

(19) World Intellectual Property
Organization
International Bureau



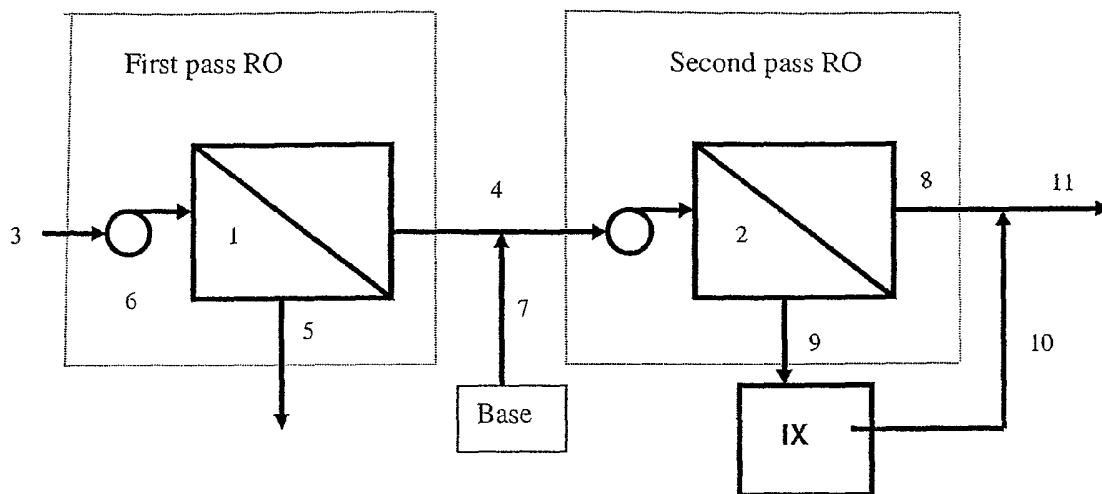
(43) International Publication Date
23 June 2005 (23.06.2005)

PCT

(10) International Publication Number
WO 2005/056166 A1

- (51) International Patent Classification⁷: **B01D 61/00**
- (21) International Application Number:
PCT/US2004/040230
- (22) International Filing Date: 2 December 2004 (02.12.2004)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/526,709 2 December 2003 (02.12.2003) US
- (71) Applicants (for all designated States except US): **HYDRANAUTICS** [US/US]; 401 Jones Road, Oceanside, CA 92054 (US). **NITTO DENKO CORPORATION** [JP/JP]; Shiga-Ken, Kusatsu-chi, Yamadera-cho, Aza Sasadani 61-7 (JP).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **WILF, Mark** [US/US]; 6204 Syracuse Lane, San Diego, CA 92122 (US). **BARTELS, Craig, R.** [US/US]; 18910-9 Caminito Cantilena, San Diego, CA 92128 (US). **HIROSE, Masahiko** [JP/JP]; 203-11, Ryousenji, Ritto, Shiga (JP).
- (74) Agents: **KATZ, Sandra, M.** et al.; Akin Gump Strauss Hauer & Feld, LLP, One Commerce Square, 2005 Market Street, Suite 2200, Philadelphia, PA 19103-7086 (US).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:
— with international search report
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHODS FOR REDUCING BORON CONCENTRATION IN HIGH SALINITY LIQUID USING COMBINED REVERSE OSMOSIS AND ION EXCHANGE



(57) Abstract: Methods are provided for increasing the recovery rate in systems (Fig.2) for treating high salinity boron-containing liquids, such as seawater, to reduce salinity and boron concentration. The methods involve applying multi-pass reverse osmosis (1, 2), combined with partial ion exchange processing utilizing a boron specific resin, for reducing the capital and operating costs of desalination systems.

TITLE OF THE INVENTION

[0001] Methods for Reducing Boron Concentration In High Salinity Liquid Using Combined Reverse Osmosis and Ion Exchange

5 CROSS-REFERENCE TO RELATED APPLICATION

[0002] This application claims the benefit of U.S. Provisional Patent Application No. 60/526,709, filed December 2, 2003.

BACKGROUND OF THE INVENTION

10 [0003] This invention relates to methods for producing reverse osmosis permeate with reduced boron concentration from seawater. Seawater typically contains about 4 to 7 ppm boron, in addition to a variety of water-soluble salts. Traditional methods for purifying (desalinating) seawater for drinking and irrigation purposes utilize reverse osmosis (RO) membranes, which are effective at significantly reducing the concentrations of all dissolved ions in the seawater. Although the
15 reduction of the majority of dissolved ions by polyamide reverse osmosis membranes is about 98% to about 99%, the rejection rate of boron by these membranes is much lower, typically in the 70%-90% range, and may be even lower at high feed water temperatures (greater than about 25 °C).

[0004] The significantly lower rejection rate of boron by polyamide membranes may be explained by the very low dissociation rate of boric species at neutral pH. However, this boric
20 species dissociation rate increases with pH and reaches 50% dissociation at a pH of 8.6 to 9.8, depending on the ionic strength of the solution and the temperature (W. Stumm, *et al.* Aquatic Chemistry, John Wiley & Sons (1981)). Consequently, an increased boron rejection rate is achievable at high pH, thus making possible appreciable boron concentration reduction by reverse osmosis.

25 [0005] Magara, *et al.* (*Desalination* 118:25-34 (1998)) and Prats, *et al.* (*Desalination* 128: 269-273 (2000)) describe methods for reducing boron concentration using two-pass reverse osmosis systems. In these systems, the pH of the permeate from the first pass is increased before it is passed through the RO membrane in the second pass in order to improve the boron rejection. The term
30 "permeate" is known in the art to refer to reverse osmosis product water. Because the RO permeate from these systems has low salinity, even adjustment of the pH to high levels does not result in scale

formation. Further, the industrial application of such a method is quite straightforward and results in effective boron reduction.

