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(54) Title: METHODS FOR REMOVING SUBSTANCES FROM AQUEOUS SOLUTIONS

(57) Abstract

Methods are provided for removing contaminants from an aqueous solution to yield a less contaminated aqueous effluent. In one embodiment of the invention, the method comprises corprecipitating non-volatile contaminants (i.e., heavy metals, light metals, cyanide, phenolics, oil and grease, TSS, BOD, COD and/or TOC) with a carrier precipitate which is formed in situ within the aqueous solution. In another embodiment of the invention, the method comprises partioning volatile organic contaminants between a liquid phase and a gas phase. In yet a further embodiment, the above versions of the invention are simultaneously performed in the same reaction vessel.

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METHODS FOR REMOVING SUBSTANCES
FROM AQUEOUS SOLUTIONS

BACKGROUND OF THE INVENTION

One aspect of this invention relates generally to the removal of heavy metals from aqueous solutions and, in particular, to the removal of heavy metals from aqueous solutions by the method of coprecipitation. As used herein, the term "heavy metals" refers to non-ferrous metals and metaloids (e.g., arsenic, selenium, and antimony) which have an atomic number greater than that of calcium.

There is increasing concern over the hazards posed by the rising levels of heavy metals within the world's water supplies. Most heavy metals are toxic to some degree to all life-forms. Aqueous concentrations of as little as 0.05 ppm can have a deleterious effect on aquatic flora and fauna. In humans, toxic heavy metal poisoning can lead to severe nervous system disorders and can cause death. Even trace amounts of heavy metals within an organism's environment are potentially dangerous, because heavy metals do not decompose over time (as do most organic pollutants) and often accumulate within the organism throughout its lifetime. This accumulative effect is accentuated in succeeding species along each food chain.

As a consequence of the increasing concern over aqueous heavy metal concentration levels, industry is being required to virtually eliminate heavy metals from its aqueous wastes. For many industries, however, this requirement is very difficult to fulfill. The metal finishing industries, for example, employ a variety of processes which generate large volumes of aqueous waste material. Many of these wastes contain high concentrations of heavy metals (often as high as 10 percent), including zinc, nickel, copper,

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chromium, lead, cadmium, tin, gold, and silver. The combined
quantity of these wastes generated daily is very large (over
one billion gallons in the United States), and the number of
plants employing metal finishing processes is also large
(nearly 8,000 in the United States). Numerous heavy metal
removal methods have been proposed for the metal finishing
industries, including dilution, evaporation,
alkali-precipitation, absorption, dialysis, electrodialysis,
reverse osmosis, and ion exchange, but none has been found to
be entirely satisfactory.

By far the most common heavy metal removal method
is alkali-precipitation. In this method, a sufficient
quantity of base is added to the aqueous waste solution to
precipitate the desired quantity of heavy metals as insoluble
metal hydroxides. However, as governmental heavy metal
regulations have become stricter, the alkali-precipitation
method has become exceedingly costly, more difficult to use,
and in some instances inappropriate.

Alkali-precipitation must be carried out at high pH
(between about 9 and about 12) in order to reduce the soluble
heavy metal concentrations to within acceptable limits.
Additive chemical volumes can therefore be quite high. Large
quantities of base are required to raise the waste solution
pH to treatment conditions and to precipitate the requisite
quantity of heavy metals. Large quantities of acid are often
required to reduce the pH of the resulting treated effluent
prior to its recycle or disposal. Additive chemical unit
costs are also quite high because a costly base, such as
caustic soda, must be employed. The most preferable base,
aqueous ammonia (because it is less expensive and easier to
handle than caustic soda), is impractical in the
alkali-precipitation method. At the high solution pH levels
required by the alkali-precipitation method, aqueous ammonia

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forms soluble complexes with many heavy metal species
(especially with copper, nickel, and zinc) thereby preventing
their precipitation.

Waste streams containing hexavalent chromium, a
common contaminant in many metal finishing industry waste
solutions, require costly pretreatment because the
alkali-precipitation method is ineffective in precipitating
hexavalent chromium. The pretreatment step entails reducing
the hexavalent chromium to the trivalent state by reaction
with a suitable reducing agent, such as sodium bisulfite, at
pH levels below 3. After pretreatment, the trivalent
chromium is precipitated from the solution as a hydroxide by
raising the solution pH to above about 9.

Waste streams containing organic and nitrogenous
complexing agents, also common contaminants in many metal
finishing industry waste solutions, require a specialized
and especially costly alkali-precipitation treatment. To
counter the tendency of the complexing agents to solubilize
heavy metals, large quantities of calcium hydroxide must be
added to the waste solution. The large quantities of base
necessarily raise the pH of the solution to very high levels,
and make necessary the eventual use of large quantities of
acid to neutralize the resulting effluent. The necessary use
of calcium hydroxide also results in significantly increased
operating costs because calcium hydroxide exists as a slurry
at treatment conditions and is, therefore, very difficult to
handle and control. Furthermore, having to use calcium
hydroxide in such high concentrations results in large
precipitate sludge disposal costs because abnormally large
volumes of sludge are produced. This abnormal sludge
production stems from (a) the fact that, in addition to the
formation of heavy metal precipitates, calcium precipitates

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are formed as well, and (b) the fact that calcium
precipitates tend to retain a large amount of water.

Various light metals, e.g., beryllium and aluminum,
are also undesirable contaminants. Prior art methods for
removing light metals from aqueous systems are not
satisfactory. For example, although aluminum can be removed
by alkaline precipitation, the resulting flocculent or
precipitate (aluminum tetrahydroxide) is very hygroscopic and
is difficult to settle. In addition, alkaline precipitation
is ineffective in treating concentrated aluminum solutions.
Furthermore, aluminum readily redissolves out of the
precipitate.

With respect to beryllium, beryllium is a small,
hydrated, unreactive atom that is generally only removal from
a solution by methods capable of removing sodium, e.g., ion
chromatography.

Cyanide is also a hazardous contaminant. Although
prior art methods for reducing the cyanide concentration in
aqueous systems exist, these methods generally require that
the cyanide be treated separately. Accordingly, if other
contaminants are present in a cyanide-containing solution, a
multi-step process is required to remove all the
contaminants. The use of separate steps to remove the
cyanide and other contaminants increases the cost of the
treatment process.

In addition, governmental regulations restrict the
amount of organic contaminants that can be present in water.
Exemplary organic contaminants include volatile organics,
phenolics, oil and grease, and organic contaminants measured
in terms of total suspended solids (TSS), biological oxygen
demand (BOD), chemical oxygen demand (COD), and total organic

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carbon (TOC). Unfortunately, compliance with these
governmental regulations is not always possible because it is
difficult to remove sufficient organic contaminants with
prior art organic contaminant removal methods.

SUMMARY OF THE INVENTION

In accordance with the present invention, methods
are provided for removing contaminants from an aqueous
solution. In one version, the method comprises
coprecipitating heavy metal ions with a carrier precipitate
which is formed in situ within the aqueous solution. In
another version, the method comprises coprecipitating light
metal ions with a carrier precipitate which is formed in situ
within the aqueous solution. In a third version, the method
entails coprecipitating cyanide ions with a carrier
precipitate which is formed in situ within the aqueous
solution. If a mixture of heavy metal ions, light metal
ions, and/or cyanide ions are present in the aqueous
solution, these contaminants can be simultaneously
coprecipitated using the same methodology.

Use of the above methods results in reducing the
presence of heavy metal ions, light metal ions, and cyanide
ions in the aqueous solution to below their thermodynamic
equilibrium concentrations. This extraordinary result
affords the user the unique ability to substantially reduce
high aqueous concentrations of heavy and light metals as well
as cyanide often to within legally acceptable concentrations,
while maintaining the aqueous solution at near neutral pH.

In addition, methods are also provided for removing
volatile organics, phenolics, oil and grease, TSS
contributors, BOD contributors, COD contributors, and TOC

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contributors from an aqueous solution. The phenolics, oil
and grease, TSS contributors, BOD contributors, and/or TOC
contributors present in an aqueous solution are removed by
adsorption onto a carrier precipitate which is formed in situ
within the aqueous solution. The carrier precipitate
preferably is the same precipitate used to remove the heavy
metals, the light metals, and/or cyanide.

        In each of the above embodiments of the invention,
the preferred method involves rapidly forming the precipitate
at a controlled pH by quickly oxidizing ferrous ions to form
a substantially completely amorphous ferric
hydroxide-containing precipitate that also contains a major
portion of the non-volatile contaminants originally present
in the aqueous solution.

        With respect to the volatile organics, these are
removed by sparging air through the aqueous solution. In
addition, the volatile organic removal process and above
discussed precipitation process can be performed
simultaneously in the same vessel.

        Accordingly, the (a) phenolics, oil and grease, TSS
contributors, BOD contributors, and/or TOC contributors, (b)
heavy metal ions, light metal ions, and/or cyanide ions,
and/or (c) volatile organics can be simultaneously removed
from the same aqueous solution in the same reaction vessel.

                BRIEF DESCRIPTION OF THE DRAWING

        The present invention will be more readily
understood by reference to the drawing which schematically
illustrates a waste water treatment system embodying features
of the invention.

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DETAILED DESCRIPTION OF THE INVENTION

The method of the invention can be used to remove the following contaminants from nearly any aqueous stream: dissolved heavy metals, light metals, TSS contributors, BOD contributors, COD contributors, TOC contributors, volatile organics, and/or iron. The invention will now be described first with respect to heavy metals, then light metals and cyanide, next phenolics, oil and grease, TSS contributors, BOD contributors, COD contributors, and TOC contributors, and finally with respect to volatile organics. Unless otherwise stated, all process and apparatus parameters disclosed for heavy metal removal are equally effective for the removal of the other contaminants as well. Likewise, unless otherwise stated, all process and apparatus parameters disclosed for the removal of the other non-volatile contaminants are equally effective for heavy metal removal as well.

With respect to heavy metals, the invention is particularly useful in removing the large concentrations of copper, nickel, zinc, gold, silver, cadmium, tin, chromium, lead, vanadium, mercury, titanium, selenium, antimony, and molybdenum from pickling acid wastes and other acidic waste streams formed in the metal finishing industries. In the method of the invention, an amorphous carrier precipitate is created within an aqueous waste solution which is contaminated with heavy metals and/or iron. The contaminants are thereby caused to coprecipitate with the carrier precipitate and are thus removed from the aqueous solution.

"Coprecipitation" as used with respect to the invention described herein refers to the chemical phenomenon where, within an aqueous solution containing a cationic carrier precipitate precursor, an anionic carrier precipitate precursor, and one or more coprecipitant precursors, the

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cationic and anionic carrier precipitate precursors are
caused to chemically react and precipitate out of the aqueous
solution as carrier precipitate particles; and, as the
carrier precipitate particles are formed, coprecipitant
precursors are removed from the aqueous solution by
adsorption onto the surface of the carrier precipitate
particle and/or by occlusion within the interior of the
carrier precipitate particle. The term "occlusion" as used
herein refers to the entrapment of foreign ions within a
precipitate particle by physical encapsulation within the
particle walls and by chemical bonding within the particle
structure.

It has been discovered that by the method of the
invention a heavy metal-rich aqueous solution can be
transformed into a liquid-solid mixture wherein the
liquid-phase heavy metal concentrations are substantially
lower than their respective equilibrium concentrations.
Although the invention is not limited to any particular
theory of operation, the reduction of heavy metal
concentrations below their equilibrium concentrations is
believed to result, in part, from the large quantities of
heavy metals which are occluded within the amorphous carrier
precipitate structure. The proportion of the dissolved heavy
metals which become occluded is typically greater than 10
weight percent, frequently greater than 50 weight percent and
often greater than 80 weight percent. By segregating the
liquid-phase of the mixture from the amorphous solid-phase, a
stable aqueous effluent is produced which is substantially
free of heavy metals. It has been further discovered that
the method of the invention results in liquid-phase heavy
metal concentrations which are so much lower than their
respective equilibrium values that environmentally innocuous
liquid effluents can be produced from heavy

metal-concentrated solutions, even when the liquid phases are
maintained at near neutral pH.

In the embodiment of the invention illustrated in
the drawing, an acid waste stream containing heavy metal ions
in concentrations usually above 50 ppmw, typically greater
than 100 ppmw, frequently greater than 1,000 ppmw and often
greater than 10,000 ppmw is generated in an industrial
process 6. This stream is transferred from the industrial
process 6 via a conduit 8. Carrier precipitate precursor
cations from a source 10 are added to the stream via a
conduit 12 to raise the concentration of such cations
sufficiently so that the molar ratio of such cations to heavy
metal ions within the stream is preferably greater than 1:1,
more preferably greater than 4:1, and most preferably greater
than 8:1. However, the molar ratio of carrier precipitate
precursor cations to heavy metal ions is typically less than
about 10:1. In a preferred embodiment of the invention,
wherein the carrier precipitate is amorphous oxyferric
hydroxide (hereinafter referred to as "ferric hydroxide"),
ferrous ions are preferably added as the carrier precipitate
precursor cations to achieve the desired molar ratio of
ferrous ions to heavy metal ions. However, since waste
streams rich in heavy metals are commonly rich in dissolved
iron as well, sometimes only little or no addition of ferrous
ions from the source 10 is necessary.

Carrier precipitate precursor anions are also added
to the waste acid stream. Preferably, such anions are added
in sufficient quantities to raise the concentration of such
anions within the waste stream to above the stoichiometric
concentration necessary to react with all solubilized carrier
precipitate precursor cations, and more preferably above 110
percent of such stoichiometric concentration. The addition
of such anions can be made by injection into the conduit 8

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(not shown) or by addition to vessels 14 and 16 (as described
hereinafter). In the embodiment shown in the drawing,
addition of the anions is made in two stages to allow for
accurate pH control. This two stage pH control is especially
preferred for use when ammonia is the selected base and
complexable metal cations are present in the waste water.
Accordingly, as illustrated in the drawing, the waste acid
stream from the industrial process 6 is transferred via the
conduit 8 to the mixing vessel 14. The anions are added as
part of a base from a source 18 to the acid waste solution
within the vessel 14 via a conduit 20. Exemplary bases
include aqueous ammonia, hydroxide containing bases (e.g.,
sodium hydroxide, calcium hydroxide, potassium hydroxide,
magnesium hydroxide, etc.), and mixtures thereof.

Rapid mixing of the solution within the vessel 14
is preferably assured by the use of a mixing device 22.
Sufficient base is added to the solution within the vessel 14
to raise the solution pH to between about 5.5 and about 6.5.
The partially neutralized waste solution is then transferred,
via a conduit 24, to the precipitation vessel 16. Via a
conduit 26, additional base from the source 18 is added to
the waste solution within the vessel 16 in sufficient
quantities to raise the solution pH to between about 6.5 and
about 9.5, preferably to between about 6.5 and about 9, e.g.,
about 6.5 to about 8 or about 6.5 to about 7.5, but most
preferably to between about 7.5 to about 8.

Within the vessel 16, the carrier precipitate
precursor cations are caused to react with the carrier
precipitate precursor anions and precipitate out of solution.
As the amorphous carrier precipitate forms, substantial
quantities of heavy metal ions coprecipitate with the carrier
precipitate and are thereby removed from the solution. In
the preferred embodiment wherein the carrier precipitate is

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ferric hydroxide, precipitation is triggered by the oxidation
of ferrous ions to ferric ions. Accordingly, as illustrated
in the drawing, an oxidizing agent, e.g., air, oxygen, and
mixtures thereof, from a source 28, is added to the acid
waste stream via a conduit 30. The preferred oxidizing agent
is air. Sufficient oxidizing agent is added to rapidly
oxidize essentially all of the dissolved ferrous ions to
ferric ions. When air is the selected oxidizing agent, the
rate of air addition is preferably sufficient to oxidize all
of the ferrous ions and to air-saturate the solution.

