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CA 2418329 C 2010/02/02

(11)(21) **2 418 329**

(12) **BREVET CANADIEN**
CANADIAN PATENT

(13) **C**

(86) Date de dépôt PCT/PCT Filing Date: 2001/07/20
(87) Date publication PCT/PCT Publication Date: 2002/02/21
(45) Date de délivrance/Issue Date: 2010/02/02
(85) Entrée phase nationale/National Entry: 2003/02/04
(86) N° demande PCT/PCT Application No.: NO 2001/000314
(87) N° publication PCT/PCT Publication No.: 2002/013955
(30) Priorité/Priority: 2000/08/04 (NO20003977)

(51) Cl.Int./Int.Cl. *B01D 69/00* (2006.01), *B01D 61/00* (2006.01), *B01D 61/02* (2006.01), *B01D 69/02* (2006.01), *F03G 7/04* (2006.01)

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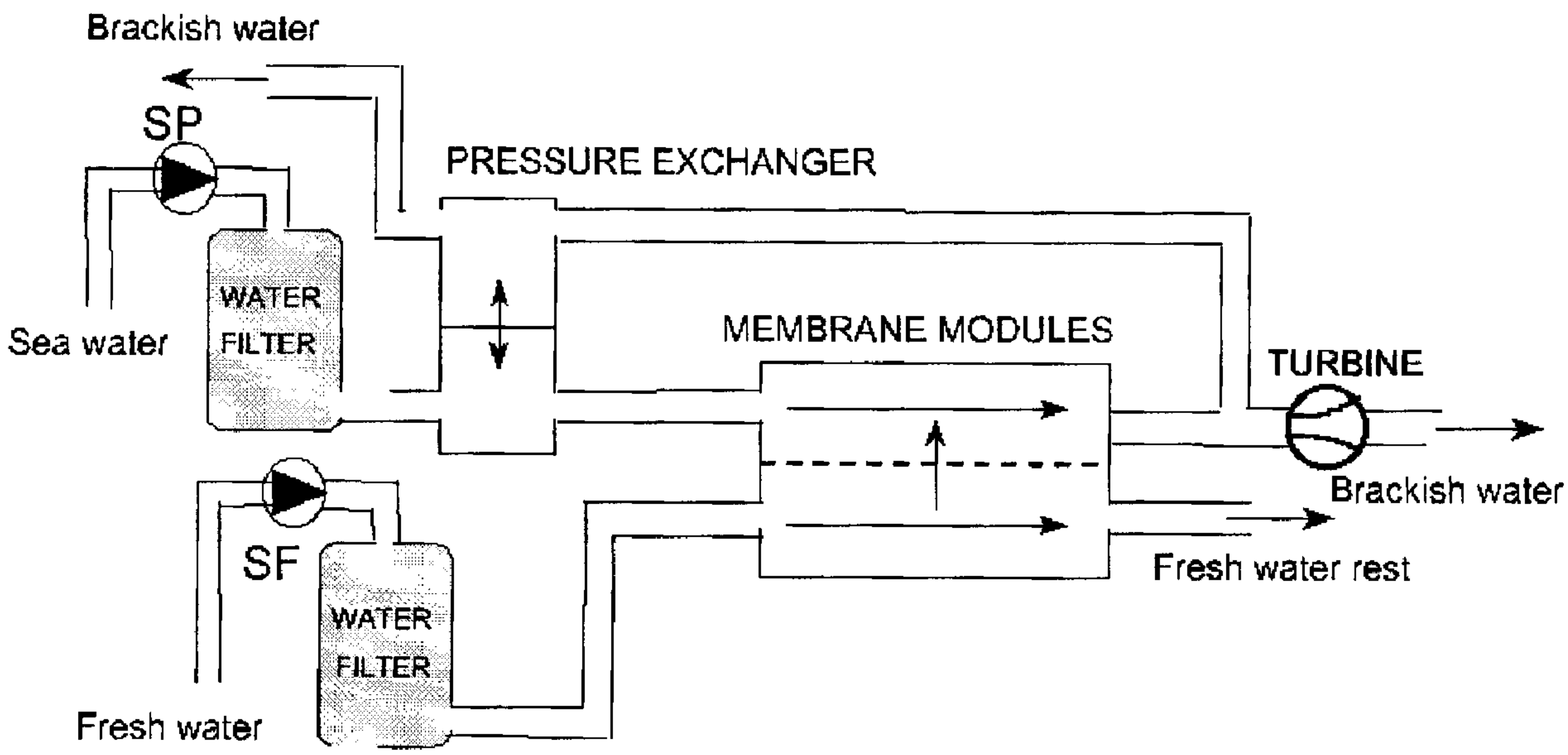
(54) Titre : MEMBRANE SEMI-PERMEABLE, PROCEDE DE PRODUCTION D'ENERGIE ET DISPOSITIF
(54) Title: SEMI-PERMEABLE MEMBRANE FOR USE IN OSMOSIS, METHOD FOR PROVIDING ELECTRIC POWER AND A DEVICE



(57) Abrégé/Abstract:
The present invention concerns a semi-permeable membrane for use in osmosis consisting of one thin layer of a non-porous material (the diffusion skin), and one or more layers of a porous material (the porous layer), where the porous layer has a structure where porosity φ, thickness of the membrane x (m), and tortuosity τ, are related to one another as given by the expression: $\chi \cdot \tau = \varphi \cdot S$ wherein S is a structure parameter having a value equal to or less than 0.0015 meter. Further a method for providing elevated pressure by osmosis as well as a device for providing an elevated osmotic pressure and electric power is described.

ABSTRACT

The present invention concerns a semi-permeable membrane for use in osmosis consisting of one thin layer of a non-porous material (the diffusion skin), and one or more layers of a porous material (the porous layer), where the porous layer has a structure where porosity ϕ, thickness of the membrane x (m), and tortuosity τ, are related to one another as given by the expression:

$$x \cdot \tau = \varphi \cdot S$$

wherein S is a structure parameter having a value equal to or less than 0.0015 meter. Further a method for providing elevated pressure by osmosis as well as a device for providing an elevated osmotic pressure and electric power is described.

SEMI-PERMEABLE MEMBRANE FOR USE IN OSMOSIS, METHOD FOR PROVIDING ELECTRIC POWER AND A DEVICE

The present invention concerns an improved semi-permeable membrane for use in osmosis with properties adapted to the object, and/or membrane modules with reduced loss of energy. More especially, the invention concerns a semi-permeable membrane consisting of one thin layer of a non-porous material (the diffusion skin), and one or more layers of a porous material (the porous layer). Further, the invention concerns a method for providing elevated pressure by osmosis (from salt gradients) in a system with pressure retarded osmosis through one or more semi-permeable membranes which are built up of several layers, whereby at least a part of the elevated osmotic pressure is maintained in the system. A plant for providing an osmotic elevated pressure and electric power is also described.

