (U.S. Patent No. 4,046,687), soluble lanthanide metal salts (U.S. Patent No. 4,566,975), lanthanum oxide (U.S. Patent No. 5,603,838), lanthanum chloride (U.S. Patent No. 6,197,201), mixtures of lanthanum oxide and one or more other rare earth oxides (U.S. Patent No. 6,800,204),
30 cerium oxides (U.S. Patent No. 6,862,825); mesoporous molecular sieves impregnated with lanthanum (U.S. Patent Application Publication No. 20040050795), and

polyacrylonitrile impregnated with lanthanide or other rare earth metals (U.S. Patent Application Publication No. 20050051492). It should be understood that such rare earth-containing fixing agents may be obtained from any source known to those skilled in the art.

5 In some embodiments, the rare-earth containing compound can comprise one or more of cerium, lanthanum, or praseodymium. Where the fixing agent comprises a compound containing cerium, the fixing agent can be derived from cerium carbonate. More specifically, such a fixing agent can be prepared by thermally decomposing a cerium carbonate or cerium oxalate in a furnace in the presence of air. When the fixing
10 agent comprises cerium dioxide, it is generally preferred to use solid particles of cerium dioxide, which are insoluble in water and relatively attrition resistant. Water-soluble cerium compounds such as ceric ammonium nitrate, ceric ammonium sulfate, ceric sulfate, and ceric nitrate can also be used as the fixing agent, particularly where the concentration of arsenic in solution is high.

15 The fixing agent comprising the rare earth-containing compound can be present the first portion of fixing agent that is contacted with the arsenic-containing solution, the second portion of fixing agent that is contacted with a partially depleted solution or in each of the first, second and any additional portions of the fixing agent. The first portion of fixing agent can be substantially free of arsenic prior to contacting the arsenic-
20 containing solution or the first portion can be partially-saturated with arsenic. When partially-saturated, the fixing agent can comprise between about 0.1 mg and about 80 mg of arsenic per gram of fixing agent.

 Optionally, a fixing agent that does not contain a rare earth compound can also be used in the methods and apparatus of the present invention. Such optional fixing agents
25 can include any solid, liquid or gel that is effective at fixing arsenic in solution through precipitation, adsorption, ion exchange or some other mechanism. These optional fixing agents can be soluble, slightly soluble or insoluble in the aqueous solution. Optional fixing agents can include particulate solids that contain cations in the +3 oxidation state that react with the arsenate in solution to form insoluble arsenate compounds. Examples
30 of such solids include alumina, gamma-alumina, activated alumina, acidified alumina such as alumina treated with hydrochloric acid, metal oxides containing labile anions

such as aluminum oxychloride, crystalline alumino-silicates such as zeolites, amorphous silica-alumina, ion exchange resins, clays such as montmorillonite, ferric salts, porous ceramics. Optional fixing agents can also include calcium salts such as calcium chloride, calcium hydroxide, and calcium carbonate, and iron salts such as ferric salts, ferrous salts, or a combination thereof. Examples of iron-based salts include chlorides, sulfates, nitrates, acetates, carbonates, iodides, ammonium sulfates, ammonium chlorides, hydroxides, oxides, fluorides, bromides, and perchlorates. Where the iron salt is a ferrous salt, a source of hydroxyl ions may also be required to promote the co-precipitation of the iron salt and arsenic. Such a process and materials are described in more detail in U.S. Patent No. 6,177,015, issued Jan. 23, 2001 to Blakey et al. Other optional fixing agents are known in the art and may be used in combination with the rare earth-containing fixing agents described herein. Further, it should be understood that such optional fixing agents may be obtained from any source known to those skilled in the art.

Particulate solids such as insoluble fixing agents and insoluble arsenic-containing compounds are separated from the various solutions described herein for further processing. Any liquid-solids separation technique, such as filtration, gravity settling, centrifuging, hydrocycloning or the like can be used to remove such particulate solids. An optional flocculant, coagulant or thickener can also be added to the solution before the particulate solids are removed. Such agents are useful for achieving a desired particle size and improving the settling properties of the arsenic-laden fixing agent. Examples of inorganic coagulants include ferric sulfate, ferric chloride, ferrous sulfate, aluminum sulfate, sodium aluminate, polyaluminum chloride, aluminum trichloride among others. Organic polymeric coagulants and flocculants can also be used, such as polyacrylamides (cationic, nonionic, and anionic), EPI-DMA's (epichlorohydrin-dimethylamines), DADMAC's (polydiallyldimethyl-ammonium chlorides), dicyandiamide/formaldehyde polymers, dicyandiamide/amine polymers, natural guar, etc.

In one embodiment, an arsenic-laden fixing agent is separated from a partially depleted solution in a first separator. The arsenic laden fixing agent is then directed to a filtration unit that is connected to the separator where the fixing agent is further filtered to produce a filtrate and arsenic-laden solids. The solids are directed out of the filtration unit for appropriate disposal or further handling. The filtration unit has an outlet in fluid

communication with a second contact zone for recycling the filtrate to the second contact zone where it is combined with the partially-depleted solution and contacted with fresh fixing agent.

5 In another embodiment, a mixture of an arsenic-depleted solution and a partially saturated fixing agent are directed out of a second contact zone and into a second separator for separating the solution from the fixing agent. The arsenic-depleted solution is directed out of the separator for use, disposal or additional processing. The separator has an outlet in fluid communication with the first contact zone for directing a slurry of the partially-saturated fixing agent to the first contact zone where it contacts in-coming
10 fresh arsenic-containing solution.

The rare earth-containing fixing agents of the present invention are particularly advantageous in their ability to remove arsenic from solution over a wide range of pH values and at extreme pH values. The pH of the arsenic-containing solution can be less than about 7 when the arsenic-containing solution is contacted with the first portion of
15 fixing agent. More specifically, the pH of the arsenic-containing solution can be less than about 4, and still more specifically, the pH of the arsenic-containing solution can be less than about 3 when the arsenic-containing solution is contacted with the first portion of fixing agent. In other embodiments, the pH of the arsenic-containing solution can be more than about 7 when the arsenic-containing solution is contacted with the first portion
20 of fixing agent. More specifically, the pH of the arsenic-containing solution can be more than about 9, and still more specifically, the pH of the arsenic-containing solution can be more than about 10 when the arsenic-containing solution is contacted with the first portion of fixing agent.

To the extent that it is desirable to adjust or control the pH, an optional acid
25 and/or alkaline addition may be added to the solution as is well known in the art. Acid addition can include the addition of a mineral acid such as hydrochloric or sulfuric acid. Alkaline addition can include the addition of sodium hydroxide, sodium carbonate, calcium hydroxide, ammonium hydroxide and the like.

When the arsenic-containing solution includes a recoverable metal, the method
30 can optionally include the step of separating the recoverable metal from the arsenic-depleted solution in a metal recovery unit connected to the second contact zone. As used

herein, recoverable metal can include virtually any metal of interest, but specifically includes metals from Group IA, Group IIA, Group VIII, and the transition metals. Where the recoverable metal is in solution in the arsenic containing solution, the fixing agent is preferably an insoluble compound that selectively adsorbs arsenic from the solution and
5 does not react or reacts only weakly with the recoverable metal to form an insoluble product. The recoverable metal can be separated from the arsenic-depleted solution by combining the arsenic-depleted solution with a process stream in a metal refining process. In some embodiments, the arsenic-depleted solution can be electrolyzed to separate the recoverable metal from solution. By way of example, the removal of
10 contaminants to form a solution for separating various metals through electrorefining processes is described in detail in U.S. Patent No. 6,569,224 issued May 27, 2003 to Kerfoot et al. In other embodiments, the recoverable metal can be precipitated from the arsenic-depleted solution in a precipitation vessel connected to the second contact zone.

When the step of contacting the partially-depleted solution with the second
15 portion of fixing agent yields a partially-saturated fixing agent, the method can optionally include separating the partially-saturated fixing agent from the arsenic-depleted solution. In such an embodiment, the method can further include the steps of contacting the partially-saturated fixing agent with a fresh portion of an arsenic-containing solution under conditions in which at least a portion of the arsenic is fixed by the partially-
20 saturated fixing agent to give a second partially-depleted solution and an arsenic-laden fixing agent. The second partially-depleted solution is separated from the arsenic-laden fixing agent. Such a method can also optionally include the step of contacting the second partially-depleted solution with a third portion of fixing agent under conditions in which at least a portion of the arsenic is fixed by the fixing agent to give an arsenic-depleted
25 solution.

