



## (51) International Patent Classification:

C02F 1/52 (2006.01)

C02F 101/10 (2006.01)

C02F 1/66 (2006.01)

## (21) International Application Number:

PCT/EP2020/061310

## (22) International Filing Date:

23 April 2020 (23.04.2020)

## (25) Filing Language:

English

## (26) Publication Language:

English

## (30) Priority Data:

201941016817

27 April 2019 (27.04.2019)

IN

## (71) Applicant (for all designated States except US): SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ

B.V. [NL/NL]; Carel van Bylandtlaan 30, 2596 HR THE HAGUE (NL).

## (71) Applicant (for US only): SHELL OIL COMPANY [US/US]; 150 N. Dairy Ashford, HOUSTON, TX 77079 (US).

## (72) Inventors: OLTHOF, Timoth  , Johannes; Grasweg 31, 1031 HW Amsterdam (NL). JANSSEN, Albert, Joseph, Hendrik; Carel van Bylandtlaan 23, 2596 HR The Hague (NL). PARTHASARATHI, Manigandan; Plot No 7, Bengaluru Hardware Park, Devanahalli Industrial Park, Mahadeva Kodigehalli, Bangalore North, Karnataka 562149 (IN). SINGLA, Mehak; Plot 7, Bengaluru Hardware Park, Devanahalli Industrial Park, Mahadeva Kodigehalli, Bangalore North, Karnataka 562149 (IN).

## (74) Agent: SHELL LEGAL SERVICES IP; PO Box 384, 2501 CJ THE HAGUE (NL).

(54) Title: A PROCESS FOR REMOVING SELENIUM FROM A WATER STREAM CONTAINING SELENIUM USING TURBULANT FLOW REACTOR SYSTEM

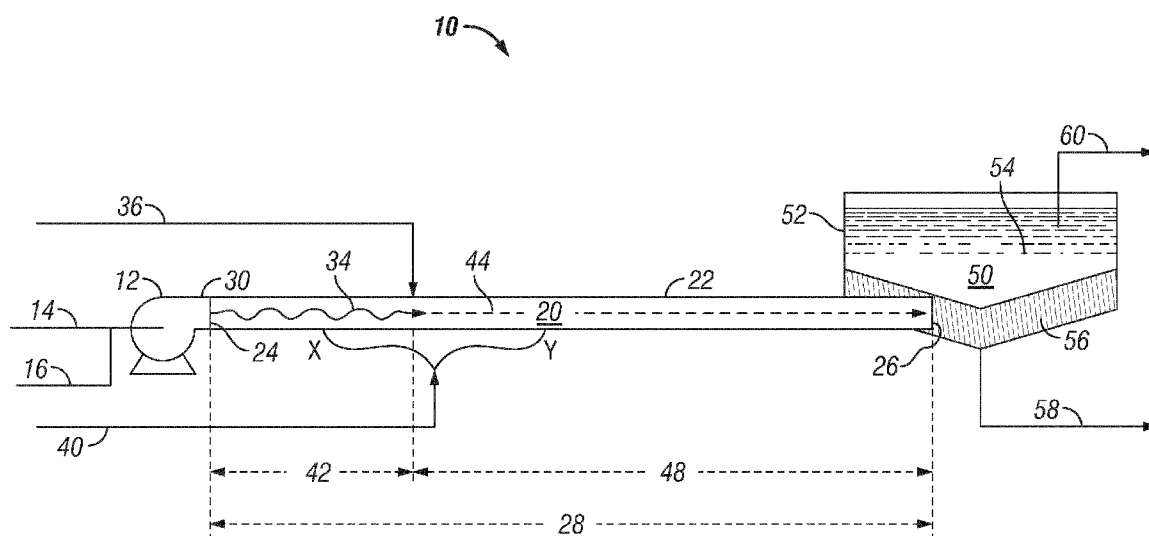


FIG. 1

(57) Abstract: Presented is a process for removing selenium from a water stream, having a selenium concentration, to yield a treated water product (54, 254) having a significantly reduced selenium concentration. The process includes use of a tubular reactor (22, 220) and multiple iron introduction stages to first remove the selenite oxyanion concentration from the water stream by the application of ferric iron and then to remove the selenate oxyanion and elemental selenium concentrations by the application of ferrous iron. The pH of the first reaction mixture (34, 234) resulting from the ferric iron introduction or first mixing step is maintained in the acidic range to prevent precipitation of iron. The pH of the second reaction mixture (44, 244) resulting from the ferrous iron introduction or second mixing step is raised to the basic range to promote precipitation of iron and the formation of iron sludge. Separation means (52, 252) provides for separation of the second reaction mixture to yield the treated water product and an iron precipitate sludge product.



**(81) Designated States** (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

**(84) Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

**Declarations under Rule 4.17:**

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

**Published:**

— *with international search report (Art. 21(3))*

---

## **A PROCESS FOR REMOVING SELENIUM FROM A WATER STREAM CONTAINING SELENIUM USING TURBULANT FLOW REACTOR SYSTEM**

### **FIELD OF THE INVENTION**

5           This invention relates to a process for removing selenium from a water stream that contains a selenium concentration using a turbulent flow reactor system.

### **BACKGROUND OF THE INVENTION**

Selenium is a naturally occurring group 16 (VIA) element and is released into the environment by various sources such as the coal burning, oil and gas, irrigated agriculture,  
10   mining, and metallurgical industries. Pertaining to the oil and gas industry, crude oil containing seleniferous marine shales is rich in selenium, which is a major source of selenium in refinery effluent. During the various crude oil refining steps, selenium and other pollutants (e.g., oil residues, benzene, sulfur, arsenic, chromium, etc.) can be transferred from oil mixtures to waste water streams, where refinery units such as the  
15   desalter, coker, hydrotreater, and sour water stripper, provide a major source for selenium-contaminated waste water. For example, during crude oil processing, sour water that contains selenium compounds is stripped from an oil mixture and flows into a waste water treatment system. During treatment, the selenium compounds within the stripped sour water are oxidized to selenium oxyanions, i.e., selenate ( $\text{SeO}_4^{2-}$ ) and selenite ( $\text{SeO}_3^{2-}$ ),  
20   which are bioavailable with a high potential for bioaccumulation and toxicity. If harmful amounts of selenium remain even after treatment, selenium-contaminated treated waste water may be discharged into natural water bodies, thus, resulting in selenium contamination and adverse effects on aquatic and aquatic dependent wild life.

Federal and state mandates dictate the removal of selenium compounds from waste  
25   water streams before being discharged into natural water bodies. Over the years, three main methods have emerged for removing selenium from waste water including physical, biological, and chemical treatments. Physical treatment includes processes like ion-exchange, reverse osmosis, and membrane filtration. Biological treatment deals with organic carbon sources (e.g. aerobic and an-aerobic bacteria, algae, fungus) for conversion  
30   of soluble species (e.g., selenate and selenite) to insoluble species (e.g., elemental selenium). Chemical treatment includes adsorption, redox transformation, electrocoagulation, and precipitation of soluble and insoluble selenium species.

There are a variety of processes described in the art that apply iron co-precipitation for removing selenium from water streams that contain selenium in its various forms. One

example of such a process is the selenium precipitation process described in U.S. Patent 9,963,360. This patent discloses processes for treating an aqueous solution to remove dissolved selenium oxyanions using an ion exchange process, a selenate precipitation process, or a combination of both the ion exchange process and the selenate precipitation process. For the selenate precipitation process, a selenate-containing aqueous solution is contacted with a ferrous iron or a ferrous/ferric iron mixture to co-precipitate or adsorb at least a portion of the selenate with the iron to thereby produce a selenium-iron precipitate and a selenium depleted discharge solution.

Another process that uses iron salts for removal of selenium species from water streams is disclosed in U.S. Patent No. 5,993,667. This process provides for removing selenium from refinery water streams by mixing an aqueous solution of ferric sulfate or other soluble ferric salt with the refinery water to produce a first stream containing a precipitate consisting of ferric hydroxide and ferric oxyhydroxide. The first stream is further mixed with an aqueous permanganate solution, causing the oxidation of the selenium to selenite and the formation of a manganese dioxide precipitate. The selenite is adsorbed on both the manganese dioxide and the ferric hydroxide to form a second stream including selenium-containing solids.

U.S. Patent Application Publication No. 2012/0241381 discloses a dual-stage selenium reduction process. A first stage treatment uses an iron co-precipitation process to remove a bulk concentration of selenium from selenium contaminated water. In particular, the ferric salt is added to form a ferric hydroxide and a ferrihydrite precipitate, which adsorbs dissolved selenite and suspended selenium particles, but not selenate. In an additional step, an oxidizing agent, i.e. potassium permanganate, may further be introduced into the selenium contaminated water to convert the selenate to selenite. Water from the first stage is treated by either a hydride generation process or an ion-exchange media, or a combination thereof, to achieve a lowered selenium concentration.

These prior art processes typically are only able to provide treated waters having concentrations of the selenium compounds down to 100-200 parts per billion ("ppbw"). None of the previously described approaches individually removes both the selenate and selenite concentrations in waste water streams to below 10 ppbw.

Accordingly, there is a need for a selenium removal process for treating water streams that are contaminated with several species of selenium oxyanions, including

selenite and selenate anions, to yield treated water having a total selenium concentration of less than 10 ppbw.

### **SUMMARY OF THE INVENTION**

Therefore, provided is a process for removing selenium from a waste water stream  
5 that has a selenium concentration. In this process, the waste water stream and a ferric salt are introduced into a tubular reaction zone of a tubular reactor and are mixed to form a first reaction mixture. The tubular reactor has an inlet end for receiving the waste water stream, an outlet end for discharging a waste water reaction mixture, and a length extending  
10 between the inlet end and the outlet end. The first reaction mixture passes through at least a portion of the length of the tubular reaction zone wherein at a first location along the length of the tubular reaction zone a ferrous salt is introduced into the first reaction mixture within the tubular reaction zone. A pH regulating composition is also introduced into the tubular reaction zone either with the introduction of the ferrous salt or at least at a second location along the length of the tubular reaction zone downstream from the introduction of the  
15 waste water stream and ferric salt where the pH regulating composition mixes with the first reaction mixture. The second reaction mixture passes from the tubular reaction zone into a separation zone defined by separation means for separating the second reaction mixture into a water product, having a reduced selenium concentration that is less than the selenium concentration of the waste water stream, and an iron precipitate sludge product.

20 In another embodiment of the inventive process, the waste water stream and a ferric salt are introduced into a tubular reaction zone of a tubular reactor and are mixed to form a first reaction mixture. The tubular reactor has an inlet end for receiving the waste water stream, an outlet end for discharging a waste water reaction mixture, and a length extending between the inlet end and the outlet end. The first reaction mixture passes  
25 through at least a portion of the length of the tubular reaction zone wherein at a first location along the length of the tubular reaction zone a ferrous salt is introduced into the first reaction mixture within the tubular reaction zone. A pH regulating composition is also introduced into the tubular reaction zone either with the introduction of the ferrous salt or at a second location along the length of the tubular reaction zone wherein it mixes with the  
30 first reaction mixture, the ferrous salt and the pH regulating composition to form a second reaction mixture. The second reaction mixture passes through at least a second portion of the length of the tubular reaction zone and from the tubular reaction zone into a mixing reaction zone defined by a mixed flow reactor. The second reaction mixture from the

mixing reaction zone then passes into a separation zone defined by separation means for separating the second reaction mixture into a water product, having a reduced selenium concentration that is less than said selenium concentration of the waste water stream, and an iron precipitate sludge product.