[0006] An example of a similar methodology applied to high salinity water is described by Tao, *et al.* (U.S. Patent No. 5,250,185), which describes the application of a high pH RO processing method to oilfield-produced water. In order to prevent scaling of the reverse osmosis system by carbonate salts, the feed water is softened prior to adjustment of the pH to a level greater than 9.5. Tao teaches that the high pH is necessary to obtain the desired increase in boron rejection. Additionally, Mukhopadhyay (U.S. Patent No. 5,925,255) describes the treatment of brackish and low salinity water by reverse osmosis, in which the hardness of the RO feed water is removed by a weak cation exchange resin.

[0007] However, the use of two pass RO processing always results in a decrease in the overall recovery rate since the overall recovery rate is the product of the recovery rates of the first and second passes. The second pass RO usually operates at a recovery rate of about 80% to 90%, so that only about 80 to 90% of the feed to the second pass is converted to the final product, while the remaining 10-20% is discharged as concentrate. The major reason for the limited recovery in the second pass RO unit is a danger of calcium carbonate and magnesium hydroxide precipitation (scaling), which occurs during operation of RO devices at the high pH required for increased boron rejection. Increased recovery results in an increased concentration of sparingly soluble salts and higher scaling potential. For example, at 50% recovery, the concentration of soluble salts in the concentrate is twice that of the feed. In contrast, when the recovery is increased to 90%, the concentration factor increases to ten. Considering that the first pass permeate is produced at relatively high capital and operating cost, the recovery rate of the second pass RO significantly affects the cost of the final purified water. Therefore, maximizing the recovery rate of the second pass RO device, while simultaneously minimizing scaling, is desirable.

[0008] An example of a conventional two pass system configuration is depicted in Fig. 1. As shown in Fig. 1, seawater feed 3 is pumped by high pressure pump 6 to a first pass RO membrane unit 1. In membrane unit 1, the seawater feed is separated into two streams: concentrate 5 and permeate 4. Membrane unit 1 operates at a recovery rate of about 45% to 55%. In seawater applications, the low recovery of the first pass is due to high osmotic pressure resulting from high salinity. If the recovery were much higher than about 45 to 55%, the system would require much higher feed pressure to produce permeate. In contrast, the feed to the second pass RO has low salinity and osmotic pressure, and the recovery is thus not limited by feed pressure but by other factors such as scaling, as previously explained.

[0009] The pH of permeate 4 is then adjusted with base 7 to a pH of about 10. Base-adjusted permeate 4 is then pumped to a second pass RO membrane unit 2, in which it is processed to produce permeate 8 and concentrate 9. The second pass membrane unit 2 operates at a recovery rate of about 80% to 90%. In some two pass system designs (not shown), concentrate 9 is returned to the feed 3 of the first pass unit 1, thereby reducing the quantity of feed water required. Typical process parameters of a conventional configuration, such as that shown in Fig. 1, are tabulated in Comparative Example 1 below.

[0010] Methods for increasing the recovery of RO systems during boron reduction processes have been previously proposed (see, for example, Rodendo *et al.* (*Desalination* 156:229 – 238 (2000) and Prats, *et al.* (*Desalination* 128:269-273 (2000)), including staging of RO units (operating RO units in series in a multi-pass system configuration). Alternative methods of boron reduction have been described in U.S. Patent Application Publications Nos. 2003/0230531 A1 and 2004/0065617 A1 of Applicants. These methods involve adjusting the pH of high salinity, boron – containing liquids to about 8.5 to about 9.5 prior to passage through a reverse osmosis device. In one embodiment, the high salinity liquid may be treated with a membrane filtration system to remove suspended solids. These methods are effective at reducing boron concentration to less than about 2 ppm or even lower.

[0011] A further known method of boron reduction involves processing first pass permeate with an ion exchange, boron specific resin. The recovery rate of ion exchange systems is quite high, about 98%. Further, boron reduction using ion exchange systems is very effective, and the boron concentration in the ion exchange effluent is normally less than 0.1 ppm. Unlike in reverse osmosis processes, the boron concentration in the ion exchange effluent is substantially unaffected by the concentration level of boron species in the influent (feed). However, water processing through boron specific ion exchange systems does not result in salinity reduction. Therefore, any additional salinity reduction must be accomplished using a second pass RO step. Further, at current resin prices and process parameters, the use of ion exchange systems is a more expensive solution for boron reduction than RO processes. There thus remains a need in the art for an efficient, cost-effective method for removing boron and reducing salinity from high salinity liquids, such as seawater.

BRIEF SUMMARY OF THE INVENTION

[0012] A method of reducing boron concentration and salinity in a high salinity, boron-containing liquid comprises:

(a) passing the high salinity, boron-containing liquid through a first pass reverse osmosis device to produce a first pass concentrate and a first pass permeate;

(b) adjusting a pH of the first pass permeate to about 8 to about 11;

(c) passing at least a portion of the pH-adjusted first pass permeate through a second pass reverse osmosis device to produce a second pass concentrate and a second pass permeate;

(d) passing the second pass concentrate through an ion exchange unit containing a boron specific resin to produce an effluent; and

(e) combining the effluent and the second pass permeate to produce a blended flow;

wherein the blended flow exhibits a lower boron concentration and a lower salinity than the high salinity liquid.

[0013] A variation of the above method of reducing boron concentration and salinity in a high salinity, boron-containing liquid comprises:

(a) passing the high salinity, boron-containing liquid through a first pass reverse osmosis device to produce a first pass concentrate and initial and final first pass permeates;

(b) passing at least a portion of the final first pass permeate through an ion exchange unit containing a boron specific resin to produce an effluent;

(c) adjusting a pH of the effluent to about 8 to above 11;

(d) passing the pH-adjusted effluent through a second pass reverse osmosis device to produce a second pass concentrate and a second pass permeate; and

(e) combining the second pass permeate and the initial first pass permeate to produce a blended flow;

wherein the blended flow exhibits a lower boron concentration and a lower salinity than the high salinity liquid.