A dispersion device 32 and/or a mixing device 34
can be used to assure rapid and thorough mixing of the waste
solution, additive base, and additive oxidant within the
vessel 16. The function of the mixing device 34 is, in part,
to shear or otherwise reduce the size of the bubbles that
emerge from the dispersion device 32. An exemplary
dispersion device 32 is a multi-perforated tube. In general,
the cross-sectional area of the multi-perforated tube is
selected so that the air flow rate divided by the
cross-sectional area is from about 50 to about 150 ft/sec.
The remaining dimensions of the multi-perforated pipe are
selected in accordance with the rule of thumb for design of
perforated-pipe distributors as discussed in Perry's Chemical
Engineers' Handbook, Perry et al. Editors, 4th ed.,
McGraw-Hill Book Company, New York, NY (1963), page 5-45, the
publication being incorporated herein by reference.

The coprecipitant reaction is very rapid.
Typically, more than 95 weight percent, and usually more than
99 weight percent, of the heavy metals are removed from the
waste solution within about 8 minutes after the formation of
the first 5 weight percent of the carrier precipitate. After
this 8 minute period, the remaining solubilized heavy metals
generally continue to be adsorbed onto the precipitate

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particles. The ideal residence time of the aqueous solution
within the vessel 16 and a separator 36 (described
hereinafter) varies with each particular operation situation,
and the optimizing of such residence time will, in each
situation, require some routine adjustment.

From the vessel 16, aqueous effluent, now
substantially reduced in dissolved heavy metal content, is
transferred together with the nascent precipitate to the
solids separator device 36 via a conduit 38. The precipitate
is essentially completely amorphous. Within the separator 36
the effluent and amorphous precipitate are segregated into
two streams. The separator 36 is comprised of a clarifier,
filter, centrifuge, settling pond or other suitable
liquid-solid separating equipment capable of segregating the
precipitate particles from the aqueous effluent. The
segregated precipitate is removed from the separator 36 as a
sludge and is transferred to a suitable disposal site (not
shown) via a conduit 40.

Although in some embodiments of the invention it is
desirable to return a portion of the sludge to either the
mixing vessel 14 or the precipitation vessel 16 via a conduit
(not shown), in the preferred version of the invention none
of the sludge is returned to any portion of the treatment
system. In fact, it is most preferred that no water
insoluble matter be added to the mixing vessel 14 or the
precipitation vessel 16 or any portion of the system feeding
into either of these vessels 14 or 16. However, some bases
suitable for use in the present invention may be only
partially water soluble. These partially water soluble bases
can be employed in the most preferred embodiment of the
present invention provided that they are substantially devoid
of iron-containing, water-insoluble compounds.

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The corresponding aqueous effluent, which typically contains less than 15 ppmw heavy metals and usually contains less than 5 ppm heavy metals, can be recycled to the industrial process 6 via a conduit 42. In those cases where it is desired that the recycled effluent be less basic than the solution within the separator 36 (e.g., where the recycled effluent is to be used as an acid makeup solution), acid from a source 44 is added to the recycled effluent via a conduit 46. Optionally, the treated effluent from the separator 36 is discharged to a disposal site (not shown) via a conduit 48. Preferably, the concentrations of heavy metals within the treated effluent are reduced to below the relevant legal limits so that non-recycled effluent can be discharged directly to a municipal sewer.

Although the preceding description of one embodiment of the invention assumes that the aqueous waste solution is an acid waste, the invention is not limited to the treatment of such wastes. Furthermore, although the preceding description of the invention describes a continuous process, the invention can also be practiced as a batch process. In addition, although the carrier precipitate precursor cations (e.g., ferrous ions) have been shown to be originally present in the acid waste stream or added to the acid waste stream via the conduit 8, in an alternative embodiment of the invention the cations are added directly to the precipitation vessel 16 or to any liquid flowing into the precipitation vessel 16. Also, although the pretreatment vessel 14 is shown in the drawing, it is more preferred to introduce the waste stream directly into the precipitation vessel 16 along with the required base, and thus avoid the need for the pretreatment vessel 14. Generally, the pretreatment vessel 14 is used when ammonia is the desired base and the waste water contains complexable metal cations,

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but even in these situations it is not critical that the two
stage pH control be used.

Preferably, the choices of carrier precipitate
precursors and operating conditions are made so as to
maximize the removal of heavy metal ions while minimizing
treatment costs. Towards that end the choices are generally
made so as to (1) produce a carrier precipitate structure
which is conducive to heavy metal occlusion, (2) produce a
carrier precipitate particle surface which is conducive to
adsorption, (3) form the carrier precipitate as rapidly as
possible, and (4) minimize extraneous reactions which
interfere with heavy metal coprecipitation.

The carrier precipitate cation and anion are
generally chosen so that, when the carrier precipitate is
forming, the developing precipitate is conducive to the
occlusion of heavy metals. The carrier precipitate cations
of choice are those which have approximately the same ionic
diameter as most of the contaminant heavy metals. The
similarity of ionic diameter makes it conducive for the
forming carrier precipitate to accept heavy metal ions in
substitution for carrier precipitate cations. When
substituted heavy metal ions are similar in size to the
cations, the precipitate structure is not unduly stressed by
the heavy metal inclusion. Thus, preferably, the ionic
diameter of the carrier precipitate precursor cation is
between about 75 percent and about 125 percent of the ionic
diameter of the most common heavy metal contaminant within
the waste solution.

The preferred carrier precipitate cations are metal
ions, with the ions of aluminum, calcium, iron (ferrous), and
magnesium being more preferred. Most preferred are iron
ions, because such ions closely approximate the size of most

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contaminant heavy metals and because it is common for large
natural concentrations of iron ions to be dissolved within
heavy metal-rich waste streams.

The carrier precipitate anions of choice are those
which form insoluble salts with the contaminant heavy metals
as well as with the carrier precipitate cations. Such anions
have a strong attraction for heavy metal ions, and the degree
of heavy metal occlusion is directly proportional to the
strength of the anion-heavy metal bonds. This
proportionality stems from the fact that, before heavy metal
occlusion can occur, the heavy metal ions must first be drawn
to and strongly held by the anions at the surface of the
carrier precipitate. When the carrier precipitate cations
are ferrous ions, the preferred carrier precipitate anions
are hydroxyl, phosphate, and carbonate ions. When the
carrier precipitate cations are calcium ions, the preferred
anions are hydroxyl, phosphate, carbonate, and sulfate ions.
When the carrier precipitate cations are aluminum, the
preferred anions are hydroxyl and phosphate ions. When the
primary precipitate cations are magnesium, the preferred
anions are hydroxyl, phosphate, and carbonate ions. The
preferred carrier precipitates are aluminum hydroxide, ferric
hydroxide, calcium sulfate, iron phosphate, and calcium
phosphate, with ferric hydroxide being most preferred.

The operating conditions are also generally
controlled so as to produce a carrier precipitate particle
surface which is conducive to the adsorption of heavy metal
ions. As explained above, the carrier precipitate anion is
chosen from among those anions which form strong bonds with
the contaminant heavy metal ions. In addition, the
concentration of carrier precipitate precursor anions in
solution is maintained in most cases at levels sufficiently
in excess of the concentration of the carrier precipitate

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precursor cations so as to assure that the carrier
precipitate particle surface is anionic. The anionic
particle surface attracts the heavy metal ions, binds them
(adsorption), and makes them available for incorporation
within the precipitate structure (occlusion). When hydroxyl
ions are the chosen carrier precipitate anions, maintaining
such anion excess is a matter of pH control. Where ferric
hydroxide is the chosen carrier precipitate, solution pH
during coprecipitation is maintained above about 6 because
solutions which are more acidic cause the ferric hydroxide
precipitate surface to take on a cationic character.

     In general, the larger the carrier precipitate
surface area, the more heavy metals are removed from
solution. Thus, the carrier precipitate and the conditions
of operation are preferably chosen so as to maximize the
surface area of each unit mass of precipitate. The total
mass quantity of produced carrier precipitate is thereafter
controlled, where possible, to the minimum value sufficient
to remove the requisite quantity of heavy metals.

     The carrier precipitate is generally formed as
rapidly as possible because the removal of heavy metal ions
by both the adsorption and occlusion mechanisms is markedly
greater at higher precipitation rates. Typically, about 95
percent of the carrier precipitate is formed within about 15
minutes, preferably within about 10 minutes, and more
preferably within about 5 minutes. The adsorption of heavy
metal ions is increased by an increase in the precipitation
rate because adsorption is surface area-dependent. When the
carrier precipitate is formed rapidly, it forms as a large
number of small individual particles, each having a high
surface area-to-mass ratio. By relative comparison, when the
carrier precipitate is formed slowly, it forms as a small
number of large particles, each having a low surface

area-to-mass ratio. Thus, for a given mass of carrier
precipitate precursors, the faster the precipitate is formed,
the larger is the combined surface area of the resulting
precipitate particles.

The occlusion of heavy metal ions is increased by
an increase in precipitation rates because occlusion is
adsorption-dependent and diffusion time-dependent. As
alluded to above, heavy metal ions are more likely to be
occluded within the carrier precipitate when they are first
adsorbed at the carrier precipitate surface. Thus, the
number of heavy metal ions occluded within the carrier
precipitate is proportional to the number of heavy metal ions
adsorbed onto the carrier precipitate surfaces during the
growth of the carrier precipitate particles. The number of
heavy metal ions which are occluded within the carrier
precipitate is inversely proportional to the relative ionic
diffusion times available in the vicinity of the forming
carrier precipitate. Heavy metal ions, which initially bond
with precipitate surface anions and which might otherwise be
eventually incorporated as a part of the particle framework,
tend to be displaced by competing carrier precipitate
precursor cations which diffuse to the precipitate surface.
Thus, if the rate of carrier precipitate formation is
relatively fast with respect to the rates of ionic diffusion
near the forming particle surfaces, the localized diffusion
times are relatively small and more heavy metals are
occluded.

The choices of carrier precipitate and operating
procedures are therefore preferably made, in part, so as to
maximize the rate at which the carrier precipitate is formed.
In the preferred embodiment wherein the carrier precipitate
is ferric hydroxide, the precipitation rate depends on two
reactions, the oxidation of ferrous ions to ferric ions and

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the reaction of ferric ions with hydroxyl ions. The
precipitation rate is almost solely controlled by the
oxidation reaction since oxidation is much the slower of the
two reactions. Thus, the basic strategy is to maximize the
rate of oxidation. Accordingly, in the case of ferrous ions,
substantially all the ferrous ions in the solution are
oxidized to ferric ions within about 30 minutes. Preferably,
the oxidation time is less than 15 minutes, and more
preferably less than 10 minutes. In order to obtain this
oxidation rate, the oxidant is rapidly introduced into the
aqueous solution. Since the more oxidant introduced into the
solution, the faster the oxidation rate, the amount of
oxidant, when air, introduced into the solution is typically
at least about 1 liter of air, preferably at least about 2
liters of air, more preferably at least about 4 liters of
air, and even more preferably at least about 10 liters of air
per 1000 ppm ferrous iron initially present in the solution
before the introduction of oxidant when operating on a batch
basis. However, when operating on a continuous basis, the
above amounts of air are per 1000 ppm ferrous present, on an
average, in the feed stream to the reactor. In rate terms,
when the oxidant is air, the air is generally introduced into
the solution at a rate of at least about 10, more typically
about 50, preferably about 90, and even more preferably about
200 liters of air per hour per liter of solution per 1000 ppm
ferrous iron (1/hr/1/1000 ppm ferrous iron) present in the
solution at the beginning or substantially at the beginning
of the residence time of the solution in the precipitation
vessel 16 when operating on a batch basis. However, when
operating on a continuous basis, the rate of air introduction
is per 1000 ppm ferrous iron present, on an average, in the
feed stream entering the precipitation vessel 16.

The oxidation reaction is also accelerated as the
solution pH is raised. Accordingly, it is preferred to

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maintain the pH of the reaction medium as high as possible
during the introduction of the oxidizing agent.

In addition, the oxidation reaction is accelerated
by the presence of a suitable catalyst. Most soft Lewis
bases can be employed as suitable catalysts, with iodine and
oxygen-containing soft Lewis bases being preferred. The most
preferred catalyst is ferric hydroxide since it is
manufactured in situ by the method of the invention.
However, no addition of catalyst is usually necessary because
ferric hydroxide is formed in situ and is thereafter
constantly present within the precipitation vessel 16.

In addition to promoting rapid precipitation, the
rapid oxidation of the ferrous ions may promote occlusion in
another way. In aqueous solutions, ferrous ions tend to form
soluble complexes with heavy metal and hydroxyl ions. If the
ferrous ions of such complexes are rapidly oxidized to ferric
ions, these complexes tend to precipitate out of solution en
masse, including the originally complexed heavy metal ions
which, during precipitation, become occluded within the
precipitate.

The operating conditions are also preferably
controlled to minimize extraneous reactions which interfere
with the heavy metal coprecipitation. Thus, the
concentration of superfluous ions is maintained as low as
practical (for instance, by dilution of the waste stream)
since such ions interact with carrier precipitate precursor
and heavy metal ions, thereby impeding the coprecipitation
reactions. Also, the pH of the aqueous solution is
maintained at sufficiently low levels to minimize the effects
of complexing agents which solubilize heavy metal ions at
high pH. For instance, certain nitrogenous compounds,
including ammonia, complex with several heavy metal ions,

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especially with copper, nickel, and zinc, at pH levels above
about 8. Where such complexing agents are present in the
aqueous solution and where "complexable" heavy metal ions are
also present, the pH of the aqueous solution is therefore
maintained below about 8, and preferably below about 7.5.
Accordingly, in the embodiment of the invention illustrated
in the drawing (wherein aqueous ammonia is used as a base),
the pH of the waste solution in the precipitation vessel 16
is preferably maintained between about 6.5 and about 7.5 in
order to oxidize the ferrous ions as rapidly as possible but
not form significant quantities of ammonia-heavy metal
complexes. Since this pH operating range is relatively
narrow, since the relation between dissolved ammonia and
solution pH is very sensitive within this operating range,
and since the pH of the acid waste stream generated in the
industrial process 6 can fluctuate significantly, it is
sometimes preferable as shown in the drawing to accomplish pH
control in two steps. First, the pH of the acid waste stream
is raised to pH levels between about 5.5 and about 6.5 within
the vessel 14. Second, the solution pH is carefully raised
to operating levels (e.g., between about 6.5 and about 7.5,
but most preferably between about 7.5 and about 8) within the
precipitation vessel 16. However, if possible, it is
generally preferred to add the waste stream directly to the
precipitation vessel 16 and adjust the pH of the waste stream
only within the precipitation vessel 16, i.e., to avoid two
step pH control.

Accordingly, the aqueous waste solution is
preferably introduced into the precipitation vessel 16 while
maintaining the vessel 16 under conditions which
substantially and immediately subject essentially all of the
ferrous ions entering the vessel 16 to oxidizing conditions
causing rapid oxidation of the ferrous ions while preferably
controlling the pH so as to coprecipitate a substantially

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completely amorphous precipitate comprising a substantial
amount of ferric hydroxide coprecipitated with a substantial
proportion of the heavy metals.

The method of the invention is unique in its
effectiveness for removing substantial quantities of heavy
metals from aqueous solutions at near neutral pH. The
effective removal of heavy metals at near neutral pH is most
advantageous to the industrial operator. It substantially
reduces problems caused by the aforementioned presence of
heavy metal complexing agents, especially nitrogenous
complexing agents, which are commonly found in aqueous waste
streams. Accordingly, it allows the additive use of aqueous
ammonia, a most cost-effective base. The ability to operate
at near neutral pH also eliminates the need to add
neutralizing acid to the treated effluent before disposal.
Likewise, it markedly reduces the consumption of fresh acid
necessary to reacidify the treated effluent when the effluent
is employed as a recycle acid. Finally, operating at near
neutral pH produces a precipitate which settles faster than
precipitates formed at higher pH levels. This last fact
allows the operator to separate the treated effluent from the
nascent precipitate particles with smaller and less expensive
separating equipment than would be required by other
precipitation methods.