U. S. Patent 4,283,913 comprises a saturated non-convective water reservoir which captures solar energy and which is used as a separation unit in combination with reverse electro dialysis or pressure retarded osmosis for energy production. From the water reservoir which partly can separate a solution, a higher concentrated stream and a less concentrated stream is passed into two chambers separated with a semi-permeable membrane. Parts of the energy which is created by permeation of the stream with lower concentration through the membrane and the subsequent mixing of the two mentioned streams is transformed into energy before the streams are returned to the water reservoir.

From U. S. Patent 4,193,267 is known a procedure and an apparatus for the production of power by pressure retarded osmosis, wherein a concentrated solution with high hydraulic pressure is passed along a semi-permeable membrane, and where a diluted solution is passed along the opposite side of said membrane. A portion of the diluted solution is transported through the membrane and creates a pressurized mixed solution. The potential energy stored in this pressurized mixture is converted into applicable energy by pressure release and pressurizing the diluted solution.

In U. S. Patent 3,978,344 a procedure is described for producing energy by pressure retarded osmosis by the use of a turbine and a semi-permeable membrane.

Further, from U. S. Patent 3,906,250 is known production of energy by pressure retarded osmosis by hydraulic pressurizing a first liquid which is introduced on one side of a membrane, whereafter another liquid with lower hydraulic pressure and a lower osmotic pressure is introduced on the other side of a membrane. Pressure retarded osmosis will lead to transport of parts of the other liquid through the semi-permeable membrane and thereby a pressurized mixed solution is formed with a larger volume than the first liquid alone. The stored energy is then transformed in a turbine into useable energy such as electric or mechanical power.

U. S. Patent 3,906,250 discloses a method and apparatus for generating power by utilizing pressure retarded osmosis. A first liquid having a relatively high osmotic pressure is introduced at a relatively high hydraulic pressure into a first pathway in which it contacts one face of a semi-permeable membrane, and a second liquid having a lower osmotic pressure is introduced at lower hydraulic pressure into a second pathway in which it contacts the opposite face of the membrane. At every point in the two pathways, the hydraulic pressure difference between the liquids on the opposite faces of the membrane is maintained at a value which is less than the osmotic pressure difference between the liquids. Part of the second liquid passes by pressure-retarded osmosis through the semi-permeable membrane, forming a pressurized mixed solution of greater volume than that of the first liquid introduced into the first pathway. The potential energy stored in the pressurized mixed solution is then converted into useful energy, such as electrical or mechanical power. This prior art also discloses that after potential energy stored in the pressurized mixed solution is converted into useful energy, the first and second liquids are recovered by separating from the mixed solution a quantity of the second liquid equal to the quantity which passed through the membrane, the original temperatures of the so-recovered first and second liquids are restored, the original hydraulic pressure difference is reapplied between the recovered first and second liquids, and the recovered first and second liquids are then recycled through the first and second pathways.

EP-0,882,493-A2 discloses a method for transferring mass between a flow of a first fluid in a gas phase such as combustion flue gas, and a flow of a second fluid in a liquid phase, where the first fluid is contacted with the outer surface of porous (semi-permeable) membranes, e.g., polytetrafluoro-ethylene (PTFE, Teflon) membranes, in the form of hollow fibres having gas-containing pores, and contacting the second fluid with the inner surface of the membranes. Useful membranes for such gas diffusion operation have a porosity (**e**) of at least 0.50, a mass transfer coefficient of e.g. at least 1 cm/s, and a tortuosity factor of e.g. at most 1.4/**e** when the porosity **e** is lower than 0.80, and at most 1.3/**e** when the porosity **e** is 0.80 or higher. This will yield a low structure parameter value (in meters) for such a membrane. However, such a prior art gas diffusion membrane cannot be used for osmosis or for that matter pressure retarded osmosis. There is accordingly no link between a gas diffusion membrane and one for use in osmosis, because the mode of operation is totally different, and therefore also the structure. The pores of the prior art porous membrane are, owing to the nature of the mechanism by which the hollow fibre membrane functions, in general gas-containing. Further, the prior art membrane as disclosed has no thin layer of non-porous material forming a skin, just the porous material.

For centuries it has been known that when salt water and fresh water are partitioned in two different chambers of a semi-permeable membrane, made for example of a biological membrane, e.g., of hog's bladder, fresh water will press itself through the membrane. The driving force is capable of elevating the salt water level above the level of the fresh water, whereby a potential energy is obtained in the form of a static water height. The phenomenon is called osmosis and belongs to the so-called colligative properties of a solution of a substance in another substance. This phenomenon can be thermodynamically described and the amount of potential energy is therefore known. In a system of fresh water and ordinary sea water, the theoretical potential expressed as pressure is approximately 26 bars. The energy potential can in principle be utilized by several technical methods where the energy can be recovered as i.e. steam pressure and stretching of polymers. Two of technical methods are using semi-permeable membranes, and these are reverse electro dialysis (energy potential as electrical DC voltage) and pressure retarded osmosis, PRO, (energy potential as water pressure).

Calculations have been made to find the costs of energy production at PRO plants. The uncertainty of such calculations is illustrated by the fact that reported values for the energy costs fluctuate over more than a magnitude. Wimmerstedt (1977) indicated a little more than 1 NOK/kWh, whereas Lee et al (1981) indicated prohibitive costs. Jellinek and Masuda (1981) indicated costs of less than 0.13 NOK/kWh. Thorsen (1996) made a cost estimate which stated 0.25 – 0.50 NOK/kWh based on an evaluation of recent data for membrane properties and prices. All of these evaluations are based on the use of fresh water and sea water. Thus, earlier conclusions indicated costs of energy produced by PRO that varied very much. A comprehensive elucidation of methods for energy production today and in the future is included in the book "Renewable Energy" (ed. L. Burnham, 1993) prior to the Rio conference about environment and development. Here salt power is only mentioned very briefly, and it is maintained that the costs are prohibitive.

When fresh water is mixed with salt water there is an energy potential (mixing energy) for PRO corresponding to a downfall of 260 meters for fresh water, and the locations of most interest are rivers flowing into the ocean. In the present invention it has been found that 35 – 40% of this energy can be recovered by PRO. In a practical power plant the energy will be liberated as water pressure by approximately 10 bars in the stream of brackish water which develops after the fresh and salt water have been mixed together. This pressure can be used for operating conventional turbines. The effective amount of energy will then be between 50 and 100% of the naturally occurring downfall energy in fresh water on a world basis.

According to the present invention, the actual potential for amounts of power seems to be 25 – 50% of the water power which today has been developed in Norway. Power plants based on the present invention do not lead to significant emissions into the air or water. Further this form of energy is fully renewable, and is only using natural water as driving force in the same manner as conventional water power plants. The object of the present invention is to make possible commercial utilization of salt power on a bigger scale.