[0014] Another variation of the above method of reducing boron concentration and salinity in a high salinity, boron-containing liquid comprises:

(a) passing the high salinity, boron-containing liquid through a first pass reverse osmosis device to produce a first pass concentrate and a first pass permeate;

(b) adjusting a pH of the first pass permeate to about 8 to about 11;

(c) passing at least a portion of the pH-adjusted first pass permeate through a lead segment of a second pass reverse osmosis device containing a first stage and a second stage to produce a second stage permeate and a second stage concentrate;

(d) adjusting a pH of the second stage concentrate to about 7 to about 8;

5 (e) passing the pH-adjusted second stage concentrate through a tail segment of the second pass reverse osmosis device containing at least a third stage to produce a third stage permeate;

(f) passing the third stage permeate through an ion exchange unit containing a boron specific resin to produce an effluent; and

(g) combining the effluent with the second stage permeate to produce a blended flow;

10 wherein the blended flow exhibits a lower boron concentration and a lower salinity than the high salinity liquid.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[0015] The foregoing summary, as well as the following detailed description of the invention, will be better understood when read in conjunction with the appended drawings. For the purpose of illustrating the invention, there are shown in the drawings embodiments which are presently preferred. It should be understood, however, that the invention is not limited to the precise arrangements and instrumentalities shown. In the drawings:

[0016] Fig. 1 is a schematic flow diagram of a conventional two pass reverse osmosis system (prior art);

[0017] Fig. 2 is a schematic flow diagram of a reverse osmosis/ion exchange configuration according to one embodiment of the invention;

[0018] Fig. 3 is a schematic flow diagram of a reverse osmosis/ion exchange system configuration according to a second embodiment of the invention; and

25 [0019] Fig. 4 is a schematic flow diagram of a reverse osmosis/ion exchange system configuration according to a third embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0020] The present invention is directed to methods for substantially decreasing boron concentration and salinity in high-salinity, boron-containing liquids, such as seawater, using a two pass reverse osmosis unit and an ion exchange unit. In order to increase the recovery rate, some streams of the RO system are partially processed by an ion exchange unit which utilizes a boron

specific resin. By processing the first stage permeate with a hybrid second pass RO device in combination with the boron specific ion exchange unit, the methods of the present invention enable a significant increase in the recovery rate of a multistage boron reduction process. Such a configuration enables the second pass RO unit to be operated at a feed pH and recovery rate conditions which reduce scaling potential in the concentrate of the second pass RO unit, while simultaneously maintaining overall high permeate recovery rate.

[0021] The term "high salinity liquid" may be understood to mean any liquid having a salt content of at least about 2000 ppm of total dissolved salts (TDS), and more preferably greater than about 10,000 ppm TDS. In one embodiment, the high salinity boron-containing liquid is seawater, but any high salinity liquid which contains boron may be treated by the methods of the invention. The presently preferred method of measuring the boron concentration is ICAP (Ion Coupled Argon Plasma). However, boron determination may be accomplished by any standard technique known to those in the art.

[0022] The methods of the invention involve treating the high salinity, boron-containing liquid with a two pass RO system. In one embodiment, the high salinity, boron-containing liquid is passed through a first pass reverse osmosis device, preferably operating at a recovery rate of about 45 to 55%, to produce a first pass concentrate and a first pass permeate. This first pass permeate is then treated with a base to elevate the pH to about 8 to about 11, preferably about 9 to about 10. As previously described, literature reports have shown that boron rejection can be greatly enhanced by raising the pH to relatively high levels, such as greater than 9.5. However, under such conditions, softening of the water is also necessary. Because high pH levels may result in calcium scaling, typical RO plants are operated at pH levels of 8.2 or less to ensure the absence of calcium scale formation. In contrast, the methods of the present invention are advantageous because they do not require pre-softening of the water and result in substantially higher boron rejection by operating the second pass reverse osmosis system at pH levels of most preferably about 9 to about 10, higher than normal.

[0023] The preferred bases for use in the methods of the invention are sodium hydroxide and calcium hydroxide. However, other common bases, such as lime (calcium oxide), may also be used. Even if the pH of the high salinity liquid is initially greater than 8, it may be desirable for some applications to raise the pH to the more preferred range of about 9 to about 11.

[0024] In a preferred embodiment, both the measurement and adjustment of the pH are performed in-line while the high salinity liquid flows. Following determination of the pH, a dosing pump which is fed from a tank injects the base into the in-line fluid. Ideally, the dosing pump has

an automatic feedback which automatically monitors and controls the amount of base which is added. No mixing is required because the base is mixed naturally with the high-salinity liquid as it flows.

[0025] Following pH adjustment, at least a portion of the pH-adjusted first pass permeate is processed at elevated pH by a second pass reverse osmosis device, preferably operating at a recovery rate of about 75 to 95%, more preferably at about 80%, to produce a second pass concentrate and a second pass permeate. The most preferred feed pH to the second pass RO device ($\text{pH} \leq 10$) and the recovery rate of the second pass RO device (about 80%) are designed to minimize the scaling tendency of calcium carbonate and magnesium hydroxide by operating at concentration and pH conditions below the saturation limits of calcium carbonate and magnesium hydroxide. Finally, the second pass concentrate is processed for boron reduction via passage through an ion exchange unit containing a boron specific resin to product an effluent. Appropriate boron exchange resins are known in the art commercially available, including without limitation Amberlite IRA 743, manufactured by Rohm and Haas. The recovery rate of the ion exchange unit is preferably about 97 to 99%, more preferably about 98%.

[0026] It is within the scope of the invention that all or a fraction of the pH-adjusted first pass permeate is processed by the second pass RO device. Since second pass processing adds cost to the operating expenses, costs can be minimized by processing with a second pass only the smallest fraction of the first pass permeate required to obtain design quality of the combined permeate (blend). However, this option (second pass treatment of a fraction of the first pass permeate) is only effective if the first pass RO achieves design reduction of dissolved constituents other than boron.

[0027] Finally, the effluent and the second pass permeate are combined to yield a blended flow exhibiting a reduced boron concentration and lower salinity than that of the high salinity, boron-containing feed liquid.