Arsenic can be extracted from solids such as contaminated soils, industrial byproducts and waste materials by leaching or extraction to release the arsenic from such solids. As a result, the method can also optionally include the step of forming the arsenic-containing solution by contacting an arsenic-bearing material with an arsenic
30 extraction agent comprising one or more of an inorganic salt, an inorganic acid, an organic acid and an alkaline agent. Specific examples of inorganic salt arsenic extraction

agents include potassium salts such as potassium phosphate, potassium chloride, potassium nitrate, potassium sulfate, sodium perchlorate and the like. Examples of inorganic acids that may be used to extract arsenic from solids include sulfuric acid, nitric acid, phosphoric acid, hydrochloric acid, perchloric acid and mixtures thereof. Organic acid extractants can include citric acid, acetic acids and the like. Alkaline agents can include sodium hydroxide among others. The arsenic-bearing material is contacted with an extraction agent in a tank, container or other vessel suitable for holding such solutions and materials. Pumps, mixers or other suitable means may be included for promoting agitation and contact between the extraction agent and the arsenic-bearing materials. A more detailed description of arsenic extraction agents and their use may be had by reference to M. Jang et al., "Remediation Of Arsenic-Contaminated Solids And Washing Effluents", *Chemosphere*, 60, pp 344-354, (2005); M. G. M. Alam et al., "Chemical Extraction of Arsenic from Contaminated Soil", *J. Environ Sci Health A Tox Hazard Subst Environ Eng.*, 41 (4), pp 631-643 (2006); and S.R. Al-Abed et al., "Arsenic Release From Iron Rich Mineral Processing Waste; Influence of pH and Redox Potential", *Chemosphere*, 66, pp 775-782 (2007).

DETAILED DESCRIPTION OF THE FIGURES

Figure 1 is a flow chart representation of method 100. Method 100 includes step 105 of contacting an arsenic-containing solution with a first portion of fixing agent under conditions in which at least a portion of the arsenic is fixed by the fixing agent to yield a partially-depleted solution and an arsenic-laden fixing agent. In step 110, the arsenic-laden fixing agent is separated from the partially-depleted solution. In step 115, the partially-depleted solution is contacted with a second portion of fixing agent under conditions in which at least a portion of the arsenic is fixed by the fixing agent to yield an arsenic-depleted solution. The fixing agent comprises a rare earth-containing compound.

Figure 2 is a schematic representation of apparatus 200. Apparatus 200 receives an arsenic-containing solution from a source 201 and directs it to a first contact zone within mixing tank 205. Tank 205 may optionally receive fresh fixing agent from a source 203 and a partially saturated fixing agent through line 229. The arsenic-

containing solution is contacted with the fixing agent in tank 205. Tank 205 may optionally include a mixer (not shown) within the tank to promote agitation and contact between the arsenic-containing solution and the fixing agent. In this first contact zone, at least a portion of the arsenic is fixed to yield a partially-depleted solution and an arsenic-laden fixing agent.

As illustrated, both the solution and fixing agent are transferred via line 209 to separator 210 where the partially-depleted solution is separated from the arsenic-laden fixing agent. Separator 210 has an overflow outlet that directs the partially-depleted solution through line 211 to tank 215. The fixing agent is directed through an outlet to filter 213. Within filter 213, the fixing agent is filtered to yield a filtrate and arsenic-laden solids. The filtrate is routed through line 219 to tank 215 where it is recombined with the partially-depleted solution from separator 210. The arsenic-laden solids produced from the fixing agent in filter 213 are directed out through line 225.

The partially depleted solution and filtrate are combined in tank 215 and contacted with fresh fixing agent from source 207. Tank 215 may optionally include a mixer (not shown) within the tank to promote agitation and contact between the partially-depleted solution and the fixing agent. In this second contact zone, at least a portion of the arsenic is fixed to yield an arsenic-depleted solution. As illustrated, the arsenic-depleted solution and fixing agent are transferred via line 221 to separator 227 wherein the arsenic-depleted solution is separated from the fixing agent. The fixing agent in separator 227 is partially saturated with arsenic and may be recycled to first contact zone within tank 205 for contacting fresh arsenic-containing solution from source 201. The arsenic-depleted solution separated from the fixing agent in separator 227 is directed out of apparatus 200 through line 223.

Example 1: Single treatment of caustic As-containing mining waste solution

These experiments were conducted to determine the surface loading: volume ratio necessary to treat the caustic As-containing solution. The caustic As-containing solution consisted of 5-7 g/L As (III), 20 g/L Na_2CO_3 , 4 g/L Sulfate, 4 mg/L Ni, and 1 mg/L Cu. The pH of the solution was approximately 10.5. The fixing agent used in these

experiments was a high surface area ceria, prepared by thermally decomposing cerium carbonate to CeO₂ at 300° C in a muffle furnace with adequate exposure to air.

Single treatment experiments were run using 200 mL of caustic As-containing solution at approximately 75° C and adding between 3-20g of the thermally decomposed cerium carbonate. Under test conditions, the ceria surface became saturated at a loading of 80 mg(As)/g(Ce). When more than 10g of ceria was added, the arsenic concentration dropped below 0.2% and the surface was no longer able to be loaded to the saturation capacity.

Results are provided in Table 1. Observations collected over the course of two hours suggest that the system rapidly reaches a steady state, particularly when the surface becomes saturated with arsenic.

Table 1

Mass ceria (g)	As(ppm) 30min	As(ppm) 1hr	As(ppm) 2hr	Capacity (mg/g)
3.0	4600	4600	4700	80
5.0	3900	3500	3800	76
7.0	3000	3000	2900	80
10	1700	1700	1600	82
15	544	521	549	70
20	133	118	112	57

Example 2: Two-stage counter-current treatment of caustic As-containing solution

A caustic As-containing solution was prepared by adding 10 g NaAsO₂, 20 g Na₂CO₃, 1 mL of 1000 ppm copper nitrate standard, 0.4 mL of 10,000 ppm nickel nitrate standard to 800 mL DI water. The caustic As-containing solution was then diluted to a full liter and the pH was titrated down to 10.5 using concentrated HCl. With the addition of the nickel sulfate and copper sulfate, a majority of nickel and copper precipitated out, due to the high pH of the caustic solution. The resulting caustic As-containing solution consisted of 5 g/L As (III), 20 g/L Na₂CO₃, 300 µg/L Ni, and 300 µg/L Cu. The fixing agent was again a high surface area ceria prepared by thermally decomposing cerium carbonate to CeO₂ at 300° C in a muffle furnace with adequate exposure to air.

The two stage counter-current procedure was carried as follows:

Cycle 1/Stage 1: 12 g of 300 thermally decomposed cerium carbonate was added to 200 mL of the caustic As-containing solution maintained at a temperature of 70-80°C.

The suspension was filtered on Watman paper, the arsenic-laden ceria was discarded, and the supernatant solution was moved to Cycle 1/Stage 2.

Cycle 1/Stage 2: The supernatant solution from Cycle 1/Stage 1 was re-treated with 12 g of fresh ceria. The twice-treated solution was filtered and the ceria was collected and transferred to Cycle 2/Stage 1.

Cycle 2/Stage 1: The ceria collected from Cycle 1/Stage 2 was added to 200 mL of fresh caustic As-containing solution. The suspension was filtered, the arsenic-saturated ceria was discarded, and the supernatant solution was advanced to Cycle 2/Stage 2.

Cycle 2/Stage 2: The supernatant solution from Cycle 2/Stage 1 was re-treated with 12g of fresh ceria. The twice-treated solution was filtered and the ceria was collected and transferred to Cycle 3/Stage 1.

Cycle 3/Stage 1: The ceria collected from Cycle 2/Stage 2 was added to 200 mL of fresh caustic As-containing solution. The suspension was filtered, the arsenic-saturated ceria was discarded, and the supernatant solution was advanced to Cycle 3/Stage 2.

Cycle 3/Stage 2: The supernatant solution filtered in Cycle 3/Stage 1 was re-treated with 12g of fresh ceria.

