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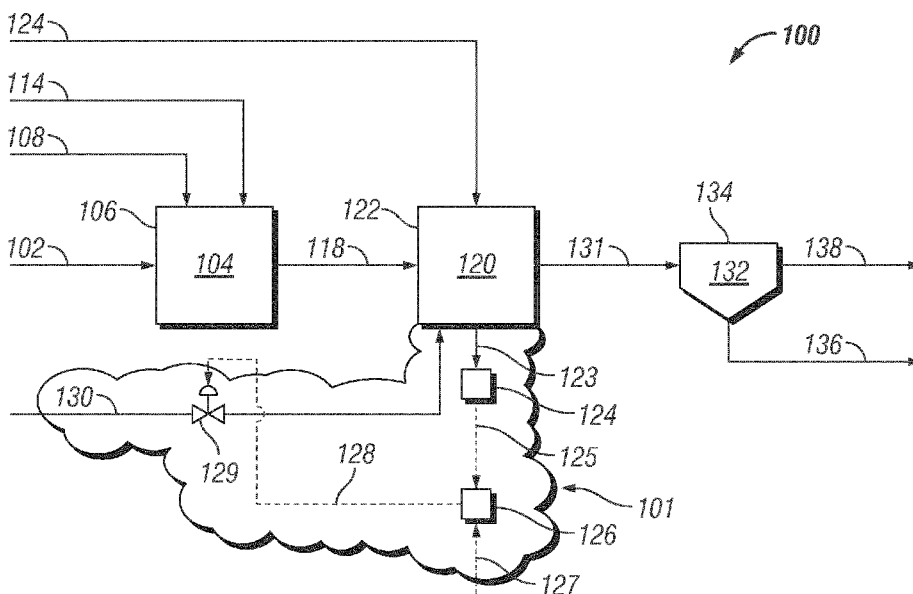


FIG. 1

(57) Abstract: Disclosed is a method of controlling the properties and yield of sludge in a process for removing selenium from a selenium-contaminated water stream to yield treated water having an ultra-low selenium concentration. The process includes two iron addition steps. The first step includes mixing ferric salt with the contaminated water that is followed by a second step of mixing ferrous salt with the mixture from the first step. The pH of the second step mixture is controlled within a range to give iron precipitate sludge having certain desired settling and compaction properties. The second step mixture then undergoes separation of the iron precipitate sludge from the treated water.



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METHOD OF CONTROLLING SLUDGE YIELD AND PROPERTIES IN A PROCESS FOR SELENIUM REMOVAL FROM WASTE WATER

FIELD OF THE INVENTION

5 This invention relates to a method of controlling sludge yield and sludge settling and compaction properties in a process for removing selenium from selenium-contaminated water streams.

BACKGROUND OF THE INVENTION

10 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, 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
15 transferred from oil mixtures to waste water streams, where refinery units such as the 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
20 water are oxidized to selenium oxyanions, i.e., selenate (SeO_4^{2-}) and selenite (SeO_3^{2-}), 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.

25 Federal and state mandates dictate the removal of selenium compounds from waste 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
30 organic carbon sources (e.g. aerobic and an-aerobic bacteria, algae, fungus) for conversion 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
5 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
10 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
15 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
20 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
25 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.

One problem with these processes is that they are unable to provide treated waters
30 having concentrations of selenium compounds down to less than 100-200 parts per billion ("ppbw). These processes are ineffective at removing contaminating concentrations of selenate and selenite from selenium-contaminated water streams to yield treated water having very low concentrations of selenium of less than 10 ppbw. Also, significantly, the

precipitates yielded from these single iron-addition step processes have poor settling properties that make separation of the yielded precipitates from the water difficult or inefficient.

There is thus a desire to have an improved process capable of removing selenium
5 from water streams contaminated with concentrations of selenium oxyanions of both selenate and selenite to yield treated waters having very low concentrations of selenium of less than 10 ppbw. It is further desirable for processes that apply precipitation methods to remove selenium from the selenium-contaminated water streams to yield precipitates that more easily and efficiently are separated from the treated water.

SUMMARY OF THE INVENTION

Accordingly, a method is provided for controlling the properties and yield of sludge
in a process providing for enhanced removal of selenium from a waste water stream,
having a selenium concentration of both selenite and selenate. This method comprises
mixing ferric chloride with the waste water stream to form a first mixture. In a second
15 mixing step ferrous chloride is mixed with the first mixture to form a second mixture having a second mixture pH. The formation and properties of iron oxide precipitate sludge within the second mixture is controlled by adjusting the second mixture pH to within a range that provides for the formation of the iron oxide precipitate sludge and that provides for the second mixture having a desired sludge volume index (SVI). The second mixture,
20 which comprises the iron oxide precipitate sludge and treated water, is then separated into a water product, having a reduced selenium concentration that is less than said selenium concentration of the waste water stream, and an iron oxide precipitate sludge product.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic block flow diagram illustrating an embodiment of the
25 inventive two-step iron addition process for removing selenium from a selenium-contaminated water stream and for controlling the properties and yield of sludge from the process.

FIG. 2 presents bar graphs comparing experimental results from testing the ability
of the inventive two-step iron addition process and of the comparative single-iron addition
30 processes to remove selenium from a simulated selenium-contaminated water. The bar graphs show that the two-step iron addition process provides treated water having a significantly lower selenium concentration than the treated water from the processes that apply a single iron addition step.

FIG. 3 presents bar graphs comparing the Sludge Volume Indexes of the reactor effluents from two-step ferric-ferrous iron addition, one-step ferric-ferrous iron co-addition, and single-step ferric iron addition processes for removing selenium from selenium-contaminated water. The bar graphs include comparisons of the SVI's of the reactor effluents having a pH of 8 and a pH of 9. These bar graphs show that the sludge settling properties from the two-step ferric-ferrous iron addition process are significantly better than such properties of the sludge from the one-step ferric-ferrous co-addition and single-step ferric addition processes.

FIG. 4 presents bar graphs comparing the SVI of the reactor effluents yielded from the two-step ferric-ferrous iron addition process when different amounts of ferrous iron is added to the second step which operated at different pH conditions of either 8 or 9. The bar graphs show that for all concentrations of iron addition the lower pH condition provides a sludge having better settling properties than the higher pH condition regardless of the amount of iron added.

DETAILED DESCRIPTION OD 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, 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
5 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.
10 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
15 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,
20 including concentrations of the selenium oxyanions of selenite (SeO_3^{-2}) and selenate (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
25 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 further provides a method of controlling the properties and yield of sludge in addition to removing both selenite and selenate from the waste water. Indeed, this sludge control and the unexpected properties of the sludge made by the
30 inventive two-step iron addition process when it is operated under specifically defined pH process conditions contribute to providing a treated water having an ultra-low selenium concentration that may be dischargeable, preferably, without further processing.

The two-step iron addition process yields treated water having a significantly reduced selenium concentration that is less than the selenium concentration of the waste water that is treated. 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 process control of the formation and properties of its iron oxide precipitate sludge contributes to removing selenium from the waste water to yield treated water having the ultra-low selenium concentrations the inventive process.

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 (SeCN^-) and selenium hydride (SeH_2). These compounds may be present in the waste water stream at a concentration in the range of from 700-5000 ppbw. The SeCN^- and SeH_2 compounds of the waste water stream are then typically reduced in biological waste water treatment under aerobic conditions to selenate (SeO_4^{2-}) and selenite (SeO_3^{2-}) compounds that require removal by a subsequent 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 times of the same refinery depending on the operations, processes, and types of treatments.