[0028] Alternatively, the first pass permeate may be passed through the ion exchange unit prior to pH adjustment and passage through the second pass RO device. This configuration is described in detail below with respect to Fig. 4. In such a configuration, the second pass permeate and a fraction of the first pass permeate are combined to yield a blended flow. The selection of a specific configuration may be determined on a case by case basis using an economic analysis.

[0029] The methods of the invention are effective at reducing the boron concentration to less than 1 ppm, preferably less than 0.5 ppm, and the total salinity to 400 to 500 ppm. However, it is possible using the methods of the invention to reduce the total salinity to significantly lower levels, such as 25 ppm.

[0030] In one embodiment of the invention, at least one of the reverse osmosis devices comprises an array or set of membrane elements arranged in a series in a pressure vessel. The parallel array of pressure vessels contains reverse osmosis membrane elements which are preferably polyamide type membranes having slight or excessive negatively charged surfaces. Other negatively charged separation membranes, such as polyacrylic acid, may also be used. The membrane elements may be arranged in a variety of packing configurations, such as a plate and frame module or a hollow fiber module, and more preferably a spiral wound configuration. Typical spiral wound reverse osmosis membrane elements which are commercially available are 4" x 40" or 8" x 40" (about 100 mm x about 1000 mm or about 200 mm x about 1000 mm), but any membrane configuration or dimension known in the art would be applicable for the methods of the invention. Typically, pressure vessels comprise about 6 to about 8 membrane elements, but under some circumstances, it may be desirable to use fewer membranes in the pressure vessel.

[0031] The liquid may be passed through the RO device(s) at ambient temperature or at slightly reduced or slightly elevated temperatures. More particularly, the methods would be effective at a normal temperature range for the membranes of about 10°C to about 45°C. It is not believed that the effect of pH on boron removal is significantly affected by changes in temperature. However, while the methods may be performed at temperatures below about 20°C, RO membranes are inherently more effective at rejecting boron at these lower temperatures and the pH adjustment step may not be needed. The methods may be performed at normal operating pressures of a reverse osmosis membrane, such as about 800 to about 1500 psi (about 5500 to about 10,000 kPa), more preferably about 800 to about 1200 psi (about 5500 to about 8200 kPa), and most preferably about 900 to about 1000 psi (about 6100 to about 6800 kPa). In an exemplary process, saline water is provided at about 12 to about 75 gpm (about 45 to about 284 liters/min) for an 8 inch (about 100 mm) diameter by 40 inch (about 1000 mm) long element.

[0032] In one embodiment, the methods of the invention further comprise adding a scale inhibitor to the high salinity liquid before passage through the first pass RO device in order to prevent the formation of carbonate or other hardness scales in the membranes, which typically occurs at high pH. The anti-scalant may be any commercial scale inhibitor known in the art to control calcium carbonate scaling or magnesium hydroxide scaling. A preferred dosage of scale inhibitor is about 0.5 to about 5 ppm.

[0033] Fig. 2 depicts a configuration containing a two pass RO system in which the second pass RO concentrate is processed by ion exchange, according to one embodiment of the invention. As shown in Fig. 2, high salinity liquid feed 3 is pumped by a high pressure pump 6 to a first pass RO

device (membrane unit) 1. In membrane unit 1, operating at a recovery rate of about 45 to 55%, the high salinity liquid is separated into two streams: concentrate 5 and permeate 4. The pH of permeate 4 is adjusted with base 7 to a pH of about 10, and then pumped to a second pass RO device (membrane unit) 2 where it is processed to produce permeate 8 and concentrate 9. The second pass membrane unit operates at recovery rate of about 80%. Concentrate 9 is then processed through an ion exchange unit IX utilizing a boron specific resin. Finally, the effluent 10 of the ion exchange unit is blended with permeate 8 to produce a blended flow 11. The recovery rate of the ion exchange unit is about 98%, so that the combined recovery rate of the second pass hybrid RO/ion exchange system (ratio of the flow rate of stream 11 to the flow rate of stream 3) is over 99%, close to 99.6%. The salinity of the combined permeate (blended flow) is reduced according to the system rejection rate of the first pass RO unit only because the permeate and the concentrate of the second pass are combined together. Typical process parameters for a configuration as shown in Fig. 2 are tabulated in Example 1.

[0034] A second embodiment of the method of the invention utilizes a two pass RO system and partial processing of the second pass permeate with an ion exchange resin. The method also involves passing a high-salinity, boron-containing liquid through a first pass RO device to produce a first pass permeate and a first pass concentrate. The first pass permeate is adjusted with base to a pH of about 8 to about 11, more preferably about 9 to about 10, as previously described. Preferred details of the RO device, the nature of the base, and the mode of base addition have been previously described. At least a portion of the pH-adjusted permeate from the first pass RO unit is then processed at elevated pH by a second pass, preferably four stage, RO unit. The term "RO stage" is understood in the art to refer to a series of pressure vessels, whereas an "RO pass" is a unit that is composed of one or more stages. The most preferred pH to the first two stages of the second pass RO unit (≤ 10) and the recovery rate (about 80%) are designed to minimize the scaling tendency of calcium carbonate and magnesium hydroxide, as previously described.

[0035] The pH-adjusted first pass permeate is passed through a lead segment of the second pass RO device containing a first and a second stage to produce a second stage permeate and a second stage concentrate. After the passage through the second stage, the method involves adjusting the pH of the second stage concentrate to about 7 to about 8, preferably by adding an acid. Appropriate acids are well known in the art and are commercially available, including without limitation hydrochloric acid and sulfuric acid. As previously described with respect to the addition of base, in a preferred embodiment, both the measurement and adjustment of the pH are performed in-line while the high salinity liquid flows. Following determination of the pH, a dosing pump which is fed

from a tank injects the acid into the in-line fluid. Ideally, the dosing pump has an automatic feedback which automatically monitors and controls the amount of acid which is added. No mixing is required because the acid is mixed naturally with the high-salinity liquid as it flows.

