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Canadian Intellectual Property Office

CA 2799294 C 2021/11/23

(11)(21) 2 799 294

(12) BREVET CANADIEN
CANADIAN PATENT

(13) C

(86) Date de dépôt PCT/PCT Filing Date: 2011/05/18
(87) Date publication PCT/PCT Publication Date: 2011/11/24
(45) Date de délivrance/Issue Date: 2021/11/23
(85) Entrée phase nationale/National Entry: 2012/11/13
(86) N° demande PCT/PCT Application No.: CA 2011/050311
(87) N° publication PCT/PCT Publication No.: 2011/143775
(30) Priorité/Priority: 2010/05/18 (US61/346,002)

(51) Cl.Int./Int.Cl. *C02F 1/58* (2006.01), *C01B 25/26* (2006.01), *C02F 1/42* (2006.01), *C02F 1/44* (2006.01), *C02F 1/52* (2006.01), *C02F 9/00* (2006.01)

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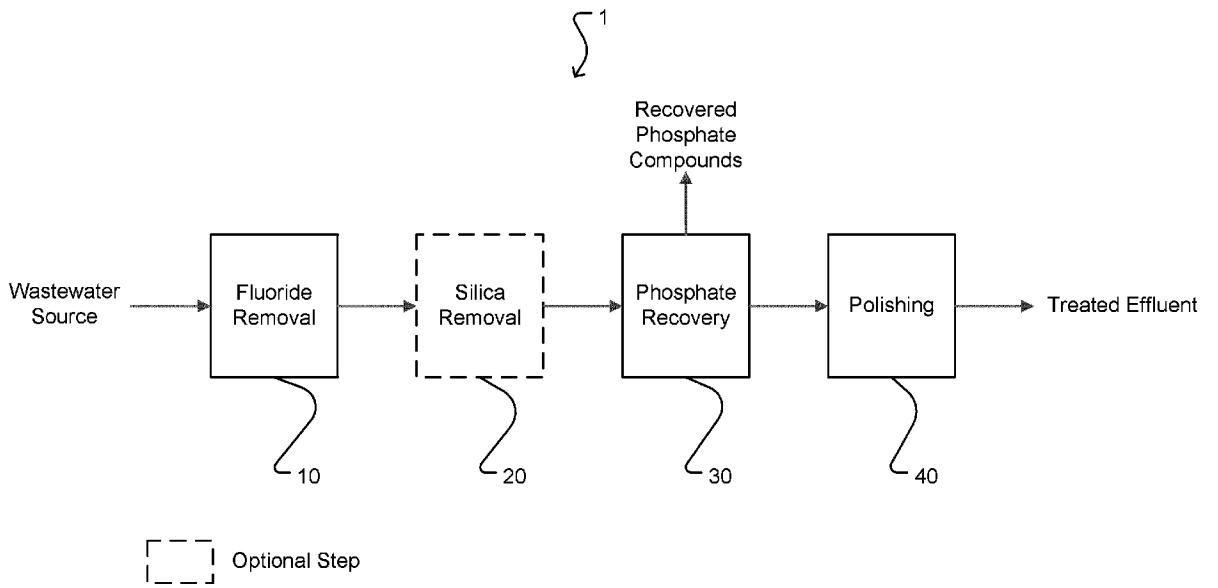
(54) Titre : TRAITEMENT D'EAUX USEES CONTENANT DES PHOSPHATES
(54) Title: TREATMENT OF PHOSPHATE-CONTAINING WASTEWATER



(57) Abrégé/Abstract:
A method for treating, and recovering phosphate compounds from, phosphate-containing wastewater. The method includes the steps of: (a) removing fluoride from the wastewater; (b) recovering a phosphate compound from the wastewater by maintaining super saturation conditions for the phosphate compound; and (c) polishing the wastewater. A silica removal step may be optionally performed after step (a) and before step (b).

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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
24 November 2011 (24.11.2011)

PCT

(10) International Publication Number
WO 2011/143775 A1

(51) International Patent Classification:
C02F 1/58 (2006.01) *C02F 1/52* (2006.01)
C02F 1/42 (2006.01) *C02F 9/00* (2006.01)
C02F 1/44 (2006.01) *C01B 25/26* (2006.01)

(21) International Application Number:
PCT/CA2011/050311

(22) International Filing Date:
18 May 2011 (18.05.2011)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/346,002 18 May 2010 (18.05.2010) US

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

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

Published:

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

(54) **Title**: TREATMENT OF PHOSPHATE-CONTAINING WASTEWATER

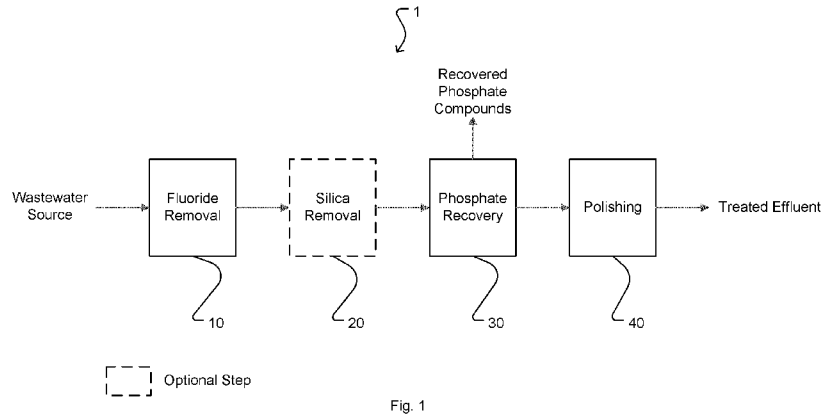

Fig. 1

(57) **Abstract**: A method for treating, and recovering phosphate compounds from, phosphate-containing wastewater. The method includes the steps of: (a) removing fluoride from the wastewater; (b) recovering a phosphate compound from the wastewater by maintaining super saturation conditions for the phosphate compound; and (c) polishing the wastewater. A silica removal step may be optionally performed after step (a) and before step (b).

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TREATMENT OF PHOSPHATE-CONTAINING WASTEWATER

Technical Field

[0002] The invention relates to treatment of phosphate-containing wastewater, such as phosphogypsum pond water, and the recovery of useful phosphate compounds, such as struvite, during treatment.

Background

[0003] Phosphogypsum is a by-product of processing phosphate rock into phosphoric acid fertilizer. The production of 1 ton of phosphoric acid generates approximately 4 to 5 tonnes of phosphogypsum. Phosphogypsum is essentially a waste product. Phosphogypsum may have low level radioactivity which prevents its use in various applications.

[0004] Phosphogypsum is typically stored by being slurried and piled into large stacks, which can be up to hundreds of feet high, in open air storage sites. Water percolating through the stacks forms ponds. In 2005, there were 24 phosphogypsum stacks in Florida alone, containing 1.2 billion tonnes of phosphogypsum and 50 billion gallons of pond water (Perpich et al, 2005).

Date Reçue/Date Received 2020-09-24

[0005] In active phosphoric acid fertilizer plants, such ponds are typically used as reservoirs for process water for use in a closed loop. The pond water is toxic and needs to be treated before it can be discharged. Furthermore, closed stacks continue to produce a contaminant-containing leachate requiring treatment.

[0006] Pond water associated with phosphogypsum stacks is strongly acidic and contains numerous contaminants including large amounts of phosphates. Data collected from a number of sources are summarized in Table 1. The column headed "Representative Value" contains results from a composite of 18 samples from 6 different plants representing the composition of saturated fresh pond water (Kennedy et al., 1991). The reported phosphorus concentration of 6,600 ppm as P is equivalent to 20,220 ppm PO_4 or 0.22 Mol/L. Pond water also contains significant amounts of ammonia (ammonia is often added to phosphoric acid in phosphoric acid plants to make di-ammonium phosphate) and magnesium.

Table 1: Typical composition of pond water

Component	Units	Range	Representative Value
pH		1.3 – 3.0	1.55
Conductivity	µS/cm	15,000 – 30,000	
Ammonia (as N)	ppm	500 – 2,000	592
Calcium	ppm	500 – 3,000	1,155
Chloride	ppm	10 -300	
Fluoride	ppm	200 – 15,000	7,600
Iron	ppm	5 - 300	216
Magnesium	ppm	200 - 500	286

Phosphorus (as P)	ppm	500 – 12,000	6,600
Potassium	ppm	100 - 400	276
Silica (as Si)	ppm	100 – 4,000	1,910
Sodium	ppm	1,000 – 3,000	1,995
Sulfate (as S)	ppm	1,000 – 4,000	1,695

[0007] Pond water treatment chemistry is relatively complex. Pond water may contain ten major components that can form numerous soluble species and precipitates when the pH is changed and cations are added. As indicated by the data under the column headed "Range" in Table 1, the composition of pond water can vary significantly.