The sources of the waste water in crude oil refineries 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
5 desired.

The inventive process applies two iron addition steps to provide for the removal of selenium from waste water streams having significantly high concentrations of selenium compounds, including concentrations of selenium oxyanions of selenite (SeO_3^{-2}) and selenate (SeO_4^{-2}). It surprisingly has been discovered that the application of the two iron
10 mixing steps in the treatment of a selenium-contaminated water stream to remove selenium provides for much higher levels of selenium removal from the water than do comparative processes that apply only a single iron mixing step.

In the first step or stage of the inventive process, a waste water stream that typically is delivered from a containment system is introduced along with a ferric salt, such as ferric
15 chloride (FeCl_3), into a first mixing or reaction zone. The ferric salt, which is preferably in the form of an aqueous iron solution, is mixed with the waste water stream that is introduced into the first mixing zone or reaction zone or is introduced with the waste water stream into the first mixing zone or reaction zone or is separately introduced into the first mixing zone or reaction zone.

Thus, in the first step or stage of the process, a ferric salt is mixed with the water
20 stream, containing both selenite and selenate oxyanions, to form a first mixture. This first mixing step is performed separately from the second mixing step or stage of the process. What is meant by performing the first mixing step separately from the second mixing step is that two steps are separated by either time of the iron additions or by space or distance
25 between the iron additions or by both time and space. The separation in time or space or both requires that the ferrous salt of the second mixing step is added to the water and ferric salt mixture, or first mixture, of the first step after they have been mixed and preferably after enough reaction time has passed to allow the reaction of the first mixing step to approach completion.

The second mixing step is performed either in the same reactor that defines one or
30 more mixing zones in which the first mixing step and second mixing step are conducted, or in a second reactor separate from the first reactor. In the later case, the second reactor defines a second mixing zone in which the second mixing and reaction step is conducted.

After allowing enough time to pass for the reaction to take place within the first mixture, the first mixture is then mixed with a ferrous salt, such as ferrous chloride, in a second mixing step or stage of the process to form the second mixture. The second mixture is allowed to react for enough time before separating the second mixture into a treated
5 water product and an iron oxide precipitate sludge product.

It is surprising and unexpected that this two-step ferric-ferrous iron addition process provides significantly greater amounts of selenium removal from selenium-contaminated water streams than does single step addition of either a ferric salt alone, or a ferrous salt alone, or both ferric-ferrous salts simultaneously as a co-addition. What is especially
10 surprising and unexpected, however, is that the iron oxide precipitate sludge produced by the two-step iron addition process has much better settling and compaction properties than the sludge produced by any of the single-step iron addition processes.

The enhanced settling properties of the sludge yielded from the two-step addition process provides numerous benefits. For example, the better settling properties allow for
15 easier and better separation of the water and iron precipitate sludge of a reactor effluent. The improved sludge settling properties may provide for better clarified treated water during separation of the second stage effluent that needs no further downstream polishing before its discharge. The treated water of the single-step processes tends to be discolored with suspended iron particles or with colloidal iron particles, or both. Other benefits may
20 include such things as smaller settler designs, quicker separation times, and fewer downstream treatment steps.

Another discovery about the iron oxide precipitate sludge resulting from the two-step addition process is that the preferred settling properties are dependent upon the specific pH conditions under which the second mixing step is conducted. It has been found
25 that the pH at which the second mixing step is operated is an important if not critical factor influencing the sludge properties and should be controlled to within a specified basic pH range to control the formation and properties of the iron oxide precipitate sludge. Controlling the pH of the second mixture is, thus, an important aspect of the inventive process and to its successful operation.

30 The inventive two-step iron addition process includes first mixing zone defined by any suitable means for mixing the waste water stream with the ferric salt to provide a first reaction mixture having a desired molar ratio of the ferric salt-to-selenite that is contained in the waste water. Suitable mixing means are those capable of providing for mixing of the

ferric salt with the waste water stream or for liquid-liquid mixing of the aqueous iron solution with the waste water stream. Such means may include a simple tubular reactor that relies on the turbulence of the fluid flow provided by pumping of the liquid feeds through the tubular conduit and the geometry of the tubular conduit, or mixing means can be any other suitable reactor system known to those skilled in the art, such as continuous stirred tank reactors. Examples of other mixing means include static mixers, in-line mixers, in-tank mixers, and an agitated tanks, vessels and other containers.

In the first mixing step, an aqueous ferric solution that is stored, for example, in a feed tank, is introduced into the first mixing zone along with the waste water stream wherein the two are mixed together to form a first reaction mixture. The mixing of the aqueous ferric solution with the waste water stream forms a first reaction mixture within the first mixing zone. The aqueous ferric solution includes dissolved soluble iron salt, ferric chloride (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 mixing zone are maintained or controlled so that at least a portion of the introduced 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 mixed with the waste water stream should be such as 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 stream and aqueous ferric solution introduced into the first mixing zone should be such to provide residence time to allow for the ferric chloride to react to form the ferric hydroxide or ferrihydrite reaction product. But, it is a feature of the inventive process for there to be little or essentially no formation of iron precipitate in the first mixing step. In fact, this is an aspect of the inventive process

that is distinguishable over the iron co-precipitation process in that the precipitation of the iron hydroxide and ferrihydrite is not desired with the inventive process, and it may be controlled by adjustments made to the pH of the first reaction mixture, if it is required, to prevent the formation of precipitate within the first reaction mixture. Normally, however, there is no need to alter the pH condition of the first mixing step or the first reaction mixture because of the acidic characteristic of the ferric salt. The pH of the first stage reaction mixture is typically acidic and can be as low as around 1.5 or 2.

To control the first pH of the first reaction mixture, a first pH-regulating solution is introduced into the first mixing zone along with the waste water stream and aqueous ferric solution in amounts necessary to maintain the first pH within the required range. Examples of suitable pH-regulating solutions include hydrogen chloride (HCl), sulfuric acid (H₂SO₄), or other similar acidic solutions. The first pH-regulating solution may be stored in a feed tank or other conventional storage device and pumped into the first mixing zone.

The residence time of the feed to the first mixing zone is then generally at least 5 seconds, but the system may be constrained by hydraulic and other factors resulting in a longer residence time than is necessarily required to provide the desired selenium conversion. The practical upper limit for the residence time is no more than 2 hours. Most desirably, the residence time of the feed to the first mixing zone is in the range of from 5 seconds to one hour, preferably, between 10 seconds to 45 minutes. For plug flow reactor systems the residence time may preferably be in the range of from 10 seconds upwardly to 45 minutes or from 10 seconds to 5 minutes.

At least a portion of the first reaction mixture may then be passed to the second mixing zone and introduced along with a ferrous salt, such as ferrous chloride (FeCl₂), into a second mixing zone. The ferrous salt is preferably introduced into the second mixing zone in the form of an aqueous iron solution. The second mixing zone is defined by any suitable means for mixing the first reaction mixture with an aqueous ferrous solution. Suitable mixing means are those capable of providing for liquid-liquid mixing of the first reaction mixture with the aqueous ferrous solution. Such means may include a simple tubular reactor, including the same tubular reactor used with the first mixing step, the tubular reactor relies on the turbulence of the fluid flow provided by pumping of the liquid feeds through the tubular conduit and the geometry of the tubular conduit. Examples of other mixing means include static mixers, in-line mixers, in-tank mixers, and an agitated tanks, vessels and other containers.

