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(54) Title: PROCESS FOR REMOVING ARSENIC FROM AQUEOUS STREAMS

(57) Abstract: Arsenic is removed from water and other aqueous feeds by (1) treating the feed with a compound containing cerium in the +4 oxidation state, preferably cerium dioxide, to oxidize arsenic in the +3 oxidation state to arsenic in the +5 oxidation state and (2) removing the arsenic in the +5 oxidation state from the aqueous phase, normally by contacting the treated feed with alumina or other precipitating agent containing cations in the +3 oxidation state.

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PROCESS FOR REMOVING ARSENIC FROM AQUEOUS STREAMSCROSS-REFERENCES TO RELATED APPLICATIONS

This application claims Convention priority to and is a  
5 U.S. continuation-in-part (CIP) patent application of U.S.  
Patent Application No. 10/353,705 (filed 29 January 2003),  
the entire contents of which are hereby expressly  
incorporated herein by this reference.

10 BACKGROUND

This invention relates generally to methods,  
compositions and devices for removing arsenic from aqueous  
streams and is particularly concerned with methods,  
compositions and devices for removing arsenic from  
15 groundwater and drinking water using cerium in the +4  
oxidation state to oxidize arsenic so it can be  
precipitated from the water.

Arsenic is a toxic element that naturally occurs  
in a variety of combined forms in the earth. Its presence  
20 in natural waters may originate, for example, from  
geochemical reactions, industrial waste discharges and past  
agricultural uses of arsenic-containing pesticides.  
Because the presence of high levels of arsenic may have  
carcinogenic and other deleterious effects on living  
25 organisms, 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). Arsenic concentrations in  
wastewaters, groundwaters, surface waters and geothermal  
30 waters frequently exceed this level. Thus, the current MCL  
and any future decreases, which may be to as low as 2.0  
ppb, create the need for new techniques to economically and  
effectively remove arsenic from drinking water, well water  
and industrial waters.

35 Arsenic occurs 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

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arsenite ( $\text{AsO}_2^{-1}$ ) and arsenate ( $\text{AsO}_4^{-3}$ ). 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 ( $\text{HAsO}_2$ ), is a weak acid and remains un-ionized at a pH between 5 and 8 where adsorption takes place most effectively.

Various technologies have been used in the past to remove arsenic from aqueous systems. Examples of such techniques include adsorption on high surface area materials, such as alumina and activated carbon, ion exchange with anion exchange resins, co-precipitation and electrodialysis. However, most technologies for arsenic removal are hindered by the difficulty of removing arsenite. The more successful techniques that have been used in large municipal water supplies are not practical for residential applications because of space requirements and the need to use dangerous chemicals. The two most common techniques for residential water treatment have been reverse osmosis and activated alumina. The former method produces arsenic-containing waste streams that must be disposed of, and the latter requires the use of caustic chemicals.

The above facts coupled with the potential for the decrease in MCL to between 2 and 10 ppb make it imperative that effective processes, compositions and devices for removing arsenic from water and other aqueous systems be developed.

### 30 SUMMARY

In accordance with the invention, it has now been found that arsenic can be efficiently and effectively removed from water and other aqueous feedstocks by treating the arsenic-containing aqueous feed with a compound containing cerium in the +4 oxidation state, preferably cerium dioxide ( $\text{CeO}_2$ ), in order to oxidize the arsenic so that it can be more easily removed by precipitation from the treated aqueous feed to produce a purified aqueous liquid with a reduced concentration of arsenic. "Precipitation" as used herein

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encompasses not only the removal of arsenic-containing ions in the form of insoluble species, but also includes the immobilization of arsenic-containing ions on or in insoluble particles. In one embodiment of the process of the invention, water or other aqueous liquid containing dissolved arsenic in the +3 and +5 oxidation states is contacted with cerium dioxide to oxidize arsenic in the +3 oxidation state to arsenic in the +5 oxidation state, and the arsenic in the +5 oxidation state is removed from the aqueous liquid by contacting the liquid with a precipitating agent that reacts with the arsenic in the +5 oxidation state to produce insoluble arsenic compounds and an aqueous liquid of reduced arsenic content.