5 In yet another embodiment of the inventive process, a waste water stream and a ferric salt are introduced into a tubular reaction zone of a tubular reactor to provide a first reaction mixture. The tubular reactor has an inlet end for receiving the waste water stream, an outlet end for discharging a waste water reaction mixture, and a length extending between the inlet end and the outlet end. The first reaction mixture passes through at least a  
10 portion of the length of the tubular reaction zone and into a mixed flow reaction zone that is defined by mixed flow reactor means. A ferrous salt and a pH regulating composition are mixed with the first reaction mixture either within the tubular reaction zone or within the mixed flow reaction zone or a combination thereof to form a second reaction mixture with the first reaction mixture, the ferrous salt and the pH regulating composition. The second  
15 reaction mixture passes from the mixed flow reaction zone into a separation zone defined by separator means for separating the second reaction mixture into a water product, having a reduced selenium concentration that is less than the selenium concentration of the waste water stream, and an iron precipitate sludge product.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

20 FIG. 1 is a schematic diagram illustrating an embodiment of the inventive process for removing selenium from a waste water stream having a concentration of selenium. The process system includes a tubular reactor that discharges a reaction mixture into a settler that provides for separating the discharged reaction mixture into a treated water product and an iron precipitate sludge product.

25 FIG. 2 is a schematic diagram illustrating another embodiment of the inventive process for removing selenium from a waste water stream having a concentration of selenium. The process system includes a tubular reactor that is connected in flow communication with a mixed flow reactor that discharges its reaction mixture into a settler that provides for separating the mixed flow reactor discharge into a treated water product  
30 and an iron precipitate sludge product.

FIG. 3 includes two plots showing the percentage selenium removal from selenium-contaminated water by the inventive two-step iron addition process and by a single-step

iron co-addition process for removing selenium from water as a function of reaction time after addition of the ferric and ferrous iron.

FIG. 4 is a photograph of three graduated cylinders containing settled effluents yielded from the various iron addition processes used for removing selenium from selenium-containing water. Cylinders 1-2 include settled effluents from the two-step iron addition processes, and cylinder 3 includes settled effluent from the single-step iron co-addition process. The discoloration of the water layer in cylinder 3 is suspended iron that has failed to settle out from the water. The water layers of cylinders 1-2 are clear indicating essentially no suspended iron.

#### **DETAILED DESCRIPTION OF THE INVENTION**

Waste water streams produced during the refining of crude oil may be introduced into the environment after conventional treatment to remove contaminants provided that the amount of selenium present in the treated waste water streams is non-existent or so small that it is of no consequence. Yet, in areas where substantial concentrations of selenium are naturally present during the refining of crude oils, waste water streams produced from these areas may present a problem when selenium concentrations exceed environmental standards. As a result, selenium-removal treatments should be performed to reduce the selenium concentration to acceptable standards prior to introducing the streams into natural water bodies.

One method that has been used to remove selenium from water streams having contaminating concentrations of selenium is the ferrihydrite co-precipitation process that is also referred to as the iron co-precipitation process. In this method, a ferric salt, e.g., ferric chloride,  $\text{FeCl}_3$ , is added to the water at proper pH and temperature conditions to form a ferric hydroxide and a ferrihydrite precipitate. Selenite oxyanions contained in the water are concurrently adsorbed onto the precipitate. The selenium is then removed from the water along with the removal of the precipitate. While this process can provide for the removal of a large portion of selenium that may be contained in a water stream, it is not able to alone provide treated water that meets the more stringent regulations requiring selenium concentration levels of less than 10 ppbw or even less than 5 ppbw in treated water.

One reason the iron co-precipitation process is unable to provide treated water having the low selenium concentration is that the iron co-precipitation process is more selective in removing selenite ions than removing selenate ions. To achieve the required

low selenium concentration in the treated water, however, it may also be necessary to remove selenate from the waste water.

Another co-precipitation process is, as discussed above, disclosed in US 9,963,360. This selenate co-precipitation process involves precipitation of selenate by a single step of contacting a water solution containing selenate with ferrous iron or a ferrous/ferric iron mixture in a single mixing chamber. The mixing chamber may be an electrolytic cell equipped with an iron anode which acts as a source of the ferrous or ferrous/ferric iron. The '360 patent supplies little detail about the mixing chamber and electrolytic cell of its process. One problem with its single-step selenate co-precipitation process is its potentially complex operation. The process is inefficient in its selenium removal especially when it requires recycling of its precipitated selenium and iron.

The inventive process provides for the efficient, low-cost removal of selenium from waste water streams having significantly high concentrations of selenium compounds, including concentrations of the selenium oxyanions of selenite ( $\text{SeO}_3^{2-}$ ) and selenate ( $\text{SeO}_4^{2-}$ ). As used herein, the term "selenium" refers to all forms of selenium, including selenium compounds, selenate and selenite anions, and elemental selenium. It is understood also that the weight concentrations and ranges (e.g. ppbw) reported in this specification for the selenium compounds, including the selenium oxyanions selenite and selenate, are based on the weight of the selenium metal component of the indicated selenium compound or selenium oxyanion as opposed to the weight of the indicated compound or oxyanion.

The inventive process provides for the removal of both selenite and selenate from the waste water to yield treated water having a significantly reduced selenium concentration that is less than the selenium concentration of the waste water. This process can even remove the selenium oxyanions from the waste water to provide treated water having concentrations of the selenium oxyanions of less than 50 ppbw, preferably less than 25 ppbw, and more preferably, less than 10 ppbw.

The inventive process is potentially applicable to any discharge water stream containing selenium, including effluents, process waste waters, aqueous solutions, and the like, generated during oil and gas operations and other industry operations. In crude processing, often a waste water stream is stripped from the crude oil where non-volatile selenium compounds within the waste water stream are converted to selenocyanate ( $\text{SeCN}^-$ ) and selenium hydride ( $\text{SeH}_2$ ). These compounds may be present in the waste water stream at a concentration in the range of from 700-5000 ppbw. The  $\text{SeCN}^-$  and  $\text{SeH}_2$  compounds

of the waste water stream are then typically reduced to selenate ( $\text{SeO}_4^{2-}$ ) and selenite ( $\text{SeO}_3^{2-}$ ) compounds that require removal by a waste water treatment facility.

The total selenium concentration in the waste water stream can be in the range of from 20 ppbw up to 5,000 ppbw. More typically, the total selenium concentration of the waste water stream is at least 50 ppbw and less than 1,000 ppbw. The selenite concentration in the waste water stream typically is at least 20 ppbw and less than 5,000 ppbw, but, more typically, the selenite concentration is in the range of from 30 to 2,000 parts per billion by weight (ppbw). The selenate concentration in the waste water stream typically is at least 20 ppbw and less than 5,000 ppbw, but, more typically, the selenate concentration is in the range of from 30 to 2,000 ppbw. The ratio of selenate to selenite varies between refineries and within different treatment facilities and different time of the same refinery depending on the operations, processes, and types of treatments.

The sources of the waste water can be found in coker effluent, extracted groundwater, boiler blowdown, cooling tower blowdown, storm water, wash water, process water wash streams, and any combination of these. Stripped sour water and desalter effluent are often the two most dominating waste water sources that contain elevated selenium levels. One or more of the source streams may originate from various production areas and can be collected from and contained within storage tanks, containment ponds, or any other type of collection/containment system. The type of containment system used may depend on the number and volume of contaminated streams generated and the degree of treatment desired.

An important and necessary feature of the inventive process is the use of a tubular reactor in the introduction of the iron salt reactants into the waste water stream for reaction with and removal of the selenium that is contained in the waste water stream. It is the rapid, first order reaction rate of the selenium oxyanions with the iron reactants of the process that allows for economic use of the tubular reactor. One advantage provided by the tubular reactor of the inventive process is its lower capital and operating costs compared to alternative reactor systems. The tubular reactor of the process also provides for an exceptionally high selenium conversion, and it allows for staged reactions of the selenite and selenate contaminant concentrations of a waste water feed stream with the iron reactants within a single length of a single reactor.

The tubular reactor of the process defines a tubular reaction zone having a geometry and a structure that when used under the conditions of the inventive process

promote turbulent fluid flow within the tubular reaction zone. This turbulent fluid flow is important to the process, because it provides for practical, cost-effective approach to theoretical plug flow within the tubular reaction zone. The onset of the turbulent flow correlates with a dimensionless number called the Reynolds number.

5 For the inventive process, flow rate of the waste water feed stream into and through the tubular reactor in combination with the cross-sectional geometry of the tubular reaction zone of the tubular reactor are preferably such that the calculated Reynolds number is greater than about 4,000. This is thought to be the point at which the waste water flow through the tubular reaction zone begins to be turbulent.

10 The references herein to the geometry and structure of the process system consider two of the factors that determine the turbulence of the waste water flow through the tubular reaction zone of the tubular reactor. These are the Reynolds number factors of the axial flow velocity of the waste water feed stream within the tubular reaction zone and the hydraulic diameter of the tubular reaction zone of the tubular reactor. The axial flow  
15 velocity of the waste water feed stream is defined as the volumetric flow rate of the waste water feed into the tubular reaction zone divided by cross sectional area of the tubular reaction zone. The hydraulic diameter is defined as the product of four multiplied by the quotient of the cross-sectional area of the tubular reaction zone divided by the wetted perimeter of the tubular reaction zone.

20 Other structural features that may be incorporated into the tubular reactor of the process to promote and provide means for promoting turbulent fluid flow within the tubular reaction zone include static mixers, baffles for directing the fluid flow within the tubular reaction zone, projections extending from the inside surfaces of the tubular reactor, and imposed surface roughness or corrugations on the inside surfaces of the tubular  
25 reactor. It is preferred, however, for the tubular reactor zone to remain open to prevent possible plugging that may result from the inclusion therein of any one or more of the various turbulence promoting means.

The tubular reactor of the process can thus have any suitable geometry that provides for the turbulent flow of the waste water stream that is introduced into the tubular  
30 reaction zone. Examples of such geometries of the cross-section of the tubular reaction zone include circles, regular and irregular polygons, such as triangles, rectangles, squares and other multisided geometries, and non-circular curved shapes, such as ovals.

The tubular reactor can also be made of any suitable material such as concrete conduits, steel pipe and conduits, PVC pipe and conduits, or any other material that can suitably provide for a tubular reactor.