[0036] The pressure of the second pass, second stage pH-adjusted concentrate is then increased using a booster pump, and is passed through the a segment of the second pass RO device, containing at least a third stage, and preferably also a fourth stage, preferably operating at a recovery rate of about 80 to 90%, to yield a third stage permeate. Due to the low pH (about 7 to 8), there is no scaling tendency of calcium carbonate or magnesium hydroxide in the tail segment of the second pass RO device. The second stage permeate (permeate from stages one and two) is sent to a permeate tank for blending, while the third stage permeate (permeate from stages three and four) is passed through an ion exchange unit containing a boron specific resin, as previously described, to yield an effluent. Finally, the effluent of the ion exchange unit is blended with the second stage permeate to produce a blended flow. In this configuration, the combined recovery rate of the second pass, hybrid system (reverse osmosis and ion exchange) is in the range of 95.6 to 97.6%. In this method, the salinity of the blended flow is reduced according to the system rejection rate of the first and second passes because the concentrate of the second pass is discharged to drain.

[0037] Fig. 3 depicts a configuration of the second embodiment of the method using a two-pass RO system in which a portion of the second pass RO permeate is processed by ion exchange. As shown in Fig. 3, high salinity liquid feed 3 is pumped by a high pressure pump 6 to a first pass RO device (membrane unit) 1. In membrane unit 1, operating at a recovery rate of about 45 to 55%, the high salinity liquid is separated into two streams: concentrate 5 and permeate 4. The pH of permeate 4 is adjusted with base 7 to a pH of about 10, and then pumped to a second pass RO device (membrane unit) where it is processed to produce permeate 8 and concentrate 9. The second pass membrane unit consists of two segments connected in series. The lead segment 2 produces low salinity, low boron permeate 8 that is sent directly to storage and a concentrate 11 which is treated with acid 12 to reduce the pH and then processed by the tail membrane segment 13 to yield low salinity permeate 9. The boron concentration of permeate 9 is only slightly lower than the concentration in the feed 11, and permeate 9 is further processed with an ion exchange unit IX containing a boron specific resin to yield an effluent 10. Finally, the effluent 10 of the ion exchange unit is blended with permeate 8 to produce a blended flow 14. Typical process parameters for a configuration as shown in Fig. 3 are tabulated in Example 2.

[0038] A third embodiment of the method of the invention involves passing the first pass permeate through the ion exchange unit prior to pH adjustment and passage through the second pass

RO device. Specifically, this method utilizes a configuration as shown in Fig. 4 containing a two pass RO system in which a fraction of the first pass permeate is processed by ion exchange to reduce boron concentration. The pH of the effluent is then increased and processed with a second pass RO for additional boron and salinity reduction. As shown in Fig. 4, high salinity liquid feed 3 is pumped by a high pressure pump 6 to a first pass RO device (membrane unit) 1. In membrane unit 1, operating at a recovery rate of about 45 to 55%, the high salinity liquid is separated into three streams: concentrate 5 and permeates 4a and 4b. Permeates 4a and 4b (low and high salinity permeates, respectively) are taken from two ends of the first pass. Stream 4a (low salinity permeate), taken from the feed side of the unit, contains low concentrations of boron and total dissolved salts, whereas stream 4b (high salinity permeate), taken from the concentrate side of the unit, contains higher concentrations of boron and total dissolved salts. The high boron and total dissolved salts stream 4b is processed by an ion exchange unit IX containing a boron specific resin to yield an effluent 10. Effluent 10 is then treated with base 7 to increase the pH to about 10, and then pumped to a second pass RO device (membrane unit) 2 where it is processed to produce permeate 8 and concentrate 9. The second pass permeate 8 is then combined with low salinity (initial) first pass stream 4a to form final blended permeate 11. The second pass concentrate 9 may be discharged or combined with the feed of the first pass RO unit (not shown).

[0039] This invention will best be understood in connection with the following, non-limiting examples.

[0040] In the following simulated Examples, the results of the various RO systems were calculated using Hydranautics projection software "IMS Design." In these calculations, a seawater temperature of 25 °C was assumed, as well as RO seawater membrane SWC4 for the first pass, brackish membrane ESPA2 for the second pass, and base adjustment using NaOH.

EXAMPLE 1

[0041] A two pass RO system, in which the second pass concentrate is processed by ion exchange, as shown in Fig. 2, was simulated. The process parameters of this configuration are tabulated below.

EXAMPLE 2

[0042] A two pass RO system utilizing partial second pass permeate processing by the ion exchange unit, as shown in Fig. 3, was simulated. The process parameters of this configuration are tabulated below.

COMPARATIVE EXAMPLE 1

[0043] A conventional two pass RO system was simulated as shown in Fig. 1. The process parameters of this configuration are tabulated below.

TABLE

Parameter	Example 1	Example 2	Comp. Ex. 1
<u>Recovery Rates</u>			
1 st pass RO (R1)	45%	45%	45%
2 nd pass RO (R2)	80%	80%	90%
Ion exchange (R3)	98%	98%	-----
3 rd pass RO (R3)	-----	90%	-----
Combined (Rt)	44.8% ¹	43.9% ²	40.5% ³
1 st pass RO permeate flow (Q1)	10,041 m ³ /day	10,242 m ³ /day	11,111 m ³ /day
1 st pass feed salinity (FC1)	35,000 ppm TDS	35,000 ppm TDS	35,000 ppm TDS
1 st pass feed boron conc. (FB1)	5 ppm	5 ppm	5 ppm
<u>1st pass permeate</u>			
salinity (TDS1)	267 ppm	267 ppm	281 ppm TDS
boron concentration (B1)	1.5 ppm	1.5 ppm	1.5 ppm
2 nd pass RO feed pH (pH F2)	10	10	10
<u>2nd pass permeate (stages 1 & 2 if applicable)</u>			
flow (Q2)	8,032 m ³ /day	8,194 m ³ /day	10,000 m ³ /day
salinity (TDS2)	8 ppm	8 ppm	12 ppm
boron concentration (B2)	0.42 ppm	0.44 ppm	0.5 ppm
<u>2nd pass permeate (stages 3&4)</u>			
flow (Q2b)	-----	1,843 m ³ /day	-----
salinity (TDS2b)	-----	98 ppm	-----
boron concentration (B2b)	-----	4.7 ppm	-----
<u>Ion exchange effluent</u>			
flow (Q3)	1,968 m ³ /day	1,806 m ³ /day	-----
salinity (TDS3)	1350 ppm	98 ppm	-----
boron concentration (B3)	0.1 ppm	0.1 ppm	-----
Combined permeate flow (Q)	10,000 m ³ /day	10,000 m ³ /day	-----
Combined flow salinity (TDS)	272 ppm	25 ppm	-----
Combined boron concentration (B)	0.36 ppm	0.38 ppm	-----
<u>2nd pass concentrate</u>			
Ca ²⁺ concentration	4 ppm	(stage 2) 4 ppm	8.4 ppm
Mg ²⁺ concentration	12.3 ppm	(stage 2) 12.3 ppm	25.9 ppm
CO ₃ ²⁻ concentration	11.8 ppm	(stage 2) 11.8 ppm	24.9 ppm
HCO ₃ ⁻ concentration	15.8 ppm	(stage 2) 15.8 ppm	32.1 ppm