In the second iron addition or mixing step, an aqueous ferrous solution stored, for example in a feed tank, is introduced into the second mixing zone along with the first reaction mixture wherein they are mixed together to form the second reaction mixture, comprising water and an iron precipitate sludge. The second mixing step may be conducted
5 in a tubular reactor or within a second mixing vessel or container or tank that is equipped with at least one agitator providing for mixing of the first reaction mixture with the aqueous ferrous solution.

Mixing of the aqueous ferrous chloride solution with the first reaction mixture results in formation of green rust reaction products within the second mixing zone that
10 comprise crystalline compounds of iron (II) and iron (III) cations, the hydroxide anion and other anions of selenate or selenite. The ferrous-ferric hydroxide formed within the second mixing zone acts as an active reducing agent to reduce selenate to selenite and to insoluble elemental selenium. Mixing of the aqueous ferrous solution within the second mixing zone with the first reaction mixture from the first stage of the process reduces its selenate
15 concentration and further reduces remaining selenite concentration to form a second reaction mixture, comprising an iron precipitate sludge and water.

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 reaction mixture. The formation of the iron precipitate sludge and its later separation
20 provides for removal and reduction of at least 50% of the selenate anions contained in the first reaction mixture. The process, however, is able to remove at least 85%, and most preferably, it provides for removing at least 95% of the selenate anions contained in the first reaction mixture.

It is understood that references in this specification to “iron” are not necessarily
25 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 to 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
30 containing at least the components selenium. The waste water may optionally contain one of 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 and heavy metals. The precipitate may also include iron oxide and iron hydroxide.

The mixing of the aqueous ferrous solution with the first reaction mixture from the first mixing step of the process forms a second reaction mixture within the second mixing zone that reduces the selenate concentration in the first reaction mixture. A commercially available aqueous ferrous chloride solution may be used in the process. Also, the ferrous chloride solution may also be prepared by dissolving a commercial 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 after mixing 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 first reaction mixture and aqueous ferrous solution introduced into the second mixing zone should be such as to provide sufficient residence time for the selenate and ferric hydroxide and ferrihydrite of the first reaction mixture to react with the ferrous chloride of the aqueous ferrous solution to produce the iron precipitate sludge of the second reaction mixture. The residence time of the feed to the second mixing zone is, thus, at least 5 minutes but no more than 2 hours. More desirably, however, the residence time of the feed to the second mixing zone is in the range of from 5 minutes to one hour, and, preferably from 5 minutes and 45 minutes.

An important feature of the inventive process is that it provides for controlling the operation of the two-step iron addition process to maximize selenium removal from a selenium-contaminated water stream to yield treated water having significantly reduced selenium concentrations below those of the selenium-contaminated water streams. One factor that provides for such enhanced selenium removal from the selenium-contaminated

water is the control of the sludge yield from the process and the settling properties of the sludge. It is unexpected that the sludge settling properties of a sludge made in a two-step ferric-ferrous addition process are materially better than the sludge settling properties of sludge made by any of the single-step iron addition processes.

5 In addition to this unexpected feature of the two-step iron addition process, it is further unexpected that the pH conditions of its second mixing and reaction step have a significant effect on the settling and compaction properties of the yielded sludge. Due to this effect, it is important, if not critical, for the second mixture pH of the second mixture of the process to be maintained and controlled within a specified second mixture pH range
10 for the sludge to have the desired settling characteristics and to properly control the overall process. Indeed, controlling or maintaining the second mixture pH to within a specific range is essential to the formation of the iron precipitate sludge having desired characteristics needed to properly operate the process for removal of selenium from the waste water stream.

15 The property of the second mixture or second reactor effluent controlled by the process and which is indicative of settling characteristics of a sludge is the Sludge Volume Index (SVI) of the reactor effluent. The term “Sludge Volume Index,” as it is used in this specification, is determined by placing a volume of the full mixture of sludge and water effluent (i.e., a reactor effluent), such as the second mixture, into a graduated cylinder and
20 allowing it to settle for 30 minutes. The volumes of the clear water layer, which lays on top of the settled sludge layer, and of the settled sludge layer are measured after a settling time of 30 minutes. The SVI is the quotient of the volume of this settled sludge layer divided by the sum of the volume of the clear water layer above the settled sludge layer and the volume of the sludge layer, reported as a percent, where the sum of the clear water layer
25 and settled sludge layer is the full mixture placed in the graduated cylinder. A smaller value for sludge volume, SV (%), represents better settling and compaction properties of the sludge. A clear water layer indicates that the precipitate has settled out of the water. A smaller sludge layer indicates that the sludge settled rapidly and compacted well.

 The desired SVI of the second mixture can be influenced by the amount of iron
30 added to the processed water. The SVI tends to be larger when larger quantities of iron are added to the water to be treated, but, generally, the desired SVI of the second mixture of the process is less than 32%. The practical lower limit for the SVI is greater than 1%. Thus, the desired SVI should be controlled within a range of from 1% to 32%. It is preferred for

the desired SVI to be controlled to less than 27%, and, more preferred, less than 22%. The lower limit for the desired SVI is typically greater than 1.5%, and more typically, greater than 2%. Thus, the desired SVI is controlled within the preferred range of from 1.5% to 27%, or within the more preferred range of from 2% to 22%.

5 Due to the relationship of the sludge settling properties and second mixture pH, the desired SVI is controlled by adjusting the second mixture pH within a range that provides the desired SVI for the second mixture. To achieve the desired SVI for the second mixture, it is important to control the second mixture pH of the second reaction mixture so that it is greater than 7 but less than 9.5. It has been found that to yield a sludge having more
10 desirable settling properties that the second mixture pH must be basic and therefore greater than 7 but otherwise a lower pH value tends to provide for a sludge having better settling properties. A preferred second mixture pH is in the range of from 7.5 to 9, and, more preferred, the second mixture pH is in the range of from 7.8 to 8.8.

 In one embodiment of the inventive process a sample of the second mixture is
15 obtained and its characteristic SVI is measured or determined by the methodology described in this specification or by any other suitable method to provide a measured sludge volume index that is representative of the SVI of the second mixture. The value for this measured sludge volume index is then compared against a desired SVI for the second mixture to identify and determine the difference between the desired SVI and the measured
20 SVI. The second mixture pH is then adjusted in response to this difference by controlling an amount of pH regulating composition, such as sodium hydroxide, that is admixed with the second mixture to provide a second mixture pH required to provide that an actual second mixture SVI that approaches the desired second mixture SVI.

 An alternative to measuring the second mixture SVI and adjusting the second
25 mixture pH in response to differences between the desired SVI and the measured SVI is to instead make adjustments in the second mixture pH in response to differences in the measured second mixture pH and the desired second mixture pH. This control method works because the second mixture SVI correlates with the second mixture pH. The second mixture pH can therefore be measured and adjusted as needed to provide the desired
30 second mixture SVI. In this embodiment, a measured second mixture pH for the second mixture is measured or determined by any known method and compared against a desired second mixture pH for the second mixture to identify and determine the difference between the desired second mixture pH and the measured second mixture pH. The second mixture

pH is then adjusted in response to this difference by controlling an amount of pH regulating composition, such as sodium hydroxide, that is admixed with the second mixture to provide a second mixture pH required to provide that an actual second mixture SVI that approaches the desired second mixture SVI.

5 In the preferred embodiment of the process, the second reaction mixture flows from the second mixing zone into a separating zone. The separating zone is defined by any suitable means for separating the second reaction mixture to yield a water product stream, having a reduced or a lowered selenium concentration that is less than the selenium concentration of the waste water stream, and an iron precipitate sludge product. Suitable
10 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,
15 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.