Assumed area expenditure for an intended salt power plant will be relatively small and in the same magnitude as for a gas power plant, and substantially smaller than for wind power. The method is therefore especially friendly to the environment. Briefly the method with regard to the environmental effects and the use properties can be characterised as follows:

– no CO_2 emissions or other big quantities of emissions other than water
– renewable, like conventional power from water
– stable production, unlike the wind and wave power

- small areas are required, a fact which leads to little influence on the landscape
- flexible operation
- suited for small as well as large plants.

The known art does not deal with effective semi-permeable membranes with reduced loss of energy, where the biggest part of the salt gradient in the membrane is present in the same layer as the flow resistance if the membrane is used for PRO. Therefore an effective and optimised membrane/membrane module has to be developed where the requirement for salt gradient in the membrane and flow resistance as mentioned above are satisfied. This cannot satisfactorily be achieved in existing membranes designed for filtering (reverse osmosis). Further a method for production of electric power from osmotic pressure with an effective semi-permeable membrane as mentioned above in a system with PRO where a satisfactory part of the osmotic pressure is maintained, has not been described.

An important feature of the present invention is that most of the salt gradient in the membrane is localized in the same layer – the diffusion skin – as the flow resistance. Further the present invention also consists of a porous carrier material for the diffusion skin with no resistance worth mentioning against water transport and salt diffusion. This is not satisfactorily achieved in existing membranes designed for filtering (reverse osmosis)/pressure retarded osmosis, PRO. Consequently, in the present invention, salt does not appear in unfavourably high concentrations in parts of the membrane other than the diffusion skin. According to the present invention, membranes with particular inner structures are also important. Further the concentration polarization of salt on the sea water side of the membranes is reduced compared to conventional membranes.

In the present PRO plant pressure energy in the brackish water is directly recovered hydraulically for pressurizing incoming sea water. Thereby a part of the loss which ordinarily would occur in an ordinary water pump for this purpose is avoided. By avoiding this loss the PRO plant according to the present invention can be built on ground level instead of below ground level and nevertheless achieve acceptable efficiency.

Recovery of pressure energy by direct hydraulic pressurizing of incoming sea water takes place in a device where the turbine pressure in half of the device is pushing sea water directly into the membrane module. In the other half the brackish water is pushed back and out of the PRO plant as the sea water is pumped in. The mentioned processes which take place in the respective halves of the device for hydraulic pressurizing of sea water alternate by rotation of the water containing part or by a controlled valve system in the mentioned device. The mentioned direct hydraulic pressure transfer leads to that sea water pumps with limited efficiency are no longer necessary.

In accordance with one aspect of the invention, there is provided a semi-permeable membrane for use in osmosis consisting of one thin layer of a non-porous material acting as diffusion skin, and at least one layer of a porous material, characterised in that the porous layer has a structure where porosity ϕ, thickness x (m), and tortuosity τ, stand in relation to one another as given by

$$x \cdot \tau = \varphi \cdot S \qquad \text{Equation (1)}$$

where S is a structure parameter having a value of 0.0015 meter or lower.

In accordance with another aspect of the invention, there is provided a method for providing an elevated pressure by osmosis in a system using pressure retarded osmosis through at least one semi-permeable membrane, which are built up of several layers, where at least one part of the osmotic pressure is maintained in the system, characterized by contacting a salt containing first water feed stream with a non-porous material or the diffusion skin in at least one semi-permeable membrane; where at the same time a second water feed stream containing less salt is brought in contact with a porous material in a porous layer of said at least one membrane, where the porous layer has a structure where porosity ϕ, thickness x (m), and tortuosity τ, are related to one another as given by the expression

$$x \cdot \tau = \varphi \cdot S \qquad \text{Equation (1)}$$

where S is a structure parameter, having a value of 0.0015 meter or lower, whereby water from the stream containing less salt naturally is driven through the semi-permeable membrane by osmosis and creates an osmotic hydraulic elevated pressure on the permeate side.

In still another aspect of the invention, there is provided a plant for providing elevated osmotic pressure, characterised by that the plant comprises at least one semi-permeable membrane or membrane module where the membrane or membrane module comprises a non-porous material or diffusion skin, and at least one layer of a porous material forming a porous layer which has a structure where porosity ϕ, thickness x, and tortuosity τ, are related to one another given by:

$$x \cdot \tau = \varphi \cdot S \qquad \text{Equation (1)}$$

wherein S is a structure parameter having a value of 0.0015 meter or lower, and that a pressure exchange arrangement is provided for direct hydraulic transfer of osmotic pressure at elevated pressure branched off from an outlet of the membrane or membrane module to an inlet thereof.

In a still further aspect of the invention, there is provided a plant for providing an elevated osmotic pressure, characterised in that the plant comprises at least one semi-permeable membrane or membrane module where the membrane or membrane module comprises a non-porous material or diffusion skin, and at least one layer of a porous material forming a porous layer which has a structure where porosity ϕ, thickness x, and tortuosity τ, are related to one another given by:

$$x \cdot \tau = \varphi \cdot S \qquad \text{Equation (1)}$$

wherein S is a structure parameter having a value of 0.0015 meter or lower, and that at least one power providing turbine is cooperative with the membrane or membrane module.

The present invention describes semi-permeable membranes or membrane modules in which the membranes include a thin diffusion skin with natural osmotic properties, and the rest of the membrane has an increased porosity, so that salt is not collected here (the porous layer).

Thus the present invention comprises a semi-permeable membrane for use in osmosis consisting of one thin layer of a non-porous material acting as diffusion skin, and at least one layer of a porous material, wherein the porous layer has a structure where porosity ϕ, thickness x (m), and tortuosity τ, stand in relation to each other as indicated by the equation

$$x \cdot \tau = \varphi \cdot S \qquad \text{Equation (1),}$$

S is a structure parameter having a value equal to or less than 0.0015 meter and can be expressed as $S = x \cdot \tau / \varphi$, which is a precise expression for the structure in the porous part of the membrane.

The membrane is suitably configured for pressure retarded osmosis.

As will be appreciated by the average expert in the art, the value of S is related to a wetted membrane.

The porous layer of the membrane, when an amount of salt containing water is brought into contact with the non-porous material or diffusion skin, has properties related to a salt permeability parameter B (in the diffusion skin) defined by:

$$B = (\varphi \cdot D \cdot (dc/dx) / \tau - J \cdot c) \cdot 1/\Delta c_s \qquad \text{Equation} \quad (2)$$

wherein:

A is the water permeability,

B is the salt permeability (m/s),

Δc_s is the difference in salt concentration over the diffusion skin (moles/cm^3),

φ is the porosity,

x is the thickness of the porous layer,

J is the water flux (m/s),

c is the salt concentration (moles/cm^3),

D is the diffusion coefficient of the salt (m^2/s),

τ is the tortuosity,

where the efficiency of the membrane in pressure retarded osmosis for a given value of a water permeability, A (m/s/Pa), can be expressed by an integration of Equation (2) to yield:

$$\Delta c_s / c_b = exp(-d_s \cdot J/D) / \{ 1 + B \cdot [(exp(d_f J/D + S \cdot J/D) - exp(-d_s \cdot J/D)] / J\} \qquad \text{Eq. (3)}$$

wherein:

c_b is the concentration of salt water salt minus the concentration of salt in the fresh water (moles/cm^3),

d_f and d_s are the thickness of the diffusion films (concentration polarizing) on the fresh water side and salt water side, respectively, of the membrane (μm),

$\Delta c_s / c_b$ expresses the efficiency of the membranes in pressure retarded osmosis for a given value of the water permeability.