The tubular reactor has an inlet end for receiving the introduction of the waste water feed stream into the tubular reaction zone and an outlet end for discharging a waste water reaction mixture from the tubular reaction zone. The tubular reaction zone also has a length that extends between the inlet end and the outlet end of the tubular reactor. The length and cross-sectional area of the tubular reaction zone together define a total volume for the tubular reaction zone of the tubular reactor.

The process of the invention includes at least two mixing steps for mixing the iron reactants of the process with the waste water stream. These mixing steps occur at different locations within and along the length of the tubular reaction zone of the tubular reactor. The first mixing step includes introducing the waste water stream and a ferric salt, such as ferric chloride ( $\text{FeCl}_3$ ), into the tubular reaction zone and passing a first reaction mixture, comprising the waste water feed stream and ferric salt, through at least a portion of the length of the tubular reaction zone.

The waste water stream is typically delivered from a containment system and mixed with a ferric salt before or along with its introduction into the tubular reaction zone, or the ferric salt is separately introduced into the tubular reaction zone where it is mixed with the waste water stream at a location near the inlet end of the tubular reactor. The ferric salt is preferably introduced into the waste water in the form of an aqueous iron solution.

This first reaction mixture passes downstream from the inlet end through at least a first portion or first section of the length of the tubular reaction zone at which point or location a ferrous salt, such as ferrous chloride ( $\text{FeCl}_2$ ), is introduced into the tubular reaction zone and mixed with the first reaction mixture.

The second mixing step further includes introducing a pH regulating composition into the tubular reaction zone at any one or more locations downstream from the first mixing step. The pH regulating composition may be introduced into the tubular reaction zone concurrently with the ferrous salt introduction. Alternatively, the pH regulating composition may be introduced into the tubular reaction zone at one or more other locations before or after the ferrous salt introduction. Within the tubular reaction zone, the ferrous salt and the pH regulating composition are mixed with the first reaction mixture to form a second reaction mixture.

The second reaction mixture that comprises the first reaction mixture, the ferrous salt and the pH regulating composition passes downstream through a second portion or second section of the length of the tubular reaction zone and is discharged as a waste water reaction mixture from the tubular reaction zone into either a separator or a continuous mixed flow reactor.

It is preferred for the ferric salt that is introduced into the tubular reaction zone to be in the form of an aqueous ferric solution that mixes with the waste water stream to form the first reaction mixture. The aqueous ferric solution includes dissolved soluble iron salt, ferric chloride ( $\text{FeCl}_3$ ), in water. The ferric chloride solution may also be prepared by dissolving commercially available ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) in the appropriate amount of water. Conditions within the tubular reaction zone are such that at least a portion of the ferric salt is converted to ferric hydroxide [ $\text{Fe}(\text{OH})_3$ ] or to ferrihydrite ( $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ ), or a combination of both compounds.

The aqueous ferric solution that is mixed with the waste water stream typically will have a molar concentration of ferric chloride in the range of from 0.5 millimoles per liter (mmol/L) to 50 mmol/L, preferably, from 1 to 30 mmol/L, and most preferably, from 1.5 to 20 mmol/L.

The amount of aqueous ferric solution introduced and mixed with the waste water stream in the first mixing step should be to provide a dosing ratio of ferric-to-selenite that is in the range of from about 1,000:1 to 10,000:1 moles of ferric-to-moles of selenite. It is preferred to apply in the first mixing step a ferric-to-selenite dosing ratio in the range of from 1,000:1 to 4,000:1 moles of ferric-to-moles of selenite and, most preferred, from 1,000:1 to 3,500:1 moles of ferric-to-moles of selenite to reduce the selenite concentration in the waste water stream.

The volumetric flow rate of the waste water feed and ferric salt introduced into the tubular reaction zone, the cross-sectional geometry of the tubular reaction zone, and the length of the tubular reaction zone through which this first reaction mixture passes should be such to provide a desired residence time for the first reaction mixture in the tubular reaction zone. The desired residence time is the time-period of the passage of the first reaction mixture through the tubular reaction zone before the first reaction mixture is mixed with either the ferrous salt or pH regulating composition, or both.

This residence time should allow for conversion and removal of a major fraction of the selenite concentration from the waste water stream before introducing the ferrous salt

into the tubular reaction zone. The selenite has been found to rapidly react with ferric chloride, and it is believed that this reaction may be modeled as a first order reaction. Therefore, the first mixture, comprising the waste water feed and ferric salt, requires only a short residence time for its passage through the tubular reaction zone to provide at least a significant conversion of the selenite anions contained in the waste water.

An important feature of the inventive process is for the residence time of the first mixture within the tubular reaction zone, before the introduction of the ferrous salt and the pH regulating composition in the second mixing step, to be long enough to provide for conversion of at least about 70 % of the selenite contained in the waste water feed.

Preferably, at least 80 %, and, more preferably, at least 90 % of the selenite is converted before the second mixing step. This residence time, however, should not be significantly longer than is necessary to provide essentially complete (*i.e.*, at least 99 %) conversion or near complete (*i.e.*, at least 99.5 %) conversion or complete (*i.e.*, at least 99.9%) conversion of the selenite before the second mixing step that includes introducing the ferrous salt and pH regulating composition into the tubular reaction zone. This is to minimize the required length of the tubular reactor and to minimize any underutilized or unused portion of the tubular reactor.

The residence time required for providing the necessary selenite conversion is at least 5 seconds, but the system may be constrained by hydraulic and other factors resulting in a longer residence time than is required to provide the desired selenite conversion. The practical upper limit for the residence time is less than 2 hours. The preferred residence time is in the range of from 5 seconds to one hour. A more preferred residence time is in the range of from 10 seconds to 5 minutes.

A desirable feature of the process is to maintain an acidic pH the first reaction mixture within the tubular reaction zone below to minimize or prevent any significant amount of iron precipitate formation in the first reaction mixture. Iron precipitate tends to form when the first reaction mixture has an elevated pH that is basic and typically that is greater than 8. So, the first pH of the first reaction mixture within the tubular reaction zone should be controlled or maintained below a pH of about 7.5 to avoid formation of iron precipitate. To achieve the best results, the pH of the first reaction mixture is kept below 7, such as, within the range of from 1 to 7. It is preferred to maintain the pH of the first reaction mixture within the range of from 1.5 to 6.5, and, most preferably, from 1.5 to 6.

Typical operation of the process requires little need to control of the pH of the first reaction mixture because of the acidity of the ferric chloride added to the waste water stream. The first reaction mixture normally will have a first pH of less than 7. If required, however, a suitable pH-regulating solution such as hydrogen chloride (HCl), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), or another similar acidic solution may be used to lower the pH to prevent iron precipitate formation.

In the second iron addition or mixing step, a ferrous salt, preferably in the form of an aqueous ferrous solution stored, for example in a feed tank, is introduced into the tubular reaction zone. The introduced ferrous salt and an introduced pH regulating composition are mixed with the first reaction mixture within the tubular reaction zone to form the second reaction mixture, comprising the first reaction mixture, a ferrous salt, and a pH regulating composition.

It is theorized that dissolved ferric hydroxide and ferrihydrite of the first reaction mixture reacts with the ferrous salt of the second mixing step to form a green rust reaction product. The green rust comprises crystalline compounds of iron (II) and iron (III) cations, the hydroxide anion and another anion such as sulfate, if sulfates are present in the waste water, or selenate or selenite. It is also thought that the green rust contributes to the reduction of selenate in the first reaction mixture to selenite that is then adsorbed onto the green rust precipitate that is formed within the tubular reaction zone of the second step of the process. Non-limiting examples of chemical formulas for several varieties of the green rust may be represented as follows:

Carbonate Green Rust  $[\text{Fe}_4^{2+}\text{Fe}_3^{3+}(\text{HO}^-)_{12}]^{2+} \cdot [\text{CO}_3^{2-} \cdot 2\text{H}_2\text{O}]^{2-}$

Chloride Green Rust:  $[\text{Fe}_3^{2+}\text{Fe}_3^{3+}(\text{HO}^-)_8]^+ \cdot [\text{Cl}^- \cdot n\text{H}_2\text{O}]^-$

Sulfate Green Rust:  $[\text{Fe}_4^{2+}\text{Fe}_3^{3+}(\text{HO}^-)_{12}]^{2+} \cdot [\text{SO}_4^{2-} \cdot 2\text{H}_2\text{O}]^{2-}$

Selenate Green Rust:  $[\text{Fe}_4^{2+}\text{Fe}_3^{3+}(\text{HO}^-)_{12}]^{2+} \cdot [\text{SeO}_4^{2-} \cdot 2\text{H}_2\text{O}]^{2-}$

Mixing of the aqueous ferrous chloride solution with the first reaction mixture therefore results in formation of the reaction products described above. The ferrous-ferric hydroxide formed within the tubular reaction zone acts as an active reducing agent to reduce selenate to selenite and to insoluble elemental selenium. Mixing of the aqueous ferrous solution with the first reaction mixture from the first stage of the process reduces its

selenate concentration and further reduces remaining selenite concentration to form a second reaction mixture.

The second stage introduction of the pH regulating composition into the first reaction mixture is a significant aspect of the operation of the inventive process. Providing  
5 for a second reaction mixture pH to within a specific range is important to the formation of the iron precipitate sludge and in the removal of selenium from the waste water stream. The pH regulating composition is introduced into the tubular reaction zone at a location along the length of the tubular reactor between its inlet end and outlet end. Preferably, introduction of the pH regulating composition into the tubular reaction zone is, as  
10 discussed above, at a second location along the tubular reactor length at which at least a significant fraction of the selenite in the waste water feed has been converted, such as at least about 70 %, or any of the other conversions noted above. This is to assure that the selenite reactions with the ferric salt are essentially complete, or near complete, or complete before the pH is raised to promote the precipitation of iron.

15 The pH of the second reaction mixture required to promote precipitation of iron sludge is in the basic range. Thus, to achieve the benefits of the inventive process, the pH of the second reaction mixture is raised to greater than 7 by the introduction of the pH regulating composition. More typically, the pH of the second reaction mixture is maintained within a range that is required to form ferrous-ferric hydroxide and elemental  
20 selenium within the second reaction mixture. Preferably, the pH of the second reaction mixture is controlled to within the range of from greater than 7 to 11. More preferably, the pH is controlled to within the range of from 7.5 to 10, and, most preferably, from 8 to 9.5.

The iron precipitate sludge comprises insoluble elemental selenium and ferrous-ferric hydroxide, both of which are later separated from the water component of the second  
25 reaction mixture. The formation of the iron precipitate sludge and its later separation provides for removal and reduction of at least 50% of the selenate anions contained in the first reaction mixture. The process, however, can remove at least 85%, and most preferably, it provides for removing at least 95% of the selenate anions contained in the first reaction mixture.

30 It is understood that references in this specification to “iron” are not necessarily directed to the elemental form of iron or to iron that is in an oxidation state of zero. Rather, the use of the term in most instances refers to a compound, or complex, or ion, or mixture of compounds having iron as a component rather than iron that is in the elemental form.