 When using a settler or clarifier as separating means, 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
20 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 and has the composition described above including formed ferrous-ferric hydroxide, which acts as an active reducing agent to reduce selenate to selenite. The iron precipitate sludge product
25 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
30 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 natural water bodies.

FIG. 1 is a schematic block flow diagram of an embodiment of the inventive process 100 for the enhanced removal of selenium from a waste water stream having a
5 contaminating concentration of selenium. The selenium content of the water includes the oxyanions of selenium, selenite and selenate. Further included is control system 101 that provides for controlling the properties and yield of sludge from process 100.

The schematic of FIG. 1 depicts the flow of the waste water stream as it is processed in two iron addition or mixing steps that are operated in series flow and
10 thereafter followed by a step for separating iron precipitate and a treated water product. The treated water product of the process has a significantly reduced selenium concentration below the selenium concentration of the waste water feed. The selenium concentration of the treated water is less than 10 ppbw and, preferably, less than 5 ppbw. Control of the sludge properties provide for better separation of the sludge and improved treated water
15 quality with enhanced reductions in contaminating selenium concentrations.

As shown in FIG. 1, the waste water stream passes via line 102 and is introduced into mixing zone 104 that is defined by first mixing means 106. The waste water stream has a concentration of selenium in the range of from 100 ppbw to 10,000 ppbw. The selenium concentration includes concentrations of the selenium oxyanions of selenite and
20 selenite.

A ferric salt, such as ferric chloride, which is preferably in the form of an aqueous ferric solution, is passed and introduced into first mixing zone 104 by way of line 108. The ferric chloride and waste water stream are mixed within first mixing zone 104 by first
25 mixing means 106 that provides for mixing of the waste water stream with the ferric salt to provide a first reaction mixture. The amount of ferric salt mixed with the waste water stream is such as 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 per moles of selenite.

It is a desirable aspect of process 100 for there to be little to no formation of an iron precipitate in first reaction mixture of first mixing zone 104. Controlling the formation of
30 iron precipitate within the first reaction mixture is done primarily by maintaining the pH of the first reaction mixture (first pH) below a pH that provides for the formation of an iron precipitate. This pH is typically less than 7.5. Preferably, the first pH is maintained within the range of from 1.5 to 6.5.

If it is needed to control the pH of the first reaction mixture, a first pH-regulating solution is introduced into first mixing zone 104 by way of line 114. The introduction of the ferric chloride into first mixing zone 104 may tend to increase the acidity of the first reaction mixture, and, therefore, there may be no need to mix any first pH-regulating
5 solution with the first reaction mixture to maintain its pH within the desired range to keep iron precipitate from forming within the first reaction mixture.

The residence time of the first reaction mixture within first mixing zone 104 should be sufficient to allow for the ferric salt to react to form either ferric hydroxide or ferrihydrite, or both, in the first reaction mixture. At least a portion, preferably a major
10 portion, or the entire flow of the first reaction mixture passes from first mixing zone 104 by way of conduit 118 and is introduced into second mixing zone 120.

It is a preferred feature of process 100 for there to be no intervening or intermediate separation of the first reaction mixture before introducing the at least a portion of first reaction mixture into second mixing zone 120 through conduit 118.

15 In the second mixing step, a ferrous salt, which is preferably in the form of an aqueous ferrous solution, and comprises water and ferrous chloride, passes through line 124 for introduction into second mixing zone 120. The ferrous salt is mixed within second mixing zone 120 with the first reaction mixture flowing from conduit 118 to form the second reaction mixture.

20 Second mixing zone 120 is defined by second mixing means 122 that provides for mixing the ferrous salt with the first reaction mixture to yield the second reaction mixture. The amount of ferrous salt mixed with the first reaction mixture in second mixing zone 120 is such as to provide a dosing ratio of ferrous-to-selenate that is in the range of from about 5,000:1 to 140,000:1 moles of ferrous per moles of selenate.

25 The residence time of the second reaction mixture within second mixing zone 120 should be sufficient to allow for the formation of the green rust reaction products or iron precipitate sludge. The residence time of the second reaction mixture within second mixing zone 120 should be sufficient to allow for the formation of the ferric-ferrous hydroxide to yield the iron precipitate sludge.

30 Control system 101 provides for controlling the formation and properties of the iron precipitate sludge. It is understood that control system 101 may be a completely automated system comprising equipment such as analyzers, controllers, computers, and valves that are electronically, pneumatically or wirelessly integrated to provide for the automatic control

of the process variables of process 100. As an alternative or in combination with the automatic system, human input may be used as a substitute for any one or more of the equipment elements or means of control system 101 for measuring, computing, and adjusting the process variables.

5 Control system 101 provides for determining the pH or SVI, or both properties, of the second reaction mixture by obtaining a sample of the second reaction mixture and transferring the sample by way of transfer means 123 to analyzer 124.

Analyzer 124 provides means for determining the pH of the second reaction mixture or the SVI of the second reaction mixture. For an automated control system 101, a
10 signal 125 is generated by analyzer 124 that is representative of the measured SVI or the measured pH. Signal 125 is input to controller or computer 126.

Provided to controller 126 is a second input signal 127 that is representative of a desired SVI or a desired pH for the second reaction mixture. Controller 126 compares the information transmitted by signals 125 and 127 and performs a computation to identify any
15 difference between the desired SVI and the measured SVI, or controller 126 performs a computation to identify any difference between the desired pH and the measured pH, or it performs both computations, and transmits signal 128 that is representative of the difference between the desired SVI and the measured SVI, or the difference between the desired pH and the measured pH, or both, to control valve 129.

20 Control valve 129 is interposed in conduit 130 through which a pH modifying composition, such as sodium hydroxide, passes and is introduced into the second reaction mixture to modify and control its pH. Control valve 129 is open or closed in response to signal 128 to adjust the flow of the pH modifying composition into the second reaction mixture to adjust its pH to within the required range to provide a second reaction mixture
25 having the desired SVI.

The second reaction mixture then passes from second mixing zone 120 by way of line 131 and is introduced into separation zone 132 defined by separator 134. Separator 134 provides means for separating the second reaction mixture to yield a water product and an iron precipitate sludge product. Separator 134 can include any conventional device,
30 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 100 from the waste water stream. The iron precipitate sludge product passes from separation zone 132 via line 136 for transportation to off-site disposal or for additional treatment before its final disposal.

5 The water product has a significantly reduced selenium concentration compared to the selenium concentration of the waste water stream that is treated by process 100. This treated water product passes from separation zone 132 via line 138 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
10 environmental standards that place restrictions on the total selenium concentration within a discharge water. Process 100 is able to treat waste water having high concentrations of both selenium and sulfates and still obtain a treated water product having exceptionally low selenium content.

15 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

20 This Example illustrates the unexpectedly greater selenium removal from a selenium-contaminated water stream provided by a two-step iron addition process when compared to the selenium removal provided by either a single-step ferric iron addition process or a single-step ferrous iron addition process.

25 This Example describes three batch experiments and presents the results of these experiments. One experiment involved the single addition of ferric chloride to simulated selenium-contaminated effluent water. The second experiment involved the single addition of ferrous chloride to simulated selenium-contaminated effluent water. The third experiment involved two separate iron addition steps that included ferric chloride addition to simulated selenium-contaminated effluent water followed by, after a reaction period, ferrous chloride addition to the water and ferric chloride reaction mixture.