¹Rt = R1 x R2 = 0.45 x [0.8 + (0.2 x 0.98)]²Rt = R2 x R2 = 0.45 x [0.8 + (0.2 x 0.9 x 0.98)]³Rt = R1 x R2 = 0.45 x 0.90

[0044] From the data in the Table, it can be seen that the use of two pass reverse osmosis in combination with ion exchange results in enhanced boron rejection (0.1 ppm in Examples 1 and 2 vs. 0.5 ppm in the Comparative Example). Further, the ion concentration of calcium, magnesium, carbonate, and bicarbonate in the combined flow is lower according to the methods of the invention.

5 [0045] In comparison with prior art systems and methods, the methods according to the present invention enable a significantly increased boron rejection rate in a high salinity liquid, particularly seawater, RO system while avoiding scaling of the second pass RO membranes by calcium carbonate or magnesium hydroxide. In the inventive designs, the concentration product of calcium and carbonate ions in the high pH concentrate is about four times lower than in a conventional
10 design, and the corresponding magnesium concentration is two times lower. Due to processing of at least a fraction of the second pass RO permeate with a boron specific ion exchange unit, low boron concentration in the combined permeate and overall high recovery rate are achieved simultaneously.

[0046] It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is
15 understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover modifications within the spirit and scope of the present invention as defined by the appended claims.

CLAIMS

We claim:

1. A method of reducing boron concentration and salinity in a high salinity, boron-containing liquid, comprising:

5 (a) passing the high salinity, boron-containing liquid through a first pass reverse osmosis device to produce a first pass concentrate and a first pass permeate;

(b) adjusting a pH of the first pass permeate to about 8 to about 11;

(c) passing at least a portion of the pH-adjusted first pass permeate through a second pass reverse osmosis device to produce a second pass concentrate and a second pass permeate;

10 (d) passing the second pass concentrate through an ion exchange unit containing a boron specific resin to produce an effluent; and

(e) combining the effluent and the second pass permeate to produce a blended flow;

wherein the blended flow exhibits a lower boron concentration and a lower salinity than the high salinity liquid.

15 2. The method according to claim 1, wherein the high salinity liquid contains at least about 2000 ppm total dissolved solids.

3. The method according to claim 1, wherein the high salinity liquid is seawater.

4. The method according to claim 3, wherein the seawater comprises about 4 to about 7 ppm of boron.

20 5. The method according to claim 1, wherein the boron concentration of the blended flow is less than about 1 ppm and the salinity of the blended flow is less than about 500 ppm total dissolved solids.

6. The method according to claim 5, wherein the boron concentration of the blended flow is less than about 0.5 ppm.

25 7. The method according to claim 1, wherein the pH in step (b) is adjusted to about 9 to about 10.

8. The method according to claim 1, wherein step (b) comprises adding to the first pass permeate at least one base selected from the group consisting of calcium hydroxide, sodium hydroxide, and lime.

9. The method according to claim 1, wherein at least one of the first pass reverse osmosis device and the second pass reverse osmosis device comprises at least one polyamide reverse osmosis membrane.

10. The method according to claim 9, wherein the at least one reverse osmosis membrane is selected from the group consisting of a spiral wound membrane and a hollow fiber membrane.

11. The method according to claim 1, further comprising adding a scale inhibitor prior to step (a).

12. The method according to claim 1, wherein the first pass reverse osmosis device exhibits a recovery rate of about 45 to about 55%.

13. The method according to claim 1, wherein the second pass reverse osmosis device exhibits a recovery rate of about 75 to about 95%.

14. The method according to claim 1, wherein the ion exchange unit exhibits a recovery rate of about 98%.

15. A method of reducing boron concentration and salinity in a high salinity, boron-containing liquid, comprising:

(a) passing the high salinity, boron-containing liquid through a first pass reverse osmosis device to produce a first pass concentrate, a low salinity first pass permeate and a high salinity first pass permeate;

(b) passing at least a portion of the high salinity first pass permeate through an ion exchange unit containing a boron specific resin to produce an effluent;

(c) adjusting a pH of the effluent to about 8 to about 11;

(d) passing the pH-adjusted effluent through a second pass reverse osmosis device to produce a second pass concentrate and a second pass permeate; and

(e) combining the second pass permeate and the low salinity first pass permeate to produce a blended flow;

wherein the blended flow exhibits a lower boron concentration and a lower salinity than the high salinity liquid.

16. A method of reducing boron concentration and salinity in a high salinity, boron-containing liquid, comprising:

5 (a) passing the high salinity, boron-containing liquid through a first pass reverse osmosis device to produce a first pass concentrate and a first pass permeate;

(b) adjusting a pH of the first pass permeate to about 8 to about 11;

(c) passing at least a portion of the pH-adjusted first pass permeate through a lead segment of a second pass reverse osmosis device containing a first stage and a second stage to produce a second
10 stage permeate and a second stage concentrate;

(d) adjusting a pH of the second stage concentrate to about 7 to about 8;

(e) passing the pH-adjusted second stage concentrate through a tail segment of the second pass reverse osmosis device containing at least a third stage to produce a third stage permeate;

(f) passing the third stage permeate through an ion exchange unit containing a boron specific
15 resin to produce an effluent; and

(g) combining the effluent with the second stage permeate to produce a blended flow;

wherein the blended flow exhibits a lower boron concentration and a lower salinity than the high salinity liquid.