[0008] A cost-effective and efficient process for treating phosphate-containing wastewater while recovering commercially useful phosphate compounds would be desirable.

Summary

[0009] The following embodiments and aspects thereof are described and illustrated in conjunction with apparatus and methods which are meant to be exemplary and illustrative, not limiting in scope. In various embodiments, one or more of the above-described problems have been reduced or eliminated, while other embodiments are directed to other improvements.

[0010] In one aspect, a method for treating, and recovering phosphate compounds from, phosphate-containing wastewater, is provided. The method comprising: (a) removing fluoride from the wastewater; (b) recovering a phosphate compound from the wastewater

by maintaining supersaturation conditions for the phosphate compound; and (c) polishing the wastewater.

[0011] Step (a) may comprise precipitating the fluoride. Precipitating the fluoride may comprise raising the pH of the wastewater to about pH 3 to 4. Raising the pH of the wastewater may comprise adding a calcium-containing base with calcium in a quantity to meet stoichiometric requirements for precipitating the fluoride. The calcium-containing base may be lime. The fluoride may be precipitated as fluorite. Raising the pH of the wastewater further may comprise adding one or more calcium-free bases with cations in a quantity to meet stoichiometric requirements for precipitating the phosphate compound. The one or more calcium-free bases may be selected from the group consisting of magnesium oxide, magnesium hydroxide, ammonium hydroxide and anhydrous ammonia.

[0012] The phosphate compound may comprise struvite or a struvite analog such as iron ammonium phosphate.

[0013] Maintaining supersaturation conditions in step (b) may comprise one or more of: maintaining a supersaturation ratio of 2 to 5; maintaining a pH of at least about pH 5; controllably introducing magnesium and/or ammonium; and maintaining a concentration of phosphate higher than concentrations of magnesium and ammonia. The struvite may be recovered in the form of crystals and aggregates ranging in size from 1 to 5 mm.

[0014] Silica may be removed from the wastewater of step (a) if the wastewater from step (a) comprises a silica concentration of greater than 100 ppm. Removing silica may comprise hydrolyzing the silica by raising the pH. Raising the pH to hydrolize the silica may comprise adding a base comprising cations in a quantity to meet stoichiometric requirements for precipitating the phosphate compound. The base may be selected from the group consisting of magnesium oxide, magnesium hydroxide, ammonium hydroxide and anhydrous ammonia.

[0015] Polishing step (c) may comprise raising the pH to about pH 8 to 10. Step (c) may comprise removing ammonia using a process selected from the group consisting of breakpoint chlorination, stripping, biological nitrification and biological denitrification.

[0016] Polishing step (c) may comprise subjecting the wastewater from step (b) to a two-stage membrane treatment comprising: (i) a first membrane treatment to obtain a first concentrate comprising divalent ions and a first permeate comprising monovalent ions; and (ii) a second membrane treatment for the first permeate to obtain a second concentrate comprising monovalent ions and a second permeate comprising effluent. The first concentrate may be recirculated to step (a). The first membrane treatment may comprise nanofiltration. The second membrane treatment may comprise reverse osmosis. Prior to the two-stage membrane treatment, the pH may be lowered to about pH 3 to 5, and suspended solids may be removed by filtration. Ammonia may be removed from the second permeate by subjecting the second permeate to ion exchange.

Ammonia-containing regeneration liquid of the ion exchange may be recirculated to step (b).

[0017] Prior to step (b) the wastewater may be subjected to a first membrane treatment to obtain a first concentrate comprising divalent ions and a first permeate comprising monovalent ions, wherein the first concentrate defines feed for step (b). Wastewater from step (b) may be recirculated to step (a). The first permeate may be subjected to a second membrane treatment to obtain a second concentrate comprising monovalent ions and a second permeate comprising effluent. The first membrane treatment may comprise nanofiltration. The second membrane treatment may comprise reverse osmosis. Prior to the two-stage membrane treatment, the pH may be lowered to about pH 3 to 5, and suspended solids may be removed by filtration. Ammonia may be removed from the second permeate by subjecting the second permeate to ion exchange. Ammonia-containing regeneration liquid of the ion exchange may be recirculated to step (b).

[0018] In addition to the exemplary aspects and embodiments described above, further aspects and embodiments will become apparent by reference to the drawings and by study of the following detailed descriptions.

Brief Description of the Drawings

[0019] The accompanying drawings illustrate non-limiting embodiments of the invention.

[0020] Figure 1 is a flowchart illustrating a process for treating phosphate-containing wastewater according to one embodiment of the present invention.

[0021] Figure 2 is a block diagram illustrating a process for treating phosphate-containing wastewater according to another embodiment of the present invention.

[0022] Figure 3 is a flowchart illustrating a process for treating phosphate-containing wastewater according to one embodiment of the present invention.

[0023] Figure 4 is a block diagram illustrating a process for treating phosphate-containing wastewater according to another embodiment of the present invention.

[0024] Figure 5 is a flowchart illustrating a process for treating phosphate-containing wastewater according to one embodiment of the present invention.

[0025] Figure 6 is a block diagram illustrating a process for treating phosphate-containing wastewater according to another embodiment of the present invention.

Description

[0026] Throughout the following description, specific details are set forth in order to provide a more thorough understanding of the invention. However, the invention may be practiced without these particulars. In other instances, well-known elements have not been shown or described in detail to avoid unnecessarily obscuring the invention. Accordingly, the specification and drawings are to be regarded in an illustrative, rather than a restrictive, sense.

[0027] Some embodiments of the invention relate to methods for treating phosphate-containing wastewater while simultaneously recovering commercially useful phosphate compounds. Bases are used to neutralize the acidity of phosphate-containing wastewater. Cations from the bases are used to remove contaminants and recover phosphate compounds. Excess cations may be recirculated to maximize contaminant removal and recovery of phosphate compounds.

[0028] Some embodiments of the invention relate to treatment processes wherein the phosphate-containing wastewater is phosphogypsum pond water and the phosphate compound is recovered in the form of granular struvite. These embodiments coincide with an aspect of the invention having significant commercial utility. The scope of the invention, however, is not limited to these embodiments.

[0029] Figure 1 illustrates in a general manner a wastewater treatment process 1 according to one embodiment of the invention. In process 1, phosphate-containing wastewater from a wastewater source undergoes a fluoride removal step 10, an optional silica removal step 20, a phosphate recovery step 30, and a polishing step 40. The wastewater may for example be phosphogypsum pond water. Phosphate recovery step 30 yields phosphate compounds in a commercially useful form. Polishing step 40 yields treated effluent ready for discharge.

[0030] Figure 2 illustrates another embodiment of the invention following process 1 but more specifically exemplifying treatment of phosphogypsum pond water and recovery of struvite.

[0031] Fluoride removal step 10 comprises raising the pH of the wastewater with one or more bases to a desired pH that promotes precipitation of contaminants such as fluoride and/or sulphates but not precipitation of phosphates. In some embodiments the pH may be raised to about pH 3.0-4.0. In some embodiments the degree to which the pH is raised may vary with the composition of the wastewater. Fluoride removal step 10 results in relatively dense precipitates that settle well. The precipitates may for example be settled and separated in a pond, a clarifier, a separation tank, or the like.

[0032] The base used in fluoride removal step 10 may be a calcium-containing base. The calcium-containing base may be added in an amount such that the calcium added to any pre-existing calcium in the

wastewater results in a concentration of calcium ions sufficient to cause precipitation of compounds such as fluorite, calcium fluorosilicate, calcium sulphate, and the like while being insufficient to precipitate significant amounts of calcium phosphate. This may be achieved by adding sufficient calcium into the wastewater solution at a rate such that the product of the calcium ion concentration, the concentration of a fluorine-containing ionic species and the concentrations of any other components of a calcium salt exceeds the k_{sp} for the calcium salt without being so high as to cause significant precipitation of calcium phosphate. The total amount of calcium added in step 10 is desirably sufficient to cause precipitation of the bulk of the fluoride in the wastewater in step 10. For example, a stoichiometric amount of calcium may be introduced during step 10. As shown in Figure 2, the calcium-containing base may comprise lime, including calcium oxides, carbonates and hydroxides. In other embodiments, the calcium-containing base may be a compound other than lime.