The value of the structure parameter S and thereby the inner structure of the membrane is decisive for its efficiency in pressure retarded osmosis. The structure should have only one thin and non-porous layer wherein salt has considerably lower diffusion velocity than water. The other layers must all be porous so that salt and water can be transported with as little resistance as possible. Usually several porous layers are present to give the membrane the correct mechanical properties and/or as a result of the production method. In those cases where the diffusion skin lies between two or more porous layers, or the membrane is laterally reversed in relation to fresh water and salt water, the expressions will be more complicated, but the following discussion will be valid in the same manner.

The structure parameter S should have a value of 0.0015 or lower. The thickness of the membrane is less than 150 μm, preferably less than 100 μm. The average value for porosity, φ, in the porous layer in the present invention is more than 50%. The semi-permeable membrane has a tortuosity, τ , which is less than 2,5. The permeability for salt, B, is less than $3 \cdot 10^{-8}$ m/s, and the water permeability, A, is more than $1 \cdot 10^{-11}$ m/s/Pa. The thickness of the diffusion film on the side containing lesser salt and the side containing more salt is less than 60 μm, preferably less than 30 μm.

Membrane modules according to the present invention comprise flow breakers consisting of threads of polymers which are forming a net with a square or rhombic pattern. Further several membranes are packed together in modules (rolled up spiral membranes) where the distance between adjacent membranes are from 0.4 to 0.8 mm.

The present invention further concerns a method where an elevated pressure is provided by osmosis (from salt gradients) in a system with pressure retarded osmosis through one or more semi-permeable membranes, which are built up of several layers, where at least one part of the osmotic pressure is maintained in the system. The method includes contacting a salt containing feed stream with a non-porous layer (the diffusion skin) in one or more semi-permeable membranes; where at the same time a feed stream containing less salt is brought in contact with the other side of the diffusion skin, and where an adjacent porous layer (the porous layer) in one or more of the mentioned semi-permeable membranes has a structure where the porosity ϕ, the thickness x (m), and the tortuosity τ, are related to one another as indicated by the expression

$$x \cdot \tau = \varphi \cdot S$$

wherein S is a structure parameter which is equal to or less than 0.0015 meter, whereby water (H_2O) from the stream containing less salt naturally is driven through the semi-permeable membrane by osmosis and creates an osmotic hydraulic elevated pressure on the permeate side.

In the stated method at least a part of the potential osmotic pressure between the two water streams is hydraulically transferred directly to the incoming salt containing feed stream. The amount of the salt containing feed stream is 1 – 3 times higher than the amount of the feed stream containing less salt, so that the ratio between the length of a flow path of the salt-containing and the less salt-containing stream is from 0.3 to 1.0. The distance between adjacent membranes is from 0.4 to 0.8 mm.

In the spiral modules the channels for the salt-containing feed stream are 10-50% filled with one or more flow breaking devices consisting of threads of polymer which form a net with square or rhombic pattern.

The pressure in the salt containing feed stream on the membrane/membrane modules is in the area from 6 – 16 bars.

As an alternative to spiral membranes parallel fibres can be placed in layers between successive streams of a less salt-containing feed stream and a salt-containing feed stream. The above mentioned will then be a little altered, but the pressure will be the same.

The invention concerns in addition a plant wherein an elevated osmotic pressure is provided, and where the plant comprises one or more semi-permeable membranes or membrane modules where the membranes comprise a non-porous layer (the diffusion skin) and at least one porous layer; and an arrangement for direct hydraulic transmission of an osmotic pressure.

Further referred to is a plant for providing elevated osmotic pressure, suitably for the purpose of generating electric power. The plant includes one or more semi-permeable membranes or membrane modules where the membranes comprise a non-porous layer (the diffusion skin) and at least one porous layer; and an arrangement for direct hydraulic transmission of an osmotic pressure, and at least a turbine with an electric generator.

The plant can be placed on the ground, or below the surface of the earth down to a level not below 200 meters.

Pressure retarded osmosis is like all osmotic processes based on selective mass transport through membranes. A chamber with fresh water is separated from a chamber with sea water by a semi-permeable membrane. This membrane allows transport of water, but not of salt.

Both water and salt will diffuse from high to low concentration, but the membrane prevents the transport of salt. The result is a net water transport from the fresh water side to the sea water side, and a pressure is building up on the sea water side. Thus the osmotic water transport is retarded by the building up of pressure. Water which has been transported to the sea water side is there at a higher pressure, and work can be extracted if the water is allowed to flow out through a turbine. In this way the free energy, by mixing fresh water and sea water, can be converted to work.

If fresh water is flowing into the sea water side without anything flowing out, the pressure will build up. Finally, the pressure on the sea water side will be so high that the transport of water comes to a stop. This happens when the difference in pressure equals the osmotic pressure of sea water given by van't Hoff's equation:

$$p_{osmotic} = 2RTC_{NaCl} \qquad \text{Equation (4)}$$

Here R is the gas constant and T is absolute temperature. For a 35 g/l NaCl solution equation (4) gives a theoretical osmotic pressure of 29 bars at 20°C. This corresponds to a water column of 296 meters. If one mole of water (0.018 kilos) is lifted 296 meters, a work of 52.2 J has to be carried out.

In a power plant based on pressure retarded osmosis, fresh water, being fed into the low pressure side, is transported by osmosis through the semi-permeable membrane to the high pressure side. From the high pressure side the water is pressure released through a turbine which generates mechanical power. To keep a necessary high salt concentration on the sea water side, sea water has to be pumped in against the working pressure. Net energy is produced because the volume stream which is expanding (fresh water + sea water) is larger than the volume stream which is compressed. Some of the fresh water is leaving the plant from the low pressure side, and provides for the transport of contaminations away from the fresh water, and possible salt which has leaked out from the high pressure side.

Another possible design of a plant for pressure retarded osmosis is to build the plant buried 0 - 200 m, suitably 50 – 150 m, most preferably 120 m below ground level. In this case fresh water is passed through pipelines downwards to the turbines, and from there into the low pressure side of the membranes. Sea water is passed into the high pressure side of the membranes which has been pressurized by hydrostatic power, and the sea water can circulate through the high pressure side with friction as the only loss. The fresh water will be transported through the membrane driven by the osmotic power, and leaves the plant mixed with sea water. The membranes can then be positioned as land based modules buried under ground level together with the turbines and other equipment. If the sea is more deep-set than the excavation the membrane modules could be placed directly in the sea.