The preferred embodiment of the invention employing
ferric hydroxide as the carrier precipitate has the
additional unique advantage over conventional hydroxide
precipitation methods of requiring less additive base to
precipitate a given quantity of iron and contaminant heavy
metals. In conventional alkali-precipitation methods, base
is consumed in the precipitation of individual iron ions, and
additional base is consumed in the precipitation of
individual heavy metal ions. In the embodiment of the

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invention illustrated in the drawing, base is consumed in the
precipitation of individual ferric ions, but little
additional base is required to precipitate the heavy metal
ions. Furthermore, in this preferred embodiment of the
invention, a substantial proportion of the base required by
the process is manufactured by the process itself. For every
ferrous ion that is oxidized to a ferric ion, a hydroxyl ion
is produced pursuant to the following reaction:

$$2Fe^{+2} + 1/2O_2 + H_2O \longrightarrow 2Fe^{+3} + 2OH^-$$

The method of the invention is also advantageous in
that chromium ions can be removed from an aqueous waste
solution without having to first reduce the hexavalent
chromium ions to trivalent ions. Typically, in a preferred
embodiment of the invention, more than about 95 percent, and
preferably more than 99 percent, of the hexavalent chromium
is removed from the aqueous waste solution at the same time
and by the same method as are other heavy metals. Thus, the
method of the invention eliminates the need for segregating
and separately treating hexavalent chromium-containing waste
streams, and saves the costs of acid, base, and reducing
agent required by such treatment.

The method of the invention is further advantageous
in that several heavy metals in the waste solution – and
oftentimes each and all of the heavy metals – can be removed
by at least about 95%, sometimes at least by about 99%, with
iron also being removed by at least about 95% and oftentimes
by virtually 100%. The examples hereafter show how readily
the invention removes two, three, and four heavy metals
simultaneously by more than about 95%, with three examples
(i.e., Examples 1, 4, and 10) showing the removal of five
such heavy metals, with a concomitant reduction in the iron
by about 100%. In addition, the data in Examples 6 to 10

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establish that, under the preferred operating conditions, each of the heavy metals (and iron) can be reduced to a concentration less than about 1 ppmw - even when the initial concentrations total more than about 400 ppmw. In addition, the present invention is capable of reducing the concentration of the heavy metals in the treated waste water to below their thermodynamic equilibrium levels. Typically, at least one heavy metal is reduced to below its thermodynamic equilibrium concentration level. Preferably, the concentrations of a plurality, e.g., at least 3 or 4, and most preferably all, of the heavy metals are reduced to below their thermodynamic levels.

In one version of the present invention, to further reduce the concentration of contaminants in the effluent from a first treatment process embodying features of the present invention, the effluent is subjected to a second treatment process in accordance with the method of the present invention. In other words, although in the vast majority of cases only a single operating stage with a single precipitation reactor vessel 16 will be needed, one may operate serially with a plurality of stages, each treating the effluent of the preceding stage.

Finally, the method of the invention is superior to conventional precipitation methods in that it produces less precipitate sludge. The lower sludge production stems, in part, from the fact that the volume of sludge is smaller when several metals are coprecipitated than when those metals are precipitated separately. The difference in sludge-production is even greater when the method of the invention and conventional precipitation methods are compared in the treatment of aqueous solutions containing significant quantities of heavy metal complexing agents. As stated above, the conventional treatment of such aqueous solutions

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requires the use of large quantities of calcium hydroxide and results in the formation of sludge volumes which are even larger than normal.

The invention can be further understood by considering the following specific examples which are illustrative of specific modes of practicing the invention and are not intended as limiting the scope of the appended claims.

EXAMPLE 1

Two aqueous waste solution samples were obtained from a commercial electroplating process. The first sample was taken from a 10,800 gal/day waste water stream containing approximately 0.6 weight percent total dissolved solids. The second sample was taken from a 1,400 gal/day waste acid stream containing approximately 15 weight percent total dissolved solids.

Twenty-three milliliters of the waste acid sample was mixed in a mechanically agitated beaker with 177 ml of the waste water sample to yield 200 ml of a combined waste solution sample. Immediately thereafter, 4.5 ml of a 28 weight percent aqueous ammonia solution was rapidly added to the beaker. Thereupon, 25 ml of an aqueous solution containing approximately 4 weight percent of a ferric hydroxide-heavy metal precipitate was added to the beaker.

Immediately thereafter, air was commenced to flow through a sintered glass tube at the bottom of the beaker so as to cause air bubbles to rise through the solution. A precipitate was observed to appear within the solution, and the solution pH was observed to begin dropping. Aqueous ammonia was periodically added to the solution over about the

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next 30 minutes in order to maintain the solution pH between
about 7.0 and about 7.5.

After about 30 minutes, the solution pH was
observed to stabilize. The flow of air was ceased but the
solution was agitated for an additional 30 minutes.

Thereafter, a pipette was used to extract a sample
of the solution-precipitate mixture. The precipitate
particles were removed by filtering the sample through #41
(coarse) filter paper. The resulting filtrate was clear and
colorless.

The filtrate was analyzed for heavy metals content
and compared to the heavy metal content of the original
combined waste solution sample. The results are presented in
TABLE 1.

TABLE 1

Sample	Metals Concentrations, ppmw							Solution pH
	Cd	Cr	Cu	Fe	Ni	Pb	Zn	
Untreated combined waste solution	0.6	2.3	5	4,850	3.5	106	953	3.5
Treated filtrate after treatment	<0.1	<0.1	1.4	<0.1	0.2	<0.5	2.8	7.3
Percent Removal	>98.3	>95.7	72.0	100	94.3	>99.5	99.7	NA[1]

1. NA denotes not applicable.

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EXAMPLE 2

A 50 ml sulfuric acid waste sample from a commercial electroplating process was diluted with distilled water to 200 ml. The waste solution was neutralized by the addition of 17.5 ml of a 28 weight percent aqueous ammonia solution, whereby the solution pH was observed to be 7.7.

The slurry was added to a mechanically agitated beaker containing 22 ml of an aqueous ferric hydroxide slurry. Air was commenced to flow through a sintered glass tube at the bottom of the beaker so as to cause air bubbles to rise through the solution. Aqueous ammonia was periodically added to the solution so as to maintain the solution pH between 7.0 and 7.5.

About 15 minutes after neutralization, the pH of the solution was stabilized at about 7.35 and a precipitate was observed within the solution. Air dispersion was terminated but mechanical agitation was continued. A sample of the solution-precipitate mixture was extracted with a pipette and filtered through coarse filter paper. About 25 minutes after neutralization, a second sample was similarly extracted and filtered. The filtrates from both samples were clear and colorless.

The filtrates from both samples were analyzed for heavy metals content. A comparison of the heavy metals content of the filtrates to the heavy metals content of the original acid waste sample is summarized in TABLE 2.

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TABLE 2

Sample	Cd	Cr	Cu	Fe	Ni	Zn	SO_4 Conc. ppmw	Solution pH
Untreated acid waste	0.75	8.75	2.0	3,625	8.5	132	66,250	N.T.[1]
Treated filtrate 15 min. after neutralization	<.01	<.01	0.2	<.01	1.7	2.1	N.T.	7.35
Percent Removal After 15 min.	>98.7	>99.9	90.0	100	80.0	98.4	NA	NA
Treated filtrate 25 min. after neutralization	<.01	<.01	0.2	<.01	1.7	2.1	N.T.	7.35

(Metals Concentrations, ppmw)

1. N.T. denotes that the parameter was not tested.

EXAMPLE 3

A 200 ml volume of a heavy metals-containing acid solution was prepared. The solution was placed in a mechanically agitated beaker and neutralized to a pH between about 7.0 and about 7.5. Immediately thereafter, 0.142 gr of ferric oxide was added to the solution and air was commenced to bubble through the solution. Additional base was periodically added to maintain the solution pH between 7.0 and 7.5. About 7 minutes after neutralization, the solution pH was observed to have stabilized and precipitate particles were visible within the solution. A sample of the solution-precipitate mixture was extracted and filtered with coarse filter paper. The filtrate, which was clear and colorless, was analyzed for heavy metals content.

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The solution-precipitate mixture was agitated for an additional 15 minutes (a total of 22 minutes after neutralization) without addition of base or air. A second sample was extracted and filtered through coarse filter paper. The filtrate, which was clear and colorless, was analyzed for heavy metals content.

The solution-precipitate mixture was agitated for an additional 7.5 hours (a total of 18 hours after neutralization). A third sample was extracted and filtered, and the clear, colorless filtrate was analyzed for heavy metals content.

A comparison of the results of the filtrate heavy metals analyses to the heavy metals content of the original acid solution is set forth in TABLE 3.

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TABLE 3

Sample	Metals Concentrations, ppmw						Solution pH
	Cd	Cr	Cu	Fe	Ni	Zn	
Untreated acid solution	102	74	96	5,684	96	101	N.T.
Treated filtrate 7 min. after neutralization	4	<.01	0.2	<.01	3.4	<0.1	7.5
Treated filtrate 22 min. after neutralization	7	<.01	0.09	<.01	7.3	0.6	7.5
Percent Removal After 22 min.	93.1	>99.9	99.9	100	92.4	99.4	NA
Treated filtrate 18 hr. after neutralization	9.3	<.01	0.09	<.01	6.7	0.8	6.9

EXAMPLE 4

A sample of an acid waste solution from a
commercial galvanizing process was placed in a mechanically
agitated beaker, neutralized with aqueous ammonia, and
oxidized with bubbled air while maintaining the solution pH
between about 7.0 and about 8.2. When the solution pH
stabilized, addition of aqueous ammonia and air was
discontinued except as noted below.

A solution-precipitate sample was extracted with a
pipette 7 minutes after neutralization. The sample was
filtered and analyzed for heavy metals. A second sample was
also extracted (60 minutes after neutralization), filtered
and analyzed for heavy metals. Additional aqueous ammonia

was thereupon added to the solution and a third sample was extracted (73 minutes after neutralization). This sample was also filtered and analyzed for heavy metals.

Two additional samples were similarly extracted, filtered and analyzed for heavy metals. The results of all analyses are summarized in TABLE 4.

TABLE 4

Sample	_____Metals Concentrations, ppmw_____							Solution pH
	Cd	Cr	Cu	Fe	Ni	Pb	Zn	
Untreated acid waste	6.25	256	72	54,400	206	5,125	354	N.T.
Treated filtrate 60 min. after neutralization	<.01	<0.01	5.6	1.3	6.6	<0.5	1.2	7.0
Percent removal 60 min. after neutralization	>99.8	100	92.2	100	96.8	100	99.7	NA
Treated filtrate after base added, 73 minutes after neutralization	<.01	<0.01	7.2	<0.01	3.2	<0.5	0.6	7.8
Treated filtrate 120 min. after neutralization	<.01	<0.01	5.4	<0.01	1.5	0.6	0.6	7.6
Treated filtrate 2 mos. after neutralization	0.2	<0.01	0.9	0.4	0.5	<2.5	<0.4	N.T.

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EXAMPLE 5

A 50 ml acid waste sample from a commercial electroplating process was added to a mechanically agitated beaker and diluted with distilled water to 200 ml. To this diluted solution was added 18 ml of a 28 weight percent aqueous ammonia solution, whereby the solution pH was observed to be 7.0. An additional 10 weight percent iron was added to the solution in the form of ferric hydroxide particles. Immediately thereafter, air was bubbled through the solution. Aqueous ammonia was periodically added to maintain the solution pH between 7.0 and 7.5.

After about 8 minutes, the solution pH was observed to have stabilized. A sample was extracted with a pipette, filtered, and analyzed for heavy metals.

Air dispersion was halted but solution agitation was continued. The pH of the solution was raised to about 9.0. A second sample was immediately extracted, filtered, and analyzed for heavy metals.

The solution was agitated for an additional 60 minutes during which time aqueous ammonia was periodically added to maintain the pH at about 9.0. A third sample was extracted, filtered, and analyzed for heavy metals.

The results are summarized in TABLE 5.

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TABLE 5

Sample	Cd	Cr	Cu	Fe	Ni	Pb	Zn	Solution pH
			Metals Concentrations, ppmw					Solution
Untreated waste acid	0.75	8.75	2	3,625	8.5	132	132	N.T.
8 min. after neutralization	0.04	<0.01	0.2	0.3	0.7	<0.05	2.4	7.0
10 minutes after neutralization	0.1	<0.01	1.6	0.3	3.3	<0.05	30	9.0
Percent removal 10 min. after neutralization	86.7	>99.9	20.0	100	61.2	100	77.3	NA
70 min. after neutralization	0.1	<0.01	1.6	0.3	2.6	<0.05	30	9.0

EXAMPLE 6

The ferrous ion concentration of an acidic waste water solution (having a composition shown in Table 6, below) was increased to 852 ppm by addition of a concentrated ferrous chloride solution, yielding a mass ratio of 3.2 ferrous ion to heavy metal. The pH of the waste water solution was then raised to 7.8 using a solution of sodium hydroxide as base. A portion (480 ml) of the resultant solution was charged to a laboratory reactor vessel, air was sparged in at the rate of 6 liters per minute, and sodium hydroxide solution was added as necessary to maintain the pH at 7.8. The solution was kept under conditions of high agitation during the oxidation-precipitation reactions, and there was no addition of any solid matter to the solution. The oxidation precipitation reactions were allowed to proceed

for 15 minutes, after which a sample of product solution was
analyzed. The results of the analysis are also set forth in
the following Table 6:

TABLE 6

	Waste Water	Product Solution	Percent Removal, %
Cr, ppm	214	0.03	>99.9
Cu, ppm	1.5	<0.01	>99.3
Ni, ppm	46	0.2	99.6
Mn, ppm	6.3	0.2	96.8
Fe+2, ppm	217	0.03	>99.9
Total Heavy Metal, ppm	484.8	<0.47	>99.9

The data in Table 6 show that the present invention removes
an assortment of heavy metals to extremely low levels.

EXAMPLE 7

An aqueous waste solution having a pH of 1.0
contained the following metals in the concentrations shown:

Calcium	375 ppm	Lead	189 ppm
Chromium	0.6 ppm	Zinc	19 ppm
Copper	2.3 ppm	Iron	1,370 ppm

Upon chemical analysis it was found that 83% of the iron
existed in the solution as ferrous ion.

Sixty gallons of the waste solution were introduced
into a tank, and while air was introduced by a sparger and
the efficiency of the air oxidation increased by mechanical
dispersion (i.e., a mixer outfitted with a high shear
turbine), the pH of the solution was increased to 7.5 and

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maintained at that level by addition of ammonia. Within 7
minutes, it was apparent by visual inspection that a red
precipitate had formed and the reaction was essentially
complete. In addition, the pH held constant after 7 minutes
(i.e., little or no additive base was required to maintain
the pH at 7.5), also indicating that the reaction was
complete. Nevertheless, the oxidation and agitation were
maintained for another 223 minutes, the temperature of the
solution being about 75° F. throughout. At the end of the
223 minutes, the precipitate still appeared visually the same
as after the first 7 minutes. A sample of this precipitate
at the end of the run was recovered, frozen in liquid
nitrogen to prevent any altering of its character, freeze-
dried under low pressure, and then analyzed by X-ray
diffraction analysis. The sample evidenced no sign of
crystallinity and, therefore, was determined to be completely
amorphous. Also, the sample did not respond to the presence
of a magnet.

    The above Example 7 demonstrates, inter alia, that
the precipitate formed in the process of the present
invention is completely amorphous and not an intermediary to
the production of a crystalline precipitate.