Results from this two-stage counter current treatment are shown in Table 2.

Capacity (C) takes into account the amount of arsenic adsorbed to the surface in stage 2 of the previous cycle. In all cases, the twice treated solutions had an arsenic

concentration of less than about 10 ppm. The two-stage counter current procedure effectively lowered arsenic concentrations 99.86% using 12g of ceria at each stage. The observations collected over two hours support the conclusion that the adsorption kinetics are favorable, especially when the ceria surface becomes saturated with arsenic. The capacity of ceria observed in Cycle 2/Stage 1, taking into account the arsenic already adsorbed in Cycle 1/Stage 2, is comparable to the saturation capacity established from the single treatment experiments. However, relative to the single treatment tests as exemplified by Example 1, the final concentration of arsenic remaining in solution in the two-stage counter current experiment is roughly two orders of magnitude lower for the same mass of ceria.

Table 2

Time (hrs)	As(ppm)	C (mg/g)	As(ppm)	C (mg/g)
Cycle 1	Stage 1		Stage 2	
0.5	1070	77	0.11	18
1	1010	78	0.1	17
2	1040	78	0.1	17
Cycle 2	Stage 1		Stage 2	
0.5	2300	74	2.71	38
1	2250	74	2.07	37
2	2250	75	2	37
Cycle 3	Stage 1		Stage 2	
0.5	2890	85	8.5	48
1	2850	85	6.9	47
2	3000	82	6.5	50

Example 3: Two-stage counter-current treatment of acidic As-containing solution

- 5 The two-stage counter-current treatment procedure used in Example 2 was also applied to an acidic As-containing solution containing 35 ppm As(III). The acidic solution was prepared by adding 18.72 mL of 5770 ppm As (III), 1074.3 g Nickel (II) Sulfate, 250 g NaCl, 0.63 g cobalt (II) sulfate, 6 mL of 1000 ppm lead nitrate standard, and 1.5 mL of 1000 ppm copper nitrate standard to 2 L of deionized water. The solution was then diluted to 3 L, to give a pH of approximately 2.
- 10 The acidic As-containing solution was then treated with thermally decomposed cerium carbonate using the two stage counter-current procedure. The process treated a liter of the acidic As-containing solution with 0.8 g of ceria. Some dissolution of the cerium fixing agent was observed and measured along with the arsenic concentration of the treated solutions. The results are provided in Table 3. In all cases, the twice treated
- 15 solutions had an arsenic concentration of less than about 5 ppm.

Table 3

Time (hrs)	As(ppm)	Ce (ppm)	As(ppm)	Ce (ppm)
Cycle 1	Stage 1		Stage 2	
0.5	15.1	5.0	0.6	9.9
1	11.7	7.4	0.3	10.6
2	9.5	8.8	0.2	10.2
Cycle 2	Stage 1		Stage 2	
0.5	22.3	6.1	2.4	10.2
1	19.2	7.3	1.4	10.8
2	18.7	8.7	1.0	10.8
Cycle 3	Stage 1		Stage 2	
0.5	25.5	5.6	4.9	9.3
1	24.2	7.3	3.5	10.0
2	24.0	8.2	2.6	10.4

The particular embodiments disclosed above are illustrative only, as the invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. It is therefore evident that the particular embodiments disclosed above may be altered or modified and all such variations are considered within the scope and spirit of the invention. Accordingly, the protection sought herein is as set forth in the claims below.

WHAT IS CLAIMED IS:

1. A method for separating arsenic from an arsenic-containing solution, the method comprising the steps of:
 - 5 contacting an arsenic-containing solution with a first portion of fixing agent under conditions in which at least a portion of the arsenic is fixed by the fixing agent to yield a partially-depleted solution and an arsenic-laden fixing agent, wherein the fixing agent comprises a rare earth-containing compound;
 - 10 separating the arsenic-laden fixing agent from the partially-depleted solution; and
 - contacting the partially-depleted solution with a second portion of fixing agent under conditions in which at least a portion of the arsenic is fixed by the fixing agent to yield an arsenic-depleted solution.
- 15 2. The method of claim 1, wherein the arsenic-depleted solution comprises a recoverable metal from Group IA, Group IIA, Group VIII and the transition metals.
3. The method of claim 2, further comprising the step of combining the arsenic-depleted solution with a process stream in a metal refining process to separate the recoverable metal.
- 20 4. The method of claim 2, further comprising precipitating the recoverable metal from the arsenic-depleted solution.
- 25 5. The method of claim 2, further comprising electrolyzing the arsenic-depleted solution to separate the recoverable metal.
6. The method of claim 1, wherein the step of contacting the partially-depleted solution with the second portion of fixing agent yields a partially-saturated fixing agent, the method further comprising the step of:
- 30

separating the partially-saturated fixing agent from the arsenic-depleted solution.

7. The method of claim 6, further comprising:
- 5 contacting the partially-saturated fixing agent with a fresh portion of an arsenic-containing solution under conditions in which at least a portion of the arsenic is fixed by the partially-saturated fixing agent to give a second partially-depleted solution and an arsenic-laden fixing agent; and
- 10 separating the second partially-depleted solution from the arsenic-laden fixing agent.
8. The method of claim 7, further comprising contacting the second partially-depleted solution with a third portion of fixing agent under conditions in which at least a
- 15 portion of the arsenic is fixed by the fixing agent to give an arsenic-depleted solution.
9. The method of claim 2, wherein the recoverable metal is in solution and the fixing agent comprises an insoluble compound that does not react with the recoverable metal to form an insoluble product.
- 20
10. The method of claim 1, wherein the rare earth-containing compound comprises one or more of cerium, lanthanum, or praseodymium.
11. The method of claim 10, wherein the rare earth-containing compound comprises a
- 25 cerium-containing compound derived from cerium carbonate.
12. The method of claim 10, wherein the rare earth-containing compound comprises cerium dioxide.

13. The method of claim 1, wherein the arsenic-containing solution has a pH of less than about 7 when the arsenic-containing solution is contacted with the first portion of fixing agent.
- 5 14. The method of claim 13, wherein the arsenic-containing solution has a pH of less than about 4 when the arsenic-containing solution is contacted with the first portion of fixing agent.
- 10 15. The method of claim 14, wherein the arsenic-containing solution has a pH of less than about 3 when the arsenic-containing solution is contacted with the first portion of fixing agent.
- 15 16. The method of claim 1, wherein the arsenic-containing solution has a pH of more than about 7 when the arsenic-containing solution is contacted with the first portion of fixing agent.
- 20 17. The method of claim 16, wherein the arsenic-containing solution has a pH of more than about 9 when the arsenic-containing solution is contacted with the first portion of fixing agent.
- 25 18. The method of claim 17, wherein the arsenic-containing solution has a pH of more than about 10 when the arsenic-containing solution is contacted with the first portion of fixing agent.
- 30 19. The method of claim 1, wherein the arsenic-containing solution comprises more than about 1000 ppm sulfate when the arsenic-containing solution is contacted with the first portion of fixing agent.
20. The method of claim 1, further comprising the step of forming the arsenic-containing solution by contacting an arsenic-bearing material with a leaching agent

comprising one or more of an inorganic salt, an inorganic acid, an organic acid and an alkaline agent.

- 5
21. The method of claim 20, wherein the alkaline agent comprises sodium hydroxide.
22. The method of claim 1, wherein the arsenic-depleted solution comprises arsenic in an amount of less than about 20 ppm.
- 10
23. The method of claim 1, wherein the first portion of fixing agent is substantially free of arsenic prior to contacting the arsenic-containing solution.
24. The method of claim 1, wherein the first portion of fixing agent is at least partially-saturated with arsenic.
- 15
25. The method of claim 24, wherein the fixing agent partially-saturated with arsenic comprises between about 0.1 mg and about 80 mg of arsenic per gram of fixing agent.
- 20
26. An apparatus for separating arsenic from an arsenic-containing solution, the apparatus comprising:
- 25
- a first contact zone adapted to receive an arsenic-containing solution, the first contact zone having fixing agent for contacting the arsenic-containing solution and fixing at least a portion of the arsenic to yield a partially-depleted solution, wherein the fixing agent comprises a rare earth-containing compound;
- 30
- a second contact zone adapted to receive the partially-depleted solution, the second contact zone having fixing agent for contacting the partially-depleted solution and fixing at least a portion of the arsenic to yield an arsenic-depleted solution; and
- a first separator disposed intermediate the first contact zone and the second contact zone for separating fixing agent from the partially-depleted solution.