[0033] Alternatively or additionally, one or more calcium-free bases may be added to raise the pH sufficiently to precipitate the fluoride at fluoride removal step 10. In some embodiments, the calcium-free base may be selected on the basis of a phosphate compound that is desired to be recovered at phosphate recovery step 30. For example, if the phosphate compound to be recovered is or comprises struvite, as shown in Figure 2, suitable calcium-free bases may include magnesium- and/or ammonium-containing bases such as magnesium oxide, magnesium hydroxide, ammonium hydroxide, and anhydrous ammonia.

[0034] Bases containing magnesium and/or ammonia may be added to simultaneously raise pH of the wastewater and increase the concentration of magnesium and/or ammonia cations to facilitate struvite production in a subsequent step. For example, magnesium oxide may be used to add magnesium in a quantity sufficient to raise a concentration of magnesium ions to or toward a concentration desired to later precipitate struvite. Addition of a magnesium-containing base may also assist in removal of fluoride ions by promoting precipitation of fluoride as sellaite (MgF_2).

[0035] In some embodiments a mixture of two or more calcium-free bases may be used to raise the pH at fluoride removal step 10. Bases may be added in a sequence that accounts for pH-dependent differences in solubility of the bases. For example, the base with better dissolution at a lower pH may be added before the base with lower dissolution at the lower pH. For example, if magnesium oxide and ammonium hydroxide are used, then magnesium oxide may be added first (because its dissolution is better at lower pH), and then ammonium hydroxide added next to reach the desired pH for fluoride removal.

[0036] Following fluoride removal step 10, process 1 may include a silica removal step 20. Silica removal may be desirable in some embodiments to avoid silica gel formation, which may interfere with recovery of phosphate compounds (e.g. struvite crystallization) at phosphate recovery step 30. In some embodiments, silica may be removed by adding base to hydrolyze the silica and then allowing the

silica to settle. Step 20 may conveniently be performed in a settling tank or the like. Settled silica may be removed. In some embodiments, silica may be hydrolyzed by adding a base to adjust the to pH to a pH optimal for subsequent phosphate recovery step 30. In some embodiments, the pH may be at least about 5 prior to phosphate recovery step 30.

[0037] One or more bases that contain cations (e.g. magnesium and/or ammonia) that will enhance phosphate precipitation at phosphate recovery step 30 may be used to raise the pH for silica removal step 20. As shown in Figure 2, the pH may be raised to a pH of about 7.5 in silica removal step 20. In some embodiments a suitable flocculent may be added after silica hydrolysis to further promote aggregation and settling of the silica.

[0038] Silica removal step 20 is unnecessary in some embodiments. Since silica gel formation tends to occur only at higher silica concentrations (e.g. Si > 100 ppm), embodiments of the invention for processing wastewater with low silica concentrations may not require the silica removal step. Even if the silica concentration is high enough for gel formation, the hydraulic retention time of the gel formation is typically on the order of hours. In contrast, the hydraulic retention time for phosphate precipitation at phosphate recovery step 30 may be shorter than this. For example, the hydraulic retention time for struvite formation is typically less than 1 hour, although with a high concentration feed the hydraulic retention time may be significantly longer in embodiments incorporating recirculation as described below. Silica gel formation and

the need for silica removal prior to phosphate recovery step 30 may therefore be avoided even in some embodiments that process wastewater with higher silica concentrations. In some embodiments where silica is not removed prior to phosphate recovery step 30, silica is hydrolyzed during phosphorus recovery step 30 and eventually removed downstream.

[0039] Silica removal step 20 is followed by phosphate recovery step 30. As shown in Figure 2, phosphate may in some embodiments be recovered in the form of struvite, struvite analogs, or other phosphate compounds, for example according to the methods and apparatus described by Koch et al. in US 7,622,047. If the wastewater was not treated by silica removal step 20 (and therefore the pH not raised since fluoride removal step 10), then a suitable base may be added to the wastewater at an initial point of phosphate recovery step 30 to raise the pH to a desired level for precipitating the desired phosphate compound(s). As shown in Figure 2, ammonium hydroxide (or other ammonium and/or magnesium containing base) may for example be used to raise the pH for phosphate recovery step 30 to raise the pH. The pH may be raised to between pH 7.0 to 8.0, for example to pH 7.5.

[0040] Supersaturation conditions for the phosphate compound are maintained to recover desired phosphate compounds during phosphate recovery step 30. Maintaining supersaturation conditions may for example include: maintaining a supersaturation ratio of 2 to 5 for

struvite; maintaining a suitable pH , for example by controllably introducing a base and/or air stripping; maintaining phosphate concentration higher than concentrations of other components of the phosphate compound; and/or controllably introducing compounds comprising at least one of the other components of the desired phosphate compound.

[0041] Supersaturation conditions for struvite may be determined in relation to the struvite solubility product K_{sp} given by:

$$K_{sp} = [Mg^{2+}]_{eq} [NH_4^+]_{eq} [PO_4^{3-}]_{eq}$$

where the activities of the different species (i.e. $[Mg^{2+}]_{eq}$, $[NH_4^+]_{eq}$, and $[PO_4^{3-}]_{eq}$) are measured respectively as soluble magnesium, ammonia and orthophosphate at equilibrium. The supersaturation ratio (SSR) may be given by:

$$SSR = [Mg^{2+}][NH_4^+][PO_4^{3-}] / K_{sp} .$$

Increases in the SSR drive crystallization of struvite.

[0042] In the case of struvite recovery, the "other components" mentioned above are magnesium and ammonia. During struvite recovery in the embodiment illustrated in Figure 2, sodium hydroxide is added to control pH and magnesium chloride is added to control magnesium concentration. Struvite recovery may be "run lean" on magnesium and/or ammonia in some embodiments. Struvite may be recovered in the

form of solid pellets ranging in size from 1 to 5 mm in some embodiments.

[0043] The methods described in US 7,622,047 may be modified and/or selected to optimize phosphate recovery step 30 in various ways including one or more of the following.

i. The hydraulic retention time during struvite recovery may be extended since phosphogypsum pond water tends to have a much higher concentration of phosphorus compared to municipal wastewater and pellet formation is rate limiting. This may be achieved, for example, by increasing a recycling ratio (a proportion of wastewater that is recycled to wastewater that exits phosphate recovery step 30).

ii. Ammonia may be added in the form of ammonium hydroxide (or alternatively as anhydrous ammonia or ammonium chloride plus caustic for pH adjustment).

iii. The flow rate of the phosphogypsum pond water feed may be decreased relative to the flow rate of wastewater being recycled in phosphate removal step 30 to achieve the desired supersaturation ratio of 2-5.

iv. Phosphate may be kept in excess so as to minimize the amounts of magnesium and ammonium lost in the final effluent.

[0044] Following phosphate recovery step 30 the wastewater undergoes polishing step 40 before being discharged as treated effluent. In some embodiments, polishing step 40 may involve one or more chemical treatment steps.

[0045] In the embodiment shown in Figure 2, polishing step 40 includes raising the pH of the wastewater from the struvite production step to about pH 8-10. This may comprise adding a base such as lime. The elevated pH causes precipitation of remaining solutes including any phosphate, sulphate, calcium, magnesium, and trace heavy metals. Polishing step 40 may also include an ammonia removal step. As shown in Figure 2, ammonia may be removed by lowering the pH to about pH 7.0 and subjecting the wastewater to breakpoint chlorination. Other suitable methods of removing ammonia include stripping, biological nitrification, biological denitrification, and the like. The ammonia removal step may not be needed if the struvite recovery step is run lean on ammonia. After polishing step 40, the treated effluent may be discharged.

[0046] Figure 3 illustrates in a general manner a wastewater treatment process 100 according to another embodiment of the invention. Fluoride removal step 110, silica removal step 120, and phosphate recovery step 130 of process 100 may be similar to the corresponding steps of process 1.

[0047] Figure 4 illustrates a further embodiment of the invention following process 100 but more specifically exemplifying treatment of phosphogypsum pond water and recovery of struvite. Following phosphate recovery step 130, wastewater in process 100 is polished by membranes 150, 160 at polishing step 140. As shown in Figure 4, prior to membrane treatment the pH of the wastewater may be lowered to about pH 3.0-5.0 to avoid scaling of the membranes, as well as to reduce

silica hydrolysis and the risk of membrane fouling. This can be particularly desirable in cases where a silica removal step is not performed upstream. Prior to membrane treatment the wastewater may be pre-filtered to remove suspended solids and to reduce the silt density index. Lowering pH and/or pre-filtration prior to membrane treatment are optional in some embodiments.