17. The method according to claim 16, wherein step (d) comprises adding to the second
20 stage concentrate at least one acid selected from the group consisting of hydrochloric acid and sulfuric acid.

18. The method according to claim 16, wherein the high salinity liquid is seawater.

19. The method according to claim 18, wherein the seawater comprises about 4 to about
7 ppm of boron.

20. The method according to claim 16, wherein the boron concentration of the blended
25 flow is less than about 1 ppm and the salinity of the blended flow is less than about 500 ppm total dissolved solids.

21. The method according to claim 20, wherein the boron concentration of the blended
flow is less than about 0.5 ppm.

22. The method according to claim 16, wherein the pH in step (b) is adjusted to about 9 to about 10.

23. The method according to claim 16, wherein step (b) comprises adding to the first pass permeate at least one base selected from the group consisting of calcium hydroxide, sodium hydroxide, and lime.

24. The method according to claim 16, wherein at least one of the first pass reverse osmosis device and the second pass reverse osmosis device comprises at least one polyamide reverse osmosis membrane.

25. The method according to claim 24, wherein the at least one reverse osmosis membrane is selected from the group consisting of a spiral wound membrane and a hollow fiber membrane.

26. The method according to claim 16, further comprising adding a scale inhibitor prior to step (a).

27. The method according to claim 16, wherein the first pass reverse osmosis device exhibits a recovery rate of about 45 to about 55%.

28. The method according to claim 16, wherein the second pass reverse osmosis device exhibits a recovery rate of about 75 to about 95%.

29. The method according to claim 16, wherein the ion exchange unit exhibits a recovery rate of about 98%.

30. The method according to claim 16, wherein the tail segment comprises at least a third and a fourth stage.

1/4

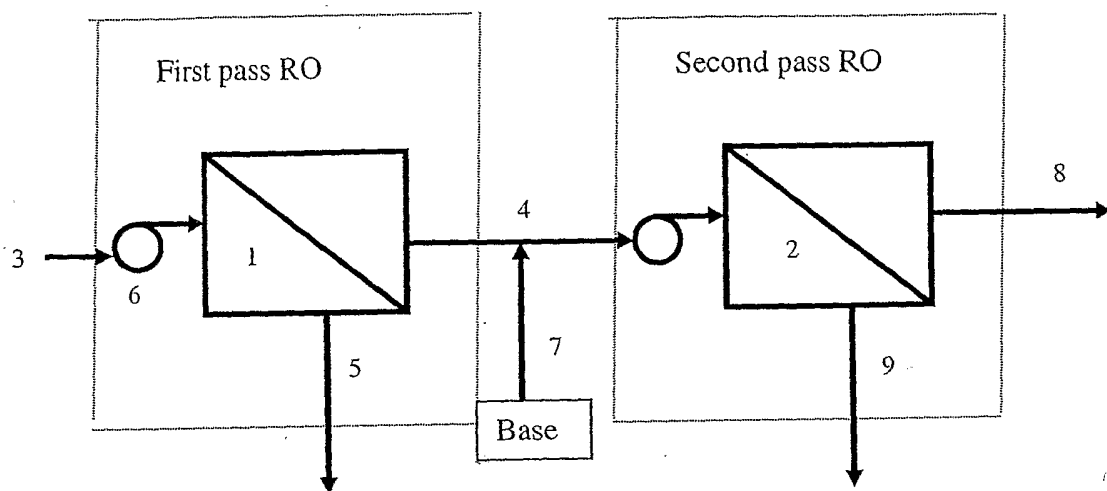


Fig. 1 (prior art)