EXAMPLE 8

    Sixty gallons of the aqueous solution described in
Example 7 were introduced into the reactor vessel employed in
Example 7, but the temperature in the reactor vessel was
maintained at about 100° F. (38° C.). Oxidation with air
sparging and dispersion was as described in Example 7, and
the pH was initially controlled to a value of around 7.75 by
addition of ammonia. The reaction was essentially complete
within about 11 minutes. (This was proven by the fact that a
sample of the solution was taken, filtered, and the resulting

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filtrate was clear, remained clear for one hour with no
change in pH, and contained only 0.2 ppm copper, less than
0.3 ppm lead, less than 0.5 ppm iron, and 0.3 ppm zinc.
Also, the pH was stable within 11 minutes, requiring no
further base addition.) Four minutes later, continuous
operation began, with the feed into and out of the reactor
vessel of the aqueous solution being 1 gpm, so that the
residence time therein was 60 minutes. pH was maintained at
about 7.5. Two samples of the contents of the reactor vessel
were taken after 70 and 75 minutes of continuous operation,
freeze-dried as in Example 7 and analyzed by X-ray
diffraction analysis. Both samples showed no evidence
whatever of crystallinity. Again, the samples were
completely amorphous. Further evidence of this was that
inspection by high resolution microscopy showed no
discernible discrete particles of regular shape and size.

     The above Example 8 demonstrates, inter alia, that
the precipitate formed when conducting the process of the
present invention at about 100° F. is completely amorphous
and not an intermediary to the production of a crystalline
precipitate. In addition, the method of the invention is
useful for removing at least about 91.3 weight percent
copper, at least about 99.8 weight percent lead, at least
about 99.9 weight percent iron, and at least about 98.4
weight percent zinc.

EXAMPLE 9

     Again, 60 gallons of the aqueous solution described
in Example 7 were introduced into the reactor vessel used in
Examples 7 and 8, but this time the temperature was
maintained at 150° F. (66° C.). With air sparging,
mechanical dispersion, and ammonia addition as in Examples 7
and 8, the reaction appeared complete about 20 minutes after

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the pH was adjusted to 7.5, i.e., after 20 minutes little or
no base was needed to maintain pH, thereby indicating that
the oxidation reaction was over. Nevertheless, oxidation by
sparging and mechanical dispersion was continued for one
hour, at which time a sample of the contents of the vessel
was taken, filtered, and the precipitate freeze-dried and
analyzed by X-ray diffraction while the filtrate was analyzed
for metals. Again, the precipitate was found to be
noncrystalline and completely amorphous. The filtrate was
found to contain only trace concentrations of metals, i.e.,
0.3 ppm copper, less than 0.05 ppm lead, 0.01 ppm iron, 0.6
ppm zinc, and less than 0.01 ppm chromium.

Example 9 therefore demonstrates, inter alia, that
even when run at about 150° F., the process of the instant
invention yields a completely amorphous precipitate and does
not form an intermediary to the production of a crystalline
precipitate. In addition, at least about 87.0 weight percent
copper, at least about 99.9 weight percent lead, at least
about 99.9 weight percent iron, at least about 96.8 weight
percent zinc, and at least about 98.3 weight percent chromium
can be removed from a contaminated waste solution.

EXAMPLE 10

One liter of an untreated waste water having the
metals content shown in Table 7 was introduced into a
laboratory-size reactor vessel. It was allowed to come to
room temperature. Air sparging through the bottom of the
vessel at a rate of 493 1/hr/1 with mechanical dispersion,
i.e., a laboratory mixer, was then commenced. The air was
sparged through a fritted disk to produce small bubbles. The
pH was then raised to 7.5 and held at that value by periodic
addition of caustic soda, as necessary, producing a brick red
precipitate.

Samples of the solution containing the precipitate were taken at 10, 15, 30, and 45 minutes after the base was first added. The four samples of solution containing the precipitate were then filtered through a Whatman #41 brand filter paper, and two samples of each filtrate were taken, so that a total of eight samples were obtained. To one set of the four samples, hydrogen peroxide was added to detect the presence of ferrous ion. No precipitate formed in any of the samples, thus proving that at the 10-, 15-, 30-, and 45-minute intervals all the ferrous ions had oxidized.

The second set of samples was allowed to stand exposed to the air for 1 hour in vials, after which they were capped. The second set of samples were acidified and analyzed for metals content. The data so obtained are shown in Table 7. Not only was iron removed in this Example 10 to extremely low levels but also all the other heavy metals. There were virtually no heavy metals left in the aqueous filtrate, and the metals data in Table 7 are all essentially below or close to their analytical detection limits.

Also, the four samples of the precipitate obtained on the Whatman #41 filter paper were subjected to X-ray diffraction analysis and found to contain no crystalline materials, i.e., they were completely amorphous.

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TABLE 7

Metal	Metal Concentration In Ppmw After A Total Elapsed Oxidation Time (Min.) of					Percent Removal After 45 Min.
	0[1]	10	15	30	45	
Cd	0.29	0.03	0.03	0.03	0.03	89.7
Cr	1.22	0.005	<0.004	<0.004	<0.004	>99.7
Cu	7.65	0.07	0.05	0.03	0.02	99.7
Fe	5,310	0.03	0.02	0.02	0.02	100
Pb	430	0.11	0.006	0.005	0.006	100
Ni	2.11	0.04	0.04	0.04	0.03	98.6
Zn	570	0.56	0.56	0.7	0.59	99.9
pH[2]	-	7.5	7.5	7.5	7.5	NA

1. Analysis of untreated waste water solution.
2. pH of reactor contents when sample taken.

EXAMPLE 11

In this experiment, Example 10 was continued under the same oxidizing conditions, but at a temperature of 60° C. for another 3 hours (i.e., a total oxidizing time of 3 hours and 45 minutes, the first 45 minutes at room temperature and the last 3 hours at 60° C.). The brick-red precipitate remained intact and, as evidenced by no significant changes in pH and oxidation-reduction potential, there was no evidence of further reaction. In addition, X-ray analysis of the precipitate at the end of the 3 hours of high temperature oxidation showed that the precipitate was still completely amorphous.

Again, as with Examples 7-9, the data of Examples 10 and 11 show that the precipitate formed in the process of the present invention is completely amorphous and not an intermediate to the formation of a crystalline, magnetic precipitate.

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EXAMPLE 12

In this experiment, another 1 liter of the untreated waste water of Example 10 was introduced into the same laboratory reactor vessel employed in Example 10 and allowed to come to room temperature. Caustic soda was added and the pH was adjusted to 7.5. The contents of the solution were allowed to stand and form a ferrous hydroxide suspension.

After forming the ferrous hydroxide suspension, the reaction conditions were altered to subject the contents of the vessel to the method of the invention. Specifically, air was sparged into the reactor vessel at a rate of 493 l/hr/l and the pH was maintained at about 7.5 so as to induce rapid and complete oxidation of ferrous ions. The ferrous hydroxide suspension was rapidly converted to the brick-red amorphous precipitate described in Example 11.

Example 12 demonstrates that rapid oxidation is essential to forming the amorphous precipitate desired in the process of the instant invention.

EXAMPLE 13

A commercial facility treats acidic waste water containing iron, lead, and zinc contaminants by bringing the pH up to 8.0 with lime followed by natural aeration in a large settling pond. The same waste was treated, on a laboratory scale, by a process within the scope of the present invention wherein the waste solution was subjected to rapid oxidation with an air stream while the pH was controlled at about 8.0 with lime. Both processes produced a sludge comprising ferric hydroxide.

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Various comparisons were then made:

(1) Settleability. The rate at which a precipitate
settles can affect the time a sludge needs to be held in a
settling zone before a purified liquid can be recovered. A
precipitate from the conventional process was blended with
deionized water so as to have a total solids content of 770
ppm--equal to that of a sample of precipitate (obtained by
the process of the present invention) in water. The samples
were put into 100 ml graduated cylinders and 3 ppm of a
standard flocculating agent (Nalco 7173 brand
polyelectrolyte) was added to each cylinder. Each cylinder
was then capped and simultaneously (a) inverted 5 times and
then simultaneously (b) placed on a bench top. The settling
rate for precipitate obtained via the process of the present
invention was about eight times faster than for the
conventional precipitate.

(2) Compaction Volume. Compaction volume of a
waste water treatment sludge is of special importance in
reducing the cost of landfilling, e.g., the less volume, the
less a disposal problem. Two samples of (a) the precipitate
from the conventional process and (b) the precipitate of the
process of the present invention were put into four different
25 ml graduated cylinders and brought to equal total solids
levels. One sample of each precipitate was then combined
with 3 ppm Nalco 7173 brand polyelectrolyte. Next, all four
samples while capped were simultaneously (a) inverted 3
times, (b) then put on a bench top, and (c) allowed to sit
for 3 weeks. The precipitate from the exemplary process of
the present invention occupied 1/3 the volume of the
conventionally produced precipitate containing an
approximately equal amount of iron.

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(3) <u>Dewaterability</u>. The less water a precipitate takes up, i.e., the less gelatinous it is, the easier it is to filter through conventional filter presses. In the conventional process described above, the final "dewatered" product contains 75 to 85% water whereas sludges produced from the exemplary process of the present invention typically run between 55 and 65% water. The difference between such values is that the conventional process requires high pressures and long filtration times and the precipitate tends to bind to the filter cloths and proves difficult to remove. In contrast, precipitates from the exemplary process of the present invention come away cleanly from the filter cloths. In addition, lower pressures and less time are required for filtration.

Example 13 accordingly demonstrates the improved settleability, compaction volume, and dewaterability characteristics of the precipitate formed by the process of the instant invention.

In addition to removing heavy metals, the process of the present invention is also useful for reducing the concentration of light metals (i.e., metals that are not heavy metals), especially aluminum and beryllium, as well as cyanide, phenolics, oil and grease, TSS contributors, BOD contributors, COD contributors, and TOC contributors present in the aqueous solution. Furthermore, any combination of these contaminants as well as any combination of these contaminants and heavy metals can be removed simultaneously from a solution in the same vessel. The process steps as well as the pH, oxidation rate, and reduction in individual contaminant concentration levels are substantially the same as discussed above with respect to heavy metals. In addition, the molar ratio of ferrous ions to light metal ions and/or cyanide ions is the same ratio as discussed above with

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respect to the molar ratio of ferrous ions to heavy metal ions.

However, with respect to contaminants selected from the group consisting of phenolics, oil and grease, TSS contributors, BOD contributors, COD contributors, and TOC contributors, the amount of ferrous ions employed to remove these contaminants from a solution is best expressed in terms of weight ratio, as opposed to molar ratio used above. Generally, the weight ratio of the ferrous ions to the total amount of contributors from this group of contaminants is at least about 1:1, but typically less than about 10:1, and preferably about 4:1 to about 6:1. When contaminants selected from a first group consisting of light metals, cyanide, and/or heavy metals and contaminants selected from a second group consisting of phenolics, oil and grease, TSS contributors, BOD contributors, COD contributors, and TOC contributors are both present in the solution, the ferrous ion concentration generally is equal to at least the sum of (A) the molar concentration of the contaminants selected from the first group plus (B) the weight of the contaminants selected from the second group. Typically, the ferrous ion concentration of the solution is equal to less than about ten times that sum. Preferably, the ferrous ions are present in the solution in a concentration that is about 2 to about 8, and more preferably about 4 to about 6, times the above sum.

As in the case of heavy metals, the method of the invention is also advantageous in typically removing at least about 95 percent, and preferably at least about 99 percent, of each these other contaminants present in the waste solution. For example, a waste stream containing at least about 0.1 ppmw, or even about about 1 ppmw, or even over about 10 ppmw aluminum, when treated by the process of the present invention can have its aluminum content reduced below

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about 0.05 ppmw. In fact, the process of the instant
invention can reduce the concentration of contaminants in a
waste stream to the following levels:

	Level, ppmw		
Contaminant	Typical	Preferred	More Preferred
Ag	<0.05	<0.01	<0.005
Al	<0.06	<0.04	<0.02
As	<0.02	<0.01	<0.005
Cd	<0.02	<0.01	<0.005
Cr	<0.01	<0.004	<0.002
Cu	<0.02	<0.01	<0.005
Fe	<0.02	<0.01	<0.005
Pb	<0.01	<0.005	<0.003
Ni	<0.1	<0.01	<0.005
Sb	<0.5	<0.2	<0.1
Se	<0.05	<0.01	<0.005
Sn	<0.5	<0.05	<0.03
V	<0.004	<0.002	<0.001
Zn	<0.02	<0.005	<0.003
Total Heavy and Light Metals	<1.5	<0.8	<0.5
TSS	<6	<4	<2
TDS	<600	<400	<200
Cyanide	<0.04	<0.02	<0.01
BOD	<40	<3	<1.5
COD	<250	<50	<25
TOC	<70	<20	<10
Oil & Grease	<0.1	<0.05	<0.03
Phenolics	<1	<0.01	<0.005

The following Examples 14 and 15 are illustrative
of some of the above additional embodiments of the invention,
as well as showing the effectiveness of the invention for
removing the heavy metal selenium.

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EXAMPLE 14

Influent and effluent waste water samples from a
biotreatment plant were collected in clean, 1-gallon amber
glass bottles with teflon-lined lids. At the collection
points, the bottles were first flushed with the waste water
to be taken, then filled to the top with a sample to
eliminate air space. The bottles were then sealed and
refrigerated at about 4° C. for preservation. Within a few
hours, the refrigerated samples were packaged in ice chests
with chilled blue ice packs wrapped around each bottle. The
samples arrived at the laboratory within 24 hours after
collection. On arrival, the samples were tested for pH,
temperature, oxidation-reduction potential (ORP), and
dissolved oxygen. The bottles were resealed and the samples
were stored in the dark at about 4° C. until further testing.
All screening tests were conducted within 4 days of sample
receipt.

Waste Water Characterization

The samples of the waste water were characterized
for heavy metals, oil and grease, inorganic and organic
compounds, total solids (suspended and dissolved), and
biochemical oxygen demand. The tests used are listed in
Table 8.

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TABLE 8

Test   Analytical Method

Heavy Metals
    Selenium   ICP[1]/MS[2]/HGAA[4]
    Aluminum   ICP
    Iron   ICP
    Vanadium   ICP
    Arsenic   GFAA[3]
    Mercury   GFAA

Inorganic Components
    Cyanide   Distillation/
                                                Colorimetry
    Soluble Sulfur   E=90.3[5]
    Thiosulfate   Titration
    Dissolved Solids (TDS)   Gravimetric

Organic Components
    Total organic carbon (TOC)   E-415[5]
    Phenolics   Distillation
    COD   Colorimetry
    BOD   Colorimetry
    Bioassay   96-hr static
                                                fish kill test
    Oil and grease   Gravimetric

1. ICP denotes inductively coupled plasma spectrophotometric
method.
2. MS denotes mass spectrometry.
3. GFAA denotes graphite furnace atomic absorption method.
4. HGAA denotes hydride generation atomic absorption method.
5. E-# denotes EPA test methods bearing the particular
number.

A summary of the characteristics of both the influent
sample and effluent sample are given in Table 9:

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TABLE 9

Summary of Waste Water Characteristics

Test	Biotreatment Plant Influent, mg/1	Biotreatment Plant Effluent, mg/1
Al	0.33	0.12
Fe	2.8	0.16
V	<0.05	<0.05
As	<0.002	<0.002
Hg	<0.001	<0.001
Se	675	2300
TSS	5	<1
TDS	778	805
Soluble S	<0.1	<0.1
Thiosulfate	24	3.6
Cyanide	0.18	0.02
COD	1.9	<1
TOC	113	25.5
BOD	150	15
Phenolics	0.12	<0.005
Oil & Grease	4.8	1.9

Treatability Studies

Laboratory treatability studies included a series of batch tests to determine the effects of specific conditions upon selenium and cyanide removal. Specifically, samples (two liters each) of the biotreatment plant effluent wastewater were treated batchwise in accordance with the invention to determine the effects of retention time and pH on the rate and extent of selenium and cyanide removal. All experiments were conducted at ambient temperature, using a 15 cm in diameter, 25 cm deep bench-scale reactor made of Lucite brand acrylic resin. The reactor was fitted with four baffles one cm wide, which extended the full length of its sides, resting on 0.5 cm spacers. The baffles functioned to minimize overdosing. Several ports were located on the side of the reactor so that continuous liquid overflow was feasible at several reactor volumes - 2, 3, and 4 liters. In

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addition, ports were available for sample collection, pH, ORP, and temperature probes. Air flow was gauged by a rotometer-type flow meter and entered the reactor vessel through a sparge ring in the bottom of the reactor. The air was then dispersed in the liquid phase with a Lightin R-100 brand, 6.2 cm diameter, 6-blade radial flow turbine stirrer powered by a 0.05 kw variable speed motor adjusted to a speed of about 500 rpm.