The references herein to iron precipitate or iron precipitate sludge or similar term are to the precipitate solids that are formed by the addition of ferric and ferrous salts to waste water containing at least the components selenium. The waste water may optionally contain one or more sulfate, chloride, or carbonate compounds that can react with the iron compounds or be absorbed upon the formed iron precipitates. The precipitate solids are thought to be a mixture of green rust compounds and further may have adsorbed thereon selenium. The precipitate may also include iron oxide and iron hydroxide.

A commercially available aqueous ferrous chloride solution may suitably be used in the process. Also, the ferrous chloride solution may also be prepared by dissolving a commercial  $\text{FeCl}_2$  salt, e.g.,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , in the appropriate amount of water to provide an aqueous ferrous chloride solution. The aqueous ferrous solution that is mixed with the first reaction mixture will have a molar concentration of ferrous chloride in the range of from 5 to about 50 mmol/L, but preferably, from 15 to 40 mmol/L.

The amount of aqueous ferrous solution mixed with the first reaction mixture should be such as to provide a dosing ratio of ferrous-to-selenate in the range from about 5,000:1 to about 140,000:1 moles of ferrous-to-moles of selenate to effectively reduce the selenate concentration in the first reaction mixture. It is preferred to apply in the second mixing step a ferrous-to-selenate dosing ratio in the range of from 10,000:1 to 27,500:1 moles of ferrous-to-moles of selenate, and, most preferred, from 15,000:1 to 26,500:1 moles of ferrous-to-moles of selenate to reduce the selenate concentration in the first reaction mixture.

The volumetric flow rate of the second mixture through the tubular reaction zone, the cross-sectional geometry of the tubular reaction zone, and the length of the tubular reaction zone should be such to provide a residence time sufficient for conversion and removal of a major fraction of the selenate concentration and selenium in the second reaction mixture. The rate of reaction of selenate with ferrous chloride is not as rapid as the reaction of selenite with ferric chloride. Therefore, a longer residence time within the tubular reaction zone for the second stage is required than for the first stage.

The residence time should be long enough to provide for conversion of at least about 70 % of the selenate contained in the second reaction mixture. Preferably, at least 80 %, and, more preferably, at least 90 % of the selenate is converted within the tubular reaction zone before discharging the waste water reaction mixture.

The residence time of the second reaction mixture in the tubular reactor should be to provide essentially complete (*i.e.*, at least 99 %) conversion or near complete (*i.e.*, at least 99.5 %) conversion or complete (*i.e.*, at least 99.9%) conversion of the selenate before discharging the second reaction mixture from the tubular reaction zone. This is to minimize the required length of the tubular reactor and to minimize the length of any underutilized or unused portion of the tubular reactor.

The residence time required for providing the necessary selenate conversion in the second stage is at least 5 minutes. The residence time in the second stage should be no more than 2 hours. The preferred residence time is in the range of from 5 minutes to one hour. A more preferred residence time is in the range of from 5 minutes to 45 minutes.

In the preferred embodiment of the process, the second reaction mixture flows from the tubular reaction zone into a separating zone. The separating zone is defined by any suitable means for separating a waste water reaction mixture such as the second reaction mixture to yield a water product stream, having a reduced selenium concentration that is less than the selenium concentration of the waste water stream, and an iron precipitate sludge product. Suitable separating means are those capable of providing for solids-liquid separation of the second reaction mixture to provide the water product stream and the iron precipitate sludge product. Examples of separating means include clarifiers such as sedimentation tanks of any suitable configuration providing for gravity separation of the iron precipitate sludge from the water component of the second reaction mixture, filter separation systems, including filter presses, and centrifugal separation systems. It is preferred for the separation step of the process to be conducted within the separating zone defined by a clarifier.

For settlers and clarifiers, the volumetric flow rate of the second reaction mixture through the separating zone should be such as to provide sufficient residence time for the iron precipitate sludge to settle for recovery as an iron precipitate sludge product. This residence time should exceed 0.5 hours. The preferred residence time is between 1 to 50 hours, or more preferably between 2 to 10 hours.

The iron precipitate sludge product comprises the iron precipitate sludge, including the formed ferrous-ferric hydroxide, which acts as an active reducing agent to reduce selenate to selenite. The iron precipitate sludge product may be transported off-site for disposal or may require additional treatment before it is suitable for final disposal.

The water product stream can include a reduced selenite concentration that is less than 5 ppbw, and, even less than 2 ppbw or 1 ppbw. The reduced selenate concentration in the water product stream is less than 10 ppbw, and, preferably, it is less than 5 ppbw. The water product stream can include a total selenium concentration of less than 10 ppbw, preferably less than 5 ppbw for both the individual selenate and selenite concentrations. The water product stream can be pumped into a second containment system where it is recycled for further use as a treated water stream in other operations or discharged into a natural water body.

In an alternative embodiment of the inventive process, the second reaction mixture can pass from the tubular reaction zone and is discharged into a mixing reaction zone of a continuous stirred or mixed flow reactor instead of directly into the separation zone of a separator. The reaction mixture of the mixed flow reactor passes from its mixing reaction zone and is introduced into the separation zone of separation means for separating the reaction mixture into the water product stream and the iron precipitate sludge product as described above. For this embodiment, the ferrous salt can be mixed with the first reaction mixture either by introducing the ferrous salt into the tubular reaction zone, or into the mixing reaction zone of the mixed flow reactor, or into a combination of the tubular reaction zone and the mixing reaction zone.

In yet another embodiment of the inventive process, the first reaction mixture passes from the tubular reaction zone and is introduced into a mixed flow reaction zone defined by mixed flow reactor means. The mixed flow reaction zone has baffles or other internal structures, or a combination thereof, that provide for locally decreased flow within the mixed flow reaction zone of iron precipitate particles contained in the first reaction mixture. This decrease in flow creates a local zone having a higher concentration of iron precipitate particles than in other locations within the mixed flow reaction zone. The baffles and other structures further provide for directing the flow of the first reaction mixture from zones within mixed flow reactor means of lower concentrations of iron precipitate particles through the local zone of higher concentration iron precipitate particles and then to separation means. This flow configuration provides for an improved reaction rate of the selenium that is contained in the first reaction mixture and improved effectiveness of the reaction within the mixed flow reaction zone.

Reference now is made to the figures. FIG. 1 is a schematic diagram illustrating process system 10 providing for an embodiment of the inventive process for removing

selenium from a water stream having a selenium concentration. The water stream may contain a total selenium concentration in the range of from 20 to 5,000 ppbw. The selenium can include a selenite anion concentration that can be in the range of from 20 to 5,000 ppbw and a selenate anion concentration that is in the range of from 20 to 5,000 ppbw. The water stream passes to the suction side of feed pump 12 through conduit 14 from any one of numerous sources (not shown) that may include a water collection and containment system or directly from an individual water source.

A ferric salt is introduced into the water stream by way of conduit 16 and is mixed with the water stream to provide a first reaction mixture that comprises the water stream and ferric salt. The amount of ferric salt introduced and mixed with the water stream provides for molar dosing ratio of ferric-to-selenite that is in the range of from 1,000:1 to 10,000:1 moles of ferric per moles of selenite.

The first reaction mixture passes through feed pump 12 that charges the first reaction mixture into tubular reaction zone 20 that is defined by tubular reactor 22. Feed pump 12 may also provide for mixing of the water stream and ferric salt in forming the first reaction mixture.

Tubular reactor 22 has inlet end 24 and outlet end 26 with tubular length 28 extending from inlet end 24 to outlet end 26. Discharge 30 of feed pump 12 is operatively connected to inlet end 24 of tubular reactor 22 and provides for the discharge and introduction of the first reaction mixture into tubular reaction zone 20. The ferric salt may alternatively be introduced into the water stream at the discharge 30 side of feed pump 12 near to inlet end 24 of tubular reaction zone 20.

The flow of the first reaction mixture through tubular reaction zone 20 is represented by wavy arrow 34. The volumetric flow rate of first reaction mixture 34 introduced into tubular reaction zone 20, the cross-sectional geometry of tubular reaction zone 20, and the portion of length 28 through which first reaction mixture 34 passes provide for a residence time of first reaction mixture 34 within tubular reaction zone 20 before introduction of either a ferrous salt or pH regulating solution, or both, into tubular reaction zone 20. This residence time is the time-period needed for allowing conversion and removal of a major fraction of the selenite concentration that is in the waste water feed or first reaction mixture. This residence time is at least 5 seconds and no more than about 2 hours.

The ferrous salt is introduced into first reaction mixture 34 of tubular reaction zone 20 through conduit 36 at a first location a distance 42 downstream from inlet end 24.

Distance 42 is at least a portion of length 28. This distance should be sufficient to provide the residence time needed for the required conversion of the selenite in the water feed. The  
5 ferrous salt is mixed with first reaction mixture 34 within tubular reaction zone 20.

A pH regulating composition is also mixed with first reaction mixture 34 by introducing it into tubular reaction zone 20 by way of conduit 40 at a location along length 28 of tubular reactor 22. The pH regulating composition is introduced into tubular reaction zone 20 at a second location between locations X and Y along tubular reactor 22. This  
10 second location should be a point along length 28 where at least a significant fraction of the selenite of the water feed has been converted.

The amount of ferrous salt introduced by way of conduit 36 into tubular reaction zone 20 and mixed with first reaction mixture 34 provides for molar dosing ratio of ferrous-to-selenate to effectively reduce the selenate concentration in first reaction mixture  
15 34 by at least 50%. This dosing ratio should be in the range of from about 5,000:1 to about 140,000:1 moles of ferrous-to-moles of selenate.

The second reaction mixture comprises first reaction mixture 34 and the ferrous salt introduced through conduit 36, and, once introduced, the pH regulating composition introduced by way of conduit 40 into and mixed with first reaction mixture 34 at a location  
20 XY along length 28 of tubular reactor 22 between locations X and Y into tubular reaction zone 20. The second reaction mixture passing through tubular reaction zone 20 is represented by dashed arrow 44.

The amount of pH regulating composition introduced by way of conduit 40 into tubular reaction zone 20 and mixed with first reaction mixture 34 raises the pH of second  
25 reaction mixture 44 to a pH that promotes the precipitation of green rust or iron sludge within second reaction mixture 44. This pH is greater than 7.

The volumetric flow rate of second reaction mixture 44, the cross-section geometry of tubular reaction zone 20, and second portion 48 of length 28 through which second reaction mixture 44 passes provide for the required residence time of second reaction  
30 mixture 44 for the conversion and removal of the selenate and selenium from the water of second reaction mixture before its discharge into separation zone 50 defined by separator 52.

Separator 52 provides means for separating the second reaction mixture to yield a water product 54 and an iron precipitate sludge product 56. Separator 52 can include any conventional device, including gravity sedimentation, mechanical pressing, or filtration devices, to separate the second reaction mixture.