The skin of the membrane can possibly be located either against the sea water or the fresh water. Locating the diffusion skin against the fresh water side will have the advantage that the contaminations in the fresh water being more readily rejected on the membrane surface because the diffusion skin has far smaller pores in comparison with the porous carrier. Since there is a net volume stream moving in towards the membrane on the fresh water side, this volume stream will be able to transport different types of impurities which can lead to fouling of the membrane. On the other hand, a continuous water stream from the membrane on the water side will contribute to keeping the surface of the membrane clean.

Because all of the pressure difference in the present process lies over the non-porous material (the diffusion skin), it can be an advantage that the diffusion skin lies on the sea water side since the overpressure will press the diffusion skin against the carrier. With the diffusion skin on the fresh water side there is a risk that the diffusion skin is loosened from the carrier, and the membrane can be destroyed.

Further, the parameters for the water permeability, A, and the salt permeability, B, are of high importance as to the performance of the membrane. For a membrane which is totally without salt leakage, the thickness, porosity and tortuosity of the carrier will not be of great importance to the energy production.

There is a considerable dependence on film thickness due to concentration polarization on the sea water side alone, as concentration polarization on the fresh water side is fully negligible for a membrane with a small salt leakage.

The thickness of this diffusion film is a critical size for the energy production by pressure retarded osmosis. This size has to be determined experimentally from transport trials where flux data are adapted to the actual model. Theoretical calculations with a more complex transport model indicate a thickness of the diffusion film of approximately 0.000025 m.

The thickness of the diffusion film on the surface of the membrane against the sea water side can be reduced by increasing the flow velocity on the sea water side, and by the use of devices which increase the stirring of the flowing sea water (turbulence promoters). Such efforts will increase the loss by friction during the flow of the sea water, and there will be an optimum point with regard to the sea water flow rate through a membrane module and the shaping of the membrane module.

As mentioned above, the concentration polarization of salt will be a small problem on the fresh water side in a good membrane module. This is a great advantage since the fresh water rate has to be low in parts of a good device as most of the fresh water is to be transported through the membrane and over to the sea water.

In pressure retarded osmosis the most important losses will be in connection with pressurizing sea water, pumping water through the membrane module and loss by conversion of pressure energy in water into electric energy by means of turbine and generator.

Because of friction loss a drop in pressure will develop over the membrane module. The water must be pumped through a narrow channel which is provided with a distance net to keep the required width of the channel, and which at the same time can promote mixing of the water phase. Thus the thickness of the diffusion film can be reduced, and the efficiency in the PRO process can be improved.

In PRO processes with a good membrane module concentration polarization will only be an essential problem on the sea water side, since the salt concentration on the fresh water side only shows a low increase. Further, the rate on the sea water side will be higher than on the fresh water side, because fresh water is transported over to the sea water, and also because there exists a desire to maintain the highest possible salt concentration in the sea water. The last mentioned is achieved by having a high through flow of salt water, but the profit of a high salt water rate has to be considered against the expenses. The rate of the salt water can be increased by recycling of salt water.

In a process according to the present invention, sea water is pressurized before it flows through the membrane module. Then the sea water together with the fresh water which has been transported through the membrane, will expand through a turbine. The pump as well as the turbine will have an efficiency of less than 1, and energy will consequently be lost in these unity operations.

To reduce the loss when large quantities of sea water first have to be compressed, and then expanded through a turbine, pressure exchange can be used. In pressure exchange the pressure in outgoing diluted sea water is used to compress incoming sea water. Only a quantity of water corresponding to the fresh water which flows through the membrane will pass through the turbine, and a far smaller turbine can therefore be used. The high pressure pump for pressurizing the sea water is completely eliminated.

Finally the invention describes a plant for the production of electric power, where the plant comprises water filters for purifying a salt containing feed stream and a feed stream containing less salt, one or more semi-permeable membranes or membrane modules, as well as an arrangement for direct hydraulic transmission of an osmotic pressure.

Figure 1 describes a PRO plant wherein fresh water as well as sea water is fed into separate water filters prior to the streams passing on each side of a semi-permeable membrane, respectively. A portion of the mixture of permeate and salt water with elevated pressure is passed to a turbine for the production of electric power. The balance of the permeate stream is passed to a pressure exchanger where incoming sea water is pressurized. The pressurized sea water is then fed into the membrane module.

Figure 2 shows the stream pattern for cross-stream in a spiral module.

Figure 3 shows stream lines in a spiral module.

Figure 4 shows the build-up of the interior structure of a membrane, a non-porous layer, called diffusion skin, and one porous layer.

Figure 5 shows the relation between pressure on the one side of the membrane which is in contact with a quantity of water containing salt (the sea water side), and osmotic flux. Figure 5 shows the values S which are acceptable for economical power production when A is 10^{-11} m/s/Pa and B is $3 \cdot 10^{-8}$ m/s. This or higher values of A are considered as necessary. Consequently S must have a value of 0.001 m or lower. Laboratory measurements have shown that the membranes intended for reverse osmosis, which gives the best performance in pressure retarded osmosis, have S-values around 0.003 m. This means that S has to be improved by a factor of 3 or better in relation to these membranes. Lower values of B will to some extent modify the requirement for S.

Figure 6 shows effect as function of pressure on the sea water side for a process with conditions as given in table 2.

Figure 7 shows concentration relations along membrane for PRO with conditions as given in table 2 (the salt concentrations on the fresh water side are hardly visible).

Figure 8 shows volume flux of water through the membrane for a process with conditions given in table 2.

The necessary values for the salt permeability, *B*, the water permeability, *A*, the structure parameter, *S*, and the thickness of the diffusion films will also apply to possible fiber membranes. A principal drawing for fibre membranes will be as for spirals with exception of that which concerns the use of flow breaking distance nets.

Examples of energy production:

The mixing zone for salt water and fresh water can be considered as adiabatic, i.e., there is no heat exchange ($dq=0$) with the surroundings. Since the mixing enthalpy is approximately zero, and work (dw), but not heat, is extracted from the mixture, it is obtained from the energy preservation law:

$$dE = c_p dT = dq + dw = dw \qquad \text{Equation (5)}$$

wherein dE is the change in the inner energy of the total system and c_p is the heat capacity of the system.

Extraction of work will according to equation (5) lead to a certain amount of cooling. If one mole of fresh water with 52.5 J/mole is reversibly mixed with three moles of salt water, the diluted salt water will be cooled down with 0.17°C. In a real process optimised for energy production per mixing unit, half of the reversible work will be taken out. This leads to a cooling of the mixture of less than 0.1°C.

As mentioned above, only 50% of the possible mixing free energy will be utilized in a practical device to maximize the energy production. Further, energy will be lost by operation of the process. With the assumption that 20% of the energy which is produced in the mixing unit is lost in the process (loss because of friction, operation of pumps, turbines, etc.) about 20 J per mole of fresh water which passes through the process could be produced. This causes an energy production for some locations based on mean flow of water transport according to the present invention as illustrated in table 1.