27. The apparatus of claim 26, wherein the rare earth-containing compound comprises one or more of cerium, lanthanum, or praseodymium.
- 5 28. The apparatus of claim 27, wherein the rare earth-containing compound comprises a cerium-containing compound derived from cerium carbonate.
29. The apparatus of claim 27, wherein the rare earth-containing compound comprises cerium dioxide.
- 10 30. The apparatus of claim 26 further comprising a second separator connected to the second contact zone for separating the arsenic-depleted solution from fixing agent.
- 15 31. The apparatus of claim 30, wherein the second separator comprises an outlet for providing fluid communication with the first contact zone for directing a partially saturated fixing agent to the first contact zone.
- 20 32. The apparatus of claim 26, further comprising a filtration unit operable connected to the first separator for receiving the arsenic-laden fixing agent and producing a filtrate.
- 25 33. The apparatus of claim 32, wherein the filtration unit comprises an outlet for providing fluid communication with the first contact zone for directing the filtrate to the first contact zone.
- 30 34. The apparatus of claim 26, further comprising a metal recovery unit connected to the second contact zone for separating a recoverable metal from the arsenic-depleted solution.
35. The apparatus of claim 34, wherein the metal recovery unit comprises one or more of a precipitation vessel and an electrolyzer.

1/2

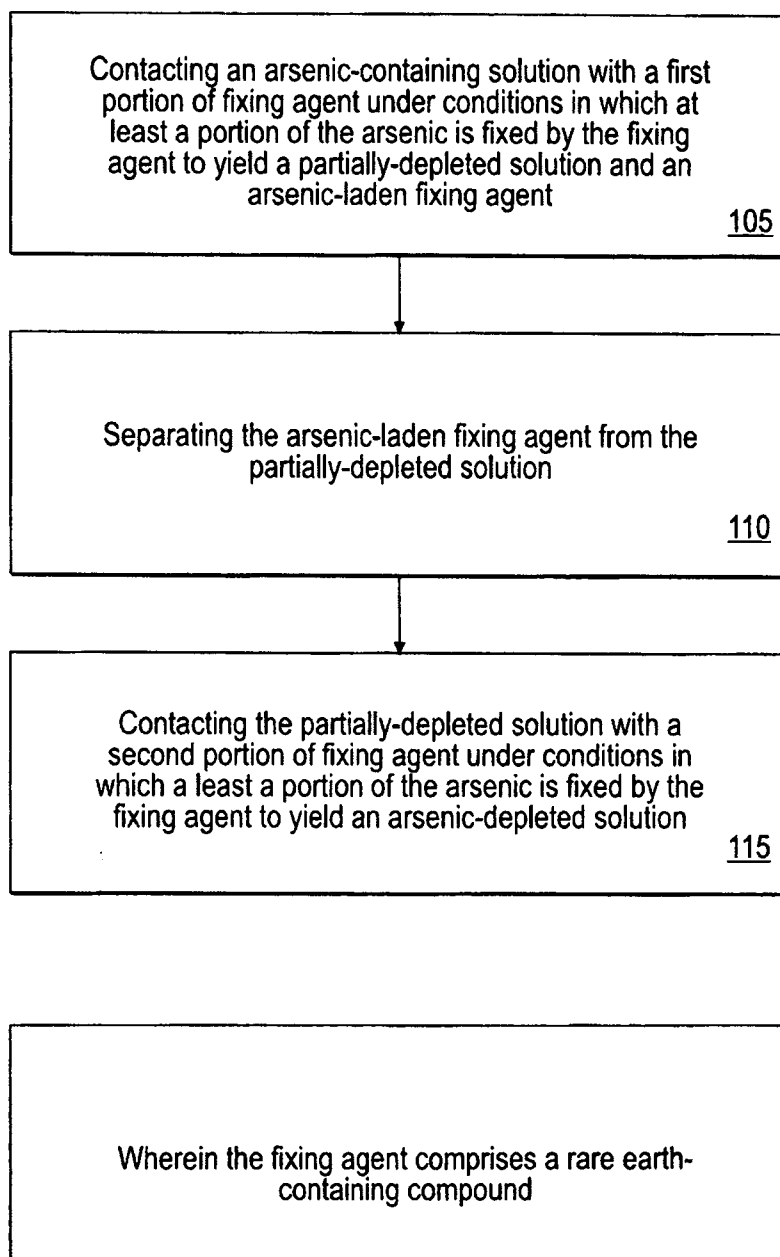


FIG. 1

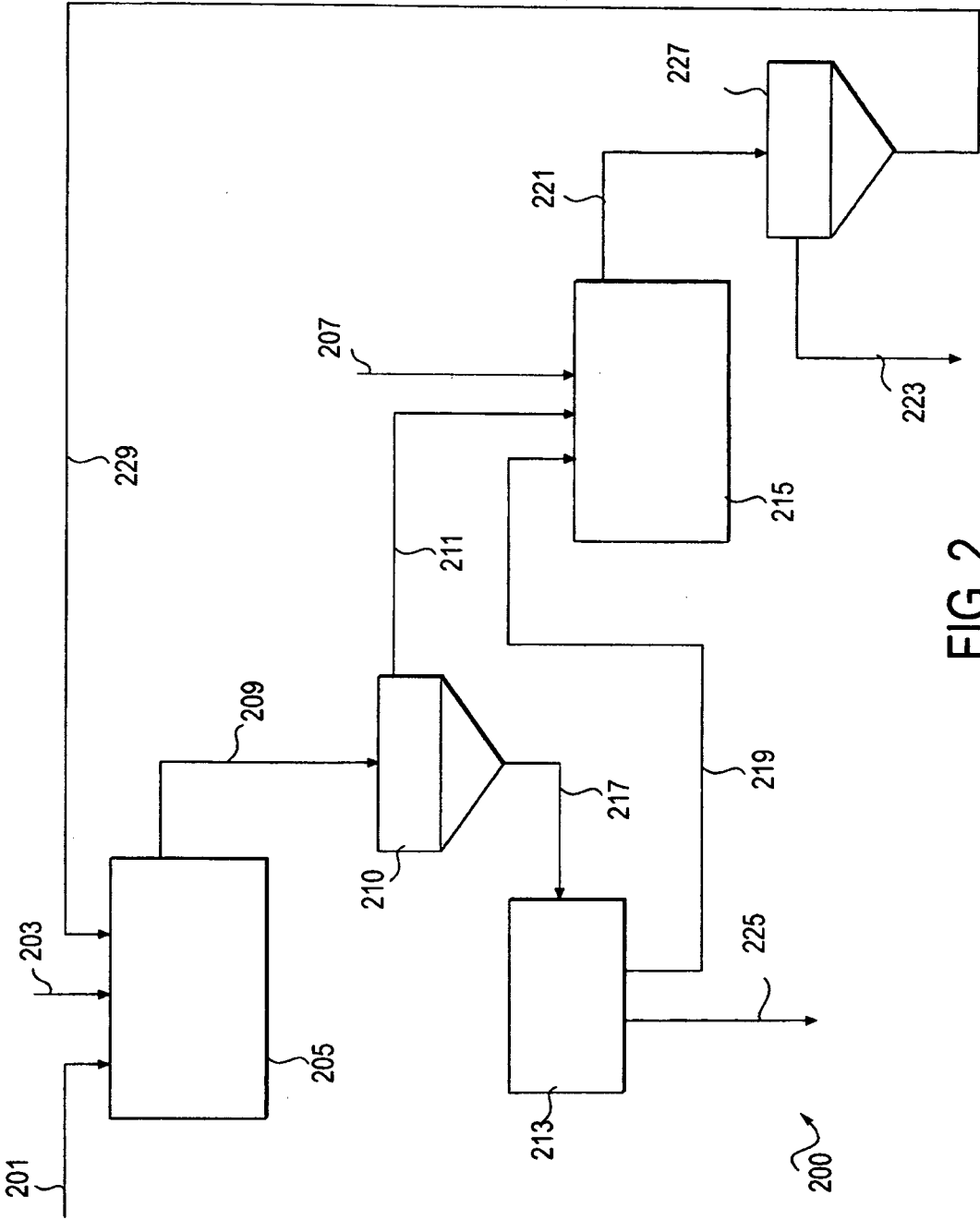


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 07/87976

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C02F 1/58 (2008.01)