[0048] First stage membrane 150 may be configured to reject divalent ions (e.g. phosphate, sulphate, magnesium) and let monovalent ions flow through (e.g. sodium, chloride, fluoride, ammonia) to second stage membrane 160. The first stage membrane may for example comprise a reverse osmosis (RO) or nanofiltration (NF) membrane. In some embodiments, the low pH concentrates (stream A) from first stage membrane 150 may be recirculated to fluoride removal step 110. As shown in Figure 4, recirculation of stream A diverts divalent ions from discharge and instead results in: further precipitation of waste components at the fluoride removal step (e.g. removal of sulphate as calcium sulphate at the fluoride removal step); and further recovery of desired components (e.g. phosphate and the magnesium as struvite) at the phosphate recovery step.

[0049] Second stage membrane 160 may be configured to reject monovalent ions (e.g. sodium, chloride, fluoride). As shown in Figure 4, the second stage membrane may comprise a reverse osmosis (RO) membrane. The pH of the permeate from the first stage membrane may be adjusted up to pH 7.5 - 8.0 before the second stage membrane to promote rejection of fluoride and obtain permeate that can be discharged

directly. In some embodiments, the second stage membrane concentrates (stream B) containing mostly monovalent ions (sodium, chloride, fluoride) may be delivered back to the wastewater source (e.g. phosphogypsum stack) or to the fluoride removal step.

[0050] An ion exchange (IX) resin bed 170 may be provided to remove ammonia from the second stage membrane permeate before discharge as treated effluent. Ion exchange regeneration liquid containing the ammonia (stream C) may be recirculated to phosphate recovery step 130 to provide pH adjustment and ammonia for recovery of phosphate compounds.

[0051] Figure 5 illustrates in a general manner a wastewater treatment process 200 according to another embodiment of the invention. Fluoride removal step 210, silica removal step 220, and phosphate recovery step 230 of process 200 are similar to the corresponding steps of process 1, and first stage membrane 250, second stage membrane 260, and ion exchange resin bed 270 are similar to the corresponding features of process 100. Figure 6 illustrates a further embodiment of the invention following process 200 but more specifically exemplifying treatment of phosphogypsum pond water and recovery of struvite.

[0052] Following silica removal step 220, wastewater is directed to first stage membrane 250. In a manner similar to process 100, the wastewater may be acidified and prefiltered prior to first stage membrane 250. Concentrate from the first stage membrane is fed to phosphate recovery step 230. This concentrate may contain most of the phosphate at

about twice the concentration compared to the feed for the phosphate recovery steps in process 1 and 100. Concentrated phosphate may improve the conditions for the recovery of phosphate compounds in some cases. The other elements of the processes illustrated in Figures 5 and 6, including the three recirculation streams A, B and C, are similar to those described above in relation to process 100, with the exception that in process 200 stream A is generated at the phosphate recovery step instead of as concentrate of the first stage membrane in process 100.

[0053] Recirculation of concentrate streams A, containing for example excess magnesium, and concentrate stream C, containing for example excess ammonia, to upstream steps may result in up to complete recovery of these components into recovered phosphate compounds, for example as struvite.

[0054] As will be apparent to those skilled in the art in the light of the foregoing disclosure, many alterations and modifications are possible in the practice of this invention without departing from the spirit or scope thereof. For example:

i. The methods for ammonia removal described for the ammonia removal step of process 1 and the ion exchange method for ammonia removal in processes 100 and 200 are interchangeable.

ii. Process 1 may be modified to provide recirculation. For example ammonia recovered at the ammonia removal step may be recirculated to phosphate recovery step 30.

iii. The two-stage membrane treatment may be substituted with a single membrane (e.g. reverse osmosis only) or more than two membranes (e.g. the two-stage membrane treatment preceded by microfiltration and/or ultrafiltration membranes).

iv. Individual features of the various embodiments disclosed herein may be combined with one another to create further example embodiments. For example, polishing stage 40 of Figure 1 may be expanded to comprise membrane treatment, as shown in Figure 3 or Figure 4 or other mechanical polishing processes.

v. Some embodiments may produce struvite analogs such as iron ammonium phosphate, wherein corresponding Fe compounds are substituted for Mg compounds during processing.

[0055] The following example provides results of laboratory scale testing of some embodiments of the invention.

EXAMPLE 1

[0056] Raw pond water samples were tested in three stages: 1) F removal with Ca, 2) pH increase, and 3) struvite precipitation.

[0057] In Stage 1, $CaCO_3$ and $Ca(OH)_2$ were added to 2L and 3L samples of pond water, mixed for 60 minutes, settled for 30 minutes, then filtered and supernatants analyzed to evaluate the effect of adding the bases on both pH and the concentrations of F and PO_4. $Ca(OH)_2$ was added in both solid and slurried form (results shown for slurried form

only). Ca:F molar ratios of 0.5 and 0.6 for both reagents were tested, respectively representing the stoichiometric amount and a 20% excess amount.

[0058] Both $CaCO_3$ and $Ca(OH)_2$ reagents raised the pH to between about 2.5 - 3.5 after 1 hour of mixing. $CaCO_3$ may be preferred in some embodiments. Test results showed that with $CaCO_3$ the F removal at 0.6 Ca:F molar ratio was lower than with $Ca(OH)_2$ at 0.6 Ca:F molar ratio but so were the PO_4 and NH_3 losses. For the remaining stages, $CaCO_3$ at 0.6 Ca:F molar ratio was used.

[0059] 24 hours after completion of the test, more solids had precipitated in the filtered supernatant, and the SO_4 concentration had decreased along with the Ca concentration, indicating gypsum formation.

Table 2: Stage 1 results

ID	F	PO4-P	NH3-N	SO4-S	Ca	pH
	mg/L	mg/L	mg/L	mg/L	mg/L	
Pond water	8800	9088.5	1215	9375	1222	1.17
J1 0.5 $CaCO_3$	7390	8262	1020	2918	4701	3.04
J2 0.6 $CaCO_3$	5197	7624	1085	3192	2091	3.23
J3 0.5 $Ca(OH)_2$	5686	7888	1024	3877	2831	3.49
J4 0.6 $Ca(OH)_2$	4409	7517	1022	7096	2616	2.66
J1 % removal	16.0%	9.1%	16.0%	68.9%		
J2 % removal	40.9%	16.1%	10.7%	66.0%		
J3 % removal	35.4%	13.2%	15.7%	58.6%		
J4 % removal	49.9%	17.3%	15.9%	24.3%		

[0060] In Stage 2, $Mg(OH)_2$ was added (in slurried 40 wt% form) to the 500 mL and 1250 mL samples of Stage 1 supernatant in Mg:P molar

ratios of 0.8, 0.9, and 1.0, to raise the pH of the solution nearer the pH required for struvite precipitation and also to put Mg ions in solution. Also, $MgCl_2$ was added in 1.0 Mg:P ratio to compare the effects of adding a non-basic Mg source at this stage.

[0061] The Mg compounds were added immediately after the completion of a repeated Stage 1 test, to prevent Ca loss through gypsum precipitation. The solutions were mixed for 60 minutes and settled for 15 minutes.

[0062] The $Mg(OH)_2$ raised the pH to 4.5 - 5.5, and caused nearly complete removal (>90%) of both Ca and F. A substantial amount of PO_4 was also removed, but the quantity remaining was still high and sufficient for struvite production downstream. A substantial amount of the added Mg was also removed in this stage. The $MgCl_2$ did not raise the pH but slightly lowered it, and had very little effect on either F removal or P loss. Increasing the Mg:P molar ratio from 0.8 to 1.0 increased F removal by only 2.8% but increased PO_4 losses by 11.5%. 0.8 Mg:P was selected for use in Stage 3.

Table 3: Stage 2 results

ID	F	PO4-P	NH3-N	SO4-S	Ca	Mg	pH
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	
Pond water	8800	9089	1215	9375	1222	551	1.17
A 0.6 $CaCO_3$	6020	7904	1152	7656	5993	502	3.06
J1 0.8 Mg(OH)2	483	5421	1135	7656	536	2208	4.47
J2 0.9 Mg(OH)2	370	4993	1123	7656	366	2234	4.86
J3 1.0 Mg(OH)2	312	4513	1068	7656	230	2242	5.27
J4 1.0 MgCl2	5430	7583	417	8975	5995	6204.7	2.79

A % removal	31.6%	13.0%	5.2%	18.3%		8.9%	
J1 % removal	92.0%	31.4%	1.5%	0%	91.0%		
J2 % removal	93.9%	36.8%	2.5%	0%	93.9%		
J3 % removal	94.8%	42.9%	7.3%	0%	96.2%		
J4 % removal	3.2%	4.7%	6.1%	0%	0%		
J1 overall removal	94.5%	40.4%	6.6%	18.3%			
J2 overall removal	95.8%	45.1%	7.6%	18.3%			
J3 overall removal	96.5%	50.3%	12.1%	18.3%			
J4 overall removal	38.3%	16.6%	65.7%	4.3%			

[0063] In Stage 3, NH_4OH was added to 500 mL samples of Stage 2 supernatant in N:P molar ratios of 0.8 and 1.0, then NaOH was used to raise the pH above 7.0. As the Mg:P ratio was approximately 0.5:1 due to the Mg loss in Stage 2, a P recovery of near 50% would be expected if the P were primarily forming struvite. The Mg was 99% removed, showing that the reaction proceeded as far as it could given the Mg limits, and the P removal was near 58%. Struvite precipitation in wastewater is Mg limited as well, and $MgCl_2$ or other sources of soluble Mg can be added.