5       The iron precipitate sludge product comprises the ferrous-ferric hydroxide and insoluble elemental selenium precipitates and possible other contaminants removed by process 10 from the waste water stream. The iron precipitate sludge product passes from separation zone 50 via line 58 for transportation to off-site disposal or for additional treatment before its final disposal.

10       The water product has a significantly reduced selenium concentration compared to the selenium concentration of the waste water stream that is treated by process 10. This treated water product passes from separation zone 50 via line 60 for flow into a containment pond, or discharge into a natural water body, or recycle as treated water for use in additional plant operations. The water product has a total selenium concentration of  
15       less than 10 ppbw, and, preferably, less than 5 ppbw, which may comply with environmental standards that place restrictions on the total selenium concentration within a discharge water. Process 10 can treat waste water having high concentrations of both selenium and sulfates and still obtain a treated water product having exceptionally low selenium content. The treated waste water may also be further treated to remove any  
20       quantities of organic selenium that have not been removed by the iron addition process. This may be done by the application of any of the known adsorption or other process for removing organic selenium from water.

FIG. 2 is a schematic diagram illustrating process system 200 providing for an embodiment of the inventive process for removing selenium from a water stream having a  
25       selenium concentration. In this process the water stream passes to the suction side of feed pump 212 through conduit 214 from any one of numerous sources (not shown) that may include a water collection and containment system or directly from an individual water source.

30       A ferric salt is introduced into the water stream by way of conduit 216 and is mixed with the water stream to provide a first reaction mixture that comprises the water stream and ferric salt. The amount of ferric salt introduced and mixed with the water stream provides for molar dosing ratio of ferric-to-selenite that is in the range of from 1,000:1 to 10,000:1 moles of ferric per moles of selenite.

The first reaction mixture passes through feed pump 212 that charges the first reaction mixture into tubular reaction zone 218 that is defined by tubular reactor 220. Feed pump 212 may also provide for mixing of the water stream and ferric salt in forming the first reaction mixture.

5           Tubular reactor 220 has inlet end 224 and outlet end 226 with tubular length 228 extending from inlet end 224 to outlet end 226. Discharge 230 of feed pump 212 is operatively connected to inlet end 224 of tubular reactor 220 and provides for the discharge and introduction of the first reaction mixture into tubular reaction zone 218. The ferric salt may alternatively be introduced into the water stream at the discharge 230 side of feed  
10       pump 212 near to inlet end 224 of tubular reaction zone 218.

The flow of the first reaction mixture through tubular reaction zone 218 is represented by wavy arrow 234. The volumetric flow rate of first reaction mixture 234 introduced into tubular reaction zone 218, the cross-sectional geometry of tubular reaction zone 218, and the portion of length 228 through which first reaction mixture 234 passes  
15       provide for a residence time of first reaction mixture 234 within tubular reaction zone 218 before introduction of either a ferrous salt or pH regulating solution, or both, into tubular reaction zone 218. This residence time is the time-period needed for allowing conversion and removal of a major fraction of the selenite concentration that is in the waste water feed or first reaction mixture. This residence time is at least 5 seconds and no more than about 2  
20       hours.

The ferrous salt is introduced into first reaction mixture 234 of tubular reaction zone 218 through conduit 236 at a first location a distance 242 downstream from inlet end 224. Distance 242 is at least a portion of length 228. This distance should be sufficient to provide the residence time needed for the required conversion of the selenite in the water  
25       feed. The ferrous salt is mixed with first reaction mixture 234 within tubular reaction zone 218.

A pH regulating composition is also mixed with first reaction mixture 234 by introducing it into tubular reaction zone 218 by way of conduit 240 at a location along length 228 of tubular reactor 220. The pH regulating composition is introduced into tubular  
30       reaction zone 218 at a second location XY between locations X and Y along tubular reactor 220. Second location XY should be a point along length 228 where at least a significant fraction of the selenite of the water feed has been converted.

The amount of ferrous salt introduced by way of conduit 236 into tubular reaction zone 218 and mixed with first reaction mixture 234 preferably provides for molar dosing ratio of ferrous-to-selenate to effectively reduce the selenate concentration in first reaction mixture 234 by at least 50%. This dosing ratio should be in the range of from about 5,000:1 to about 28,000:1 moles of ferrous-to-moles of selenate.

The second reaction mixture comprises first reaction mixture 234 and the ferrous salt introduced through conduit 236, and, once introduced, the pH regulating composition introduced by way of conduit 240 into and mixed with first reaction mixture 234 at a location along length 228 of tubular reactor 220 between locations X and Y into tubular reaction zone 218. The second reaction mixture passing through tubular reaction zone 218 is represented by dashed arrow 244.

The amount of pH regulating composition introduced by way of conduit 240 into tubular reaction zone 218 and mixed with first reaction mixture 234 raises the pH of second reaction mixture 244 to a pH that promotes the precipitation of green rust or iron sludge within second reaction mixture 244. This pH is greater than 7.

Second reaction mixture 244 passes from tubular reaction zone 218 and discharges into mixing zone 270. Mixing zone 270 is defined by mixing means 272 that provides for continuous stirred mixing and reaction of the ferrous salt with the selenate and selenium of second reaction mixture 244.

The combined residence time of the second reaction mixture within tubular reaction zone 218 and mixing zone 270 should be sufficient to allow for the continuous formation of the green rust reaction products or iron precipitate sludge and conversion of a major fraction of the selenate and selenium of second reaction mixture 244. The residence time of the second reaction mixture in mixing zone 270 should be sufficient to allow for the continued formation of the ferric-ferrous hydroxide to yield the iron precipitate sludge. This second reaction mixture then passes from mixing zone 270 by way of line 274 and is introduced into separation zone 250 defined by separator 252.

Separator 252 provides means for separating the second reaction mixture to yield a water product 254 and an iron precipitate sludge product 256. Separator 252 can include any conventional device, including gravity sedimentation, mechanical pressing, or filtration devices, to separate the second reaction mixture.

The iron precipitate sludge product comprises the ferrous-ferric hydroxide and insoluble elemental selenium precipitates and possible other contaminants removed by

process 200 from the waste water stream. The iron precipitate sludge product passes from separation zone 250 via line 258 for transportation to off-site disposal or for additional treatment before its final disposal.

The water product has a significantly reduced selenium concentration compared to the selenium concentration of the waste water stream that is treated by process 200. This treated water product passes from separation zone 250 via line 260 for flow into a containment pond, or discharge into a natural water body, or recycle as treated water for use in additional plant operations. The water product has a total selenium concentration of less than 10 ppbw, and, preferably, less than 5 ppbw, which may comply with environmental standards that place restrictions on the total selenium concentration within a discharge water. Process 200 can treat waste water having high concentrations of both selenium and sulfates and still obtain a treated water product having exceptionally low selenium content.

The treated waste water may also be further treated to remove any quantities of organic selenium that have not been removed by the iron addition process. This may be done by the application of any of the known adsorption or other process for removing organic selenium from water.

In another embodiment of the inventive process, instead of introducing the ferrous salt directly into tubular reaction zone 218 through conduit 236 and the pH regulating composition into tubular reaction zone 218 through conduit 240, the ferrous salt is introduced into mixing zone 270 through conduit 276 and the pH regulating composition is introduced into mixing zone 270 through conduit 278. Mixing means 272 provides for mixing the ferrous salt, first reaction mixture 234 and the pH regulating composition to provide second reaction mixture that passes downstream through conduit 274 and is introduced into separation zone 250 of separator 252.

The following examples are provided to illustrate certain features of the inventive process, but they should not be interpreted as limiting the scope of the invention.

### **EXAMPLE 1**

This Example illustrates the unexpectedly greater selenium removal from a selenium-contaminated water stream provided by the inventive two-step iron addition

process when compared to the selenium removal provided by a single-step ferric iron addition process.

In the comparison single-step ferric iron addition process a 5-liter vessel was filled with simulated waste water having a selenium concentration of 180 ppbw that included 90 ppbw selenite and 90 ppbw selenate. The simulated waste water also includes 260 ppmw sulfate, 250 ppmw carbonate, and 40 ppmw nitrate. These are ions that are typically found in waste water. A single application of a known amount of ferric chloride ( $\text{FeCl}_3$ ) required to provide an  $\text{Fe(III)}$  concentration of 2 mmol/liter in the water was added with stirring. Samples of the water-ferric chloride mixture were taken at different time intervals and analyzed for their selenium content.

The batch reaction simulated a plug flow reactor scheme with the selenium concentration of the water versus time in the batch reactor being representative of the selenium concentration of the water versus reactor length in a plug flow reactor.

The following Table 1 presents the results of this experiment.

Table 1. Selenium Concentration Versus Time  
After the Ferric Chloride Addition to Water

| Sampling Time<br>After Ferric Iron<br>Addition to Water<br>(minutes) | Selenium<br>Concentration<br>of Sampled<br>Water<br>(ppbw) |
|----------------------------------------------------------------------|------------------------------------------------------------|
| 0                                                                    | 180                                                        |
| 0.167 (10 seconds)                                                   | 85                                                         |
| 0.75 (45 seconds)                                                    | 85                                                         |
| 6                                                                    | 86                                                         |
| 10                                                                   | 84                                                         |
| 20                                                                   | 86                                                         |
| 30                                                                   | 88                                                         |

As is seen from the data shown in Table 1, the essentially complete reaction of the selenium with the ferric chloride rapidly occurs within about 10 seconds, and, thereafter, essentially no further reaction occurs. The selenite component of the water reacts with the ferric chloride but very little of the selenate component reacts with the ferric chloride. So, a major portion of the selenite initially reacts with the ferric chloride in the very short time period with no further reaction of the selenate occurring afterward.

### Method 1

In an embodiment of the inventive two-step ferric-ferrous addition process, a 5-liter vessel was filled with 4 liters of simulated waste water having a selenium concentration of 180 ppbw that included 90 ppbw selenite and 90 ppbw selenate. The simulated waste water also includes 260 ppmw sulfate, 250 ppmw carbonate, and 40 ppmw nitrate. An amount of ferric chloride ( $\text{FeCl}_3$ ) to provide an Fe(III) concentration in the water of 2 mmol/liter was added with stirring. After the passage of a specified time-period, an amount of ferrous chloride ( $\text{FeCl}_2$ ) to provide an Fe(II) concentration of 22.8 mmol/liter was added with continued stirring to the water simultaneously with the addition of caustic to provide a solution pH of 8.5. Samples of the water/ferric chloride/ferrous chloride/caustic mixture were taken at different time intervals and analyzed for their selenium content.

The batch reaction simulated a plug flow reactor scheme. The selenium concentration of the water versus time in the batch reactor is representative of the selenium concentration of the water versus reactor length in a plug flow reactor. The time of the introduction of the iron and caustic compounds is representative of the location along the reactor length of a plug flow reactor at which these were introduced into the plug flow reactor zone.

The following Table 2 presents the results of this experiment.