USPC - 210/714; 208/251H

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)

USPC: 210/714; 208/251H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
All Classes (text search - see terms below)

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

WEST (PGPB,USPT,USOC,EPAB,JPAB); Google

Search Terms: arsenic solution, removal, rare earth, cerium, group VI, group I, group II

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,891,067 A (Rappas et al.) 2 January 1990 (02.01.1990) fig. 3, 7, 8; col 2, ln 47-51; col 5, ln 11-12; col 6, ln 14; col 7, ln 62-64; col 8, ln 8-16; col 9, ln 10-42; col 10, ln 35-44; col 11, ln 52-60; col 12, ln 15-59	1-35
Y	US 2006/0207945 A1 (Witham et al.) 21 September 2006 (21.09.2006) para [0006]; [0016]-[0017]	1-35
Y	US 2004/0089841 A1 (Green) 13 May 2004 (13.05.2004) para [0052]-[0053]	5, 35
Y	US 6,428,705 B1 (Allen et al.) 6 August 2002 (06.08.2002) fig. 1; col 4, ln 12-21; col 5, ln 23-41	32-33

☐ Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

01 April 2008 (01.04.2008)

Date of mailing of the international search report

30 APR 2008

Name and mailing address of the ISA/US

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P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

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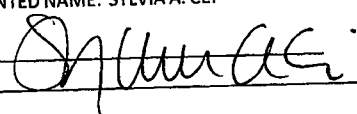
In Re the Application of:
CHEVRON U.S.A. INC.
Int'l Serial No.: PCT/US2007/087976
Intl'l Filing Date: 18 December 2007
Priority Date: 28 December 2006
Atty. File No.: 6062-37-PCT (previously
11/958,968)
Entitled: "METHOD AND
APPARATUS FOR REMOVING
ARSENIC FROM A SOLUTION"

**SUBSEQUENT COMMUNICATION TO
THE INTERNATIONAL BUREAU
CONCERNING PUBLICATION UNDER
RULE 26bis.2(e)**

FEDEX MAILING LABEL NO.: 7967 1746 0533
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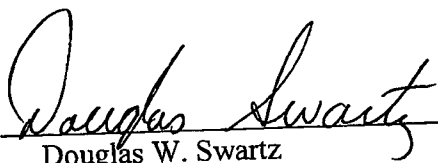
Dear Sir:

Applicant notes that in the Communication to the International Bureau Concerning Publication Under Rule 26bis.2(e) filed on May 6, 2009, an error in the priority filing date was made. The correct filing date of the priority application is December 28, 2006. A copy of the Communication is attached, with the corrections shown.

Applicant hereby respectfully requests the International Bureau publish the corrected priority claim prior to June 28, 2009, the expiration of the international phase.

The International Bureau is hereby authorized to charge any fees associated with the publication of the corrected priority claim to **Deposit Account 42640**.

Respectfully submitted,
SHERIDAN ROSS P.C.

By: 
Douglas W. Swartz
Registration No. 37,739
1560 Broadway, Suite 1200
Denver, Colorado 80202-5141
(303) 863-9700

Date: June 22, 2009

IN THE UNITED STATES RECEIVING OFFICE
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In Re the Application of:)
CHEVRON U.S.A. INC.)
Int'l Serial No.: PCT/US2007/087976)
Intl'l Filing Date: 18 December 2007)
Priority Date: 28 December 2006)
Atty. File No.: 6062-37-PCT (previously)
11/958,968))
Entitled: "METHOD AND)
APPARATUS FOR REMOVING)
ARSENIC FROM A SOLUTION")

COMMUNICATION TO THE
INTERNATIONAL BUREAU
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RULE 26bis.2(e)

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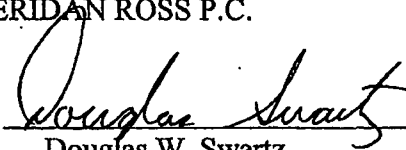
Dear Sir:

The above-referenced application was filed on 18 December 2007, incorrectly claiming priority to U.S. Provisional Application No. 60/882,376 filed December 28, ~~2008~~ 2006. The error was clerical in nature and was discovered after the time limit under Rule 26bis had expired. **The correct priority claim for PCT/US2007/087976 is 60/882,401 filed December 28, 2008.** 2006

Applicant hereby respectfully requests the International Bureau publish the corrected priority claim prior to June 28, 2009, the expiration of the international phase.

The International Bureau is hereby authorized to charge any fees associated with the publication of the corrected priority claim to **Deposit Account 42640**.

Respectfully submitted,
SHERIDAN ROSS P.C.

By: 

Douglas W. Swartz
Registration No. 37,739
1560 Broadway, Suite 1200
Denver, Colorado 80202-5141
(303) 863-9700

Date: May 5, 2009

*** TX REPORT ***

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IN THE UNITED STATES RECEIVING OFFICE
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In Re the Application of:

CHEVRON U.S.A. INC.

Int'l Serial No.: PCT/US2007/087976

Int'l Filing Date: 18 December 2007

Priority Date: 28 December 2006

Atty. File No.: 6062-37-PCT (previously
11/958,968)Entitled: "METHOD AND
APPARATUS FOR REMOVING
ARSENIC FROM A SOLUTION"

**COMMUNICATION TO THE
INTERNATIONAL BUREAU
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ALEXANDRIA, VA 22313-1450

VIA EFS-WEB (courtesy copy)

Dear Sir:

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Applicant hereby respectfully requests the International Bureau publish the corrected priority claim prior to June 28, 2009, the expiration of the international phase

From: Origin ID: TEXA (303) 863-9700
Sylvia A. Cai
Sheridan Ross P.C.
1580 BROADWAY
SUITE 1200
DENVER, CO 80202
UNITED STATES



Ship Date: 06MAY09
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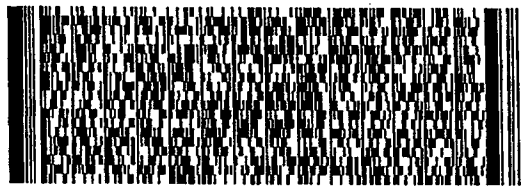
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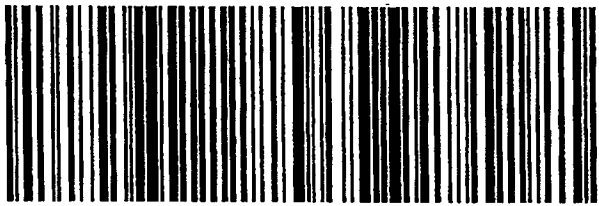
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11/958,968

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PCT REQUEST

Original (for SUBMISSION)

0	For receiving Office use only	
0-1	International Application No.	
0-2	International Filing Date	
0-3	Name of receiving Office and "PCT International Application"	
0-4	Form PCT/RO/101 PCT Request	
0-4-1	Prepared Using	PCT-SAFE [EASY mode] Version 3.51.022.197 MT/FOP 20071101/0.20.5.10
0-5	Petition The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
0-6	Receiving Office (specified by the applicant)	United States Patent and Trademark Office (USPTO) (RO/US)
0-7	Applicant's or agent's file reference	11/958,968
I	Title of Invention	METHOD AND APPARATUS FOR REMOVING ARSENIC FROM A SOLUTION
II	Applicant	
II-1	This person is	applicant only
II-2	Applicant for	all designated States except US
II-4	Name	CHEVRON U.S.A. INC.
II-5	Address	6001 Bollinger Canyon Road - 3rd Floor SAN RAMON, CA 94583 United States of America
II-6	State of nationality	US
II-7	State of residence	US
II-8	Telephone No.	925 842-0991
II-9	Facsimile No.	925 842-2051
II-10	e-mail	fctu@chevron.com

11/958,968

2/5

PCT REQUEST

Original (for SUBMISSION)