Table 4: Stage 3 results:

ID	**F**	**PO4-P**	**NH3-N**	**SO4-S**	**Ca**	**Mg**	**pH**	**Final pH**
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L		
Pond water	8800	9088.5	1215	9375	1222	551.1	1.17	
J1 0.6 $CaCO_3$	5608	7957	444*	6099	5450	496.94	3.13	
J2 0.8 $Mg(OH)_2$	477	5194	412	8756	554.9	2080.6	4.62	
J3-1 0.8 NH_4OH	277	2190	558	8948	67.6	13.158	5.52	7.40
J3-2 1.0 NH_4OH	267	2150	788	6729	65.7	13.0	5.84	7.36
J1 % removal	36.3%	12.4%	63.5%	34.9%		9.8%		
J2 % removal	91.5%	34.7%	7.2%	0%	89.8%			
J3-1 % removal	41.9%	57.8%		0%	87.8%	99.4%		
J3-2 % removal	44.0%	58.6%		23.1%	88.2%	99.4%		
J3-1 overall removal	96.9%	75.9%						
J3-2 overall removal	97.0%	76.3%						

* This number (and the ones below it) are anomalous, and should be similar to the numbers obtained at the end of the Stage 2 test wherein ammonia levels were about 1100mg/L.

EXAMPLE 2

[0064] An overall pH test was also conducted. 250 mL of the pond water sample was placed in a beaker. The blade of an overhead mixer was placed in the sample and rotated at 70 rpm. 6.95 g $CaCO_3$ was added to obtain a 0.6 Ca:F ratio. The pH was monitored every 15 minutes. The pH was recorded at 60 minutes.

[0065] 3.95 g $Mg(OH)_2$ slurried in 5.4 g water was added to obtain a 1:1 Mg:P ratio, based on previous jar test results from Example 1. The pH was monitored every 15 minutes. The pH was recorded at 60 minutes.

[0066] 2.16g dry basis/7.17g 30wt% NH_4OH was slowly added to obtain a 1:1 NH_4OH:P ratio based on P after the $CaCO_3$ precipitation.

Table 5: pH test results

ppt with CaCo3		ppt with Mg(OH)2		ppt with NH4OH		
Time (min.)	pH	Time (min.)	pH	Time (min.)	pH	Cum. NH4OH dry basis added
0	1.8	0	3.09	0	5.17	0.54
15	3.2	15	4.31	10	5.85	1.08
30	3.2	30	4.77	20	7.61	
45	3.2	45	5.03	60	7.3	2.16
60	3.1	60	5.17	120	9.49	

References

Kennedy, G.A., Soroczak, M.M. and Clayton, J.D., "Chemistry of Gypsum Pond Systems", Florida Institute of Phosphate Research (FIPR) Project #85-05-025R, 1991.

Perpich, B, Jr., Soule, C., Zamani, S. Timchak, L., Uebelhoer, G., Nagghappan, L. and Helwick, R., "Mobile Wastewater Treatment Helps Remediate Concentrated Acidic Process Water at Fertilizer Plant", Florida Water Resources Journal, July 2005.

Claims

1. A method for treating, and recovering phosphate compounds from, wastewater, the method comprising:

   (a) measuring, precipitating and removing fluoride from the wastewater by raising the pH of the wastewater by adding a calcium-containing base with a stoichiometric amount of calcium to precipitate the fluoride, and then further raising the pH of the wastewater by adding one or more calcium-free bases;

   (b) recovering struvite from the wastewater from which fluoride has been removed by maintaining supersaturation conditions for the struvite; and

   (c) polishing the wastewater,

   wherein step (c) comprises subjecting the wastewater from step (b) to a two stage membrane treatment comprising:

   (i) a first membrane treatment to obtain a first concentrate comprising divalent ions and a first permeate comprising monovalent ions, wherein the first concentrate is recirculated to step (a); and

   (ii) a second membrane treatment for the first permeate to obtain a second concentrate comprising monovalent ions and a second permeate consisting of treated effluent.

2. A method according to claim 1 wherein the first membrane treatment comprises nanofiltration.

3. A method according to claim 1 or 2 wherein the second membrane treatment comprises reverse osmosis.

4. A method according to any one of claims 1 to 3 comprising lowering the pH to pH 3 to 5 prior to the two stage membrane treatment.

5. A method according to any one of claims 1 to 4 comprising removing suspended solids by filtration prior to the two stage membrane treatment.

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6. A method according to any one of claims 1 to 5 comprising removing ammonia from the second permeate.

7. A method according to claim 6 wherein removing ammonia comprises subjecting the second permeate to ion exchange.

8. A method according to claim 7 wherein ammonia-containing liquid of the ion exchange is recirculated to step (b).

Date Reçue/Date Received 2021-04-23

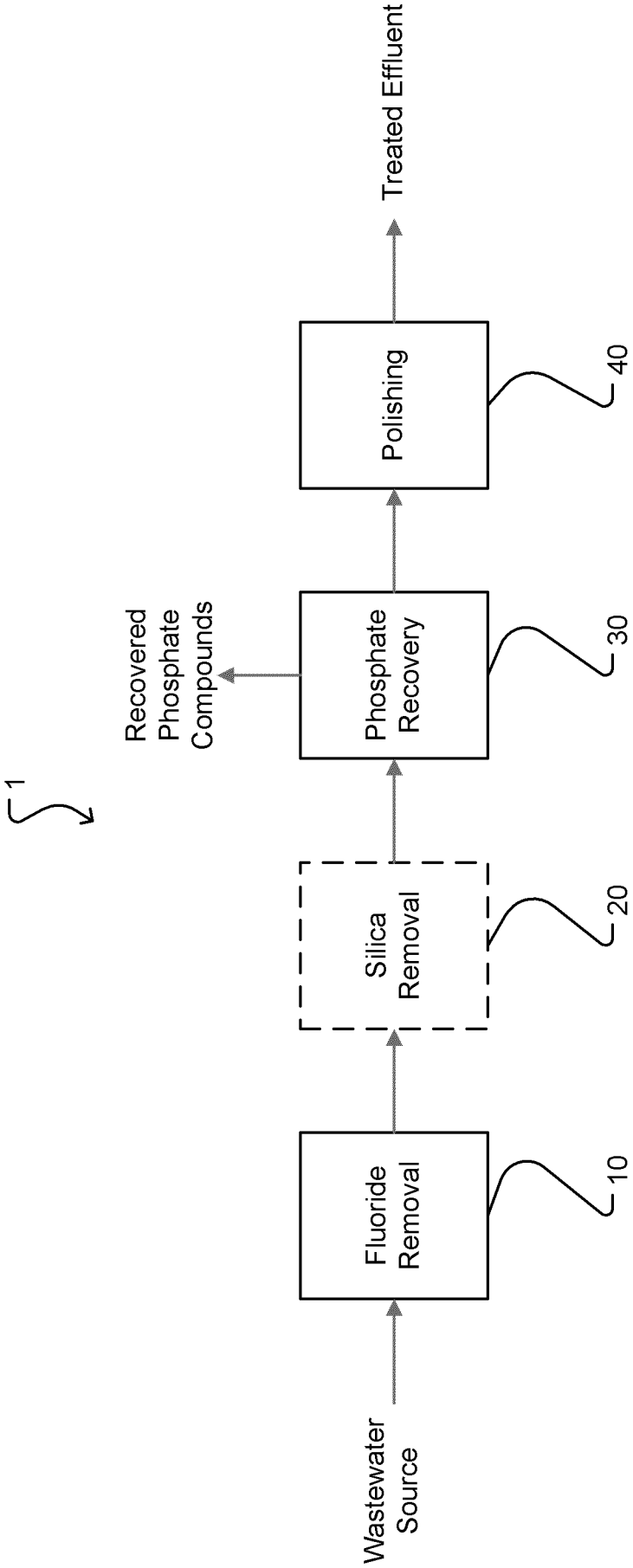

Wastewater Source
Fluoride Removal
10
Silica Removal
20
Phosphate Recovery
30
Recovered Phosphate Compounds
Polishing
40
Treated Effluent
1
Optional Step