2/4

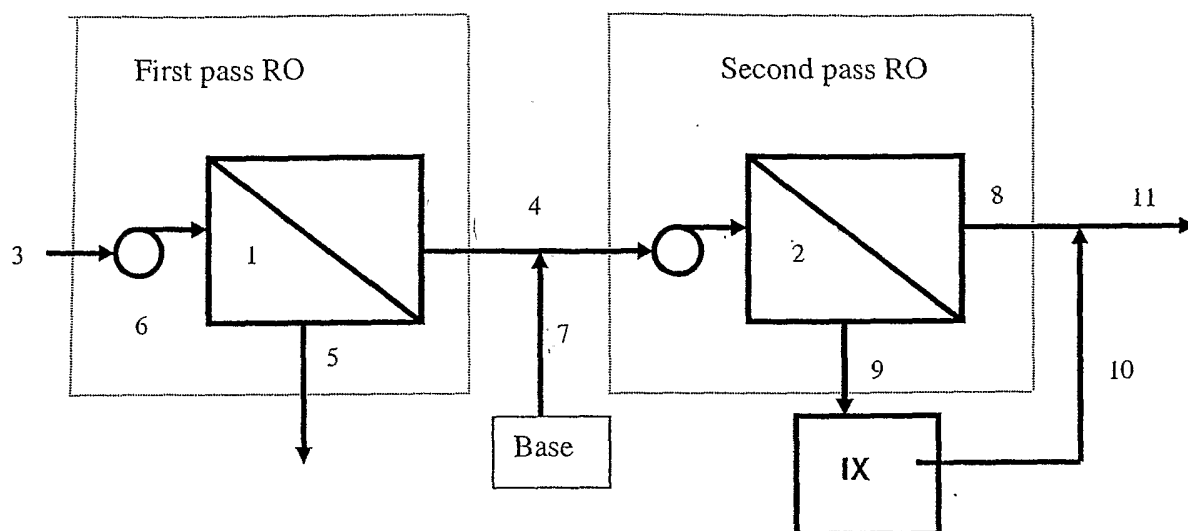


Fig. 2

3/4

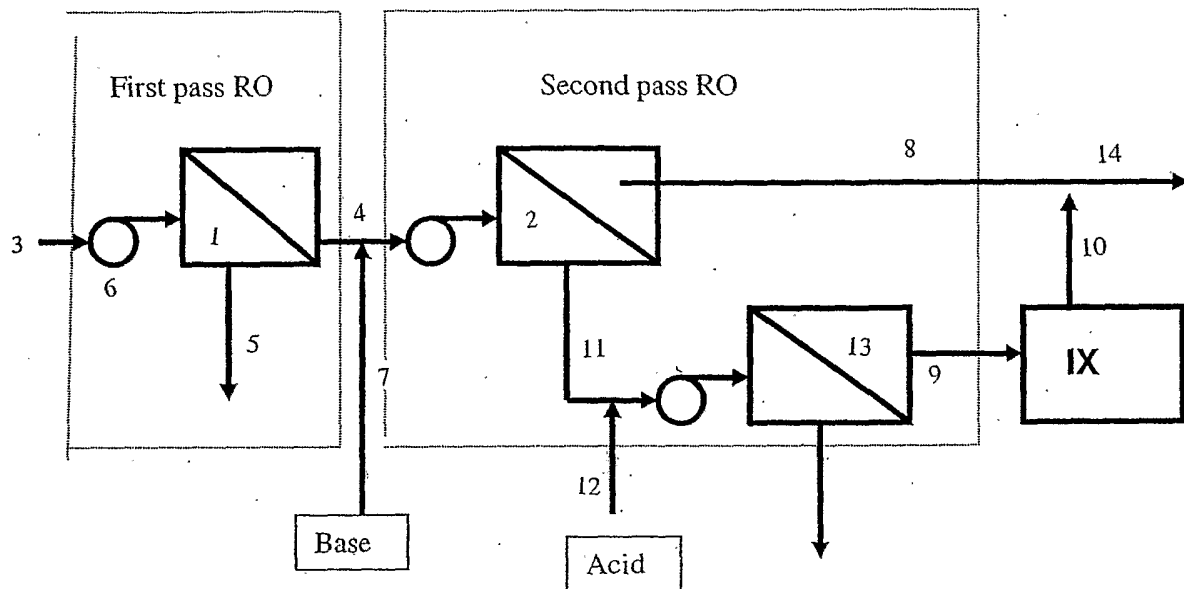


Fig. 3

4/4

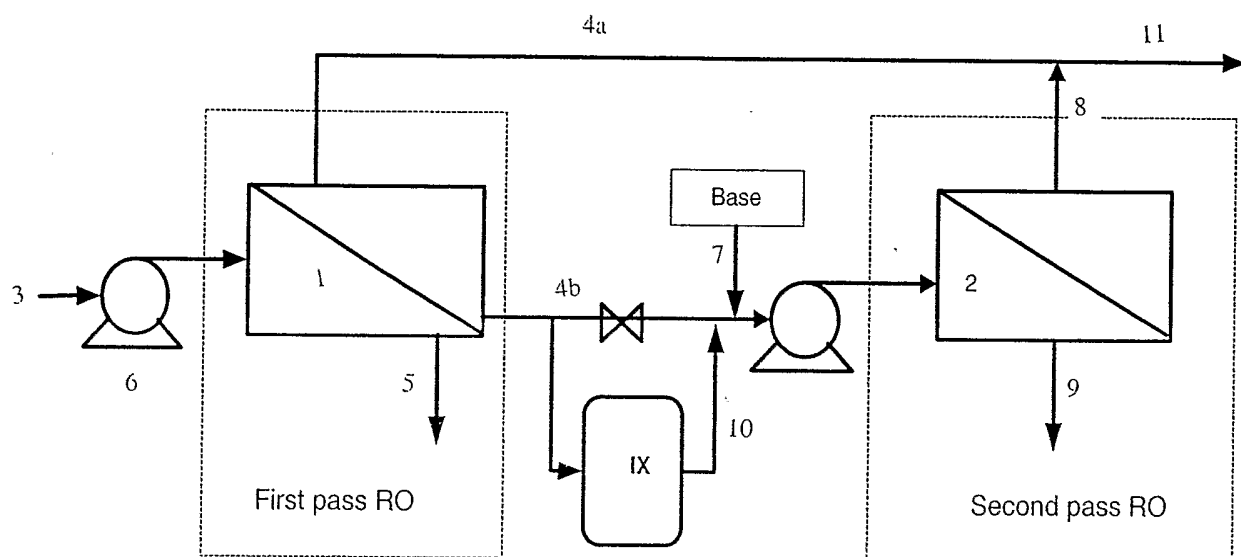


Fig. 4

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US04/40230

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B01D 61/00
US CL : 210/652, 639, 663

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : B01D 61/00

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
West, search boron, boron specific same resin, water, reverse osmosis, removing boron

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,206,048 A (GUTER) June 03 1980, column 3, lines 22-68, column 4, lines 43-53).	1-30
Y	US 5,811,012 A (TANBE et al) 22 September 1998, abstract, Fig. 17, column 13, lines 52-64.	1-30
A	US 6,398,965 a (ARBA et al.) 04, June 2002, abstract, Figures 2A-2B.	1-30
A	US 4,755,298 A (GRINSTEAD) 05 July 1998, entire disclosure.	1-30
A	US 5,250,185 A (TAO et al) 05 October 1993, entire disclosure.	1-30
Y	Yasumoto Magara et al., Development of boron reduction system for sea water desalination, Desalination 118 (1998) 25-34., pages 25-23.	1-30
Y	D. Prats et al., analysis of the influence of pH and pressure on the elimination of boron in reverse Osmosis, Desalination 128 (2000) 269-273.	1-30
A	US 6,100,375 A (BACCHUS et al) 29 August 2000, abstract and fig. 1.	1-30



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:		"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier application or patent published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

30 March 2005 (30.03.2005)

Date of mailing of the international search report

19 MAY 2005

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Facsimile No. (703) 305-3230

Authorized officer

Ana M. Fortuna

Telephone No. (571) 272-1700