Typically, the oxidized arsenic is in the +5 oxidation state and dissolved in the water or other aqueous liquid in the form of arsenate ( $\text{AsO}_4^{-3}$ ). The precipitating agent used to remove the oxidized arsenic from the aqueous liquid can be anything that reacts with the arsenate or other form of oxidized arsenic to produce insoluble arsenic compounds. For example, the precipitating agent can be cerium in the +3 oxidation state produced in the arsenic oxidation step when cerium in the +4 oxidation state is reduced. Alternatively, the precipitating agent can be any particulate solid containing cations in the +3 oxidation state, such as alumina, aluminosilicates, ion exchange resin and clays.

The oxidation and precipitation steps can be carried out in the same or separate zones. If the steps are carried out in the same zone, the compound containing cerium in the +4 oxidation state is usually mixed with the precipitating agent. Although this mixture can be made by supporting the cerium compound on the surface and/or in the pores of the precipitating solids, it is usually preferred that the cerium compound in particulate form be physically mixed with particles of the precipitating agent. A preferred composition of the invention

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comprises a mixture of cerium dioxide and alumina.

In a preferred embodiment of the process of the invention, an aqueous liquid containing dissolved arsenic in the form of arsenate and arsenite is contacted with a mixture of cerium dioxide particulates and alumina particulates in an oxidation zone such that the cerium dioxide oxidizes the arsenite to arsenate and the alumina reacts with the arsenate to form insoluble aluminum arsenate that sorbs onto the particles of alumina. The aqueous liquid exiting the oxidation zone contains a substantially reduced concentration of arsenic, usually less than about 2.0 ppb.

#### DETAILED DESCRIPTION

Although the process of the invention is primarily envisioned for removing dissolved arsenic from drinking water and groundwater, it will be understood that the process can be used to treat any aqueous liquid feed that contains undesirable amounts of arsenic. Examples of such liquid feeds include, among others, well water, surface waters, such as water from lakes, ponds and wetlands, agricultural waters, wastewater from industrial processes, and geothermal fluids. The arsenic-containing feed can also contain other inorganic contaminants, such as selenium, cadmium, lead and mercury, and certain organic contaminants. Generally, the process of the invention can be used to treat any aqueous liquid feedstock containing more than 2.0 ppb arsenic and is effective for treating feeds containing more than 500 ppb arsenic. The process is effective in decreasing the arsenic levels in such feeds to below 5.0 ppb, usually to below 2.0 ppb.

The arsenic contaminating the aqueous feed is normally dissolved in the aqueous phase and usually exists in both the +3 and +5 oxidation states, respectively, as arsenite ( $\text{AsO}_2^-$ ) and arsenate ( $\text{AsO}_4^{3-}$ ).

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Techniques for removing arsenate exist and are quite effective, but removing the arsenite is a more difficult proposition because the present technologies for doing so are not greatly effective. It has now been found that

5 substantially all of the dissolved arsenite can be easily oxidized to arsenate by treating the aqueous feed with cerium in the +4 oxidation state and the resulting arsenate, along with the arsenate originally present in the aqueous feed, precipitated from the treated feed to

10 produce an arsenic-depleted aqueous liquid.

In the process of the invention, the aqueous feed contaminated with arsenic is passed through an inlet into an oxidation vessel at a temperature and pressure, usually ambient conditions, such that the water in the

15 feed remains in the liquid state. If the feed is contaminated with particulate solids, it is usually treated to remove the solids before it is passed into the oxidation vessel. Any liquid-solids separation technique, such as filtration, centrifuging and

20 hydrocycloning, can be used to remove the particulate solids.

In the oxidation vessel the aqueous feed is contacted with a compound containing cerium in the +4 oxidation state (hereinafter referred to as cerium +4),

25 which Ce +4 is an extremely strong oxidizing agent and oxidizes any arsenite or other arsenic present in the +3 oxidation state to arsenate or other species containing arsenic in the +5 oxidation state. All of the arsenic species containing arsenic in the +5 oxidation state is

30 then precipitated from the aqueous phase by contacting the oxidized aqueous feed with a precipitating agent.

The oxidizing agent can be any solid or liquid containing cerium in the +4 oxidation state. Although it is generally preferred to use solid particles of cerium

35 dioxide, which are insoluble in water and relatively attrition resistant as the oxidizing agent, water-soluble

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cerium compounds can also be used. Examples of such compounds include ceric ammonium nitrate, ceric ammonium sulfate, ceric sulfate, and ceric nitrate.