Fig. 1

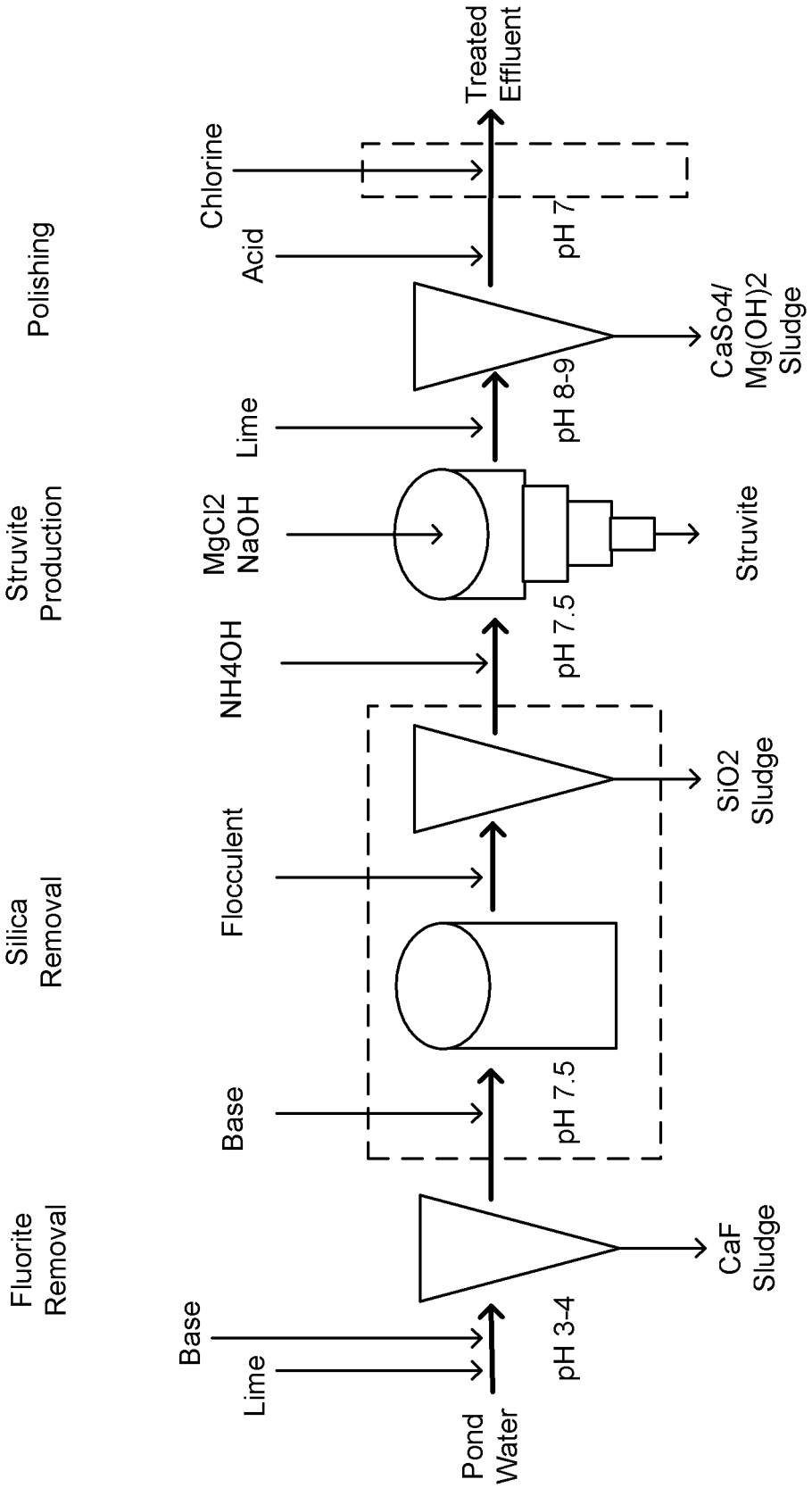
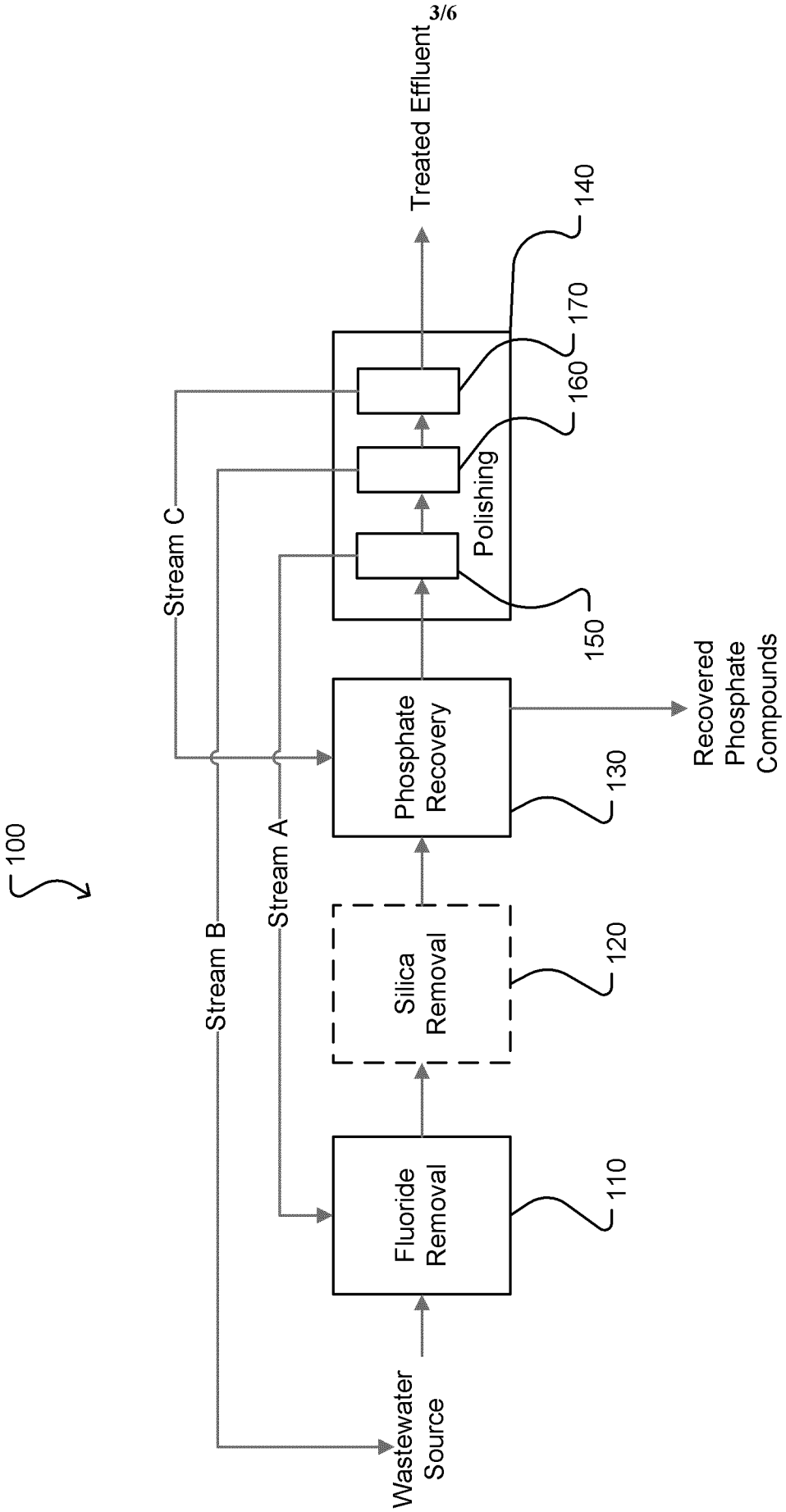

Fluorite Removal
Silica Removal
Struvite Production
Polishing
Pond Water
Lime
Base
pH 3-4
CaF Sludge
Base
Flocculent
pH 7.5
SiO2 Sludge
NH4OH
MgCl2
NaOH
pH 7.5
Struvite
Lime
pH 8-9
CaSo4/ Mg(OH)2 Sludge
Acid
Chlorine
pH 7
Treated Effluent
Optional Steps