30 The simulated selenium-contaminated effluent water used in the experiments contained 50 ppbw selenite, 50 ppbw selenate, 40 ppmw nitrate, 260 ppmw sulfate, and 250 ppmw bicarbonate.

In the first experiment, a volume of the simulated selenium-contaminated effluent water was placed in a vessel. A ferric chloride solution was mixed with the water in an

amount to provide a dosing equivalent of 14.1 mmol of iron/liter of water and with a quick adjustment of the pH of the reaction mixture to 9. The mixture was stirred for 30 minutes, which allowed the reaction to go to completion. An aliquot of the reaction mixture was then filtered, and the recovered treated water was analyzed for its selenium content, which was 55 ppbw total selenium.

The second experiment was like the first experiment, except that, it was dosed with ferrous chloride instead of with ferric chloride. In this experiment, a volume of the simulated selenium-contaminated effluent water was placed in a vessel. A ferrous chloride solution was mixed with the water in an amount to provide a dosing equivalent of 14.1 mmol iron/liter of water and with a quick adjustment of the pH of the reaction mixture to 9. This mixture was stirred for 30 minutes, which allowed the reaction to go to completion. An aliquot of the reaction mixture was then filtered, and the recovered treated water was analyzed for its selenium content, which was 20 ppbw total selenium.

The third experiment involved two separate and distinct steps of iron addition to the simulated selenium-contaminated effluent water. In the first step, the volume of water was dosed with a ferric chloride solution in an amount to provide a dosing equivalent of 4.7 mmol ferric iron/liter of water and with a quick adjustment of the pH of the reaction mixture to 9. This mixture was stirred for 15 minutes, which allowed the reaction to go to completion. In the second step, a ferrous chloride solution was mixed with the water and ferric chloride reaction mixture in an amount to provide a dosing equivalent of 9.4 mmol of ferrous iron/liter of water (the ferric-to-ferrous molar addition ratio was 1:2 and the total ferric and ferrous addition was 14.1 mmol/liter of water) and with a quick adjustment of the pH of the reaction mixture to 9. This mixture was stirred for 30 minutes, which allowed the reaction to go to completion. An aliquot of the final reaction mixture was then filtered, and the treated water was analyzed for its selenium content, which was 4 ppbw of total selenium.

FIG. 2 presents the results of these experiments in the form of bar graphs. As can be seen, the two-step iron addition unexpectedly provides significantly better selenium removal than does single-step iron addition.

EXAMPLE 2

This Example describes and presents results from (1) a two-step iron addition experiment using two continuous flow stirred tank reactors (CFSTR) connected in series
5 flow; (2) a one-step ferric-ferrous iron co-addition experiment using a single CFSTR; and
(3) a single-step ferric iron addition experiment using a single CFSTR. This Example
further demonstrates the unexpectedly enhanced settling properties of the sludge made by
the two-step iron addition process compared to the properties of the sludge made by either
the one-step ferric-ferrous iron co-addition process or the single-step ferric iron addition
10 process.

The two-step process applies ferric iron salt in the first step and ferrous iron salt in
the second step to remove selenium from a selenium-containing water feed. This process
yields in addition to treated water having a significantly reduced selenium concentration a
sludge by-product having enhanced settling properties over the sludges yielded from the
15 comparative one-step ferric-ferrous iron co-addition and single-step ferric iron addition
processes.

1. The Two-Step Iron Addition Experiment

This experiment used two five-liter continuous stirred tank reactors connected in
20 series flow. A simulated waste water feed, having a selenite concentration and a selenate
concentration, was charged to the first reactor to which a 45 wt.% aqueous ferric chloride
solution (0.45 g/ml water) was added. No pH adjustment was made to the reaction mixture
of the first reaction stage. The effluent from the first reactor was charged to the second
reactor into which a 15 wt.% aqueous ferrous chloride solution (0.15 g/ml water) along
25 with an amount of 10% NaOH solution to maintain a reaction mixture pH of either 8 or 9,
depending upon the experimental run. Effluent from the second reactor was passed to a
tank for holding treated effluent and sludge. The Sludge Volume Index (SVI) for the
second reactor effluent was measured.

The SVI of the second reactor effluent recovered from the process operating at a
30 pH of 9 was 20% and for the second reactor effluent recovered from the process operating
at a pH of 8 the SVI was 15%. The process operating at the lower pH of 8 yielded a sludge
having much better settling and compaction properties than the sludge yielded from the
process operating at a higher pH of 9.

2. The One-Step Ferric-Ferrous Iron Co-Addition Experiment

This experiment used a single five-liter continuous stirred tank reactor that was charged with simulated waste water feed, having a selenite concentration and a selenate concentration. A 45 wt.% aqueous ferric chloride solution (0.45 g/ml water), a 15 wt.% aqueous ferrous chloride solution (0.15 g/ml water), and a 10% NaOH solution in an amount to maintain a reaction mixture pH of either 8 or 9, depending upon the experimental run, were simultaneously mixed in the reactor with the water feed. The effluent from the reactor was passed to a tank for holding treated effluent and sludge. The Sludge Volume Index (SVI) of the reactor effluent was measured.

The SVI for the reactor effluent from the process operating at a pH of 9 was 40% and for the reactor effluent from the process operating at a pH of 8 the SVI was 35%. The process operating at the lower pH of 8 yielded a sludge having much better settling and compaction properties than the sludge yielded from the process operating at a higher pH of 9.

3. The Single-Step Ferric Iron Addition Experiment

This experiment used a single five-liter continuous stirred tank reactor that was charged with simulated waste water feed, having a selenite concentration and a selenate concentration. A 45 wt.% aqueous ferric chloride solution (0.45 g/ml water) and a 10% NaOH solution in an amount to maintain a reaction mixture pH of 7 was mixed in the reactor with the water feed. The effluent from the reactor was passed to a tank for holding treated effluent and sludge. The Sludge Volume Index (SVI) of the reactor effluent was measured and was 80%.

FIG. 3 presents the results of the above experiments in the form of bar graphs. As can be seen, the two-step iron addition process provides a sludge having significantly better settling and compaction properties than the sludge resulting from either the one-step ferric-ferrous iron co-addition process or the single-step ferric iron addition process. These results also demonstrate that the sludge settling and compaction properties are influenced by the pH conditions of the reaction mixture. They further show that the sludge resulting from the process operating at the lower pH of 8 has much better settling and compaction properties than a sludge yield from a process operating at higher pH of 9.

EXAMPLE 3

This Example describes and presents the results from operating a two-step iron addition experiment as described above but with differing ferrous chloride dosing rates in the second step and with different pH conditions for each dosing level. This Example further demonstrates that operating the second step at the lower pH of 8 versus a pH of 9 provides sludge with better settling properties. It also suggests that higher doses of ferrous chloride results in the formation of more sludge.

This experiment used two five-liter continuous stirred tank reactors connected in series flow. A simulated waste water feed, having a selenite concentration of 80 ppbw and a selenate concentration of 80 ppbw, was charged to the first reactor to which a 45 wt.% aqueous ferric chloride solution (0.45 g/ml water) was added to provide a fixed ferric chloride dosing rate of 5 mmol/liter that remained the same for all the experiments. No pH adjustment was made to the reaction mixture of the first reaction stage. The effluent from the first reactor was charged to the second reactor into which an amount of a 15 wt.% aqueous ferrous chloride solution (0.15 g/ml water) was added to provide a ferrous chloride dosing rate of one of five different levels (7.6 mmol/liter, 15.2 mmol/liter, 22.8 mmol/liter, 30.4 mmol/liter, and 38.01 mmol/liter,) for each of the experiments along with an amount of 10% NaOH solution to maintain a reaction mixture pH of either 8 or 9, depending upon the experimental run. Effluent from the second reactor was passed to a tank for holding treated effluent and sludge. The Sludge Volume Index (SVI) for the second reactor effluent was measured.