The precipitating agent that reacts with the  
5 arsenate containing arsenic in the +5 oxidation state to form insoluble arsenic compounds can be present in the oxidation vessel with the cerium +4 compound so that the precipitation occurs essentially simultaneously with the oxidation. Alternatively, it can be in a separate vessel  
10 into which the treated liquid exiting the oxidation vessel passes. For simplicity purposes, it is normally preferred for both the cerium compound and precipitating agent to be present in the oxidation vessel. This embodiment of the invention eliminates the need for an  
15 extra vessel and thereby reduces the cost of installing and operating the process of the invention.

Although the precipitating agent can be any material, solid or liquid, that reacts with arsenate or other species containing arsenic in the +5 oxidation  
20 state to form insoluble arsenic compounds, it is usually a particulate solid that contains cations in the +3 oxidation state, which cations react with arsenate to form insoluble arsenate compounds. Examples of such solids containing cations in the +3 oxidation state  
25 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 aluminosilicates such as zeolites, amorphous silica-alumina, ion  
30 exchange resins, clays such as montmorillonite, ferric sulfate, porous ceramics, and cerium compounds containing cerium in the +3 oxidation state, such as cerous carbonate. Although lanthanum oxide and other rare earth compounds can be used as the precipitating agent, these  
35 materials are typically not employed (except of course for cerium compounds) in the process of the invention

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because it is preferred to use a precipitating agent that has a much smaller  $K_{sp}$  than that of the rare earth compounds.

As mentioned above it is normally preferable  
5 that the cerium +4 compound and precipitating agent both be present in the oxidation vessel so that the arsenic is oxidized and precipitated essentially simultaneously in the same vessel. Although the cerium +4 compound and precipitating agent can both be water-soluble, it is  
10 normally preferred that the cerium +4 compound and precipitating agent both be water-insoluble particulate solids that are either slurried with the aqueous feed in the oxidation vessel or physically mixed together in a fixed bed through which the aqueous feed is passed during  
15 the oxidation step. In an alternative embodiment of the invention, the cerium +4 compound can be deposited on the surface and/or in the pores of the solid precipitating agent. This embodiment is normally not preferred over a physical mixture because supporting the cerium compound  
20 on or in the precipitating solids requires the cerium compound to be dissolved in a liquid, the resultant solution mixed with the support solids, and the wet solids dried. Such steps add significantly to the cost of practicing the process of the invention.

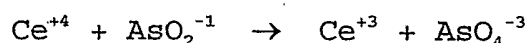
25 Normally, a sufficient amount of the cerium +4 compound is present in the oxidation vessel with the particulate precipitating agent so that the mixture of the two contains between about 8 and 60 weight percent of the cerium +4 compound calculated as the oxide. Prefer-  
30 ably, the mixture will contain between about 10 and 50 weight percent, more preferably between about 20 and 30 weight percent, of the cerium +4 compound calculated as the oxide. However, in some instances, it may be desirable for the mixture to contain greater than 40 to  
35 45 weight percent of the cerium +4 compound calculated as the oxide.



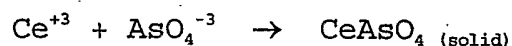
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Regardless of whether the cerium +4 compound is present in the oxidation vessel in admixture with the particulate precipitating agent or supported on or in the pores of the precipitating agent, the solids will typically range in diameter between about 0.25 and 1.5, preferably from 0.5 to 1.0, millimeters. When the cerium +4 compound and precipitating agent are present in the oxidation zone as a fixed bed, it is normally preferred that the particles be spherical in shape so the flow of the aqueous feed through the bed is evenly distributed. However, if desired, the particles may take other shapes including that of extrudates. Such extrudates would typically have a length between about 0.2 and about 3.0 millimeters.

During the oxidation step of the process of the invention, arsenite in the aqueous feed is oxidized to arsenate according to the following equation:



As the cerium +4 oxidizes the arsenite, it is reduced to cerium in the +3 oxidation state, which then reacts with the arsenate formed during the oxidation step to produce insoluble cerium arsenate as shown in the following equation:



Although theoretically there is enough cerium +3 formed by reduction of cerium +4 to react with all of the arsenate formed in the oxidation reaction to precipitate the arsenate, it is normally preferred that an additional precipitating agent be present. This agent, which can be a compound containing cerium +3, reacts with any unreacted arsenate to form an insoluble precipitate, which is removed from the aqueous feed to produce the desired arsenic-depleted aqueous liquid.