Fig. 2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Wastewater Source
Fluoride Removal
110
Silica Removal
120
Phosphate Recovery
130
Recovered Phosphate Compounds
Polishing
150
160
170
140
Treated Effluent
Stream A
Stream B
Stream C

Fig. 3

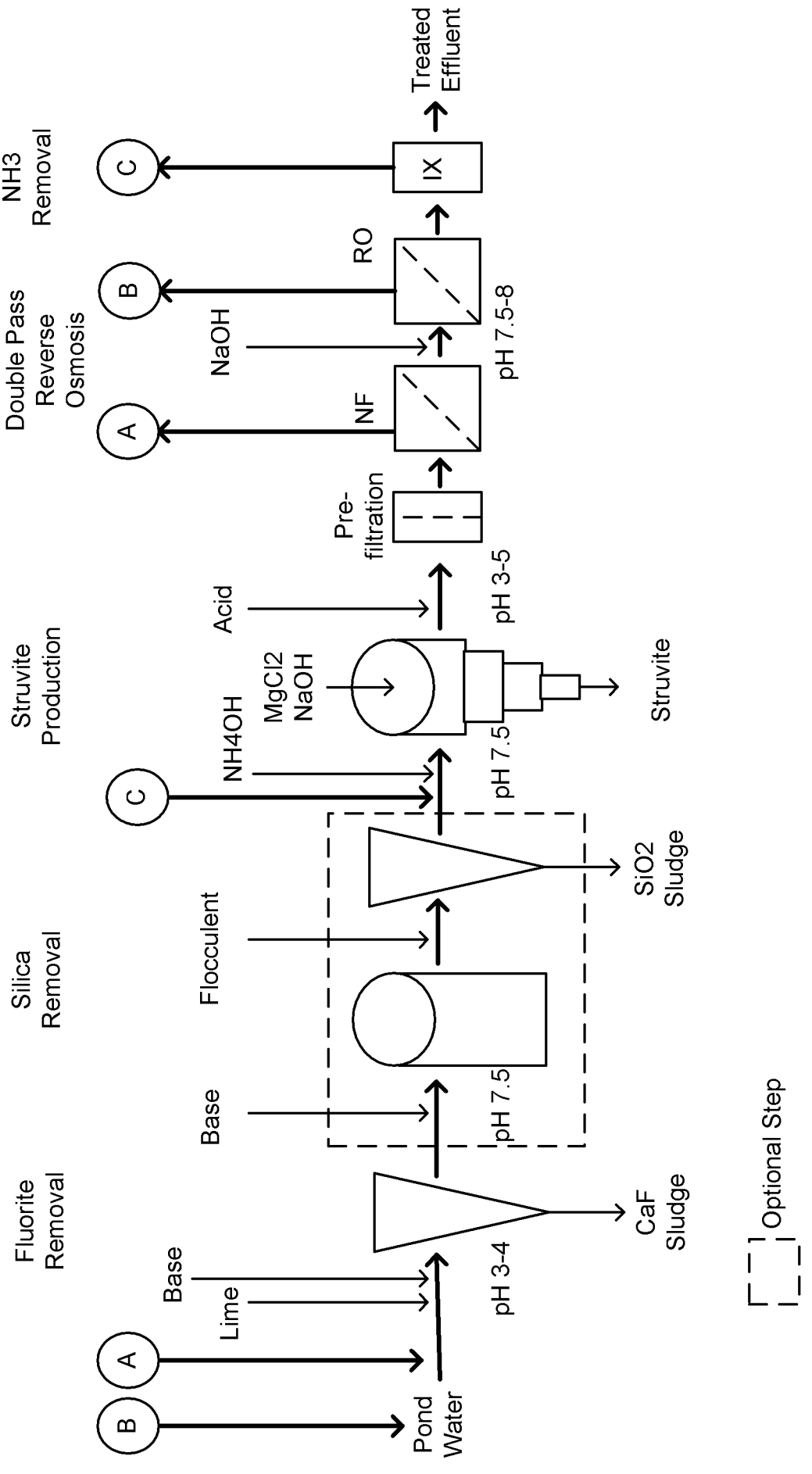
Pond Water
B
A
Fluorite Removal
Base
Lime
pH 3-4
CaF Sludge
Silica Removal
Base
Flocculent
pH 7.5
SiO2 Sludge
Struvite Production
C
NH4OH
MgCl2 NaOH
pH 7.5
Struvite
Acid
pH 3-5
Pre-filtration
Double Pass Reverse Osmosis
A
NF
NaOH
RO
pH 7.5-8
B
NH3 Removal
C
IX
Treated Effluent
Optional Step

Fig. 4

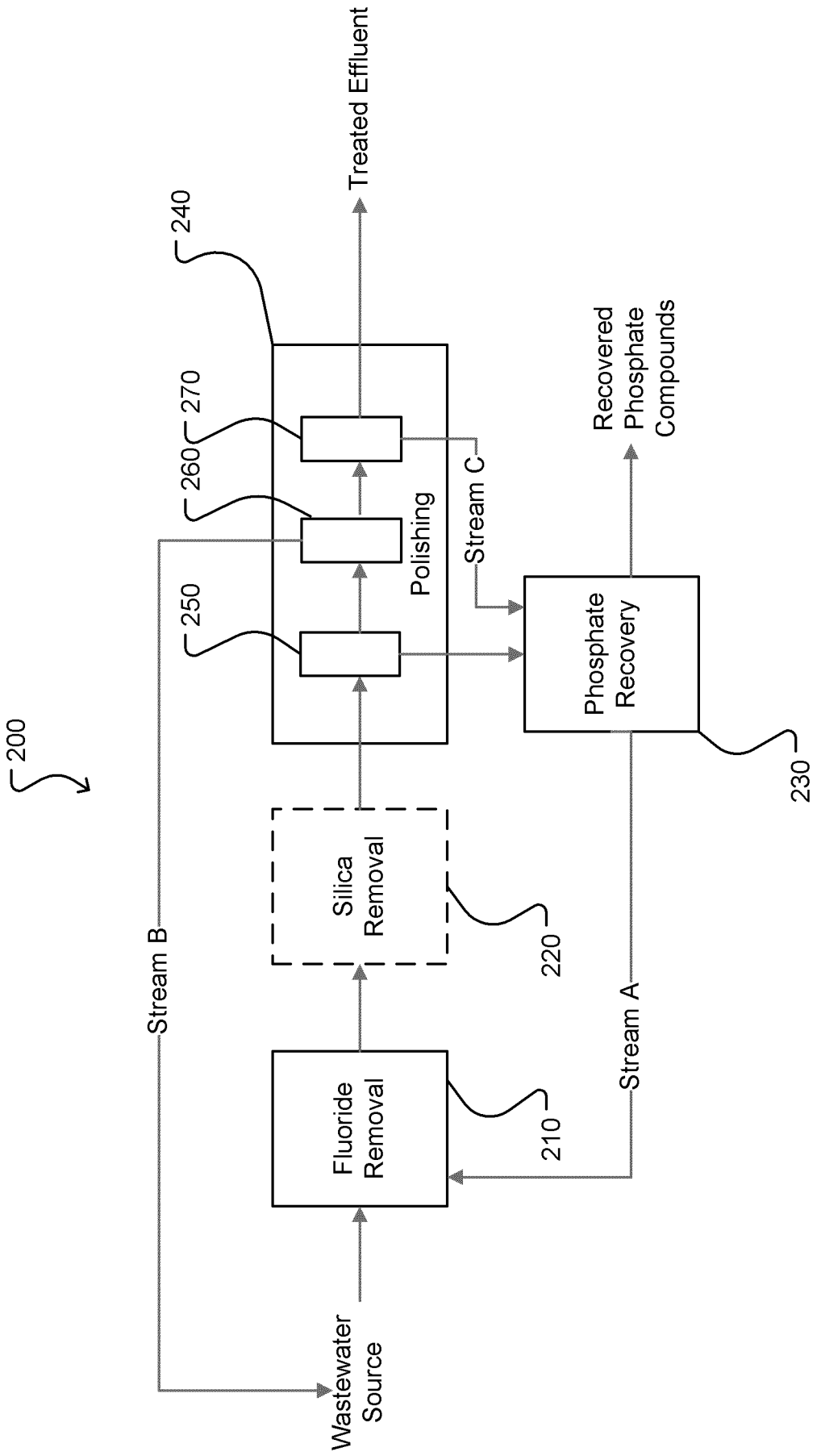
200
Wastewater Source
Fluoride Removal
210
Silica Removal
220
Phosphate Recovery
230
Recovered Phosphate Compounds
Stream A
Stream B
Stream C
Polishing
240
250
260
270
Treated Effluent