The following Table presents the SVIs for each of the sludges recovered from the ten experiments. These results demonstrate that the process operating at the lower pH of 8 yielded sludges having better settling and compaction properties than sludges yielded from the process operating at a higher pH of 9. The increases in the SVI for a given pH condition are due to the increases in the amounts of ferrous iron added to the water in each of the experiments.

Table – Sludge Volume Index of Second Stage Reactor Effluent for Different pH Conditions and for Different Ferrous Iron Dosing Ratios

	12.6 mol total Fe per Liter	20.2 mol total Fe per Liter	27.8 mol total Fe per Liter	35.4 mol total Fe per Liter	43.0 mol total Fe per Liter
pH = 8	2%	3%	5%	10%	12%
pH = 9	6%	10%	12%	15%	20%

5 FIG. 4 presents in bar graph form the summary data contained in the above Table. The bar graphs clearly illustrate that settling and compaction properties of sludge made by the two-step iron addition process in which the second mixing step is operated at a lower pH condition of 8 instead of 9 are much better. This is the case regardless of the amount of total ferrous iron that is added to the second mixing step. In all cases of iron addition, the

10 lower pH condition of the second iron addition step provides a sludge having better settling and compaction properties than sludge from the second iron mixing step operated at the higher pH condition.

THAT WHICH IS CLAIMED IS:

1. A method of controlling the properties and yield of sludge in a process providing for enhanced removal of selenium from a waste water stream, having a selenium concentration, wherein said method comprises:
 - mixing ferric chloride with said waste water stream to form a first mixture;
 - mixing ferrous chloride with said first mixture to form a second mixture having a second mixture pH;
 - controlling the formation and properties of an iron oxide precipitate sludge within said second mixture by adjusting said second mixture pH to within a range that provides for the formation of said iron oxide precipitate sludge and said second mixture having a desired sludge volume index; and
 - separating said second mixture, comprising said iron oxide precipitate sludge, into a water product, having a reduced selenium concentration that is less than said selenium concentration, and an iron oxide precipitate sludge product.
2. A method as recited in claim 1, wherein said selenium concentration is in the range of from 50 ppbw to 5,000 ppbw, including a selenite concentration of selenite anions (SeO_3^{2-}) in the range of from 20 ppbw to 5,000 ppbw and a selenate concentration of selenate anions (SeO_4^{2-}) in the range of from 20 ppbw to 5,000 ppbw.
3. A method as recited in claim 2, wherein said reduced selenium concentration is less than 10 ppbw.
4. A method as recited in claim 3, wherein the molar ratio of ferric chloride-to-selenite mixed with said waste water is in the range of from 1,000 to 10,000 moles of ferric per mole of selenite.
5. A method as recited in claim 4, wherein the molar ratio of ferrous chloride-to-selenate mixed with said first mixture is in the range of from 5,000 to 150,000 moles of ferrous per mole of selenate.

6. A method as recited in claim 5, wherein said first mixture is formed within a first mixing zone and said second mixture is formed within a second mixing zone.
7. A method as recited in claim 6, further comprising:
 - passing and introducing at least a portion of said first mixture from said first mixing zone to said second mixing zone.
8. A method as recited in claim 7, further comprising:
 - passing said second mixture to a separation zone defined by a separator providing for said separating of said second mixture into said water product and said iron oxide precipitate sludge.
9. A method as recited in claim 1, further comprising:
 - determining a measured sludge volume index for said second mixture;
 - comparing said desired sludge volume index and said measured sludge volume index to identify a difference between said desired sludge volume index and said measured sludge volume index; and
 - adjusting said second mixture pH in response to said difference to provide said desired sludge volume index.
10. A method as recited in claim 9, wherein said second mixture pH is adjusted within the range of from 7 to 11.
11. A method as recited in claim 10, wherein said step of adjusting said second mixture pH is achieved by adding a pH regulating composition to said second mixture.
12. A method as recited in claim 11, wherein said desired sludge volume index is less than 40%.
13. A method as recited in claim 12, further comprising:
 - adjusting a first mixture pH of said first mixture to within a range to inhibit iron precipitation in said first mixture.

14. A method as recited in claim 13, wherein said first mixture pH is adjusted by admixing an amount of a first mixture pH regulating composition with said first mixture that provides said first mixture pH that is less than about 7.
15. A method as recited in claim 14, wherein said second mixture pH is adjusted within the range greater than 7.5 to 9.
16. A method as recited in claim 15, wherein said second mixture pH is adjusted within the range of from about 7.8 to about 8.8.
17. A method as recited in claim 16, wherein said first mixture is formed within a first mixing zone and said second mixture is formed within a second mixing zone.
18. A method as recited in claim 17, further comprising:
 passing and introducing at least a portion of said first mixture from said first mixing zone to said second mixing zone.
19. A method as recited in claim 18, further comprising:
 passing said second mixture to a separation zone defined by a separator providing for said separating of said second mixture into said water product and said iron oxide precipitate sludge.
20. A method as recited in claim 1, further comprising:
 determining a measured second mixture pH for said second mixture; and
 comparing a desired second mixture pH for said second mixture and said measured second mixture pH to identify a difference between said desired second mixture pH and said measured second mixture pH; and
 adjusting said second mixture pH in response to said difference to provide said desired sludge volume index.
21. A method as recited in claim 20, wherein said second mixture pH is adjusted within the range of from 7 to 11.

22. A method as recited in claim 21, wherein said step of adjusting said second mixture pH is achieved by adding a pH regulating composition to said second mixture.
23. A method as recited in claim 22, wherein said desired sludge volume index is less than 40%.
24. A method as recited in claim 23, further comprising:
adjusting a first mixture pH of said first mixture to within a range to inhibit iron precipitation in said first mixture.
25. A method as recited in claim 24, wherein said first mixture pH is adjusted by admixing an amount of a first mixture pH regulating composition with said first mixture that provides said first mixture pH that is less than about 7.
26. A method as recited in claim 25, wherein said second mixture pH is adjusted within the range greater than 7.5 to 9.
27. A method as recited in claim 26, wherein said second mixture pH is adjusted within the range of from about 7.8 to about 8.8.
28. A method as recited in claim 27, wherein said first mixture is formed within a first mixing zone and said second mixture is formed within a second mixing zone.
29. A method as recited in claim 28, further comprising:
passing and introducing at least a portion of said first mixture from said first mixing zone to said second mixing zone.
30. A method as recited in claim 29, further comprising:
passing said second mixture to a separation zone defined by a separator providing for said separating of said second mixture into said water product and said iron oxide precipitate sludge.