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The oxidation step that takes place in the oxidation vessel is normally carried out at ambient pressure, at a temperature from about 4° to 100° C., preferably from about 5° to 40 °C., and at a pH greater than about 3.0. The residence time of the aqueous feed in the oxidation vessel typically ranges from about 2.0 to about 30 minutes. When the cerium +4 compound and arsenic precipitant are both solid particulates and present together as a fixed bed in the oxidation vessel, the precipitated arsenic compounds will be sorbed by or otherwise associated with the solid particles of the precipitating agent so that the aqueous fluid exiting the oxidation vessel will contain essentially no solids and very little arsenic, usually less than about 10 ppb and quite frequently less than 2.0 ppb. If the precipitating agent is not in the oxidation vessel, the effluent from the vessel is passed to another vessel where it is treated separately with the arsenic precipitating agent. Finally, if the cerium +4 compound and precipitating agent are particulate solids that are slurried with the aqueous feed in the oxidation vessel, the effluent from the vessel is normally treated to separate the solids, including the insoluble arsenic compounds formed in the vessel, from the arsenic-depleted liquid. Although the separation can be carried out in any type of device capable of removing particulates from liquids, a filtration system is typically employed.

If the aqueous feed to the process of the invention contains other contaminants that must be removed in addition to arsenic to produce the desired purified aqueous product, the removal of these contaminants is typically carried either before or after the oxidation step. If the other contaminants will interfere with the oxidation of the arsenic, they should be removed prior to the oxidation step. In some cases the process of the invention is also effective for removing other

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contaminants from the aqueous feed in addition to or to the exclusion of arsenic.

In a preferred embodiment of the invention, an arsenic purifying device containing a cartridge or filter  
5 is used to treat residential drinking water. The treating device can be a free standing container with a filtering device containing the composition of the invention or a cartridge type device designed to fit under a sink. These devices are situated so that the  
10 water entering the home or business location passes through the filter or cartridge before it enters the sink faucet. The filter and cartridge devices are quite simple and comprise a inlet attached to the source of the drinking water, a filter or cartridge containing the  
15 cerium +4 oxidizing agent, usually in the form of a fixed bed and in admixture with an arsenic precipitant, and an outlet in communication with the sink faucet to direct the arsenic-depleted drinking water exiting the cartridge or filter to the entrance of the faucet. Alternatively,  
20 a cartridge or filter type device can be designed to fit onto the faucet so that water exiting the faucet passes through the cartridge or filter device before it is consumed.

In the filter or cartridge, arsenic in the +3  
25 oxidation state is oxidized to arsenic in the +5 oxidation state, and substantially all of the dissolved arsenic +5 present reacts with cerium in the +3 oxidation state and the arsenic precipitating agent to form insoluble arsenic compounds that are sorbed onto the  
30 fixed bed solids. The precipitating agent is preferably alumina or an ion exchange resin. The effluent exiting the fixed bed and the outlet of the cartridge or filter device will typically have an arsenic concentration less than about 2.0 ppb. After the fixed bed in one of the  
35 cartridge or filter devices becomes saturated with arsenic, the cartridge or filter is replaced with a new

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cartridge or filter of the same or similar design. The spent cartridge or filter is then disposed of in a legally approved manner.

In another embodiment, the process of the invention is used in community water treatment facilities to remove arsenic from drinking water before the water is distributed to local homes and businesses. For such use the cerium +4 oxidizing agent is typically present in large tanks in either slurry form or in a fixed bed so that relatively large amounts of arsenic-containing water can be treated either in a continuous or batch mode. The arsenic precipitant can be present either in the tank with the cerium +4 oxidizing agent or in a separate vessel fed by the effluent from the tank. The water exiting the process typically has an arsenic concentration less than about 10 ppb, usually less than 5.0 ppb, and preferably less than 2.0 ppb.