Table 1. Examples of possible power plants based on average water flow

Example of rivers	Water flow (m^3/s)	Power production (MW)
Small local river	10	10
Namsen (Norway)	290	300
Glomma (Norway)	720	750
Rhine (Germany)	2 200	2 400
Mississippi (USA)	18 000	19 000

Examples of operating variables:

For calculation of water and salt transport through the membrane as well as energy production per area unit of membrane, it is necessary to have real values of the different parameters which describe the actual membrane, the shape of the membrane module, parameters describing the process conditions, as well as some physical data. Necessary parameters for the calculations are summarized in table 2.

All calculations in the following are carried out on the basis of 1 m^2 membrane area. Because the water and salt fluxes through the membrane in most cases are considerable in relation to the incoming rates of salt water and fresh water, the concentrations, and therefore also the fluxes through the membrane, will vary along the membrane. To allow for this the membrane is divided into 20 cells of equal size for calculation purposes. The concentrations and rates of salt water and fresh water, respectively, to the first cell, and the sea water pressure on the membrane, are given by the input conditions, see table 2. The fluxes of water and salt for these conditions are then calculated iteratively from cell to cell by means of the necessary equations.

The salt water rate, Q, out from the last cell, defines the rate out of the process. The difference between out-rate and in-rate for salt water, and the pressure on the salt water side indicates the produced work. The exploitation ratio of fresh water is indicated by the difference between fresh water rate in and out in relation to fresh water rate in.

Table 2.

Necessary parameters for model calculations of pressure retarded osmosis.

Symbol	Unit	Example value	Parameter
A	m/Pa/s	10^{-11}	Water permeability in the membrane
B	m/s	10^{-8}	Salt permeability through the membrane
x	m	0.0005	Thickness of the porous layer
φ		0.5	Porosity in porous layer
τ		1.5	Tortuosity in porous layer
$d_{sjø}$	m	0.00005	Thickness of diffusion film on the sea water side
d_f	m	0.00005	Thickness of diffusion film on the fresh water side
T	°C	3	Process (water) temperature
$p_{sjø}$	Pa	$13 \cdot 10^5$	Pressure on the sea water side
$c_{sjø}^{inn}$	mol/m^3	549	Incoming concentration of salt in salt water
c_f^{inn}	mol/m^3	0	Incoming concentration of salt in fresh water
Q_{inn}	m^3/s	$9 \cdot 10^{-6}$	Volume rate of fresh water in on the membrane
F		3	Feed ratio between salt water and fresh water
D_s	m^2/s	$7.5 \cdot 10^{-10}$	Coefficient of diffusion for salt (NaCl)
S	m	≤0.0015	Structure parameter

For each single set of parameters fluxes and rates are calculated as stated above. For determination of optimal sea water pressure the sea water pressure is always varied with other conditions constant.

In the calculations pressure loss through the membrane module because of the flow resistance has not been considered. Neither has the efficiency of the pump which pressurizes the sea water and the turbine which produces energy from the process been considered. Produced work as presented is therefore related to the energy production during the mixing process, and is not equal to the real work that can be extracted from a real process. Such dimensions have to be estimated for the plants in question.

The coefficient of diffusion for salt is increasing by approximately 80% when the temperature increases from 3 to 20°C, but does not change much with the concentration of salt. The coefficient of diffusion at 0.1 moles/l is therefore used in all calculations. As an example of calculations a basis point has been taken in the conservative parameter values stated in table 2. At these conditions the membrane produces 2.74 W/m^2, and 23% of the fresh water which is supplied to the membrane is transported over to the sea water side. Figure 1 shows the effect per area unit of membrane as a function of the pressure on the sea water side. As shown on the figure the effect has a relatively flat optimum area between 13 and 18 bars. By selecting a little more favourable values for the membrane thickness, film thickness and temperature, the energy production can easily be higher than 5 W/m^2.

The concentrations over the membrane from the inlet side and to the outlet are shown on Figure 7 for a sea water pressure of 13 bars. Because the salt leakage through this membrane is small in this example, the increase of the salt concentration on the fresh water side is hardly noticeable, and reaches a discharge concentration of 0.5 moles/m^3. Correspondingly the concentration polarization on the fresh water side can be fully neglected.

On the other hand, the concentration polarization on the sea water side is considerable, and gives a concentration drop just below 100 moles/m^3. Correspondingly there is a concentration drop of almost 150 moles/m^3 over the carrier. The driving concentration difference over the skin of the membrane corresponds to the concentration difference between the surface of the skin against the sea water and the side of the adjacent porous layer which faces against the sea water, see Figure 7, and amounts to approximately 320 moles/m^3, or barely 60% of the concentration difference between sea water and fresh water. This illustrates the importance of reducing the polarization effects. This is achieved by minimizing the thickness of the diffusion film on the sea water side (high flow velocity and good stirring), and the thickness of the carrier.

Figure 8 shows the volume flux of water through the membrane as a function of dimensionless position from the inlet side. As the figure shows, the water flux changes relatively little, and the reason for this is that the driving concentration difference also is relatively constant along the membrane, see Figure 7.

CLAIMS:

1. A semi-permeable membrane for osmosis comprising one thin layer of a non-porous material as a diffusion skin, and at least one porous layer of a porous material, characterised in that the porous layer has, when wetted, a porosity φ, thickness x (m), and tortuosity τ in relation to one another as given by

$$x \cdot \tau = \varphi \cdot S \qquad \text{Equation (1)}$$

where S has a value of 0.0015 meter or lower.

2. The semi-permeable membrane according to claim 1, for pressure retarded osmosis, wherein the porous layer, when an amount of a first water feed stream containing salt is contacted with the diffusion skin, has properties related to a salt permeability parameter B defined by:

$$B = (\varphi \cdot D \cdot (dc/dx) / \tau - J \cdot c) \cdot 1/\Delta c_s \qquad \text{Equation (2)}$$

wherein:

A is the water permeability,

B is the salt permeability (m/s),

Δc_s is the salt concentration difference over the diffusion skin (moles/cm^3),

φ is the porosity,

x is the thickness of the porous layer,

J is the water flux (m/s),

c is the salt concentration (moles/cm^3),

D is the diffusion coefficient of the salt (m^2/s),

τ is the tortuosity,

where the efficiency of the membrane in pressure retarded osmosis for a given value of a water permeability, A (m/s/Pa), can be expressed by an integration of Equation (2) to yield:

$$\Delta c_s / c_b = exp(-d_s \cdot J/D) / \{ 1 + B \cdot [(exp(d_f J/D + S \cdot J/D) - exp(-d_s \cdot J/D)] / J\}$$

wherein:

c_b is the difference in salt concentration between a second water feed stream and said first water feed stream, wherein said second water feed stream contains less salt than said first water feed stream (moles/cm^3),

d_f and d_s are the thickness (µm) of the diffusion films on a side of the membrane contacting the second water feed stream and a side of the membrane contacting the first water feed stream fresh, respectively, and

$\Delta c_s / c_b$ is the efficiency of the membrane in pressure retarded osmosis for a given value of the water permeability.