Approximately 100 ppm of ferrous iron were added and during the batch runs. The air sparge rate was about 3 l/min for the batch runs. The agitation was used during the treatments was enough to disperse the air sparged into the reactor and provide sufficient mixing for pH control. A pH control setpoint was maintained with a dilute sodium hydroxide solution.

1)   Effects of pH on Selenium Removal

In order to determine the influence of pH on treatability, split waste water samples were taken from the the biotreatment plant effluent sample and neutralized to a specific pH (either pH 6.5 or 7.8) using the sodium hydroxide solution.

Batch treatments were then carried out while maintaining the solution within ±0.2 pH units of the initial setpoint. The results depicted in Table 10 indicate that there is no significant effect of pH upon selenium removal within the pH range of 6.5 and 7.8.

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TABLE 10

Effect of pH on Selenium Removal

Sampling Time (min.):	(Se) mg/l at pH 6.5	(Se) mg/l at pH 7.8
0	2300	2300
30	140	93
60	81	82
120	79	79

    2)   Effects of Retention Time on Selenium Removal

    To test the effect of contact time on selenium
removal, batch experiments employing two aliquot from the
biotreatment plant effluent were conducted by subjecting each
aliquot to varying hydraulic retention times. The pH of each
aliquot was adjusted to pH 6.5. The results are set forth in
Table 11:

TABLE 11

Effect of Retention Time on Selenium Removal

Sampling Time (min.):	Aliquot A Se, mg/l	Aliquot B Se, mg/l
0	2300	2300
30	82	140
60	79	81
120		79

    Removal of selenium to residual level was completed
within the first 60 minutes. Therefore, extensive hydraulic
retention time is not necessary.

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    3) Effects of Continuous Flow on Selenium and
Cyanide Removal

    Based on the results from the above batch
experiments, operating parameters were determined for
bench-scale continuous flow experiments. In the continuous
flow mode, liquid was introduced into the reactor with a
metering pump which discharged into the bottom of the
reactor. The reactor was adjusted so that about two liters
of sample were constantly present in the reactor during the
continuous flow experiments. The conditions used in a
continuous flow treatment were short residence time (about
one hour) and a pH of about 7.8. In addition, the amount of
ferrous iron added, the air sparge rate, and the rpm of the
stirrer were the same as employed in the batch runs. Both
the biotreatment plant influent and effluent samples were
tested under these conditions. The results are shown below
in Table 12:

                          TABLE 12

        Effect of Continuous Flow on Selenium Removal

| | Biotreatment Plant | |
Sampling Time (min.):	Effluent, Se, mg/l	Influent, Se, mg/l
0	2300	675
60	22	221

    Table 12 shows that selenium can be effectively
removed using a continuous-flow treatment.

    The following Table 13 shows that cyanide removal
is equally effective for both samples under continuous-flow
conditions.

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TABLE 13

Effect of Continuous Flow on Cyanide Removal

	Biotreatment Plant	
	Effluent,	Influent,
Sampling Time (min.):	CN, mg/l	CN, mg/l
0	0.02	0.18
60	<0.01	0.01

4)   Biotoxicity Reduction

Bioassay testing was performed on the treated waste water from the continuous-flow treatments to determine the effects of the treatment upon the level of residual biotoxicity.

Results from Bioassay 96-hr static fish kill tests showed that the process of the present invention is capable of enhanced reduction of biotoxicity over biotreatment alone (i.e., 100% survival in the biotreatment plant effluent treated by the process of the present invention versus 90% survival for the untreated biotreatment plant effluent.)

Treatment of the biotreatment plant influent by the process of the present invention alone achieved an LC_{50} of 45%, which, in terms of Toxicity-Concentration represents over one third of the biotoxicity reduction achieved by the biotreatment plant system. This is a remarkable level of toxicity reduction given the relatively short reactor residence times used with the process of the present invention. Accordingly, placing the treatment process of the present invention upstream of biotreatment augments biotoxicity reduction as well as buffers the biotreatment system from peaks of toxicants that might otherwise inhibit biological treatment.

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EXAMPLE 15

A sample of a biotreatment plant influent (BI) and
a sample of the biotreatment plant effluent (BE) were taken
and stored in a refrigerated room (about 4° C.) upon receipt.
A bench scale continuous treatment system was used to test
about 12 liters each of samples BI and BE by the method of
the invention. The continuous treatment system used the
reaction vessel and stirrer employed in Example 14 to test
both samples. The pH of each sample was initially adjusted
to about 7.8. Sodium hydroxide (0.25 N) was employed in both
continuous treatments to help maintain the pH at about 7.8.
The total sodium hydroxide added during sample BI's treatment
was about 0.0024 eq/l and the total amount of sodium
hydroxide added during sample BE's treatment was about 0.0020
eq/l. About 0.042 gram of Colloidal 691 brand anti-foam was
added to sample BI, but no anti-foam was added to sample BE.
The air sparge rate used in treating sample BI was maintained
at about 0.9 l/min (uncalibrated). However, the air sparge
rate used in treating sample BE was about 2 l/min
(uncalibrated) with slight foaming. The stirrer was run at
about 500 rpm for both samples and the reactor residence time
used in treating both samples was about 30 minutes. Ferrous
iron was metered in-line to each sample stream. A ferrous
iron dosage of 100 ppm was employed in treating sample BI and
sufficient ferrous iron was added to sample BE to raise
sample BE's ferrous iron content to about 100 ppm.

Nalco 8173 brand flocculant was used to flocculate
samples BI and BE. The flocculant was added at 6 ppm for
each test. The flocculations were each performed in a
2-liter graduated cylinder. The solids generated from sample
BE were allowed to settle out overnight, and the solids
generated from sample BI were allowed to settle out for 3
nights prior to removing the solids by filtering each sample

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through a Whatman #1 brand filter paper. Ten liters of the
supernatant obtained from each treated sample were separately
stored in plastic containers for the bioassay fish kill test,
and about 1 liter of the supernatant obtained from each
treated sample was stored in nalgene plastic bottles for the
other tests. The final pH of the supernatant obtained from
samples BI and BE were about 7.18 and about 7.57,
respectively. The results obtained from this experiment are
set forth in Table 14 below.

TABLE 14

TEST	UNITS	BI RAW	BI TREATED	PERCENT REMOVED	BE RAW	BE TREATED	PERCENT REMOVED
Al	mg/l	0.18	0.04	77.8	0.24	0.06	75.0
Fe	mg/l	0.71	0.25	64.8	0.77	0.28	63.6
Na	mg/l	117	183	-56.4	121	169	-39.7
V	mg/l	0.01	<0.004	>60.0	0.01	<0.004	>60.0
As (furnace)	mg/l	2	<1	>50.0	3	1	66.7
Hg	ug/l	1.3	1.6	-23.1	2.0	0.5	75.0
Se (furnace)	mg/l	0.43	0.59	-37.2	0.44	<0.05	>88.6
pH		7.05	7.18	NA	6.92	7.57	NA
TSS	mg/l	52	6	88.5	8	4	50.0
TDS	mg/l	476	681	-43.1	472	598	-26.7
Cyanide	mg/l	0.25	0.17	32.0	0.20	<0.04	>80.0
BOD	mg/l	225	40	82.2	230	3	98.7
COD	mg/l	542	244	55.0	318	42	86.8
TOC	mg/l	227.5	63	72.3	74	19	74.3
Oil & Grease	mg/l	50	<0.1	>99.8	30	<0.1	>99.7
Phenolics	mg/l	16.4	1.1	93.3	9.63	0.01	99.9
Bioassay, Fish kill LC_{50} (fish=Flathead minnows)		500 mg/l	100,000 mg/l	19,900	100%	100%	——

Table 14 shows that the process of the present
invention is capable of simultaneously achieving significant
reductions in light metals (e.g., aluminum), heavy metals

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(e.g., vanadium, mercury, arsenic, selenium), cyanide, TSS, BOD, COD, TOC, oil and grease, as well as phenolics.

In yet another version of the invention, volatile organics are removed from the aqueous solution simultaneously with the removal of any of the above discussed contaminants that may be present in the solution. In general, the method of the present invention can reduce the concentration in the aqueous solution of any volatile organic having a Henry's Law constant of at least about 0.02. Since substances having higher Henry's Law constants are more volatile, and therefore usually easier to remove from a solution, it is preferred that each volatile organic have a Henry's Law constant of at least about 0.05, and more preferably at least about 0.25. Exemplary volatile organics that can be treated by the instant invention include, but are not necessarily limited to, benzene, xylene, ethylbenzene, t-1,2-dichloroethene, trichloroethene, tetrachloroethene, 1,1,1-trichloroethene, 1,1-dichloroethene, vinyl chloride, 1,2-dichlorobenzene, and 1,4-dichlorobenzene.

Typically, the oxidant gas employed to oxidize the ferrous ions serves a dual function in that it (a) oxidizes the ferrous ions and (b) acts as a gaseous phase. Accordingly, the volatile organics are partitioned between the gaseous phase and a liquid phase comprising the aqueous solution.

Usually, the gas is introduced proximate the bottom of a treatment vessel at a rate sufficient to achieve an average volumetric flux ratio of gas to water of at least about 20, i.e., on an average at least about 20 unit volumes of gas cross a unit area of a given surface in a specified time interval for each unit volume of water that crosses the same unit area of the surface in the same time interval. It

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is preferred to use a higher average volumetric flux ratio
because the higher the average flux ratio, the faster the
removal of the volatile organic from the aqueous solution,
all other factors being constant. However, economics
dictates a maximum average volumetric flux ratio of about
100. Preferably, the average volumetric flux ratio is about
30 to about 90, and more preferably about 40 to about 80.

One of the major advantages resulting from the
present invention's ability to simultaneously remove volatile
organic contaminants and non-volatile contaminants is that
the same reaction vessel accomplishes both results. This
eliminates additional capital costs. In addition, the vessel
need not, and preferably does not, contain any packing
material conventionally used in volatile organic removal
equipment. By avoiding the use of packing material, the
present invention is effective for removing volatile organics
without exhibiting the typical decrease in efficiency common
to packed towers. The decrease in efficiency is due to the
build-up of substances on the packing material and
necessitates the periodic cleaning or replacement of the
packing material.

The vessel preferably employed in the present
invention to simultaneously remove volatile organic and
non-volatile contaminants has an internal diameter to
internal height ratio much greater than that of vessels
conventionally used to remove volatile organics. Typically,
the vessel employed in the present invention has an internal
diameter to internal height ratio of about 1:1 to about 1:4,
preferably about 1:1.1 to about 1:3, and more preferably
about 1:1.2 to about 1:2. For example, very desirable
vessels have internal diameter to internal height ratios of
about 6 feet to about 9 feet, about 8 feet to about 12 feet,
and about 11 feet to about 15 feet. In addition, the

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impeller of the mixer employed to shear the gas bubbles
generally has a diameter of about 30 to about 40 percent of
the internal diameter of the vessel, and the sparger employed
to distribute the bubbles generally has a diameter about 75
to about 85 percent of the diameter of the impeller.

The removal of volatile organics from the aqueous
solution can be performed either by a batch or a continuous
process. In the batch process, the solution is generally
sparged with the oxidant gas for a least about 15 minutes.
In the continuous process, the average residence time that
the solution is sparged with the oxidant gas is also about 15
minutes. The maximum sparge or treatment time for both
methods is also dictated by economics and is generally about
2 hours. Preferably, the treatment time is about 0.5 to
about 1.5 hours.

Another parameter affecting the volatile organic
removal efficacy of the process of the present invention is
the pH of the aqueous solution being treated. Preferably,
the pH of the aqueous solution is maintained with a range of
about 6 to about 9.5, more preferably within a range of about
6.5 to about 9, and optimally within a range of about 7.5 to
about 8. The pH can be maintained within these ranges with a
base, 'such as one selected from the group consisting of
ammonia, hydroxide containing bases, and mixtures thereof.
When necessary, the pH can be maintained within these ranges
with an acid.

The size of the bubbles being sparged or introduced
into the aqueous solution can also affect the ability of the
present invention to remove volatile organics from aqueous
solutions. In general, the smaller the bubble size the more
surface area available for mass transfer of the volatile
organics between the liquid and gas phases. Accordingly, it

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is preferred to reduce the average bubble diameter by
strongly agitating the solution.

Typically, the process of the present invention
reduces the concentration of each volatile organic present
(as well as the total volatile organics) in an aqueous
solution by at least about 80 percent. Depending on the type
of volatile organic being removed, the treatment time, the
average volumetric flux ratio of gas to water, the pH of the
aqueous solution being treated, and the volatile organic mass
transfer rate between the liquid and gas phases, the process
of the instant invention is capable of removing more than
about 90 percent, preferably more than about 95 percent, and
even substantially all of the volatile organics initially
present in the aqueous solution.

The volatile organic removal efficiency in present
invention the can also be increased by repeatedly treating an
aqueous solution. For example, the effluent from a first
treatment stage can be subjected to a similar treatment to
obtain comparable further reductions of any volatile organic
and/or other above described contaminant.

The following examples illustrate embodiments of
the invention wherein volatile organics and other
contaminants are simultaneously removed from an aqueous
solution.

EXAMPLE 16

A sample of waste water combined from different
sources was characterized for heavy metals and inorganic and
organic compounds using the analytical methods listed in
Table 15.

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TABLE 15

Test Methods

Test	Analytical Method
Heavy Metals	
Copper	ICP
Lead	ICP
Iron	ICP
Mercury	GFAA
Selenium	HGAA
Inorganic Components	
Cyanide	Distillation/ Colorimetry
Phenolics	E-402.1
Organic Components	
Benzene	E-8020/5030
Toluene	E-8020/5030
Xylene	E-8020/5030
Ethylbenzene	E-8020/5030

A summary of the raw waste water characteristics is given in Table 16.

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TABLE 16

Benzene, mg/l	17.9
Toluene, mg/l	41.9
Xylenes, mg/l	32.6
Ethylbenzene, mg/l	5.57
1,3 Dichlorobenzene, mg/l	7.65
1,4 Dichlorobenzene, mg/l	3.1
1,2 Dichlorobenzene, mg/l	2.3
Chlorobenzene, mg/l	<2.5
Iron, mg/l	47.8
Copper, mg/l	0.15
Lead, mg/l	0.77
Selenium, ug/l	3
Mercury, ug/l	<1
Cyanide, mg/l	0.05
Oil & Grease, mg/l	9.1
Phenolics, mg/l	21

The reactor vessel and stirrer used to evaluate waste water treatability were the same as employed in Examples 14 and 15. All treatments were carried out on a batch basis under steady state conditions with respect to temperature, air-flow rate, and turbine speed. Samples were taken with a syringe, flocculated with 0.5 ml of 0.3 g/l Nalco 8173 brand flocculent, filtered, and transferred to a 40 ml volatile organic analysis (VOA) vial.

Analyses for benzene, toluene, xylene, and ethylbenzene (BTXE) were done by liquid chromatography and metals analyses were done by emission spectroscopy.

Simultaneous Treatment

Enough caustic was added to the slightly acidic sample to bring its pH up to about 7.7. Although analysis of the raw sample indicated that the sample contained a considerable amount of iron, ferrous iron (100 ppm) was added. Treatment began with the initiation of air flow

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(about 2.8 l/min) and continued for a period of about 80 minutes. Treatment results are given in Table 17.