III-1	Applicant and/or inventor	
III-1-1	This person is	applicant and inventor
III-1-2	Applicant for	US only
III-1-4	Name (LAST, First)	BURBA, John L., III
III-1-5	Address	9359 Hidden Pines Ct. Parker, Colorado 80134 United States of America
III-1-6	State of nationality	US
III-1-7	State of residence	US
III-2	Applicant and/or inventor	
III-2-1	This person is	applicant and inventor
III-2-2	Applicant for	US only
III-2-4	Name (LAST, First)	HASSLER, Carl R.
III-2-5	Address	12408 Tanager Drive Northwest Gig Harbor, Washington 98332 United States of America
III-2-6	State of nationality	US
III-2-7	State of residence	US
III-3	Applicant and/or inventor	
III-3-1	This person is	applicant and inventor
III-3-2	Applicant for	US only
III-3-4	Name (LAST, First)	O'KELLEY, C. Brock
III-3-5	Address	3620 W. Pebble Rd. Las Vegas, Nevada 89139 United States of America
III-3-6	State of nationality	US
III-3-7	State of residence	US
III-4	Applicant and/or inventor	
III-4-1	This person is	applicant and inventor
III-4-2	Applicant for	US only
III-4-4	Name (LAST, First)	WHITEHEAD, Charles F.
III-4-5	Address	875 East Silverado Ranch Blvd., Apt #2063 Las Vegas, Nevada 89183 United States of America
III-4-6	State of nationality	US
III-4-7	State of residence	US

PCT REQUEST

Original (for SUBMISSION)

IV-1	Agent or common representative; or address for correspondence The person identified below is hereby/ has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:	agent
IV-1-1	Name (LAST, First)	TURNER, Frank C.
IV-1-2	Address	CHEVRON CORPORATION, LAW DEPARTMENT POST OFFICE BOX 6006 SAN RAMON, California 94583-0806 United States of America
IV-1-3	Telephone No.	925 842-0991
IV-1-4	Facsimile No.	925 842-2051
IV-1-5	e-mail	FCTU@CHEVRON.COM
IV-1-6	Agent's registration No.	39,863
IV-2	Additional agent(s)	additional agent(s) with same address as first named agent
IV-2-1	Name(s)	ROTH, Steven H. (28,467); UZZELL, Allen H. (27,602)
V	DESIGNATIONS	
V-1	The filing of this request constitutes under Rule 4.9(a), the designation of all Contracting States bound by the PCT on the international filing date, for the grant of every kind of protection available and, where applicable, for the grant of both regional and national patents.	
VI-1	Priority claim of earlier national application	
VI-1-1	Filing date	28 December 2006 (28.12.2006)
VI-1-2	Number	60/882,376
VI-1-3	Country	US
VI-2	Priority document request The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) identified above as item(s):	VI-1

*error - should have
revised 60/882,401
FCT*

PCT REQUEST

Original (for SUBMISSION)

VI-3	Incorporation by reference : where an element of the international application referred to in Article 11(1)(iii)(d) or (e) or a part of the description, claims or drawings referred to in Rule 20.5(a) is not otherwise contained in this international application but is completely contained in an earlier application whose priority is claimed on the date on which one or more elements referred to in Article 11(1)(iii) were first received by the receiving Office, that element or part is, subject to confirmation under Rule 20.6, incorporated by reference in this international application for the purposes of Rule 20.6.		
VII-1	International Searching Authority Chosen	United States Patent and Trademark Office (USPTO) (ISA/US)	
VIII	Declarations	Number of declarations	
VIII-1	Declaration as to the identity of the inventor	-	
VIII-2	Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent	-	
VIII-3	Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application	-	
VIII-4	Declaration of inventorship (only for the purposes of the designation of the United States of America)	-	
VIII-5	Declaration as to non-prejudicial disclosures or exceptions to lack of novelty	-	
IX	Check list	number of sheets	electronic file(s) attached
IX-1	Request (including declaration sheets)	5	✓
IX-2	Description	17	-
IX-3	Claims	5	-
IX-4	Abstract	1	✓
IX-5	Drawings	2	-
IX-7	TOTAL	30	
	Accompanying Items	paper document(s) attached	electronic file(s) attached
IX-8	Fee calculation sheet	✓	-
IX-17	PCT-SAFE physical media	-	✓
IX-19	Figure of the drawings which should accompany the abstract	1	
IX-20	Language of filing of the international application	English	

PCT REQUEST

Original (for SUBMISSION)

X-1	Signature of applicant, agent or common representative	/TURNER, FRANK C. Reg. No. 39,863/
X-1-1	Name (LAST, First)	TURNER, Frank C.
X-1-2	Name of signatory	
X-1-3	Capacity	

FOR RECEIVING OFFICE USE ONLY

10-1	Date of actual receipt of the purported international application	
10-2	Drawings:	
10-2-1	Received	
10-2-2	Not received	
10-3	Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application	
10-4	Date of timely receipt of the required corrections under PCT Article 11(2)	
10-5	International Searching Authority	ISA/US
10-6	Transmittal of search copy delayed until search fee is paid	

FOR INTERNATIONAL BUREAU USE ONLY

11-1	Date of receipt of the record copy by the International Bureau	
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11/958,968

1/2

PCT (ANNEX - FEE CALCULATION SHEET)Original (for **SUBMISSION**)

(This sheet is not part of and does not count as a sheet of the international application)

0	For receiving Office use only		
0-1	International Application No.		
0-2	Date stamp of the receiving Office		
0-4	Form PCT/RO/101 (Annex)		
0-4-1	PCT Fee Calculation Sheet Prepared Using	PCT-SAFE [EASY mode] Version 3.51.022.197 MT/FOP 20071101/0.20.5.10	
0-9	Applicant's or agent's file reference		11/958,968
2	Applicant		CHEVRON U.S.A. INC.
12	Calculation of prescribed fees	fee amount/multiplier	Total amounts (USD)
12-1	Transmittal fee T	⇒	300
12-2-1	Search fee S	⇒	1800
12-2-2	International search to be carried out by	US	
12-3	International filing fee (first 30 sheets) i1	1163	
12-4	Remaining sheets	0	
12-5	Additional amount (X)	0	
12-6	Total additional amount i2	0	
12-7	i1 + i2 = i	1163	
12-12	EASY Filing reduction R	-83	
12-13	Total International filing fee (i-R) I	⇒	1080
12-14	Fee for priority document		
	Number of priority documents requested	1	
12-15	Fee per document (X)	0	
12-16	Total priority document fee: P	⇒	
12-17	Fee for restoration of priority rights F		
	Number of requests for restoration of priority rights	0	
	Total amount of fees for restoration of priority rights		
12-18	TOTAL FEES PAYABLE (T+S+I+P+F)	⇒	3180

11/958,968

2/2

PCT (ANNEX - FEE CALCULATION SHEET)Original (for **SUBMISSION**)

(This sheet is not part of and does not count as a sheet of the international application)

12-20	Mode of payment	authorization to charge deposit account
12-21	Deposit account instructions	
	The receiving Office	United States Patent and Trademark Office (USPTO) (RO/US)
12-21-1	Authorization to charge the total fees indicated above	✓
12-21-2	Authorization to charge any deficiency or credit any overpayment in the total fees indicated above	✓
12-21-3	Authorization to charge the fee for priority document	✓
12-22	Deposit account No.	03-1620
12-23	Date	18 December 2007 (18.12.2007)
12-24	Name and signature	/TURNER, Frank C./

PATENT COOPERATION TREATY

PCT/US2007/087976

SAC/DWS

From the INTERNATIONAL BUREAU

PCTNOTIFICATION OF THE RECORDING
OF A CHANGE(PCT Rule 92bis.1 and
Administrative Instructions, Section 422)

To:

SWARTZ, Douglas, W.
Sheridan Ross P.C.
1560 Broadway, Suite 1200
Denver, CO 80202
ETATS-UNIS D'AMERIQUE

RECEIVE

MAY - 4 2009

SHERIDAN ROSS P.C.
DOCKETING DEPT.

Date of mailing (day/month/year)

20 April 2009 (20.04.2009)

Applicant's or agent's file reference

11/958,968 6062-37-PCT

IMPORTANT NOTIFICATION

International application No.