Table 2. Selenium Concentration Versus Time  
After the Ferrous and Caustic Addition

| Sampling Time<br>After the Ferrous<br>Iron Addition to<br>Water<br>(minutes) | Selenium<br>Concentration<br>of Sampled<br>Water<br>(ppbw) |
|------------------------------------------------------------------------------|------------------------------------------------------------|
| 0                                                                            | 180                                                        |
| 0.167 (10 seconds)                                                           | 47                                                         |
| 1                                                                            | 44                                                         |
| 2                                                                            | 42                                                         |
| 10                                                                           | 31                                                         |
| 20                                                                           | 27                                                         |
| 30                                                                           | 26                                                         |

A comparison of the results from the two-step ferric/ferrous iron addition process with those of the single-step ferric iron addition process indicates that the two-step process provides for a significantly greater selenium removal. The addition of the ferrous chloride

to the water with pH control by the addition of caustic provides for removal of greater than 20 percent more selenium from the treatment waste water than that provided by the single addition of ferric chloride. This greater percentage of selenium removal occurs quickly after the addition of the ferrous chloride and the selenium conversion continuing for up to about 30 minutes. Incremental selenium removal levels off after about 30 minutes of reaction time.

## **EXAMPLE 2**

This Example presents descriptions of experiments representing various embodiments of the inventive two-step iron addition process and a single-step ferric/ferrous iron co-addition process. These processes both provide for selenium removal from a water stream having a contaminating concentration of selenium.

Also presented in this Example are comparisons of the selenium removal capabilities of various embodiments of the inventive two-step iron addition process and the single step iron co-addition process.

The sludge settling properties of the treated water resulting from the two-step iron addition processes and the single step iron co-addition process are also compared.

### **Method No. 2**

In this embodiment of the inventive two-step ferric-ferrous addition process, 4 liters of the simulated selenium-containing waste water was placed in a 5-liter vessel. An amount of ferric chloride ( $\text{FeCl}_3$ ) required to provide an Fe (III) concentration in the water of 2 mmol/liter was added with stirring. The pH of this mixture was about 2. After the passage of a specified time-period, an amount caustic was admixed with the mixture of water and ferric chloride to raise the pH of the mixture to 8.5. One minute after the addition of the caustic to the ferric-containing water, an amount of ferrous chloride ( $\text{FeCl}_2$ ) to provide an Fe (II) concentration of 22.8 mmol/liter was added with continued stirring to the water simultaneously with the addition of an amount of caustic to maintain a solution pH of 8.5. Samples of the water/ferric chloride/ferrous chloride/caustic mixture were taken at different time intervals after the addition of the ferrous chloride and analyzed for their selenium content.

### Method 3

This method applies a single step co-addition of ferric chloride, ferrous chloride and caustic to the simulated selenium-containing waste water. Four liters of the simulated selenium-containing waste water was placed in a 5-liter vessel. The ferric chloride, ferrous chloride, and caustic were simultaneously admixed at one time with the water. The amount of ferric chloride ( $\text{FeCl}_3$ ) mixed was that necessary to provide an Fe (III) concentration in the water of 2 mmol/liter. The amount of ferrous chloride ( $\text{FeCl}_2$ ) mixed was that necessary to provide an Fe (II) concentration in the water of 22.8 mmol/liter. The amount of caustic mixed with the water was that required to provide for a pH of 8.5 of the mixture of water, ferric chloride, and ferrous chloride. Samples of the water/ferric chloride/ferrous chloride/caustic mixture were taken at different time intervals after the addition of the ferric chloride, ferrous chloride and caustic.

Table 3. Selenium Concentration in Treated Water versus Time of Reaction After Addition of Ferrous Chloride in Two-Step Iron Addition Process and Single Step Iron Co-Addition Process

| Time After Ferrous Addition to Water (Minutes) | Method 2 ppbw Selenium (% Se Removal) | Method 3 ppbw Selenium (% Se Removal) |
|------------------------------------------------|---------------------------------------|---------------------------------------|
| 0 (Raw Water)                                  | 180                                   | 180                                   |
| 0.5                                            | 59 (67.2%)                            | 52 (71.1%)                            |
| 1                                              | 43 (76.1%)                            | 43 (76.1%)                            |
| 2                                              | 32 (82.2%)                            | 37 (79.4%)                            |
| 5                                              | 19 (89.4%)                            | 27 (85.0%)                            |
| 10                                             | 14 (92.2%)                            | 23 (87.2%)                            |
| 20                                             | 13 (92.8%)                            | 20 ((88.9%)                           |
| 30                                             | 11 (93.9%)*                           | 19 (89.4%)**                          |

\*% Se in Waste Water Remaining in Treated Water = 6.1%

\*\*% Se in Waste Water Remaining in Treated Water = 10.6%

FIG. 3 presents plots of the data shown in Table 3 for the Method 2 process (two-step iron addition) and for the Method 3 process (single-step iron co-addition). This figure helps illustrate the significant improvement in selenium removal from selenium-contaminated water that the two-step iron addition process provides over the selenium removal provided by the comparative single-step iron co-addition process.

While both processes provide almost the same selenium removal after about one minute of reaction time, the two-step process begins to provide significantly better selenium removal than the co-addition process after about two minutes of reaction time. After 10 minutes of reaction time the incremental selenium removal per unit of reaction time begins to level off and at about 30 minutes of reaction time there is little incremental improvement in selenium removal. At 30 minutes the two-step process removes at least 4.5% more selenium from the water than does the co-addition process. The single-step co-addition process, thus, leaves more than 73% of the selenium that is in the waste water in its treated water than the amount of selenium left in the treated water of the two-step process. The two-step iron addition process leaves only 6.1% of the waste water selenium in its treated water. However, on the other hand, the single-step co-addition process leaves a significantly higher amount of 10.6% of the waste water selenium in its treated water. The above percentage difference is calculated as follows:  $(10.6 - 6.1) * 100 / 6.1$ . These differences are significant considering the difficulty of removing such large percentage of selenium concentrations that are at low parts per billion concentration levels.

The settling properties of the water and sludge (effluent) yielded from each of the four methods presented above were studied. From this, it was found that the settling properties of the iron precipitate sludge of the effluent yielded from the single iron co-addition process do not provide good settling that allows for complete separation of the sludge from the water. On the other hand, the iron precipitate sludge of the effluent yielded from the two-step iron addition process has good settling properties and allows for complete separation of the sludge from the water.

A sample of the effluent from each of the experiments was placed in a graduated cylinder. This effluent sat for a long enough time to allow complete settling of the iron precipitate sludge, i.e., until no further settling occurred. FIG. 4 is a photograph of three cylinders showing the treated water after the settling of the sludge. One can see from the photographs that cylinders 1-2 containing treated water from the two-step iron addition process include much clearer water layers than the water layer in the third cylinder. The third cylinder water layer is discolored with unsettled precipitate. This indicates that the iron precipitate sludge produced in the two-step process has different and improved settling properties over those of the iron precipitate sludge produced by the co-addition process. The improved settling properties of sludge yielded in the two-step process allow better and easier water and sludge separation of the treated water product.

## THAT WHICH IS CLAIMED IS:

1. A process for removing selenium from a waste water stream, having a selenium concentration, wherein said process comprises:

introducing said waste water stream and a ferric salt into a tubular reaction zone of a tubular reactor to provide a first reaction mixture, wherein said tubular reactor has an inlet end for receiving said waste water stream, an outlet end for discharging a waste water reaction mixture, and a length extending between said inlet end and said outlet end;

passing said first reaction mixture through at least a portion of said length of said tubular reaction zone;

introducing a ferrous salt into said first reaction mixture within said tubular reaction zone at a first location along said length of said tubular reaction zone;

introducing a pH regulating composition into said tubular reaction zone either with the introduction of said ferrous salt or at a second location along said length of said tubular reaction zone and forming a second reaction mixture with said first reaction mixture, said ferrous salt and said pH regulating composition; and

passing from said tubular reaction zone said second reaction mixture into a separation zone defined by separation means for separating said second reaction mixture into a water product, having a reduced selenium concentration that is less than said selenium concentration, and an iron precipitate sludge product.

2. A process as recited in claim 1, wherein said selenium concentration includes a selenite concentration of selenite anions ( $\text{SeO}_3^{2-}$ ) exceeding 20 ppbw and a selenate concentration of selenate anions ( $\text{SeO}_4^{2-}$ ) exceeding 20 ppbw with a total selenium concentration in the range of from 100 ppbw to 5,000 ppbw.

3. A process as recited in claim 2, wherein said tubular reaction zone has a geometry and said waste water stream is introduced into said tubular reaction zone at a flow rate that provide for turbulent flow within said tubular reaction zone.

4. A process as recited in claim 3, wherein said ferric salt introduced into said tubular reaction zone is an amount that provides a molar ratio of said ferric salt-to-selenite contained in said waste water stream that is in the range of from 100:1 to 10,000:1 in said first reaction mixture.
5. A process as recited in claim 4, wherein said first location is at a first distance from said inlet end of said tubular reactor that is sufficient to provide a first residence time of said first reaction mixture within said tubular reaction zone that provides for a conversion of at least 70 % of said selenite anions in said waste water stream.
6. A process as recited in claim 5, wherein said ferrous salt introduced into said tubular reaction zone at said first location is an amount that provides a molar ratio of said ferrous salt-to-selenate contained in said first reaction mixture that is in the range of from 200:1 to 150,000:1.
7. A process as recited in claim 6, wherein said second location is between a second distance from said inlet end of said tubular reactor at which at least a portion of said selenite anions in said waste water stream are converted and the outlet end of said tubular reactor.
8. A process as recited in claim 7, wherein said pH regulating composition introduced into said tubular reaction zone at said second location provides for said second reaction mixture having a pH within a range that promotes the formation of iron precipitate within said second reaction mixture.
9. A process as recited in claim 8, wherein said pH regulating composition introduced into said tubular reaction zone at said second location provides for said second reaction mixture having a pH greater than 7.
10. A process as recited in claim 9, wherein said second reaction mixture has a second residence time within said tubular reaction zone that is sufficient to provide a conversion of at least 70 % of said selenate anions in said waste water stream.
11. A process as recited in claim 10, wherein said space time (tubular reactor volume/volumetric flow rate of said waste water stream) of said waste water stream in said

tubular reaction zone is sufficient to provide for a desired overall conversion of said selenium in said waste water stream.

12. A process as recited in claim 11, wherein said reduced selenium concentration is less than 10 ppbw.

13. A process for removing selenium from a waste water stream, having a selenium concentration, wherein said process comprises:

introducing said waste water stream and a ferric salt into a tubular reaction zone of a tubular reactor to provide a first reaction mixture, wherein said tubular reactor has an inlet end for receiving said waste water stream, an outlet end for discharging a waste water reaction mixture, and a length extending between said inlet end and said outlet end;

passing said first reaction mixture through at least a portion of said length of said tubular reaction zone;

introducing a ferrous salt into said first reaction mixture within said tubular reaction zone at a first location along said length of said tubular reaction zone;

introducing a pH regulating composition into said tubular reaction zone either with the introduction of said ferrous salt or at a second location along said length of said tubular reaction zone and forming a second reaction mixture with said first reaction mixture, said ferrous salt and said pH regulating composition;

passing from said tubular reaction zone said second reaction mixture into a mixing reaction zone defined by a mixed flow reactor; and

passing said second reaction mixture from said mixing reaction zone into a separation zone defined by separation means for separating said second reaction mixture into a water product, having a reduced selenium concentration that is less than said selenium concentration, and an iron precipitate sludge product.