3. The semi-permeable membrane according to claim 2, wherein the salt permeability, B, is less than $3 \cdot 10^{-8}$ m/s.

4. The semi-permeable membrane according to claim 2 or 3, wherein the water permeability, A, is more than $1 \cdot 10^{-11}$ m/s Pa.

5. The semi-permeable membrane according to any one of claims 1 to 4, wherein the membrane has a thickness of less than 150 µm.

6. The semi-permeable membrane according to claim 5, wherein the membrane has a thickness of less than 100 µm.

7. The semi-permeable membrane according to any one of claims 1 to 6, having an average porosity, φ, in the porous layer of more than 50%.

8. The semi-permeable membrane according to any one of claims 1 to 7, wherein the tortuosity, τ, is less than 2.5.

9. The semi-permeable membrane according to any one of claims 1 to 8, forming a set of several membranes, with flow breakers located between the membranes of the set of several membranes, said flow breakers consisting of threads of polymer which form a net with square or rhombic pattern.

10. The semi-permeable membrane according to claim 9, wherein said several membranes have been packed together in layers to form modules where the distance between adjacent membranes are from 0.4 to 0.8 mm.

11. The semi-permeable membrane according to any one of claims 1 to 8, wherein the porous layer of the membrane comprises hollow fibres with an outside diameter from 0.05 to 0.5 mm.

12. The semi-permeable membrane according to claim 1, for pressure retarded osmosis, wherein the membrane is configured for creating electric power through use of osmotic hydraulic elevated pressure created by said pressure retarded osmosis for driving at least one power turbine.

13. A method for providing an elevated pressure by osmosis in a system using pressure retarded osmosis through at least one semi-permeable membrane which is built up of several layers, where at least one part of the osmotic pressure is maintained in the system, comprising:

- contacting a first water feed stream containing salt with a non-porous material as a diffusion skin of said at least one semi-permeable membrane; where at the same time a second water feed stream containing less salt is contacted with a porous material in a porous layer of said at least one membrane, where the porous layer has, when wetted, a porosity φ, thickness x (m), and tortuosity τ, related to one another as given by the expression

$$x \cdot \tau = \varphi \cdot S \qquad \text{Equation (1)}$$

  where S has a value of 0.0015 meter or lower, and
- whereby water from the second water feed stream is driven through the semi-permeable membrane by forward osmosis and creates an osmotic hydraulic elevated pressure on a permeate side of the membrane defined by the diffusion skin.

14. The method according to claim 13, wherein the porous layer of the membrane, when the first water feed stream is contacted with the diffusion skin, has properties related to a salt permeability parameter B defined by:

$$B = (\varphi \cdot D \cdot (dc/dx) / \tau - J \cdot c) \cdot 1/\Delta c_s \qquad \text{Equation (2)}$$

wherein:

A is the water permeability,

B is the salt permeability (m/s),

Δc_s is the salt concentration difference over the diffusion skin (moles/cm^3),

φ is the porosity,

x is the thickness of the porous layer,

J is the water flux (m/s),

c is the salt concentration (moles/cm^3),

D is the diffusion coefficient of the salt (m^2/s),

τ is the tortuosity,

where the efficiency of the membrane in pressure retarded osmosis for a given value of a water permeability, A (m/s/Pa), can be expressed by an integration of Equation (2) to yield:

$$\Delta c_s / c_b = exp(-d_s \cdot J/D) / \{ 1 + B \cdot [(exp(d_f J/D + S \cdot J/D) - exp(-d_s \cdot J/D)] / J\}$$

wherein:

c_b is the difference in salt concentration between the second water feed stream and the first water feed stream, wherein said second water feed stream contains less salt than said first water feed stream, (moles/cm^3),

d_f and d_s are the thickness (µm) of the diffusion films on a side of the membrane contacting the second water feed stream and a side of the membrane contacting the first water feed stream, respectively, and

$\Delta c_s / c_b$ is the efficiency of the membrane in pressure retarded osmosis for a given value of the water permeability.

15. The method according to claim 14, wherein the salt permeability, B, is less than $3 \cdot 10^{-8}$ m/s.

16. The method according to claim 14 or 15, wherein the water permeability, A, is more than $1 \cdot 10^{-11}$ m/s Pa.

17. The method according to any one of claims 13 to 16, wherein at least a part of the osmotic pressure over the membrane is directly hydraulic transferred to the incoming first water feed stream.

18. The method according to any one of claims 13 to 17, wherein the membrane has a thickness of less than 150 μm.

19. The method according to claim 18, wherein the membrane has a thickness of less than 100 μm.

20. The method according to any one of claims 13 to 19, having an average porosity, φ, in the porous layer of more than 50%.

21. The method according to any one of claims 13 to 20, wherein the tortuosity, τ, is less than 2.5.

22. The method according to any one of claims 13 to 21, wherein the first water feed stream is in an amount 1 – 3 times higher than an amount of the second water feed stream.

23. The method according to any one of claims 13 to 22, wherein a channel for the first water feed stream between the membranes comprises flow breakers consisting of threads of polymer which form a net with square or rhombic pattern which fills the channel 10-50%.

24. The method according to any one of claims 13 to 23, wherein several membranes are packed together in layers to form modules where the distance between adjacent membranes are from 0.4 to 0.8 mm.

25. The method according to any one of claims 13 to 24, wherein a ratio between the length of a flow path of the first water feed stream and the second water feed stream is from 0.3 to 1.0.

26. The method according to any one of claims 13 to 25, wherein the porous layer of the membrane comprises hollow fibres with an outside diameter from 0.05 to 0.5 mm.

27. The method according to any one of claims 13 to 26, wherein the pressure of the first water feed stream flowing into the membrane or membrane module is in the range of 6 – 16 bars.

28. The method according to any one of claims 13 to 27, wherein the osmotic hydraulic elevated pressure is used for driving at least one power turbine.

29. The method according to claim 28, wherein the power turbine is used for creating electric power.

30. A plant for providing elevated osmotic pressure through use of pressure retarded osmosis, wherein the plant comprises at least one semi-permeable membrane or membrane module where the membrane or membrane module comprises a non-porous material as a diffusion skin, and at least one porous layer of a porous material, wherein the porous layer has, when wetted, a porosity φ, thickness x, and tortuosity τ, are related to one another as given by:

$$x \cdot \tau = \varphi \cdot S \qquad \text{Equation (1)}$$

wherein S has a value of 0.0015 meter or lower.