PCT/US2007/087976

International filing date (day/month/year)

18 December 2007 (18.12.2007)

1. The following indications appeared on record concerning:

☒ the applicant ☐ the inventor ☐ the agent ☐ the common representative

Name and Address

CHEVRON U.S.A. INC.
6001 Bollinger Canyon Road
3rd Floor
San Ramon, CA 94583
United States of America

State of Nationality

US

State of Residence

US

Telephone No.

Facsimile No.

E-mail address

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☒ the person ☐ the name ☐ the address ☐ the nationality ☐ the residence

Name and Address

MOLYCORP MINERALS, LLC
HC1 Box 224
Mountain Pass, CA 92366
United States of America

State of Nationality

US

State of Residence

US

Telephone No.

Facsimile No.

E-mail address

☐ Notifications by e-mail authorized

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

☒ the receiving Office
☐ the International Searching Authority
☐ the Authority(ies) specified for supplementary search☐ the International Preliminary Examining Authority
☒ the designated Offices concerned
☐ the elected Offices concerned
☐ other:The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Authorized officer

Vannier James

Facsimile No. +41 22 338 70 80

e-mail pt11.pct@wipo.int

Telephone No. +41 22 338 74 11

PATENT

THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re International Application of
CHEVRON U.S.A. INC.
International Application No.
PCT/US2007/087976
International Filing Date
18 December 2007
(Applicant's Ref. No. 11/958,968)

:
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: MAIL STOP PCT
:
: OFFICER: MISTY WALKER
:
:
:
:
:

P. O. Box 6006
San Ramon, CA 94583-0806

RESPONSE TO INVITATION TO CORRECT DEFECTS UNDER PCT RULE 11.13
IN PCT INTERNATIONAL APPLICATION

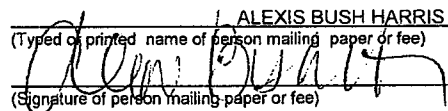
Commissioner for Patents
Mail Stop PCT
P.O. Box 1450
Alexandria, VA 22313-1450
Attention: Ms. Misty Walker

Dear Ms. Walker:

This is in response to the Invitation to Correct Defects mailed February 25, 2008 for the subject International Application, PCT/US2007/087976 (copy attached).

The Receiving Office in the Invitation to Correct Defects, Annex C1 to Form PCT/RO/106, finds that the drawings of the international application as filed do not comply with the physical requirements under, Rule 11.13.

"Express Mail" mailing label No. EV 461467605 US
Date of Deposit April 18, 2008
I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Address" service under 37 CFR 1.10 on the date indicated above and is addressed to the Commissioner for Patents Alexandria, VA 22313-1450

ALEXIS BUSH HARRIS
(Typed or printed name of person mailing paper or fee)

(Signature of person mailing paper or fee)

Applicant has enclosed a fresh set of drawings Figures 1-2 to correct the defect in Rule 11.13, which Applicant believes are in compliance with the PCT requirements. Applicant requests the Officer to replace the original drawings in the International Application with the enclosed fresh set of drawings Figures 1-2.

If Officer desires to discuss this matter, the Officer is most earnestly solicited to undersigned.

Respectfully submitted,



Frank C. Turner
Attorney for Applicant
Reg. No. 39,863
(925) 842-0991

Enclosures

April 18, 2008

ANNEX C1 TO FORM PCT/RO/106

International application No.

PCT/US2007/087976

This receiving Office has found that, with regard to the presentation of the drawings of the international application as filed, the physical requirements are not complied with to the extent that compliance therewith is necessary for:

1. ☒ reasonably uniform international publication (Rules 11 and 26.3(a)(i)) (*defects to be specified*):

Sheets containing drawings:

- a. ☐ the sheets do not admit of direct reproduction
- b. ☐ the sheets are not free from creases, cracks, folds
- c. ☐ one side of the sheets is not left unused
- d. ☐ the paper of the sheets is not flexible/strong/white/smooth/non-shiny/durable
- e. ☐ the drawings do not commence on a new sheet
- f. ☐ the sheets are not connected as prescribed (Rule 11.4(b))
- g. ☐ the sheets are not A4 size (29.7cm x 21cm)
- h. ☐ the minimum margins on the sheets are not as prescribed (top: 2.5cm; left side: 2.5cm; right side: 1.5cm; bottom: 1cm)
- i. ☐ the file reference number indicated on the sheets does not appear in the left-hand corner of the sheets, within 1.5 cm of the top of the sheets
- j. ☐ the file reference number exceeds the maximum of 12 characters
- k. ☐ the sheets are not free from frames around usable or used surfaces
- l. ☐ the sheets are not numbered in consecutive Arabic numerals (e.g. 1/3, 2/3, 3/3)
- m. ☐ the sheet numbers are not centered at the top or bottom of the sheets
- n. ☐ the sheet numbers are in the margin (see h. above for the size of the margins)
- o. ☐ the sheets contain alterations/overwritings/interlineations/too many erasures
- p. ☒ the sheets contain photocopy marks

Drawings (Rule 11.13):

- a. ☐ do not admit of direct reproduction
- b. ☐ contain unnecessary text matter
- c. ☐ contain words so placed as to prevent translation without interference with lines thereof
- d. ☒ are not executed in durable black color; the lines are not uniformly thick and well-defined
- e. ☐ contain cross-sections not properly hatched
- f. ☐ would not be properly distinguishable in reduced reproduction
- g. ☐ contain scales not represented graphically
- h. ☐ contain numbers, letters and reference lines lacking simplicity and clarity
- i. ☐ contain lines drafted without the aid of drafting instruments
- j. ☐ contain disproportionate elements of a figure not necessary for clarity
- k. ☐ contain numbers and letters of height less than 0.32 cm
- l. ☐ contain letters not conforming to the Latin, and where customary, Greek alphabets
- m. ☐ contain figures on two or more sheets which form a single complete figure but which are not able to be assembled without concealing parts thereof
- n. ☐ contain figures which are not properly arranged and clearly separated
- o. ☐ contain different figures not numbered in consecutive Arabic numerals
- p. ☐ contain different figures not numbered independently of the numbering of the sheets
- q. ☐ are not restricted to reference signs mentioned in the description
- r. ☐ do not contain reference signs that are mentioned in the description
- s. ☐ contain the same feature denoted by different reference signs
- t. ☐ are not arranged in an upright position, clearly separated from one another
- u. ☐ are not presented sideways with the top of the figures at the left side of the sheets

2. ☐ satisfactory reproduction (Rules 11 and 26.3(b)(i))

Further observations (if necessary):

Drawings are unclear. New drawings required.