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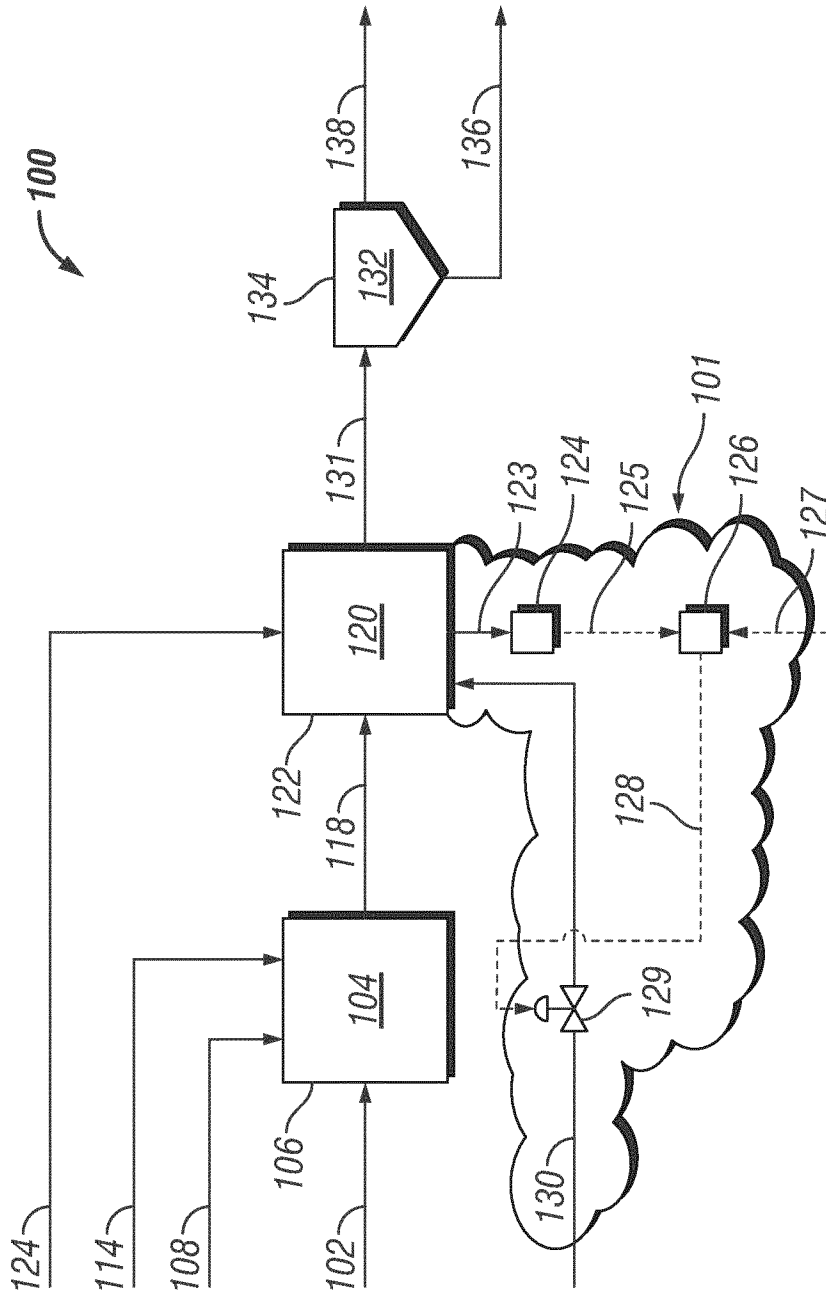


FIG. 1

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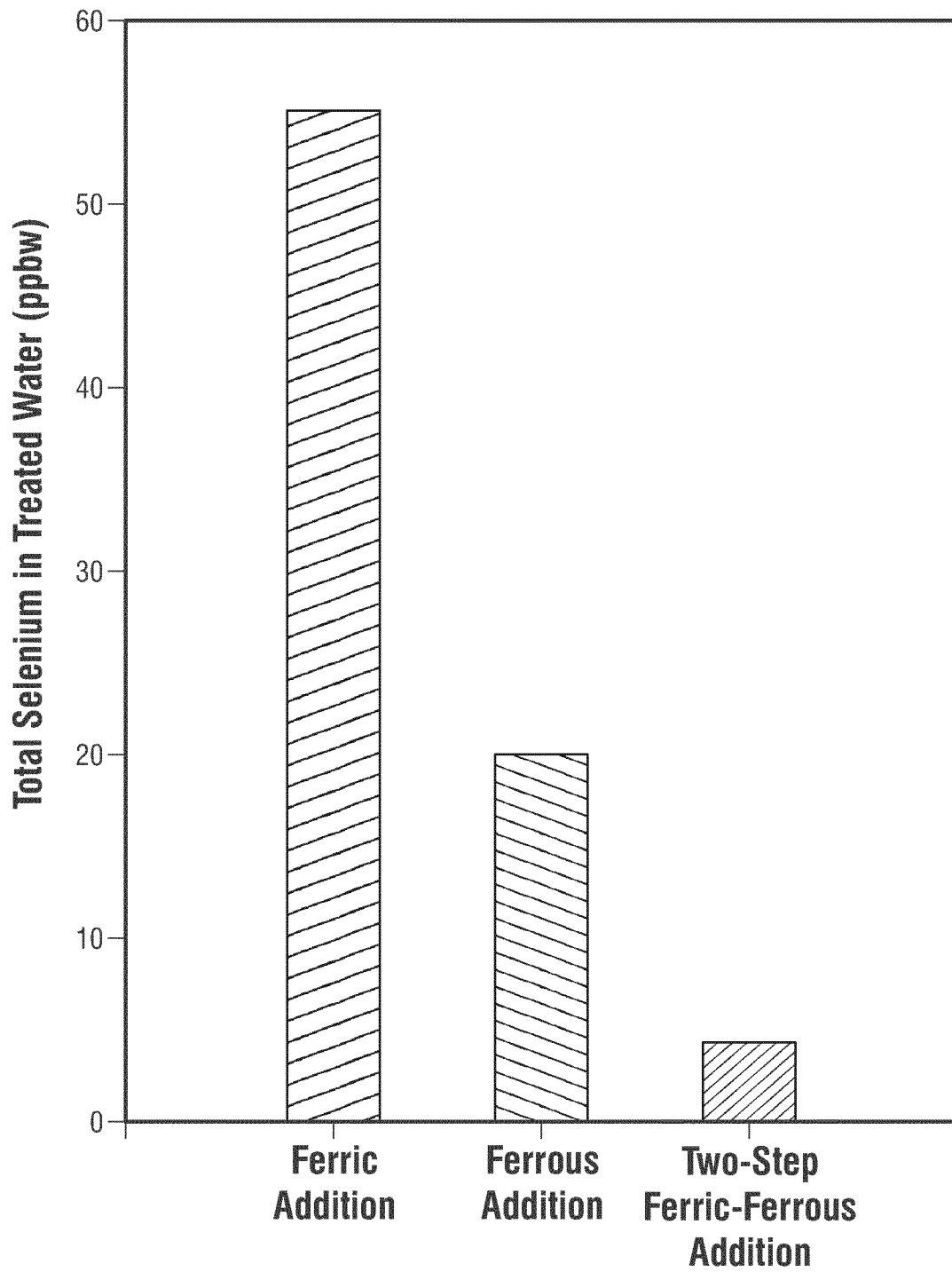