14. A process as recited in claim 13, wherein said selenium concentration includes a selenite concentration of selenite anions ( $\text{SeO}_3^{2-}$ ) exceeding 20 ppbw and a selenate

concentration of selenate anions ( $\text{SeO}_4^{2-}$ ) exceeding 20 ppbw with a total selenium concentration in the range of from 100 ppbw to 5,000 ppbw.

15. A process as recited in claim 14, wherein said tubular reaction zone has a geometry and said waste water stream is introduced into said tubular reaction zone at a flow rate that provide for turbulent flow within said tubular reaction zone.

16. A process as recited in claim 15, wherein said ferric salt introduced into said tubular reaction zone is an amount that provides a molar ratio of said ferric salt-to-selenite contained in said waste water stream that is in the range of from 100:1 to 10,000:1 in said first reaction mixture.

17. A process as recited in claim 16, wherein said first location is at a first distance from said inlet end of said tubular reactor that is sufficient to provide a first residence time of said first reaction mixture within said tubular reaction zone that provides for a conversion of at least 70 % of said selenite anions in said waste water stream.

18. A process as recited in claim 17, wherein said ferrous salt introduced into said tubular reaction zone at said first location is an amount that provides a molar ratio of said ferrous salt-to-selenate contained in said first reaction mixture that is in the range of from 200:1 to 150,000:1.

19. A process as recited in claim 18, wherein said second location is between a second distance from said inlet end of said tubular reactor at which at least a portion of said selenite anions in said waste water stream are converted and the outlet end of said tubular reactor.

20. A process as recited in claim 19, wherein said pH regulating composition introduced into said tubular reaction zone at said second location provides for said second reaction mixture having a pH within a range that promotes the formation of iron precipitate within said second reaction mixture.

21. A process as recited in claim 20, wherein said pH regulating composition introduced into said tubular reaction zone at said second location provides for said second reaction mixture having a pH greater than 7.

22. A process as recited in claim 21, wherein said second reaction mixture has a second residence time within said tubular reaction zone that is sufficient to provide a conversion of at least 70 % of said selenate anions in said waste water stream.

23. A process as recited in claim 22, wherein said space time (tubular reactor volume/volumetric flow rate of said waste water stream) of said waste water stream in said tubular reaction zone is sufficient to provide for a desired overall conversion of said selenium in said waste water stream.

24. A process as recited in claim 23, wherein said reduced selenium concentration is less than 10 ppbw.

25. A process as recited in claim 24, wherein said mixing reaction zone provides for a residence time of said second reaction mixture of at least 15 minutes.

26. A process for removing selenium from a waste water stream, having a selenium concentration, wherein said process comprises:

introducing said waste water stream and a ferric salt into a tubular reaction zone of a tubular reactor to provide a first reaction mixture, wherein said tubular reactor has an inlet end for receiving said waste water stream, an outlet end for discharging a waste water reaction mixture, and a length extending between said inlet end and said outlet end;

passing said first reaction mixture through at least a portion of said length of said tubular reaction zone and into a mixed flow reaction zone defined by mixed flow reactor means;

mixing a ferrous salt and a pH regulating composition with said first reaction mixture either within said tubular reaction zone or within said mixed flow reaction zone or

a combination thereof and forming a second reaction mixture with said first reaction mixture, said ferrous salt and said pH regulating composition; and

passing said second reaction mixture from said mixed flow reaction zone into a separation zone defined by separator means for separating said second reaction mixture into a water product, having a reduced selenium concentration that is less than said selenium concentration, and an iron precipitate sludge product.

27. A process as recited in claim 26, wherein said selenium concentration includes a selenite concentration of selenite anions ( $\text{SeO}_3^{2-}$ ) exceeding 20 ppbw and a selenate concentration of selenate anions ( $\text{SeO}_4^{2-}$ ) exceeding 20 ppbw with a total selenium concentration in the range of from 100 ppbw to 5,000 ppbw.

28. A process as recited in claim 27, wherein said tubular reaction zone has a geometry and said waste water stream is introduced into said tubular reaction zone at a flow rate that provide for turbulent flow within said tubular reaction zone and to provide a first residence time of said first reaction mixture within said tubular reaction zone that provides for a conversion of at least 70 % of said selenite anions in said waste water stream.

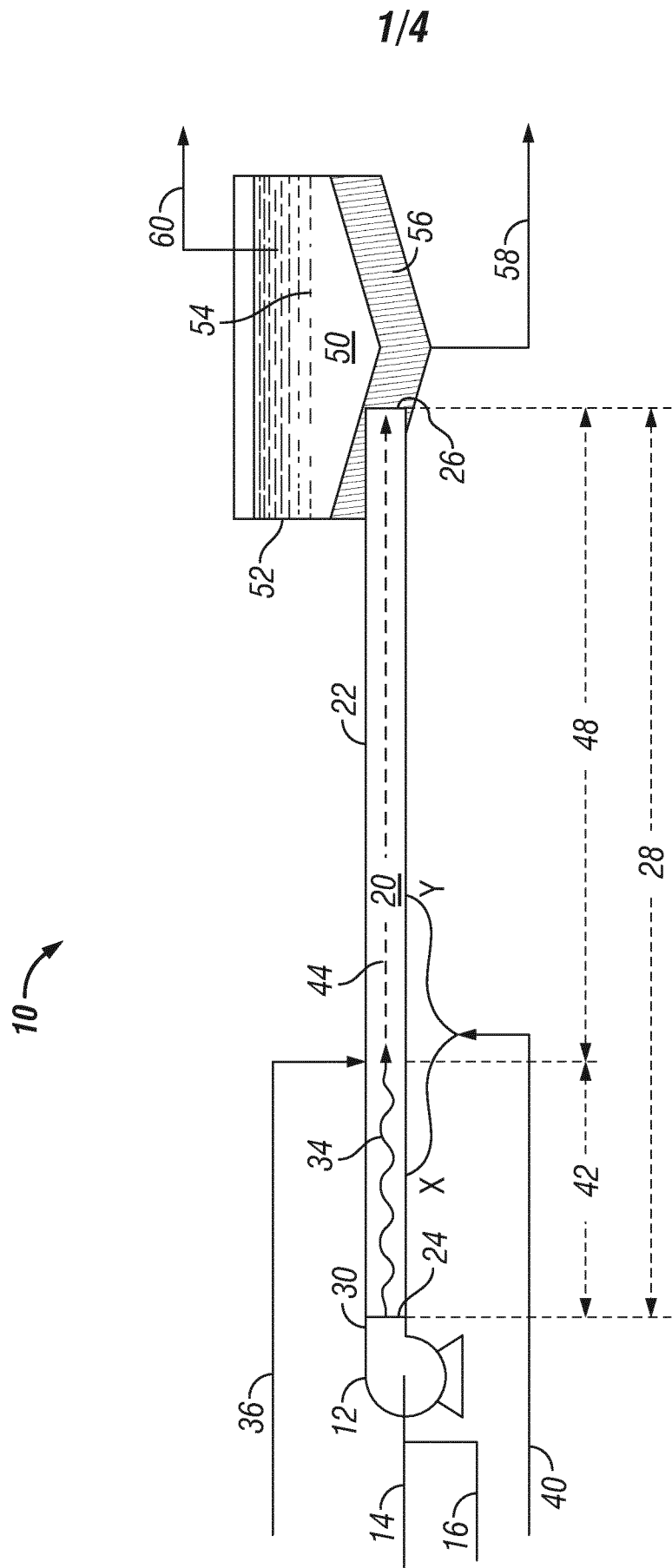
29. A process as recited in claim 28, wherein said ferric salt introduced into said tubular reaction zone is an amount that provides a molar ratio of said ferric salt-to-selenite contained in said waste water stream that is in the range of from 100:1 to 10,000:1 in said first reaction mixture.

30. A process as recited in claim 29, wherein said ferrous salt introduced into said mixed flow reaction zone provides a molar ratio of said ferrous salt-to-selenate contained in said first reaction mixture that is in the range of from 200:1 to 150,000:1.

31. A process as recited in claim 30, wherein said pH regulating composition introduced into said mixed flow reaction zone to provide for said second reaction mixture having a pH within a range that promotes the formation of iron precipitate within said second reaction mixture.

32. A process as recited in claim 31, wherein said pH regulating composition introduced into said mixed flow reaction zone to provide for said second reaction mixture having a pH greater than 7.