The nature and objects of the invention are further illustrated by the following example, which is provided for illustrative purposes only and not to limit the invention as defined by the claims. The example shows that arsenic in the +3 and +5 oxidation state can be completely removed from water using cerium dioxide.

25

#### EXAMPLE

Test solutions were prepared to mimic arsenic-containing groundwater by mixing certified standard solutions of arsenic in the +3 and +5 oxidation states with tap water containing no arsenic. Twenty grams of lanthanum oxide ( $\text{La}_2\text{O}_3$ ), 20 grams of cerium dioxide ( $\text{CeO}_2$ ), and a mixture of 10 grams of lanthanum oxide and 10 grams of cerium dioxide were separately placed in a sealed 100 milliliter glass container and slurried with about 96 milliliters of test solutions containing 100 ppb of arsenic +3, 100 ppb of arsenic +5, and 50 ppb of both arsenic +3 and arsenic +5. The resultant slurries were

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agitated with a Teflon coated magnetic stir bar for 15 minutes. After agitation, the tap water was separated from the solids by filtration through Whatman #41 filter paper and sealed in 125 milliliter plastic sample bottles. The bottles were then sent to a certified drinking water analysis laboratory where the amount of arsenic in each sample was determined by graphite furnace atomic absorption spectroscopy. The results of these tests are set forth below in Table 1.

10

TABLE 1

Test No.	Arsenic in Water Before Test		Slurried Material <u>percent</u>	Arsenic in Water After Test <u>ppb</u>	Arsenic Removed <u>percent</u>
	<u>ppb</u> <u>As<sup>+3</sup></u>	<u>ppb</u> <u>As<sup>+5</sup></u>			
15	1	0	0	0	NA
	2	50	50	0	100
20	3	50	50	100% La <sub>2</sub> O <sub>3</sub>	45
	4	50	50	100% CeO <sub>2</sub>	0
	5	50	50	50% La <sub>2</sub> O <sub>3</sub> 50% CeO <sub>2</sub>	0
	6	100	0	50% La <sub>2</sub> O <sub>3</sub> 50% CeO <sub>2</sub>	0
25	7	0	100	50% La <sub>2</sub> O <sub>3</sub> 50% CeO <sub>2</sub>	0
	8	0	0	50% La <sub>2</sub> O <sub>3</sub> 50% CeO <sub>2</sub>	0
30					NA

The data for test 3 in the table show that, when lanthanum oxide is used by itself, only 55 percent of the arsenic present in the arsenic-spiked tap water is removed. Since the solubility of lanthanum arsenate, which contains arsenic +5, is very small, it was assumed that the arsenic remaining in solution was primarily arsenic +3 in the form of arsenite. The results of test 4, on the other hand, show that cerium dioxide can remove all of the arsenic from the water. The disparity in these results is attributed to the fact that cerium

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exists in the +4 oxidation state in cerium dioxide and is a strong oxidizing agent, whereas the lanthanum in the lanthanum oxide, which is in the +3 oxidation state, is not an oxidizing agent. Although the lanthanum +3 reacts  
5 with arsenic in the +5 oxidation state to precipitate it from the water, the lanthanum does not react with the arsenic in the +3 oxidation state. The cerium in the cerium dioxide oxidizes the arsenic +3 to arsenic +5, which then reacts with cerium +3 formed by the reduction  
10 of cerium +4 to precipitate all of the arsenic dissolved in the water. Tests 5-7 show that equal mixtures of cerium dioxide and lanthanum oxide are also effective in removing all of the arsenic from the tap water.

This application discloses that arsenic is  
15 removed from water and other aqueous feeds by (1) treating the feed with a compound containing cerium in the +4 oxidation state, preferably cerium dioxide, to oxidize arsenic in the +3 oxidation state to arsenic in the +5 oxidation state and (2) removing the arsenic in  
20 the +5 oxidation state from the aqueous phase, normally by contacting the treated feed with alumina or other precipitating agent containing cations in the +3 oxidation state.

Although this invention has been described by  
25 reference to several embodiments of the invention, it is evident that many alterations, modifications and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, it is intended to embrace within the invention all such  
30 alternatives, modifications and variations that fall within the spirit and scope of the appended claims.

The Applicant reserves the right to claim or disclaim now or in the future any feature, combination of features, or subcombination of features that is disclosed  
35 herein.