TABLE 17

Simultaneous Treatment (Metals and VOC)

Results: VOC (as BTXE)

Time, Min.	Ben- zene mg/l	% Reduc- tion	Tolu- ene mg/l	% Reduc- tion	Xylene mg/l	% Reduc- tion	Ethyl benzene mg/l	% Reduc- tion
0	11	–	13	–	8.1	–	5.6	–
6	2.9	73.6	3.8	70.1	1.8	77.8	0.63	88.8
12	0.79	92.8	0.92	92.9	0.57	93.0	0.15	97.3
18	0.29	97.4	0.21	98.4	0.086	98.9	0.041	99.3
24	0.22	98.0	0.065	99.5	0.086	98.9	0.010	99.8
30	0.19	98.3	0.027	99.8	0.043	99.5	0.010	99.8

Results: Metals

Time, Min.	Copper, mg/l	% Reduc- tion	Lead mg/l	% Reduc- tion	Iron mg/l	% Reduc- tion
0	0.15	–	0.77	–	147.8	–
7	<0.03	80.0	<0.04	94.8	17.8	88.0
13	<0.03	80.0	<0.04	94.8	0.3	99.8
25	<0.03	80.0	<0.04	94.8	1.1	99.3
31	0.04	73.3	<0.04	94.8	0.6	99.6

Sequential Treatment

Treatment was carried out as described above for simultaneous treatment with the exception that the ferrous iron was added after air stripping for about 60 minutes. Treatment results are given in Table 18.

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TABLE 18

Sequential Treatment (Metals and VOC)

Results: VOC (as BTXE)

Time, Min.	Ben- zene mg/l	% Reduc- tion	Tolu- ene mg/l	% Reduc- tion	Xylene mg/l	% Reduc- tion	Ethyl benzene mg/l	% Reduc- tion
0	8.3	–	14.2	–	4.4	–	2.8	–
10	0.87	89.5	1.3	90.8	1.2	72.7	0.3	89.3
20	0.22	97.3	0.092	99.4	0.15	96.6	0.040	98.6
60	0.14	98.3	0.023	99.8	0.050	98.9	0.015	99.5
90	0.11	98.7	0.012	99.9	0.014	99.7	0.010	99.6
120	0.06	99.3	0.011	99.9	0.011	99.8	0.006	99.8

Results: Metals

Time, Min.	Copper, mg/l	% Reduction	Lead mg/l	% Reduction	Iron mg/l	% Reduction
0	0.15	–	0.77	–	47.8	–
30	<0.03	80.0	<0.04	94.8	1.2	97.5
60	<0.03	80.0	<0.04	94.8	1.6*	96.7
70	0.07	53.3	<0.04	94.8	0.3	99.7

* Measured prior to the addition of 100 ppm soluble iron, i.e., after taking an aliquot of the treated sample 60 minutes into the run, 100 ppm of ferrous iron were added to raise the iron content of the the sample to about 101.6 ppm.

The data set forth in Tables 17 and 18 indicate that simultaneous and sequential treatments yield comparable results. In addition, the fact that (a) the composite sample contained a relatively large amount of iron and (b) the metals treatment took place within the initial 60-minute period indicates that metal encapsulation and VOC stripping are occurring simultaneously, even when additional ferrous iron is added sequentially. Since a substantial reduction in the metals content was obtained prior to the addition of ferrous iron (see Table 18), the waste iron found in the raw sample is suitable as a ferrous iron source for use in the treatment process of the instant invention.

The data set forth in Tables 17 and 18 also indicate that an aqueous sample can be treated first to remove the volatile organics and then to remove the non-volatile organic contaminants or can be treated to simultaneously remove both the volatile organic and non-volatile organic contaminants. Accordingly, in a further embodiment of the present invention an aqueous solution is treated to remove its volatile organic contents irrespective

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of whether any non-volatile contaminants are also
simultaneously removed.

The parameters discussed above with respect to
simultaneously removing volatile organic and non-volatile
organic contaminants, i.e., the treatment time, the average
volumetric flux ratio of gas to water, the pH of the aqueous
solution being treated, and the average size of the gas
bubbles, are equally applicable when the only contaminant of
concern are volatile organics. In addition, the above
discussed reactor vessel is also preferably employed to
remove volatile organics. However, since there is no need to
oxidize any ferrous ions, the gas employed to remove volatile
organics need not be limited to oxidizing gases. A
commercially available non-oxidizing gas that can be used in
this version of the invention is nitrogen. Nevertheless,
since air is the cheapest available gas, air is still the gas
of choice.

In the following example, a solution is treated to
reduce its volatile organic content.

EXAMPLE 17

The system used to evaluate diffused air stripping
were the same as employed in Examples 14-16. Two samples
were treated in a batch mode. In the batch mode test, the
air flow control valve was adjusted to give the desired flow
and then the main shutoff valve was closed. The reactor was
filled with a predetermined amount of liquid. The turbine
was adjusted to a rotation speed of about 500 rpm. An
initial sample was taken with the timer started when the gas
shutoff valve was opened. Gas flow rate, temperature, and
turbine speed were monitored throughout the run. Samples
were taken with a syringe and transferred to a 40 ml VOA

vial. The parameters used in each batch mode run are set
forth in Table 19.

One sample was treated in a continuous mode. In
the continuous mode, liquid was pumped into the reactor via a
tube that opened at the bottom of the reactor and exited from
an overflow port on the side of the reactor. The reactor was
filled with liquid and air stripping was run on a volume
(air) to volume (liquid) ratio basis using previous batch
test results to estimate the proper ratio. The objective was
to get close to steady state conditions. After the liquid
metering pump was started and the system operated for at
least three volume changes, the inlet and outlet liquid flows
were sampled and analyzed. The parameters used in the
continuous mode run are also set forth in the following Table
19.

TABLE 19

Experimental Conditions

	Run Number		
	Batch Mode		Continuous Mode
	1	2	3
Reactor volume - liter	2	2	2
Air flow rate - $1\ \text{min}^{-1}$	1.0	2.0	1.2
Water flow rate - ml min^{-1}	-	-	15
Temperature - °C.	10	10	10
Mixer - RPM	500	500	500

The 40 ml VOA samples were analyzed by EPA methods 601 and
602. The results are set forth in Tables 20-22.

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TABLE 20
Run 1

Volatile Organics	Time, minutes							
	0	15		30		45	
	(ug/l)	(ug/l)	% Reduction	(ug/l)	% Reduction	(ug/l)	% Reduction
Toluene	410	150	36.6	52	87.3	19	95.4
Benzene	12	3.9	67.5	1.5	87.5	0.7	94.2
Xylenes	180	60	66.7	25	86.1	10	94.4
Ethyl-benzene	32	8.8	72.5	2.7	91.6	0.9	97.2
t-1, 2-dichloro-ethene	6.3	1.0	84.1	ND[1]	100	ND	100
tri-chloro-ethene	7300	1500	79.5	480	93.4	148	98.0
tetra-chloro-ethene	2300	450	80.4	55	97.6	9.1	99.6
1,1,1-tri-chloro-ethene	3.2	ND	100	ND	100	ND	100
1,1-dichloro-ethene	5.8	ND	100	ND	100	ND	100
vinyl chloride	32	ND	100	ND	100	ND	100
1,2-dichloro-benzene	110	83	24.5	73	33.6	48	56.4
1,4-dichloro-benzene	19	12	36.8	5.1	73.2	5.2	72.6

1. ND denotes none detected.

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Run 1, Continued

	Time, minutes					
	60		75		90	
Volatile Organics	(ug/l)	% Reduction	(ug/l)	% Reduction	(ug/l)	% Reduction
Toluene	10	97.6	3.1	99.2	1.8	99.6
Benzene	0.7	94.2	ND	100	0.6	95.0
Xylenes	3	98.3	0.9	99.5	1.0	99.4
Ethyl-benzene	ND	100	ND	100	ND	100
t-1, 2-dichloro-ethene	ND	100	ND	100	ND	100
tri-chloro-ethene	25	99.7	18	99.8	11	99.8
tetra-chloro-ethene	2.5	99.9	2.3	99.9	1.7	99.9
1,1,1-tri-chloro-ethene	ND	100	ND	100	ND	100
1,1-dichloro-ethene	ND	100	ND	100	ND	100
vinyl chloride	ND	100	ND	100	ND	100
1,2-dichloro-benzene	41	62.7	36	67.2	12	89.1
1,4-dichloro-benzene	2	89.5	1.2	93.7	1.3	93.2

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TABLE 21

Run 2

Volatile Organics	Time, minutes							
	0	15		30		45	
	(ug/l)	(ug/l)	% Reduc- tion	(ug/l)	% Reduc- tion	(ug/l)	% Reduc- tion
Toluene	84,000	61,000	27.4	28,000	66.7	19,000	77.4
Benzene	150	47	68.7	13	91.3	ND	100
Xylenes	15,000	11,000	26.7	8,300	44.7	6,000	60.0
Ethyl- benzene	2,300	1,500	34.8	990	57.0	580	74.8
tri- chloro- ethene	1,700	490	71.2	100	94.1	26	98.5
tetra- chloro- ethene	7,900	3,900	50.6	1,800	77.2	790	90.0
1,1,1- tri- chloro- ethene	3,800	540	85.8	47	98.8	4.6	99.9
1,1- dichloro- ethene	11	2.9	73.6	0.6	94.5	ND	100
vinyl chloride	16	ND	100	ND	100	ND	100
1,2- dichloro- benzene	2,300	2,100	8.7	2,500	-8.7	2,700	-17.4
1,4- dichloro- benzene	380	300	21.1	391	-2.9	690	-81.6

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Run 2, Continued

Time, minutes

Volatile Organics	60		75		90	
	(ug/l)	% Reduction	(ug/l)	% Reduction	(ug/l)	% Reduction
Toluene	8,700	89.6	790	99.1	1.0	100
Benzene	ND	100	ND	100	ND	100
Xylenes	4,000	73.3	1,900	87.3	760	94.9
Ethyl-benzene	344	85.0	130	94.3	44	98.1
tri-chloro-ethene	ND	100	ND	100	ND	100
tetra-chloro-ethene	330	95.8	72	99.1	10	99.9
1,1,1-tri-chloro-ethene	1.1	100	ND	100	0.7	100
1,1-dichloro-ethene	ND	100	ND	100	ND	100
vinyl chloride	ND	100	ND	100	ND	100
1,2-dichloro-benzene	2,600	-13.0	2,100	8.7	1,900	17.4
1,4-dichloro-benzene	710	-86.8	260	31.6	200	47.4

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TABLE 22

Run 3

Volatile Organics	Reactor 1			Reactor 2			Overall % Reduction
	In (ug/l)	Out (ug/l)	% Reduction	In (ug/l)	Out (ug/l)	% Reduction	
Toluene	32,000	9,500	70.3	9,200	1,100	88.0	96.6
Benzene	28	2.9	89.6	1.8	ND	100	100
Xylenes	10,000	1,000	90.0	880	59	93.3	99.4
Ethyl-benzene	1,900	140	92.6	110	8.7	92.1	99.5
tri-chloro-ethene	1,500	60	96.0	45	3.5	92.2	99.8
tetra-chloro-ethene	4,400	180	95.9	134	7.9	94.1	99.8
1,1,1-tri-chloro-ethene	1,400	35	97.5	27	1.1	95.9	99.9
1,1-dichloro-ethene	12	3.2	73.3	ND	ND	–	–
vinyl chloride	18	ND	100	ND	ND	100	100
1,2-dichloro-benzene	2,600	560	78.5	540	87	83.9	96.7
1,4-dichloro-benzene	610	170	72.1	150	12	92.0	98.0

The data set forth in Tables 20 to 22 indicate that excellent reductions in volatile organic concentrations are obtainable by the process of the present invention.

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Other aspects of this invention are described in
United States patent applications Serial No. 477,212, filed
March 21, 1983, now abandoned, and Serial No. 042,565, filed
April 16, 1987, as well as European patent application
84901534.2, filed November 20, 1984, these documents being
incorporated herein by reference.

Although the present invention has been described
in considerable detail with reference to certain preferred
versions thereof, other versions are possible. For example,
the reactor vessel, although described as having an average
diameter to height length ratio, can have a cross-sectional
area shape that is polygonal as well as circular. In
addition, the volatile organic removal embodiment of the
present invention can be employed with prior art processes
adapted to remove non-volatile contaminants, e.g., the
mercury and sulfide precipitation processes. In general, an
aqueous solution is treated by the prior art process with the
simultaneous introduction of a gas into the aqueous solution
as taught herein. Furthermore, the processes of the present
invention can be use to treat effluents from prior art waste
water treatment processes. Therefore, the spirit and scope
of the appended claims should not necessarily be limited to
the description of the preferred versions contained herein.

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What is claimed is:

1.   A method for removing a contaminant from an
aqueous solution comprising the contaminant and ferrous ions,
the method comprising the steps of:
        (a) rapidly oxidizing substantially all the ferrous
ions in the solution to ferric ions so as to rapidly form a
substantially completely amorphous precipitate comprising a
substantial portion of ferric hydroxide and a substantial
portion of the contaminant; and
        (b) separating the amorphous precipitate from the
solution so as to form an effluent solution having a
substantially reduced contaminant concentration,
wherein the contaminant is selected from the group consisting
of (i) light metal ions, (ii) cyanide ions, (iii) phenolics,
(iv) oil and grease, (v) TSS contributors, (vi) BOD
contributors, (vii) COD contributors, (viii) TOC
contributors, and (ix) mixtures thereof.

2.   The method of claim 1 wherein step (a)
includes the step of controlling the pH of the solution.

3.   The method of claim 1 wherein step (a)
includes the step of controlling the pH of the solution with
a base selected from the group consisting of ammonia,
hydroxide containing bases, and mixtures thereof.

4.   The method of claim 1 wherein substantially
all of the ferrous ions in the solution are oxidized to
ferric ions within a period of less than about 30 minutes.

5.   The method of claim 1 wherein substantially
all of the ferrous ions in the solution are oxidized to
ferric ions within a period of less than about 15 minutes.

6. The method of claim 1 wherein substantially
all of the ferrous ions in the solution are oxidized to
ferric ions within a period of less than about 10 minutes.

7. The method of claim 1 wherein step (a)
includes the step of introducing air into the solution at a
rate of at least about 1 l air per 1000 ppm ferrous ion
present in the solution prior to step (a).

8. The method of claim 1 wherein step (a)
includes the step of introducing air into the solution at a
rate of at least about 2 l air per 1000 ppm ferrous ion
present in the solution prior to step (a).

9. The method of claim 1 wherein step (a)
includes the step of introducing air into the solution at a
rate of at least about 4 l air per 1000 ppm ferrous ion
present in the solution prior to step (a).

10. The method of claim 1 wherein step (a)
includes the step of introducing air into the solution at a
rate of at least about 10 l air 1000 ppm ferrous ion present
in the solution prior to step (a).

11. The method of claim 1 wherein step (a)
includes the step of introducing air into the solution at a
rate of about 1 to about 10 l air per about 1,000 ppm ferrous
ion present in the solution prior to step (a).

12. The method of claim 1 wherein step (a)
includes the step of introducing air into the solution at a
rate of about 2 to about 8 l air per about 1000 ppm ferrous
ion present in the solution prior to step (a).

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13.   The method of claim 1 wherein step (a) includes the step of mixing the aqueous solution.

14.   The method of claim 1 wherein step (a) includes the step of controlling the pH of the solution so that the pH of the solution is about 6 to about 9.5.

15.   The method of claim 1 wherein step (a) includes the step of controlling the pH of the solution so that the pH of the solution is about 6.5 to about 9.

16.   The method of claim 1 wherein step (a) includes the step of controlling the pH of the solution so that the pH of the solution is about 7.5 to about 8.

17.   The method of claim 1 wherein the light metal ions are selected from the group consisting of beryllium, aluminum, and mixtures thereof.

18.   The method of claim 17 wherein the total concentration of the contaminants in the effluent solution is less than about 10% of the concentration of the contaminants in the aqueous solution prior to step (a).