33. A process as recited in claim 32, wherein said reduced selenium concentration is less than 10 ppbw.



**2/4**

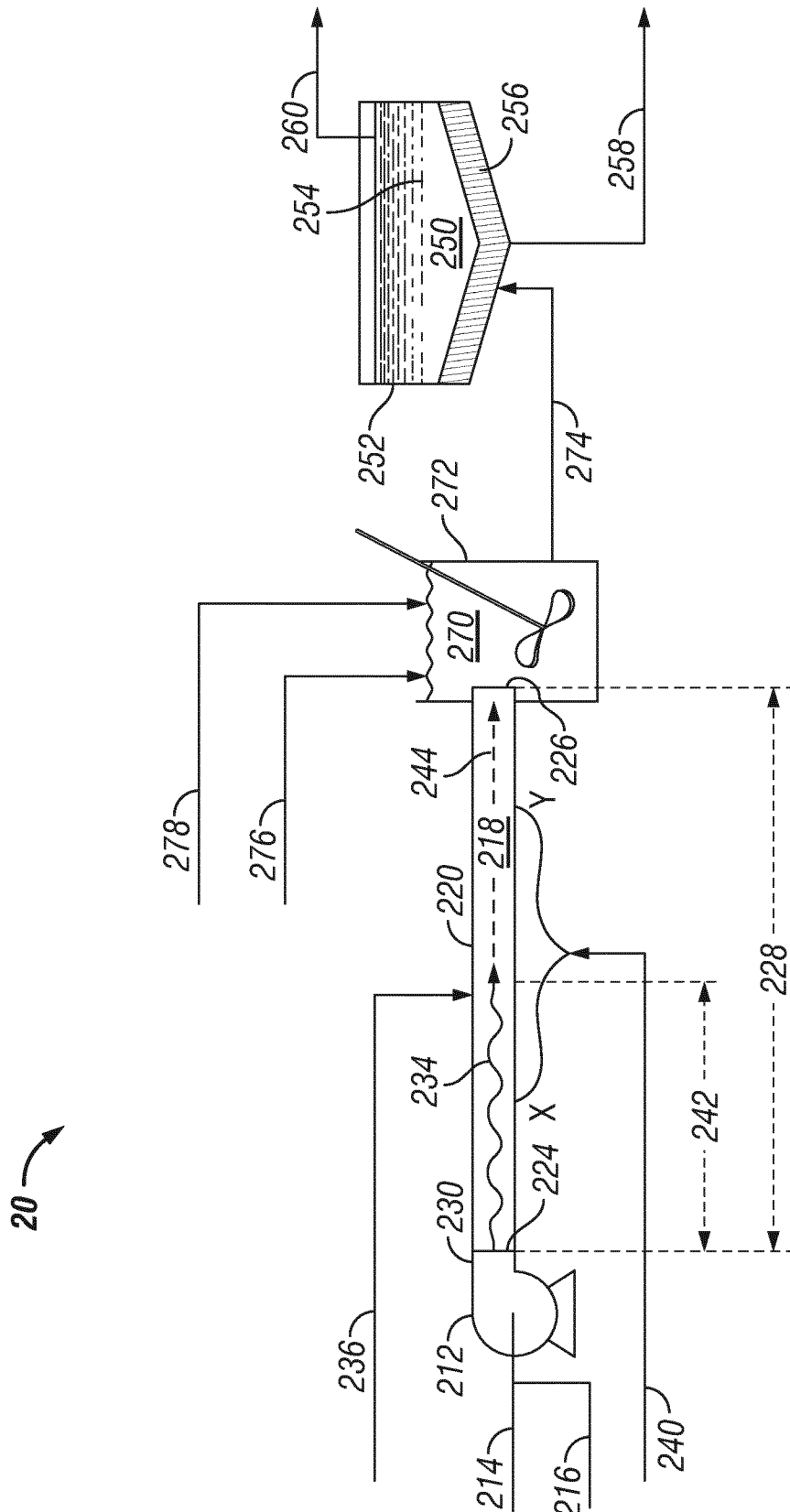
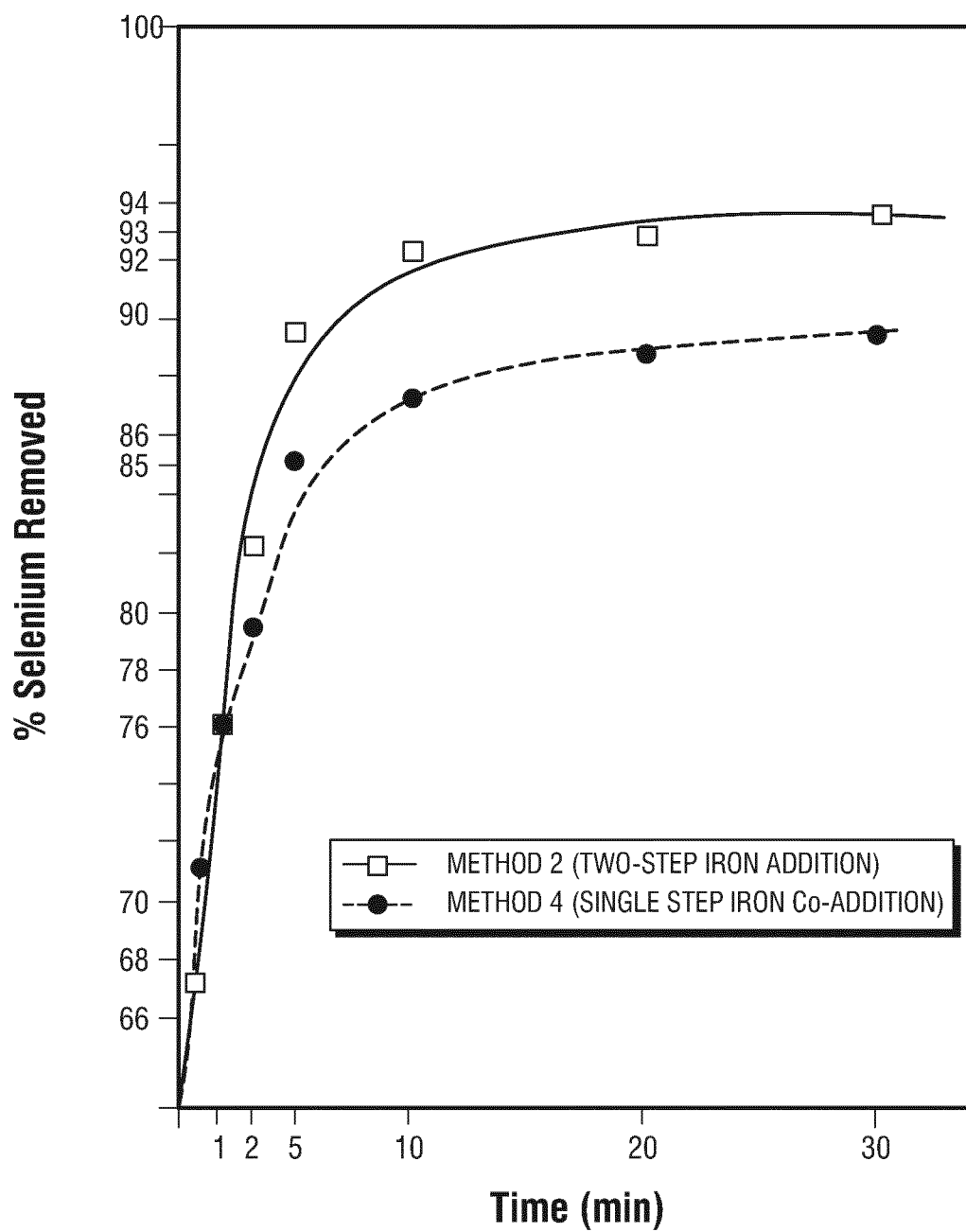


**FIG. 2**

**3/4****FIG. 3**

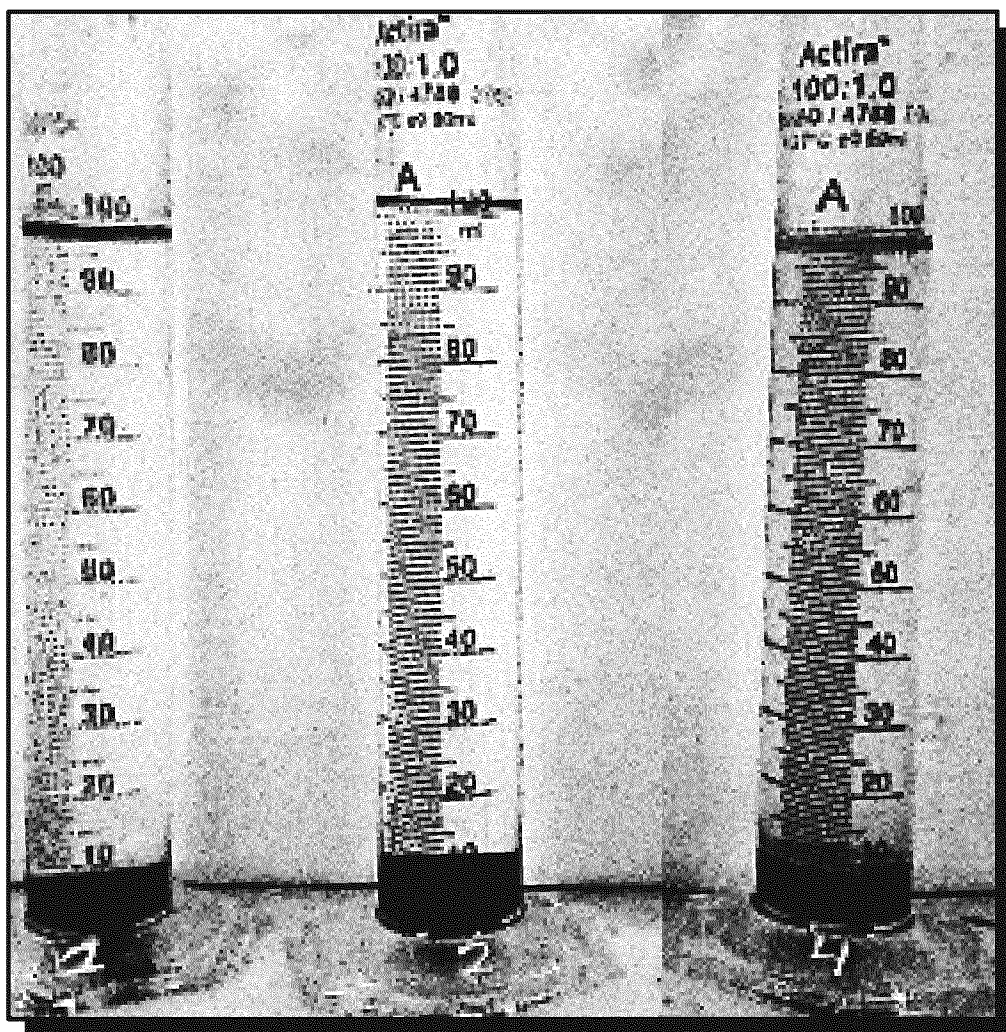


**FIG. 4**

## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2020/061310

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C02F1/52 C02F1/66  
 ADD. C02F101/10

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)  
 C02F

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

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

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | Relevant to claim No. |
|-----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X         | <p>Lipi Jain ET AL: "Removal of Selenium from Industrial Waste Water by Ferrous-Ferric Salt MS Thesis Report submitted towards the partial fulfillment for the award of Integrated BS MS degree program Shell New Technology Center, Bangalore Under the guidance of",</p> <p>30 March 2017 (2017-03-30), XP055638358, Retrieved from the Internet:<br/>           URL:http://dr.iiserpune.ac.in:8080/xmlui/bitstream/handle/123456789/778/20121020_Lipijain.pdf?sequence=1&amp;isAllowed=y [retrieved on 2019-11-01]<br/>           figure 9<br/>           page 26 - page 37</p> <p style="text-align: center;">-----<br/>           -/--</p> | 1-33                  |



Further documents are listed in the continuation of Box C.



See patent family 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 application or patent but published on or after the international filing date

"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)

"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

20 July 2020

Date of mailing of the international search report

30/07/2020

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040,  
 Fax: (+31-70) 340-3016

Authorized officer

Châtellier, Xavier

## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2020/061310

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                              | Relevant to claim No. |
|-----------|---------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| A         | US 6 139 753 A (TAYLOR REGINALD MORTON<br>[AU]) 31 October 2000 (2000-10-31)<br>claim 4<br>column 6, line 57 - line 63<br>----- | 1-33                  |
| A         | US 2012/241381 A1 (BRUSO BRUCE L [US])<br>27 September 2012 (2012-09-27)<br>cited in the application<br>figure 2<br>-----       | 1-33                  |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2020/061310

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date         |
|-------------------------------------------|---------------------|----------------------------|-----------------------------|
| US 6139753                                | A                   | 31-10-2000                 | NONE                        |
| -----                                     |                     |                            |                             |
| US 2012241381                             | A1                  | 27-09-2012                 | US 2012241381 A1 27-09-2012 |
|                                           |                     |                            | WO 2012129213 A1 27-09-2012 |
| -----                                     |                     |                            |                             |