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All of the numerical and quantitative measurements set forth in this application (including in the description, claims, abstract, drawings, and any appendices) are approximations.

5           The invention illustratively disclosed or claimed herein suitably may be practiced in the absence of any element which is not specifically disclosed or claimed herein. Thus, the invention may comprise, consist of, or consist essentially of the elements  
10 disclosed or claimed herein.

          The following claims are entitled to the broadest possible scope consistent with this application. The claims shall not necessarily be limited to the preferred embodiments or to the embodiments shown in the  
15 examples.

          All patents, prior-filed patent applications, and any other documents and printed matter cited or referred to in this application are incorporated in their entirety herein by this reference.

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WE CLAIM

1. A method for removing arsenic from an aqueous feed comprising the following steps:

(a) treating said aqueous feed in an oxidation zone with a compound containing a sufficient amount of cerium in the +4 oxidation state to oxidize said arsenic and thereby reduce said cerium to the +3 oxidation state; and

(b) removing said oxidized arsenic from said treated aqueous feed to form a purified aqueous liquid having a reduced arsenic concentration as compared to said aqueous feed.

2. The method defined by claim 1 wherein arsenic in the +3 oxidation state in said aqueous feed is oxidized to arsenic in the +5 oxidation state in said oxidation zone.

3. The method defined by claim 2 wherein arsenite ( $\text{AsO}_2^{-1}$ ) in said aqueous feed is oxidized to arsenate ( $\text{AsO}_4^{-3}$ ) in said oxidation zone.

4. The method defined by claim 1 wherein said cerium-containing compound is a particulate solid.

5. The method defined by claim 4 wherein said cerium-containing compound comprises cerium dioxide ( $\text{CeO}_2$ ).

6. The method defined by claim 1 wherein said steps (a) and (b) both take place in said oxidation zone.

7. The method defined by claim 3 wherein said arsenate ( $\text{AsO}_4^{-3}$ ) is removed from said aqueous feed by reaction with said cerium in the +3 oxidation state to



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produce insoluble cerium arsenate.

8. The method defined by claim 1 wherein said oxidized arsenic is removed from said aqueous feed by contacting said aqueous feed with an arsenic precipitating agent containing ions that react with said oxidized arsenic to form insoluble arsenic compounds.

9. The method defined by claim 8 wherein said arsenic precipitating agent comprises a particulate solid containing cations in the +3 oxidation state selected from the group consisting of alumina, ion exchange resins, crystalline aluminosilicates, clays and porous ceramics.

10. The method defined by claim 9 wherein said steps (a) and (b) both take place in said oxidation zone.

11. The method defined by claim 10 wherein said arsenic precipitating agent containing cations in the +3 oxidation state is present in said oxidation zone in combination with said cerium compound containing cerium in the +4 oxidation state.

12. The method defined by claim 1 wherein said steps (a) and (b) are carried out in the substantial absence of lanthanum.

13. The method defined by claim 1 wherein step (a) is carried out in said oxidation zone at a temperature between about 5° C. and about 40° C.

14. The method defined by claim 1 wherein said aqueous feed is selected from the group consisting of groundwater, drinking water, industrial wastewater, agricultural water, lake water, wetlands water and

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geothermal water.

15. The method defined by claim 1 wherein the concentration of arsenic in said purified aqueous liquid is less than about 10 ppb.

16. The method defined by claim 4 wherein said cerium-containing particulate solid is present in said oxidation zone in the form of a fixed bed or a slurry.

17. A method for removing arsenic from an aqueous feed comprising the following steps:

(a) treating said aqueous feed in an oxidation zone with cerium dioxide ( $\text{CeO}_2$ ) to oxidize arsenic in an oxidation state less than +5 to arsenic in the +5 oxidation state; and

(b) removing arsenic in the +5 oxidation state from said treated aqueous feed by contacting said treated feed in said oxidation zone with particulate solids that react with said arsenic in the +5 oxidation state to form an insoluble arsenic compound, thereby forming a purified aqueous liquid having a reduced arsenic concentration as compared to said aqueous feed.

18. The method defined by claim 17 wherein said cerium dioxide ( $\text{CeO}_2$ ) is supported on said particulate solids.