19.   The method of claim 17 wherein the total concentration of the contaminants in the effluent solution is less than about 5% of the concentration of the contaminants in the aqueous solution prior to step (a).

20.   The method of claim 17 wherein the total concentration of the contaminants in the effluent solution is less than about 1% of the concentration of the contaminants in the aqueous solution prior to step (a).

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21. The method of claim 1 wherein substantially all of the ferrous ions in the solution are oxidized to ferric ions within a period of less than about 30 minutes; step (a) includes the steps of introducing air into the solution at a rate of about 1 to about 10 1 air per about 1,000 ppm ferrous ion present in the solution prior to step (a), and controlling the pH of the solution so that the pH of the solution is about 6 to about 9.5; the light metal ions are selected from the group consisting of beryllium, aluminum, and mixtures thereof; and the total concentration of the contaminants in the effluent solution is less than about 10% of the concentration of the contaminants in the aqueous solution prior to step (a).

22. The method of claim 1 wherein substantially all of the ferrous ions in the solution are oxidized to ferric ions within a period of less than about 15 minutes; step (a) includes the steps of introducing air into the solution at a rate of about 2 to about 8 1 air per about 1000 ppm ferrous ion present in the solution prior to step (a), and controlling the pH of the solution so that the pH of the solution is about 6.5 to about 9; the light metal ions are selected from the group consisting of beryllium, aluminum, and mixtures thereof; and the total concentration of the contaminants in the effluent solution is less than about 5% of the concentration of the contaminants in the aqueous solution prior to step (a).

23. The method of claim 1 wherein substantially all of the ferrous ions in the solution are oxidized to ferric ions within a period of less than about 10 minutes; step (a) includes the steps of introducing air into the solution at a rate of about 4 to about 10 1 air per about 1000 ppm ferrous ion present in the solution prior to step (a), and controlling the pH of the solution so that the pH of

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the solution is about 7.5 to about 8; the light metal ions
are selected from the group consisting of beryllium,
aluminum, and mixtures thereof; and the total concentration
of the contaminants in the effluent solution is less than
about 1% of the concentration of the contaminants in the
aqueous solution prior to step (a).

24. The method of claim 1 wherein the contaminant
is selected from the group consisting of (i), (ii), mixtures
thereof, and heavy metal ions admixed with (i), (ii), or
mixtures of (i) and (ii), and the light metal ions are
selected from the group consisting of beryllium, aluminum,
and mixtures thereof.

25. The method of claim 24 wherein the molar ratio
of the ferrous ions to the contaminant in the aqueous
solution is at least about 1:1.

26. The method of claim 24 wherein the molar ratio
of the ferrous ions to the contaminant in the aqueous
solution is at least about 4:1.

27. The method of claim 24 wherein the molar ratio
of the ferrous ions to the contaminant in the aqueous
solution is at least about 8:1.

28. The method of claim 24 wherein the molar ratio
of the ferrous ions to the contaminant in the aqueous
solution is about 1:1 to about 10:1.

29. The method of claim 24 further comprising the
step of adding ferrous ions to the aqueous solution to
increase the ferrous ion-contaminant molar ratio to at least
about 1:1.

30. The method of claim 24 further comprising the
step of adding ferrous ions to the aqueous solution to
increase the ferrous ion-contaminant molar ratio to at least
about 4:1.

31. The method of claim 24 further comprising the
step of adding ferrous ions to the aqueous solution to
increase the ferrous ion-contaminant molar ratio to at least
about 8:1.

32. The method of claim 1 wherein the contaminant
is selected from the group consisting of (i), (ii), mixtures
thereof, and heavy metal ions admixed with (i), (ii), or
mixtures of (i) and (ii); the molar ratio of the ferrous ions
to the contaminant in the aqueous solution is about 1:1 to
about 10:1; substantially all of the ferrous ions in the
solution are oxidized to ferric ions within a period of less
than about 30 minutes; step (a) includes the steps of
introducing air into the solution at a rate of about 1 to
about 10 l air per about 1,000 ppm ferrous ion present in the
solution prior to step (a), and controlling the pH of the
solution so that the pH of the solution is about 6 to about
9.5; the light metal ions are selected from the group
consisting of beryllium, aluminum, and mixtures thereof; and
the total concentration of the contaminants in the effluent
solution is less than about 10% of the concentration of the
contaminants in the aqueous solution prior to step (a).

33. The method of claim 1 wherein the contaminant
is selected from the group consisting of (i), (ii), mixtures
thereof, and heavy metal ions admixed with (i), (ii), or
mixtures of (i) and (ii); the molar ratio of the ferrous ions
to the contaminant in the aqueous solution is about 2:1 to
about 8:1; substantially all of the ferrous ions in the
solution are oxidized to ferric ions within a period of less

than about 15 minutes; step (a) includes the steps of
introducing air into the solution at a rate of about 2 to
about 8 l air per about 1000 ppm ferrous ion present in the
solution prior to step (a), and controlling the pH of the
solution so that the pH of the solution is about 6.5 to about
9; the light metal ions are selected from the group
consisting of beryllium, aluminum, and mixtures thereof; and
the total concentration of the contaminants in the effluent
solution is less than about 5% of the concentration of the
contaminants in the aqueous solution prior to step (a).

34.   The method of claim 1 wherein the contaminant
is selected from the group consisting of (i), (ii), mixtures
thereof, and heavy metal ions admixed with (i), (ii), or
mixtures of (i) and (ii); the molar ratio of the ferrous ions
to the contaminant in the aqueous solution is about 4:1 to
about 8:1; substantially all of the ferrous ions in the
solution are oxidized to ferric ions within a period of less
than about 10 minutes; step (a) includes the steps of
introducing air into the solution at a rate of about 4 to
about 10 l air per about 1000 ppm ferrous ion present in the
solution prior to step (a), and controlling the pH of the
solution so that the pH of the solution is about 7.5 to about
8; the light metal ions are selected from the group
consisting of beryllium, aluminum, and mixtures thereof; and
the total concentration of the contaminants in the effluent
solution is less than about 1% of the concentration of the
contaminants in the aqueous solution prior to step (a).

35.   The method of claim 1 wherein the contaminant
is selected from the group consisting of (iii), (iv), (v),
(vi), (vii), (viii), and mixtures thereof.

36. The method of claim 35 wherein the weight ratio of the ferrous ions to the contaminant in the aqueous solution is at least about 1:1.

37. The method of claim 35 wherein the weight ratio of the ferrous ions to the contaminant in the aqueous solution is less than about 10:1.

38. The method of claim 35 wherein the weight ratio of the ferrous ions to the contaminant in the aqueous solution is about 1:1 to about 10:1.

39. The method of claim 35 wherein the weight ratio of the ferrous ions to the contaminant in the aqueous solution is about 4:1 to about 6:1.

40. The method of claim 1 wherein the contaminant is selected from the group consisting of (iii), (iv), (v), (vi), (vii), (viii), and mixtures thereof; the weight ratio of the ferrous ions to the contaminant in the aqueous solution is at least about 1:1; substantially all of the ferrous ions in the solution are oxidized to ferric ions within a period of less than about 30 minutes; step (a) includes the steps of introducing air into the solution at a rate of about 1 to about 10 l air per about 1000 ppm ferrous ion present in the solution prior to step (a), and controlling the pH of the solution so that the pH of the solution is about 6 to about 9.5; and the total concentration of the contaminants in the effluent solution is less than about 10% of the concentration of the contaminants in the aqueous solution prior to step (a).

41. The method of claim 1 wherein the contaminant is selected from the group consisting of (iii), (iv), (v), (vi), (vii), (viii), and mixtures thereof; the weight ratio

of the ferrous ions to the contaminant in the aqueous
solution is about 1:1 to about 10:1; substantially all of the
ferrous ions in the solution are oxidized to ferric ions
within a period of less than about 15 minutes; step (a)
includes the steps of introducing air into the solution at a
rate of about 2 to about 8 l air per about 1000 ppm ferrous
ion present in the solution prior to step (a), and
controlling the pH of the solution so that the pH of the
solution is about 6.5 to about 9; and the total concentration
of the contaminants in the effluent solution is less than
about 5% of the concentration of the contaminants in the
aqueous solution prior to step (a).

42. The method of claim 1 wherein the contaminant
is selected from the group consisting of (iii), (iv), (v),
(vi), (vii), (viii), and mixtures thereof; the weight ratio
of the ferrous ions to the contaminant in the aqueous
solution is about 4:1 to about 6:1; substantially all of the
ferrous ions in the solution are oxidized to ferric ions
within a period of less than about 10 minutes; step (a)
includes the steps of introducing air into the solution at a
rate of about 4 to about 10 l air per about 1000 ppm ferrous
ion present in the solution prior to step (a), and
controlling the pH of the solution so that the pH of the
solution is about 7.5 to about 8; and the total concentration
of the contaminants in the effluent solution is less than
about 1% of the concentration of the contaminants in the
aqueous solution prior to step (a).

43. The method of claim 1 wherein the light metal
ions are selected from the group consisting of beryllium,
aluminum, and mixtures thereof, and the concentration of the
ferrous ions in the aqueous solution is equal to at least
about the sum of (A) the molar concentration of the
contaminants selected from the group consisting of (i), (ii),

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and heavy metal ions, plus (B) the weight of the contaminants
is selected from the group consisting of (iii), (iv), (v),
(vi), (vii), (viii).

44. The method of claim 1 wherein the light metal
ions are selected from the group consisting of beryllium,
aluminum, and mixtures thereof, and the concentration of the
ferrous ions in the aqueous solution is equal to less than
about ten times the sum of (A) the molar concentration of the
contaminants selected from the group consisting of (i), (ii),
and heavy metal ions, plus (B) the weight of the contaminants
is selected from the group consisting of (iii), (iv), (v),
(vi), (vii), (viii).

45. The method of claim 1 wherein the light metal
ions are selected from the group consisting of beryllium,
aluminum, and mixtures thereof, and the concentration of the
ferrous ions in the aqueous solution is equal to about one to
about ten times the sum of (A) the molar concentration of the
contaminants selected from the group consisting of (i), (ii),
and heavy metal ions, plus (B) the weight of the contaminants
is selected from the group consisting of (iii), (iv), (v),
(vi), (vii), (viii).

46. The method of claim 1 wherein the light metal
ions are selected from the group consisting of beryllium,
aluminum, and mixtures thereof, and the concentration of the
ferrous ions in the aqueous solution is equal to about two to
about eight times the sum of (A) the molar concentration of
the contaminants selected from the group consisting of (i),
(ii), and heavy metal ions, plus (B) the weight of the
contaminants is selected from the group consisting of (iii),
(iv), (v), (vi), (vii), (viii).

47. The method of claim 1 wherein the light metal
ions are selected from the group consisting of beryllium,
aluminum, and mixtures thereof, and the concentration of the
ferrous ions in the aqueous solution is equal to about four
to about six times the sum of (A) the molar concentration of
the contaminants selected from the group consisting of (i),
(ii), and heavy metal ions, plus (B) the weight of the
contaminants is selected from the group consisting of (iii),
(iv), (v), (vi), (vii), (viii).

48. The method of claim 1 wherein the
concentration of the ferrous ions in the aqueous solution is
equal to about one to about ten times the sum of (A) the
molar concentration of the contaminants selected from the
group consisting of (i), (ii), and heavy metal ions, plus (B)
the weight of the contaminants is selected from the group
consisting of (iii), (iv), (v), (vi), (vii), (viii);
substantially all of the ferrous ions in the solution are
oxidized to ferric ions within a period of less than about 30
minutes; step (a) includes the steps of introducing air into
the solution at a rate of about 1 to about 10 l air per about
1,000 ppm ferrous ion present in the solution prior to step
(a), and controlling the pH of the solution so that the pH of
the solution is about 6 to about 9.5; the light metal ions
are selected from the group consisting of beryllium,
aluminum, and mixtures thereof; and the total concentration
of the contaminants in the effluent solution is less than
about 10% of the concentration of the contaminants in the
aqueous solution prior to step (a).

49. The method of claim 1 wherein the
concentration of the ferrous ions in the aqueous solution is
equal to about two to about eight times the sum of (A) the
molar concentration of the contaminants selected from the

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group consisting of (i), (ii), and heavy metal ions, plus (B)
the weight of the contaminants is selected from the group
consisting of (iii), (iv), (v), (vi), (vii), (viii);
substantially all of the ferrous ions in the solution are
oxidized to ferric ions within a period of less than about 15
minutes; step (a) includes the steps of introducing air into
the solution at a rate of about 2 to about 8 1 air per about
1000 ppm ferrous ion present in the solution prior to step
(a), and controlling the pH of the solution so that the pH of
the solution is about 6.5 to about 9; the light metal ions
are selected from the group consisting of beryllium,
aluminum, and mixtures thereof; and the total concentration
of the contaminants in the effluent solution is less than
about 5% of the concentration of the contaminants in the
aqueous solution prior to step (a).

        50.   The method of claim 1 wherein the
concentration of the ferrous ions in the aqueous solution is
equal to about four to about six times the sum of (A) the
molar concentration of the contaminants selected from the
group consisting of (i), (ii), and heavy metal ions, plus (B)
the weight of the contaminants is selected from the group
consisting of (iii), (iv), (v), (vi), (vii), (viii);
substantially all of the ferrous ions in the solution are
oxidized to ferric ions within a period of less than about 10
minutes; step (a) includes the steps of introducing air into
the solution at a rate of about 4 to about 10 1 air per about
1000 ppm ferrous ion present in the solution prior to step
(a), and controlling the pH of the solution so that the pH of
the solution is about 7.5 to about 8; the light metal ions
are selected from the group consisting of beryllium,
aluminum, and mixtures thereof; and the total concentration
of the contaminants in the effluent solution is less than
about 1% of the concentration of the contaminants in the
aqueous solution prior to step (a).

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51. The method of claim 1 further comprising the
steps of:

(c) introducing additional ferrous ions into the
effluent solution to form a modified effluent solution;

(d) rapidly oxidizing substantially all the ferrous
ions in the modified effluent solution to ferric ions so as
to rapidly form a second substantially completely amorphous
precipitate comprising a substantial portion of ferric
hydroxide and a substantial portion of any contaminant
present in the effluent solution; and

(e) separating the second precipitate from the
modified effluent solution so as to form a second effluent
solution having a contaminant concentration less than the
contaminant concentration of the effluent solution.

52. The method of claim 51 wherein step (d)
includes the step of controlling the pH of the modified
effluent solution.

53. The method of claim 51 wherein substantially
all of the ferrous ions in the solution are oxidized to
ferric ions within a period of less than about 30 minutes.

54. The method of claim 51 wherein step (d)
includes the step of introducing air into the modified
effluent solution at a rate of at least about 1 l air per
1000 ppm ferrous ion present in the modified effluent
solution prior to step (d).

55. The method of claim 51 wherein step (d)
includes the step of introducing air into the modified
effluent solution at a rate of at least about 10 l air 1000
ppm ferrous ion present in the modified effluent solution
prior to step (d).

56.   The method of claim 51 wherein step (d)
includes the step of mixing the aqueous solution.

57.   The method of claim 51 wherein step (d)
includes the step of controlling the pH of the modified
effluent solution so that the pH of the modified effluent
solution is about 6 to about 9.5.

58.   The method of claim 1 wherein the method is a
continuous process.

59.   The method of claim 1 wherein the method is a
batch process.

60.   A method for removing volatile organics from
an aqueous solution, the method comprising the steps of:
        (a) introducing a solution into a vessel having
having an internal diameter to internal height height ratio
of about 1:1 to about 1:4;
        (b) introducing a gas into the solution proximate
the bottom of the vessel at a rate sufficient to achieve an
average volumetric flux ratio of gas to water of at least
about 20; and
        (c) withdrawing a primary effluent from the vessel,
the effluent having a reduced volatile organic concentration.