1/2

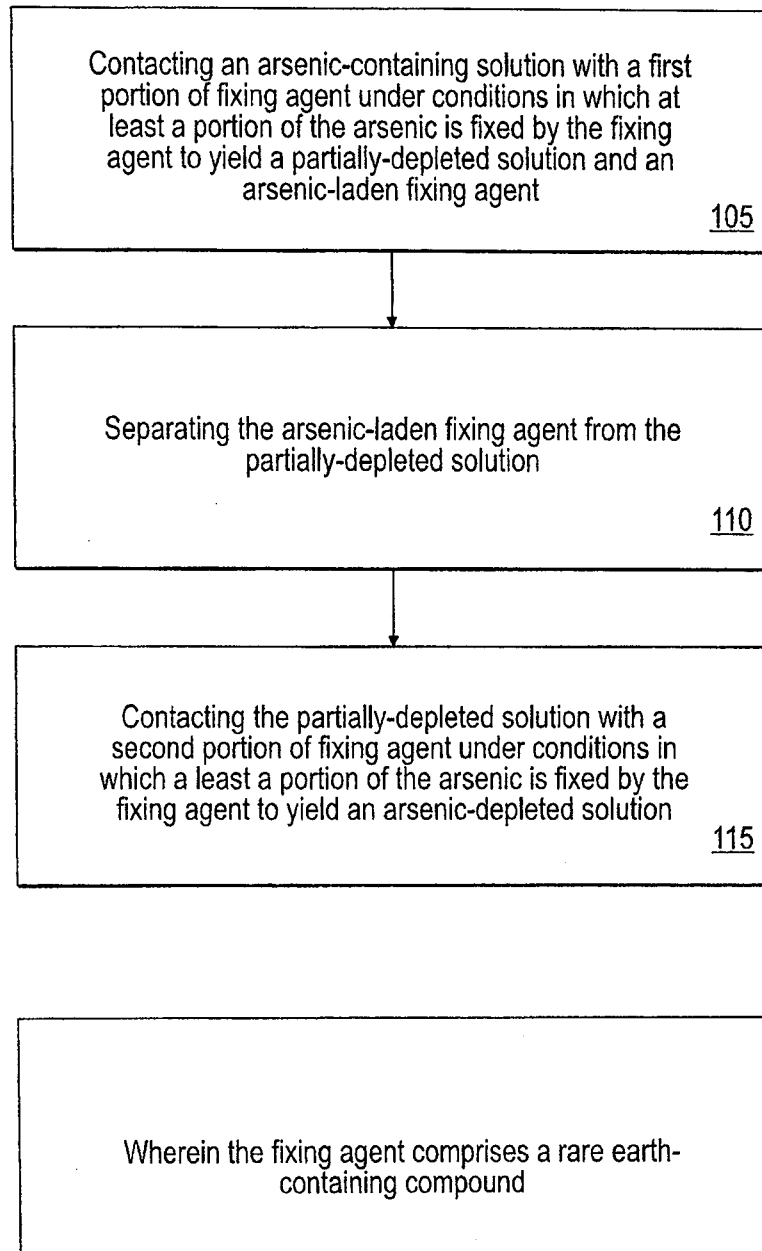


FIG. 1

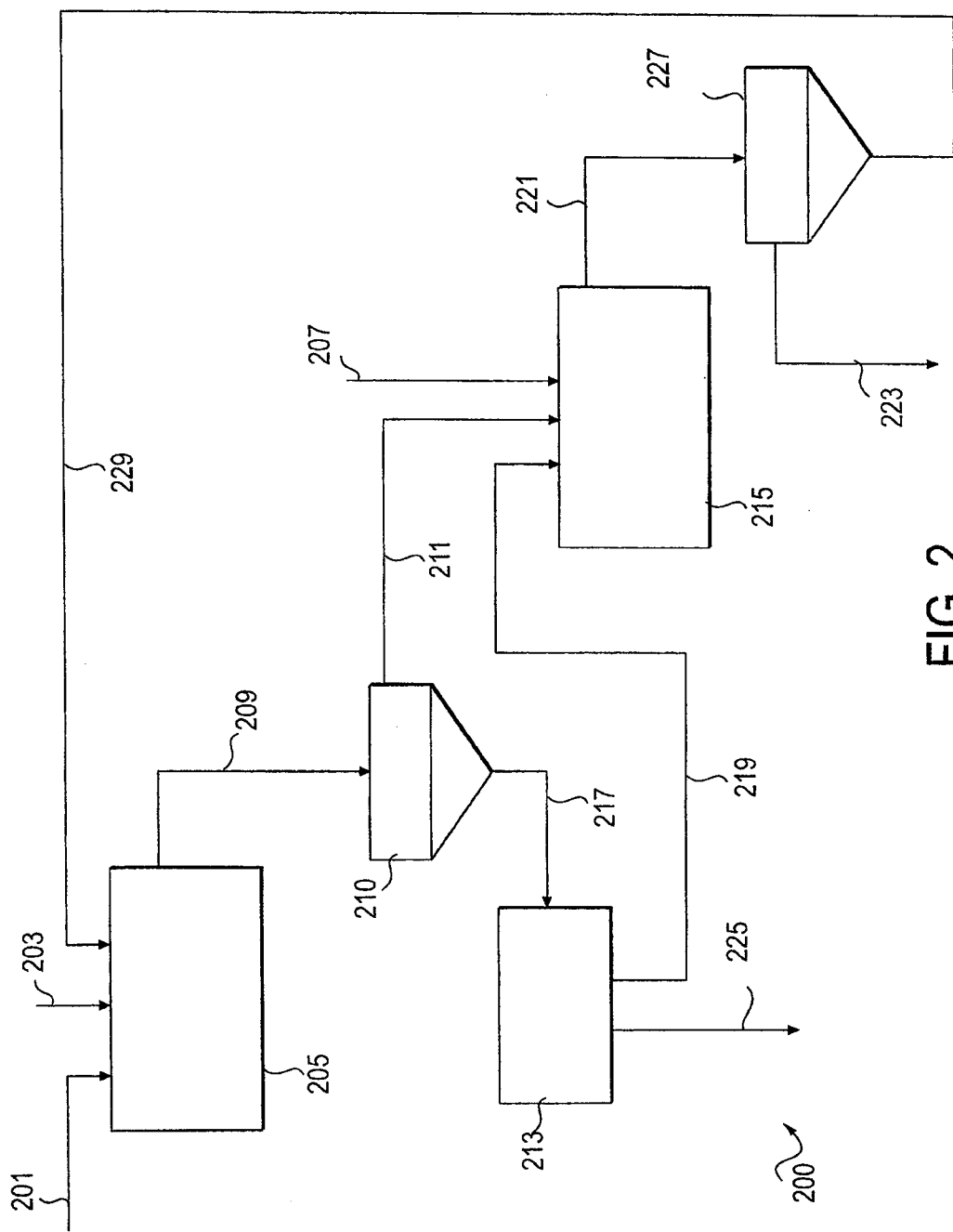


FIG. 2

Poner en contacto una solución que contiene arsénico con una primera porción de un agente fijador en condiciones en las que por lo menos una porción del arsénico es fijada por el agente fijador para obtener una solución parcialmente empobrecida y un agente fijador enriquecido en arsénico

105

Separar el agente fijador enriquecido en arsénico de la solución parcialmente empobrecida

110

Poner en contacto la solución parcialmente empobrecida con una segunda porción de agente fijador en condiciones en las que por lo menos una porción del arsénico es fijada por el agente fijador para obtener una solución empobrecida en arsénico

115

En donde el agente fijador comprende un compuesto que contiene tierras raras

Poner en contacto una solución que contiene arsénico con una primera porción de un agente fijador en condiciones en las que por lo menos una porción del arsénico es fijada por el agente fijador para obtener una solución parcialmente empobrecida y un agente fijador enriquecido en arsénico

105

Separar el agente fijador enriquecido en arsénico de la solución parcialmente empobrecida

110

Poner en contacto la solución parcialmente empobrecida con una segunda porción de agente fijador en condiciones en las que por lo menos una porción del arsénico es fijada por el agente fijador para obtener una solución empobrecida en arsénico

115

En donde el agente fijador comprende un compuesto que contiene tierras raras



No. 09-079285- -00000-0000

Fecha: 2009-07-30 12:19:21 Dep. 2020 NUECREACION
Tra. 11 PATENTE IYII Eve: 378 FASE NACIONAL I
Act. 411 PRESENTACION Folios: 110

SUPERINTENDENCIA

REQUISITOS MÍNIMOS PARA ADMISIÓN A TRAMITE PCT

PATENTE DE INVENCION

☒

MODELO DE UTILIDAD ☐

- ◆ Indicación de que se solicita la concesión de una patente ☒
- ◆ Datos de identificación del solicitante o de la persona que presenta la solicitud ☒
- ◆ Descripción de la invención ☒
- ◆ Dibujos de ser estos pertinentes ☒
- ◆ Comprobante de pago de las tasas establecidas ☒

COMPLETA ☐

INCOMPLETA ☐

DISEÑO INDUSTRIAL ☐

- ◆ Indicación de que se solicita el registro de Diseño Industrial ☐
- ◆ Datos de identificación del solicitante o de la persona que presenta la solicitud ☐
- ◆ Representación gráfica y fotográfica del Diseño Industrial o muestra del material que incorpora el diseño ☐
- ◆ Comprobante de pago de las tasas establecidas ☐

COMPLETA ☐

INCOMPLETA ☐

ESQUEMA DE TRAZADO ☐

- ◆ Indicación de que se solicita el registro de un Esquema de Trazado ☐
- ◆ Datos de identificación del solicitante o de la persona que presenta la solicitud ☐
- ◆ Representación gráfica del esquema trazado ☐
- ◆ Comprobante de pago de las tasas establecidas ☐

COMPLETA ☐

INCOMPLETA ☐

Edgar Navarro

Firma Responsable

Fecha 30-07-09

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