19. The method defined by claim 17 wherein said cerium dioxide ( $\text{CeO}_2$ ) is mixed with said particulate solids.

20. The method defined by claim 17 wherein arsenic in the +3 oxidation state in the form of arsenite ( $\text{AsO}_2^{-1}$ ) is oxidized in said oxidation zone to arsenic in the +5 oxidation state in the form of arsenate ( $\text{AsO}_4^{-3}$ ).

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21. The method defined by claim 20 wherein said particulate solids comprise alumina.

22. The method defined by claim 17 wherein said steps (a) and (b) are carried out in the substantial absence of lanthanum.

23. The method defined by claim 19 wherein the combination of said cerium dioxide ( $\text{CeO}_2$ ) and said particulate solids contains between about 10 weight percent and about 50 weight percent cerium dioxide ( $\text{CeO}_2$ ) calculated as the oxide.

24. The method defined by claim 17 wherein the concentration of arsenic in said purified aqueous liquid is less than about 2.0 ppb

25. A composition comprising a mixture of cerium dioxide ( $\text{CeO}_2$ ) and particulate solids containing cations in the +3 oxidation state, wherein said cerium dioxide is not supported on said particulate solids.

26. The composition defined by claim 25 wherein said particulate solids comprise alumina.

27. The composition defined by claim 26 essentially devoid of lanthanum.

28. The composition defined by claim 26 essentially devoid of all rare earths except cerium.

29. The composition defined by claim 26 wherein particles in said mixture range in diameter from about 0.5 to 1.0 millimeters.

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30. A device for removing arsenic from drinking water comprising:

(a) an inlet communicating with a source of said drinking water;

5 (b) a vessel containing cerium dioxide ( $\text{CeO}_2$ ) and having an entry portion and an exit portion, said entry portion communicating with said inlet; and

(c) an outlet communicating with said exit portion of said vessel.

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31. The device defined by claim 30 wherein said vessel contains cerium dioxide ( $\text{CeO}_2$ ) in combination with particulate solids that react with arsenic in the +5 oxidation state to form insoluble arsenic compounds.

32. The device defined by claim 31 wherein said vessel comprises a cartridge containing said cerium dioxide ( $\text{CeO}_2$ ), and said device is designed to fit beneath a sink or on the outlet of a faucet.

33. The device defined by claim 31 wherein said vessel comprises a tank containing said cerium dioxide ( $\text{CeO}_2$ ).

34. A method for removing arsenic from an aqueous feed comprising:

(a) treating said aqueous feed with a compound containing a sufficient amount of cerium to oxidize said arsenic; and

(b) removing said oxidized arsenic from said treated aqueous feed.

35. A method for removing arsenic from an aqueous feed comprising:

(a) treating said aqueous feed with cerium dioxide ( $\text{CeO}_2$ ) to oxidize arsenic; and

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(b) removing arsenic from said treated aqueous feed.

36. A composition comprising a mixture of cerium dioxide ( $\text{CeO}_2$ ) and particulate solids, wherein said cerium dioxide is not supported on said particulate solids.

37. A device for removing arsenic from drinking water comprising:

(a) an inlet communicating with a source of said drinking water;

(b) a vessel containing cerium dioxide ( $\text{CeO}_2$ ) and communicating with said inlet; and

(c) an outlet communicating with said vessel.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US2004/002430

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C02F1/28 C02F1/52 C02F1/62 C02F1/72

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)

IPC 7 C02F B01D B01J

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

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

BIOSIS, EPO-Internal, INSPEC, COMPENDEX, PAJ, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 916 585 A (BARKS RONALD E) 4 November 1975 (1975-11-04) column 5, line 10 - line 55 --- -/-	25-29, 36



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

° 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 document but published on or after the international filing date
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- \*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
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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US2004/002430

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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P,A	<p>--- ZHANG YU ET AL: "Arsenic(V) removal with a Ce(IV)-doped iron oxide adsorbent." CHEMOSPHERE, vol. 51, no. 9, June 2003 (2003-06), pages 945-952, XP001181786 ISSN: 0045-6535 (ISSN print) abstract page 946, right-hand column</p>	1-37
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P,A	<p>--- US 2003/155303 A1 (HARCK JOHN F ET AL) 21 August 2003 (2003-08-21) paragraphs '0042!, '0048!; claims 1-7</p>	1-37

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International Application No  
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