61.   The method of claim 60 wherein the gas is
selected from the group consisting of air, oxygen,
nitrogen,and mixtures thereof.

62.   The method of claim 60 further comprising the
step of controlling the pH of the solution.

63.   The method of claim 62 further comprising the
step of controlling the pH of the solution with the base is

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selected from the group consisting of ammonia, hydroxide
containing bases, and mixtures thereof.

64. The method of claim 60 further comprising the
step of controlling the pH of the solution so that the
solution has a pH within the range of about 6 to about 9.5.

65. The method of claim 60 further comprising the
step of controlling the pH of the solution so that the
solution has a pH within the range of about 6.5 to about 9.

66. The method of claim 60 further comprising the
step of controlling the pH of the solution so that the
solution has a pH within the range of about 7.5 to about 8.

67. The method of claim 60 wherein the average
volumetric flux ratio of gas to water is less than about 100.

68. The method of claim 60 wherein the average
volumetric flux ratio of gas to water is about 20 to about
100.

69. The method of claim 60 wherein the average
volumetric flux ratio of gas to water is about 30 to about
90.

70. The method of claim 60 wherein the average
volumetric flux ratio of gas to is about 40 to about 80.

71. The method of claim 60 wherein the method is a
batch process and the gas is introduced into the solution for
at least about 15 minutes.

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72. The method of claim 60 wherein the method is a batch process and the gas is introduced into the solution for less than about 2 hours.

73. The method of claim 60 wherein the method is a batch process and the gas is introduced into the solution for about 0.25 to about 2 hours.

74. The method of claim 60 wherein the method is a batch process and the gas is introduced into the solution for about 0.5 to about 1.5 hours.

75. The method of claim 60 wherein the method is a continuous process and the portion of the solution being treated by the gas has an average residence time of at least about 15 minutes.

76. The method of claim 60 wherein the method is a continuous process and the portion of the solution being treated by the gas has an average residence time of less than about 2 hours.

77. The method of claim 60 wherein the method is a continuous process and the portion of the solution being treated by the gas has an average residence time of about 0.25 to about 2 hours.

78. The method of claim 60 wherein the method is a continuous process and the portion of the solution being treated by the gas has an average residence time of about 0.5 to about 1.5 hours.

79. The method of claim 60 wherein the effluent volatile organic concentration is less than about 20 percent of the solution volatile organic concentration.

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80. The method of claim 60 wherein the effluent volatile organic concentration is less than about 10 percent of the solution volatile organic concentration.

81. The method of claim 60 wherein the effluent volatile organic concentration is less than about 5 percent of the solution volatile organic concentration.

82. The method of claim 60 wherein the volatile organics have a Henry's Law constant of at least about 0.02.

83. The method of claim 60 wherein the volatile organics have a Henry's Law constant of at least about 0.05.

84. The method of claim 60 wherein the volatile organics have a Henry's Law constant of at least about 0.25.

85. The method of claim 60 wherein the volatile organics are selected from the group consisting of benzene, toluene, xylene, ethylbenzene, and mixtures thereof.

86. The method of claim 60 wherein the method further comprises the step of mixing the aqueous solution.

87. The method of claim 60 further comprising the steps of:

(d) introducing the primary effluent into a second vessel having having an average diameter greater than about 10 percent of the vessel's height;

(e) introducing a gas into the primary effluent proximate the bottom of the second vessel at a rate sufficient to achieve an average volumetric flux ratio of gas to water of at least about 20; and

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(f) withdrawing a secondary effluent from the vessel, the secondary effluent having a volatile organic concentration less than that of the primary effluent.

88. The method of claim 87 wherein the gas is selected from the group consisting of air, oxygen, nitrogen, and mixtures thereof.

89. The method of claim 87 further comprising the step of controlling the pH of the solution.

90. The method of claim 87 further comprising the step of controlling the pH of the solution so that the pH of the solution is maintained within the range of about 6 to about 9.5.

91. The method of claim 87 wherein the average volumetric flux ratio of gas to water is less than about 100.

92. The method of claim 87 wherein the primary effluent is treated by a batch process and the gas is introduced into the primary effluent for at least about 15 minutes.

93. The method of claim 87 wherein the primary effluent is treated by a continuous process and the portion of the primary effluent being treated by the gas has an average residence time of at least about 15 minutes.

94. The method of claim 87 wherein the secondary effluent volatile organic concentration is less than about 20 percent of the primary effluent volatile organic concentration.

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95. A method for removing volatile organics and a
contaminant from an aqueous solution comprising the volatile
organics, the contaminant, and ferrous ions, the method
comprising the steps of:

(a) rapidly oxidizing substantially all the ferrous
ions in the solution to ferric ions so as to rapidly form a
substantially completely amorphous precipitate comprising a
substantial portion of ferric hydroxide and a substantial
portion of the contaminant;

(b) introducing a gas into the solution at a rate
sufficient to achieve an average volumetric flux ratio of gas
to water of at least about 20; and

(c) separating the precipitate from the solution so
as to form an effluent solution having a reduced contaminant
and volatile organic concentration,
the contaminant being selected from the group consisting of
(i) light metal ions, (ii) cyanide ions, (iii) phenolics,
(iv) oil and grease, (v) TSS contributors, (vi) BOD
contributors, (vii) COD contributors, (viii) TOC
contributors, (ix) mixtures thereof, and (x) heavy metal ions
admixed with (i), (ii), (iii), (iv), (v), (vi), (vii),
(viii), or (ix).

96. The method of claim 95 wherein steps (a) and
(b) are preformed simultaneously.

97. The method of claim 95 wherein step (b) is
preformed prior to step (a).

98. The method of claim 95 wherein step (a)
includes the step of controlling the pH of the solution.

99. The method of claim 95 wherein step (b)
includes the step of controlling the pH of the solution.

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100. The method of claim 95 wherein substantially all of the ferrous ions in the solution are oxidized to ferric ions within a period of less than about 30 minutes.

101. The method of claim 95 wherein step (a) includes the step of introducing air into the solution at a rate of at least about 1 l air per 1000 ppm ferrous ion present in the solution prior to step (a).

102. The method of claim 95 wherein steps (a) and (b) are performed simultaneously and include the step of mixing the aqueous solution.

103. The method of claim 95 wherein steps (a) and (b) are performed simultaneously and include the step of controlling the pH of the solution so that the pH of the solution is about 6 to about 9.5.

104. The method of claim 95 wherein the light metal ions are selected from the group consisting of beryllium, aluminum, and mixtures thereof, and the total concentration of the contaminants in the effluent solution is less than about 10% of the concentration of the contaminants in the aqueous solution prior to step (a), and the concentration of the volatile organics in the effluent is less than about 20% of the concentration of the volatile organics in the aqueous solution prior to step (b).

105. The method of claim 95 wherein steps (a) and (b) are preformed simultaneously and include the steps of introducing air into the solution at a rate of about 1 to about 10 l air per about 1,000 ppm ferrous ion present in the solution prior to step (a), and controlling the pH of the solution so that the pH of the solution is about 6 to about 9.5; substantially all of the ferrous ions in the solution

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are oxidized to ferric ions within a period of less than
about 30 minutes; the light metal ions are selected from the
group consisting of beryllium, aluminum, and mixtures
thereof; and the total concentration of the contaminants in
the effluent solution is less than about 10% of the
concentration of the contaminants in the aqueous solution
prior to step (a), and the concentration of the volatile
organics in the effluent is less than about 20% of the
concentration of the volatile organics in the aqueous
solution prior to step (b).

106. The method of claim 95 wherein the contaminant
is selected from the group consisting of (i), (ii), mixtures
thereof, and heavy metal ions admixed with (i), (ii), or
mixtures of (i) and (ii), and the light metal ions are
selected from the group consisting of beryllium, aluminum,
and mixtures thereof.

107. The method of claim 106 wherein the molar
ratio of the ferrous ions to the contaminant in the aqueous
solution is at least about 1:1.

108. The method of claim 106 further comprising the
step of adding ferrous ions to the aqueous solution to
increase the ferrous ion-contaminant molar ratio to at least
about 1:1.

109. The method of claim 95 wherein the contaminant
is selected from the group consisting of (i), (ii), mixtures
thereof, and heavy metal ions admixed with (i), (ii), or
mixtures of (i) and (ii); the molar ratio of the ferrous ions
to the contaminant in the aqueous solution is about 1:1 to
about 10:1; substantially all of the ferrous ions in the
solution are oxidized to ferric ions within a period of less
than about 30 minutes; steps (a) and (b) are performed

simultaneously and include the steps of introducing air into the solution at a rate of about 1 to about 10 1 air per about 1,000 ppm ferrous ion present in the solution prior to step (a), and controlling the pH of the solution so that the pH of the solution is about 6 to about 9.5; the light metal ions are selected from the group consisting of beryllium, aluminum, and mixtures thereof; and the total concentration of the contaminants in the effluent solution is less than about 10% of the concentration of the contaminants in the aqueous solution prior to step (a), and the concentration of the volatile organics in the effluent is less than about 20% of the concentration of the volatile organics in the aqueous solution prior to step (b).

110. The method of claim 95 wherein the contaminant is selected from the group consisting of (iii), (iv), (v), (vi), (vii), (viii), and mixtures thereof.

111. The method of claim 110 wherein the weight ratio of the ferrous ions to the contaminant in the aqueous solution is at least about 1:1.

112. The method of claim 95 wherein the contaminant is selected from the group consisting of (iii), (iv), (v), (vi), (vii), (viii), and mixtures thereof; the weight ratio of the ferrous ions to the contaminant in the aqueous solution is at least about 1:1; substantially all of the ferrous ions in the solution are oxidized to ferric ions within a period of less than about 30 minutes; steps (a) and (b) are performed simultaneously and include the steps of introducing air into the solution at a rate of about 1 to about 10 1 air per about 1,000 ppm ferrous ion present in the solution prior to step (a), and controlling the pH of the solution so that the pH of the solution is about 6 to about 9.5; and the total concentration of the contaminants in the

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effluent solution is less than about 10% of the concentration
of the contaminants in the aqueous solution prior to step
(a), and the concentration of the volatile organics in the
effluent is less than about 20% of the concentration of the
volatile organics in the aqueous solution prior to step (b).

113. The method of claim 95 wherein the light metal
ions are selected from the group consisting of beryllium,
aluminum, and mixtures thereof, and the concentration of the
ferrous ions in the aqueous solution is equal to at least
about the sum of (A) the molar concentration of the
contaminants selected from the group consisting of (i), (ii),
and heavy metal ions, plus (B) the weight of the contaminants
is selected from the group consisting of (iii), (iv), (v),
(vi), (vii), (viii).

114. The method of claim 95 wherein the
concentration of the ferrous ions in the aqueous solution is
equal to about one to about ten times the sum of (A) the
molar concentration of the contaminants selected from the
group consisting of (i), (ii), and heavy metal ions, plus (B)
the weight of the contaminants is selected from the group
consisting of (iii), (iv), (v), (vi), (vii), (viii);
substantially all of the ferrous ions in the solution are
oxidized to ferric ions within a period of less than about 30
minutes; steps (a) and (b) are performed simultaneously and
include the steps of introducing air into the solution at a
rate of about 1 to about 10 1 air per about 1,000 ppm ferrous
ion present in the solution prior to step (a), and
controlling the pH of the solution so that the pH of the
solution is about 6 to about 9.5; the light metal ions are
selected from the group consisting of beryllium, aluminum,
and mixtures thereof; and the total concentration of the
contaminants in the effluent solution is less than about 10%
of the concentration of the contaminants in the aqueous

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solution prior to step (a), and the concentration of the
volatile organics in the effluent is less than about 20% of
the concentration of the volatile organics in the aqueous
solution prior to step (b).

115.   The method of claim 95 further comprising the
steps of:
            (d) introducing additional ferrous ions into the
effluent solution to form a modified effluent solution;
            (e) rapidly oxidizing substantially all the ferrous
ions in the modified effluent solution to ferric ions so as
to rapidly form a second substantially completely amorphous
precipitate comprising a substantial portion of ferric
hydroxide and a substantial portion of any contaminant
present in the effluent solution; and
            (f) separating the second precipitate from the
modified effluent solution so as to form a second effluent
solution having a contaminant concentration less than the
contaminant concentration of the effluent solution.

116.   The method of claim 95 further comprising the
steps of introducing additional gas into the effluent
solution at a rate sufficient to achieve an average
volumetric flux ratio of gas to water of at least about 20 so
that any volatile organic content to the effluent is further
reduced.

117.   The method of claim 95 further comprising the
steps of:
            (d) introducing additional ferrous ions into the
effluent solution to form a modified effluent solution;
            (e) rapidly oxidizing substantially all the ferrous
ions in the modified effluent solution to ferric ions so as
to rapidly form a second substantially completely amorphous
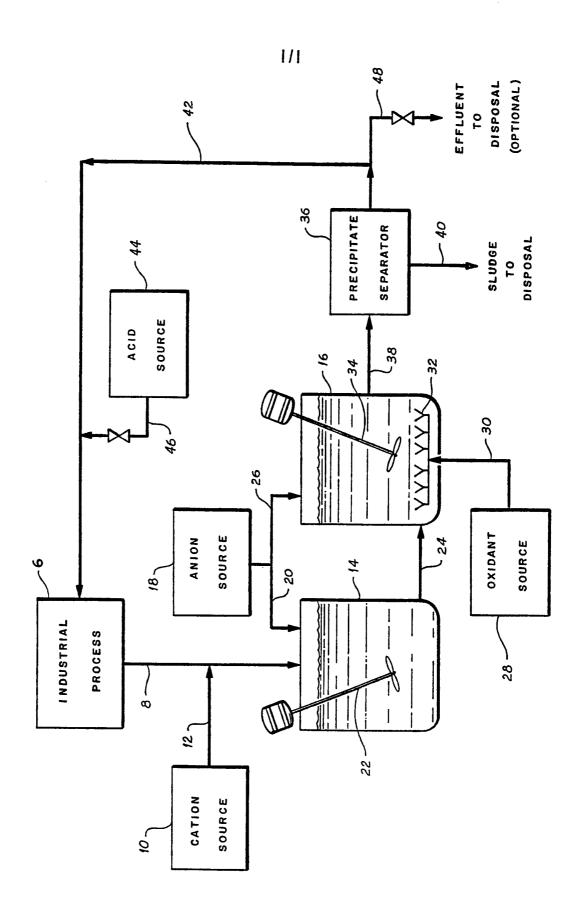precipitate comprising a substantial portion of ferric

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hydroxide and a substantial portion of any contaminant present in the effluent solution;

(f) introducing additional gas into the effluent solution at a rate sufficient to achieve an average volumetric flux ratio of gas to water of at least about 20; and

(g) separating the precipitate from the modified effluent solution so as to form an second effluent solution having a contaminant and volatile organic concentration less than the contaminant and and volatile organic concentration of the effluent solution.

118. A method for simultaneously removing volatile organics and a contaminant from an aqueous solution comprising the volatile organics and the contaminant, the method comprising the steps of:

(a) precipitating the contaminants in the solution while simultaneously introducing a gas into the solution at a rate sufficient to achieve an average volumetric flux ratio of gas to water of at least about 20; and

(c) separating the precipitate from the solution so as to form an effluent solution having a reduced contaminant and volatile organic concentration, the contaminant being selected from the group consisting of (i) light metal ions, (ii) cyanide ions, (iii) phenolics, (iv) oil and grease, (v) TSS contributors, (vi) BOD contributors, (vii) COD contributors, (viii) TOC contributors, (ix) heavy metal ions, and (x) mixtures thereof.

119. The method of claim 1 wherein the amorphous precipitate contains essentially all of the ferric ions formed in step (a).

120. The method of claim 1 wherein the amorphous precipitate consists essentially of an amorphous material.

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121.   The method of claim 1 wherein at least one of
the contaminants in the waste water is a heavy metal and step
(a) includes the step of occluding a substantial portion of
the heavy metal contaminant in the amorphous precipitate.