Fig. 5

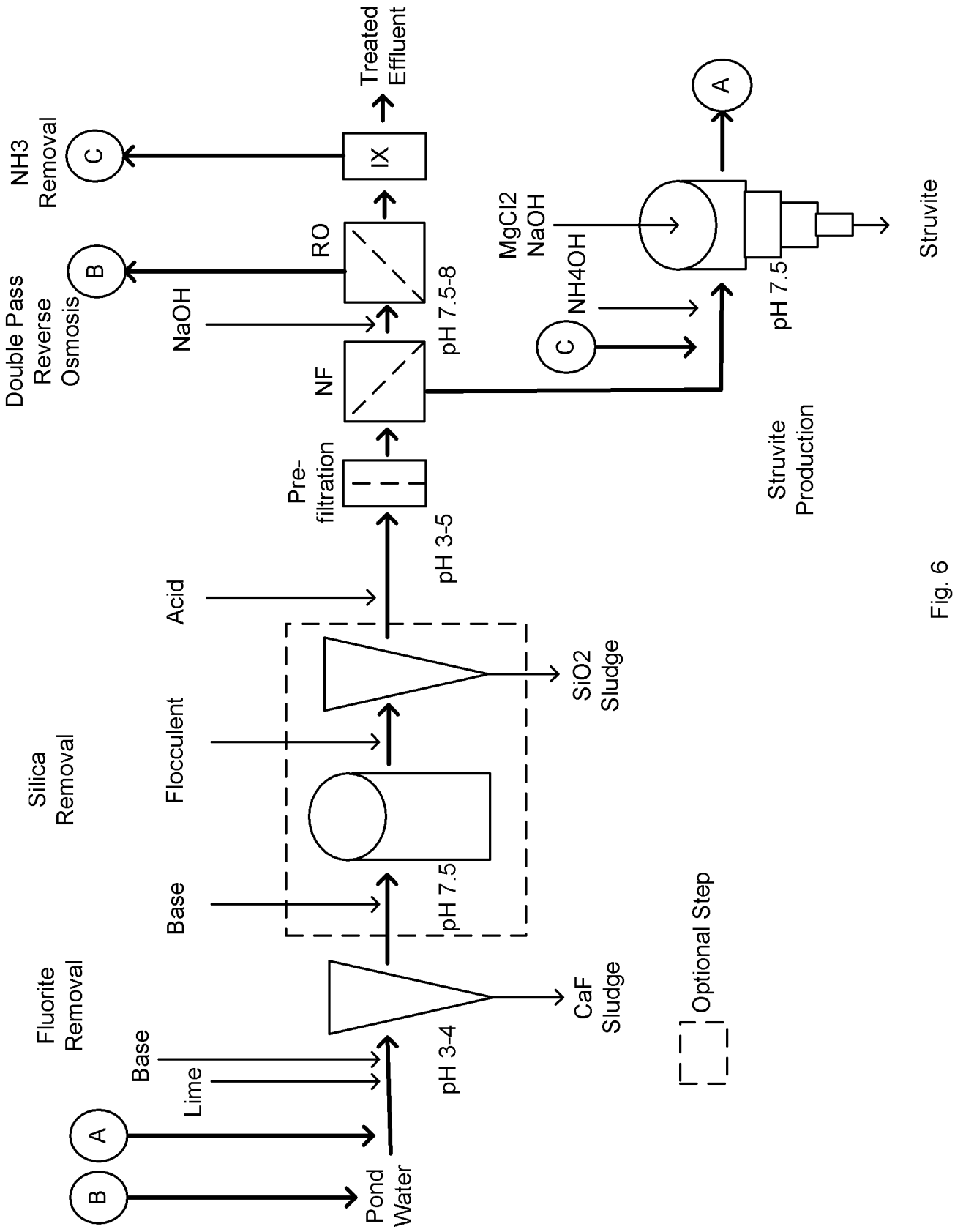
Pond Water
B
A
Base
Lime
pH 3-4
CaF Sludge
Fluorite Removal
Base
Flocculent
pH 7.5
SiO2 Sludge
Silica Removal
Acid
pH 3-5
Pre-filtration
NF
pH 7.5-8
NaOH
RO
B
Double Pass Reverse Osmosis
IX
C
NH3 Removal
Treated Effluent
Optional Step
Struvite Production
C
NH4OH
MgCl2
NaOH
pH 7.5
A
Struvite

Fig. 6

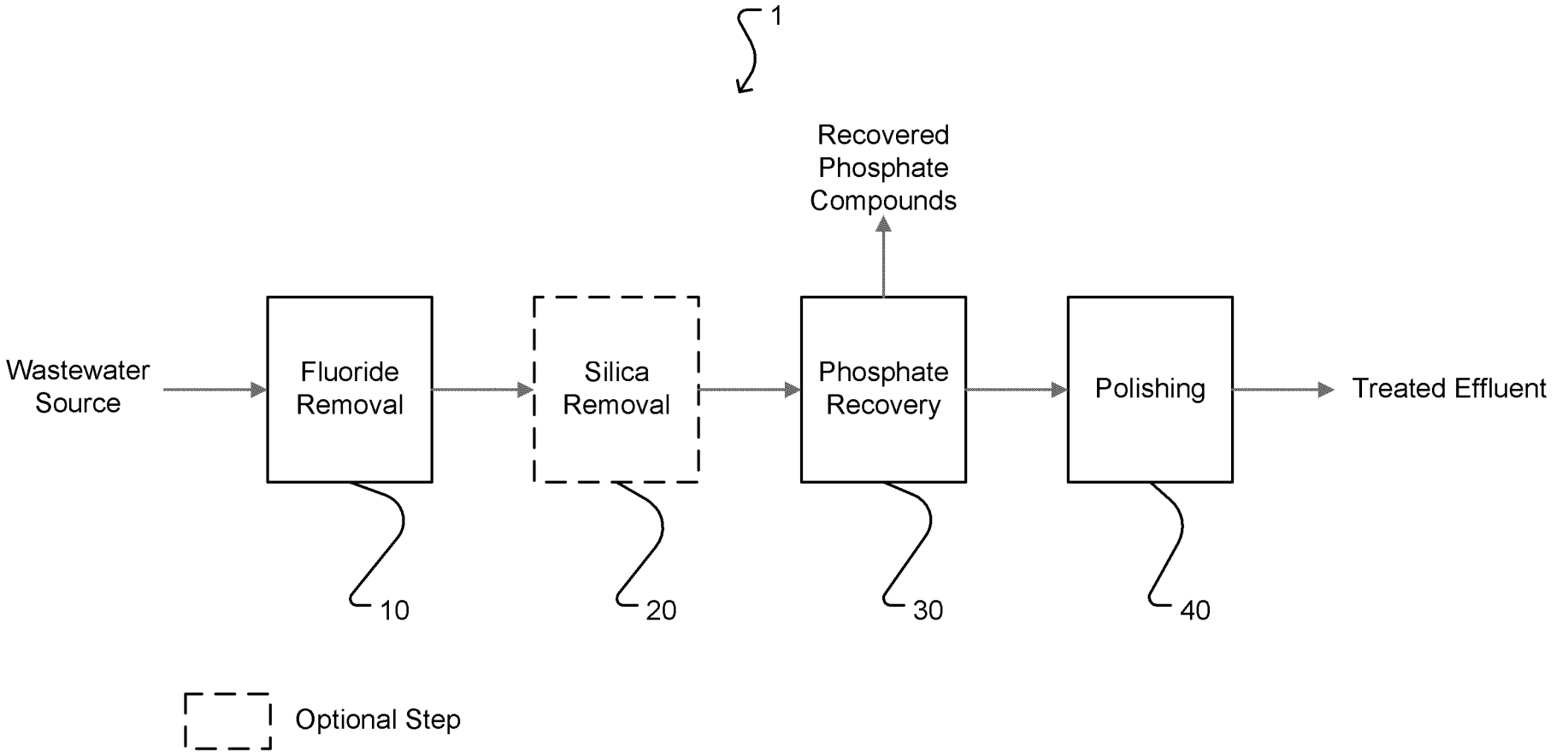
1
Recovered
Phosphate
Compounds
Wastewater
Source
Fluoride
Removal
Silica
Removal
Phosphate
Recovery
Polishing
Treated Effluent
10
20
30
40
Optional Step

Fig. 1