FIG. 2

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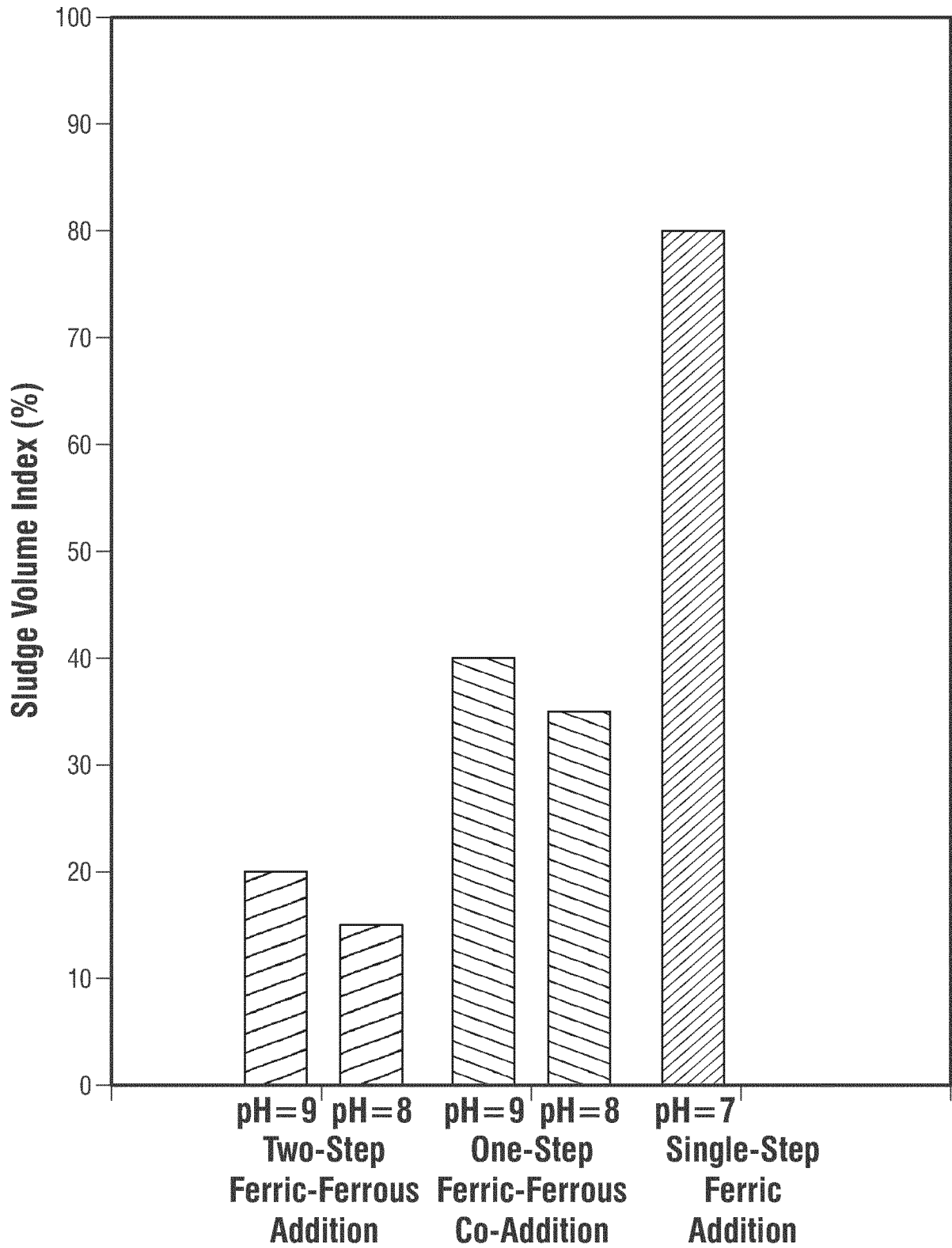


FIG. 3

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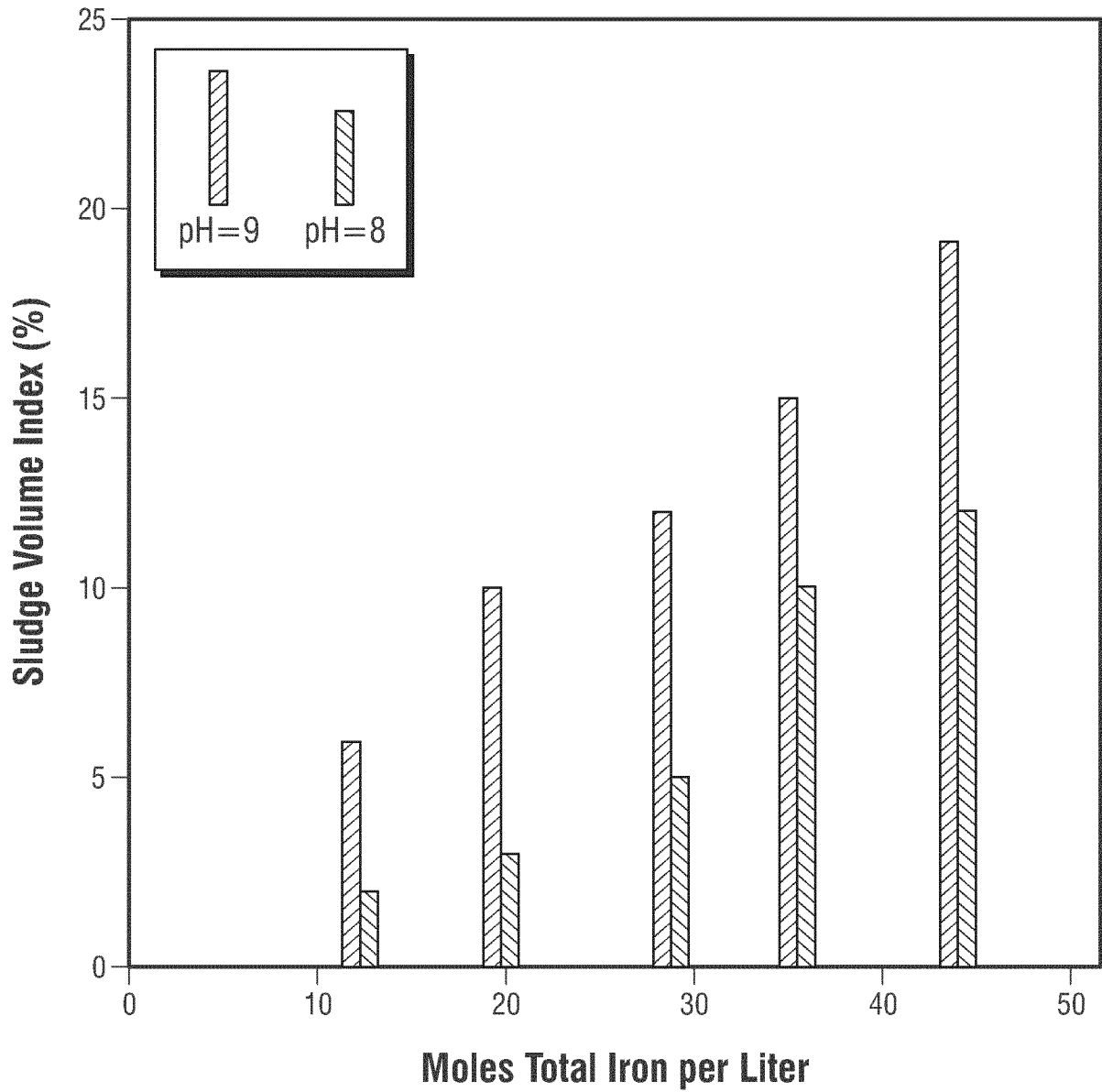


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/061301

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

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: URL:http://dr.iiserpune.ac.in:8080/xmlui/bitstream/handle/123456789/778/20121020_Lipi_Jain.pdf?sequence=1&isAllowed=y [retrieved on 2019-11-01] figure 9 page 26 - page 37</p> <p style="text-align: center;">-----</p>	1-30

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
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Date of the actual completion of the international search
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