31. The plant according to claim 30, wherein the porous layer of the membrane, when first water feed stream containing salt is contacted with the diffusion skin, has properties related to a salt permeability parameter B defined by:

$$B = (\varphi \cdot D \cdot (dc/dx) / \tau - J \cdot c) \cdot 1/\Delta c_s \qquad \text{Equation (2)}$$

wherein:

A is the water permeability,

B is the salt permeability (m/s),
Δc_s is the salt concentration difference over the diffusion skin (moles/cm^3),
φ is the porosity,
x is the thickness of the porous layer,
J is the water flux (m/s),
c is the salt concentration (moles/cm^3),
D is the diffusion coefficient of the salt (m^2/s),
τ is the tortuosity,
where the efficiency of the membrane in pressure retarded osmosis for a given value of a water permeability, A (m/s/Pa), can be expressed by an integration of Equation (2) to yield:

$$\Delta c_s / c_b = exp(-d_s \cdot J/D) / \{ 1 + B \cdot [(exp(d_f J/D + S \cdot J/D) - exp(-d_s \cdot J/D)] / J\}$$

wherein:
c_b is the difference in salt concentration between the second water feed stream and the first water feed stream, wherein said second water feed stream contains less salt than said first water feed stream, (moles/cm^3),
d_f and d_s are the thickness (μm) of the diffusion films on a side of the membrane contacting the second water feed stream and a side of the membrane contacting the first water feed stream, respectively, and
$\Delta c_s / c_b$ is the efficiency of the membrane in pressure retarded osmosis for a given value of the water permeability.

32. The plant according to claim 30 or 31, wherein the elevated osmotic pressure is applied to at least one turbine for creating electric power.

33. The plant according to claim 30, further comprising a pressure exchange arrangement connected to an outlet of the membrane or membrane module configured to receive direct hydraulic transfer of osmotic pressure at elevated pressure branched off therefrom to provide increased pressure to water delivered to an inlet of the membrane or membrane module at a diffusion skin side.

34. The plant according to claim 33, wherein at least one power providing turbine is located downstream of where a pressure transfer is branched off from the outlet.

35. The plant according to claim 30, further comprising at least one power providing turbine operably linked with the membrane or membrane module.

36. The plant according to any one of claims 30 to 35, wherein:

the plant is located 0 - 200 m below ground level,

fresh water is passed through pipelines downwards to said at least one turbine,

fresh water is further passed from the turbine into a low pressure side of said at least one membrane or membrane module,

sea water is passed into a high pressure side of said at least one membrane or membrane module, said sea water having been pressurized by hydrostatic power,

sea water is allowed to circulate through said high pressure side of said at least one membrane or membrane module,

fresh water is transported through said at least one membrane or membrane module by osmotic power, and

water leaving the plant is the fresh water mixed with sea water.

37. The plant according to any one of claims 30 to 36, wherein the porosity, φ, has an average value of more than 50%, and the tortuosity, τ, is less than 2.5.

38. The plant according to any one of claims 30 to 37, wherein the membrane has a thickness of less than 150 μm.

39. The plant according to any one of claims 30 to 38, wherein a diffusion skin side of the membrane or membrane module is configured to be contacted with a first water feed stream, and the porous layer of the membrane is configured to be contacted with a second water feed stream, said second water feed stream having less salt content than the first water feed stream, and

wherein the first water feed stream is at a pressure higher than that of the second water feed stream.

40. The plant according to any one of claims 30 to 39, which is operably linked to at least one turbine, and wherein the membrane or membrane module is configured to provide elevated osmotic pressure to drive the at least one turbine.

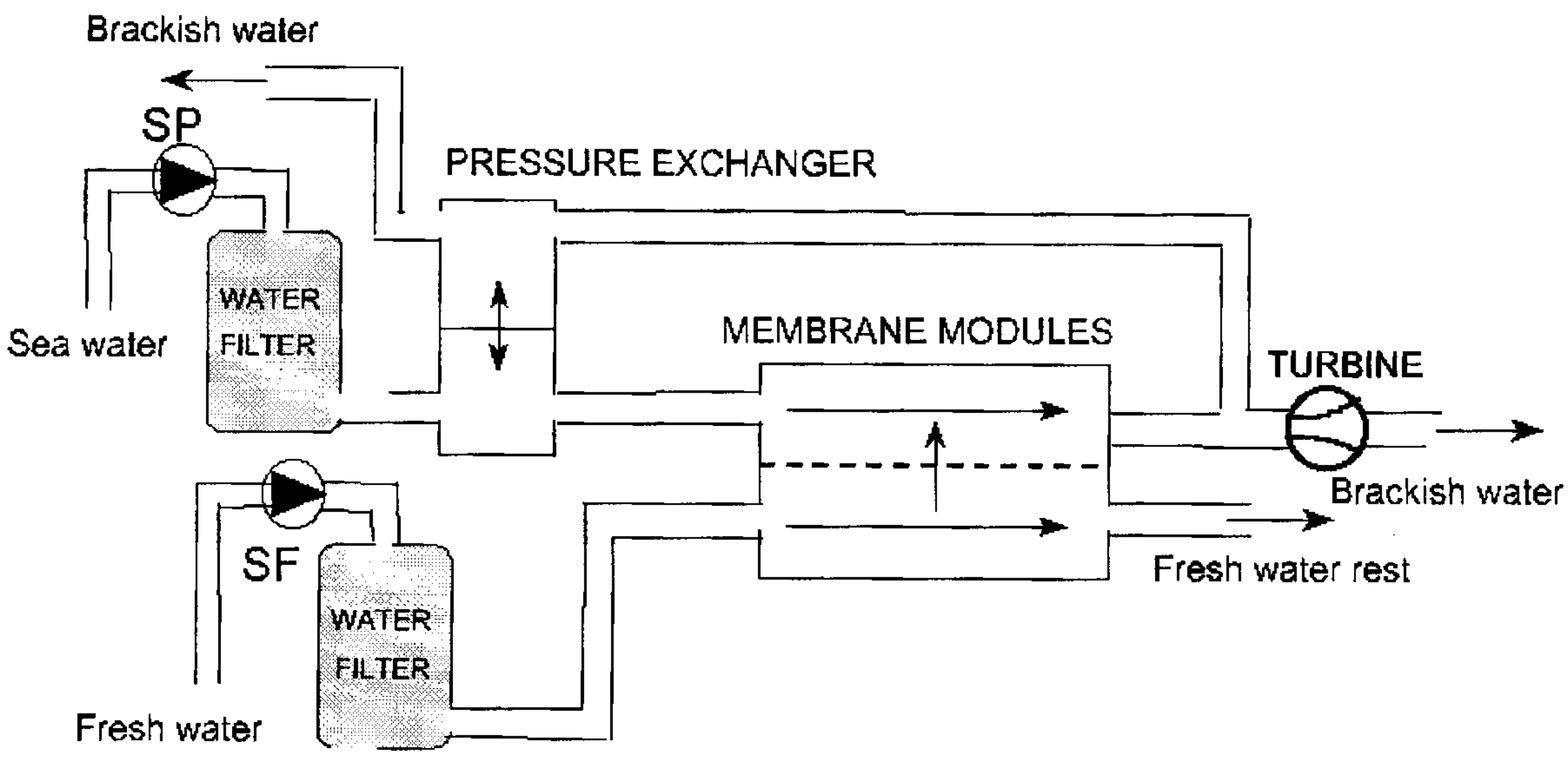


Figure 1.

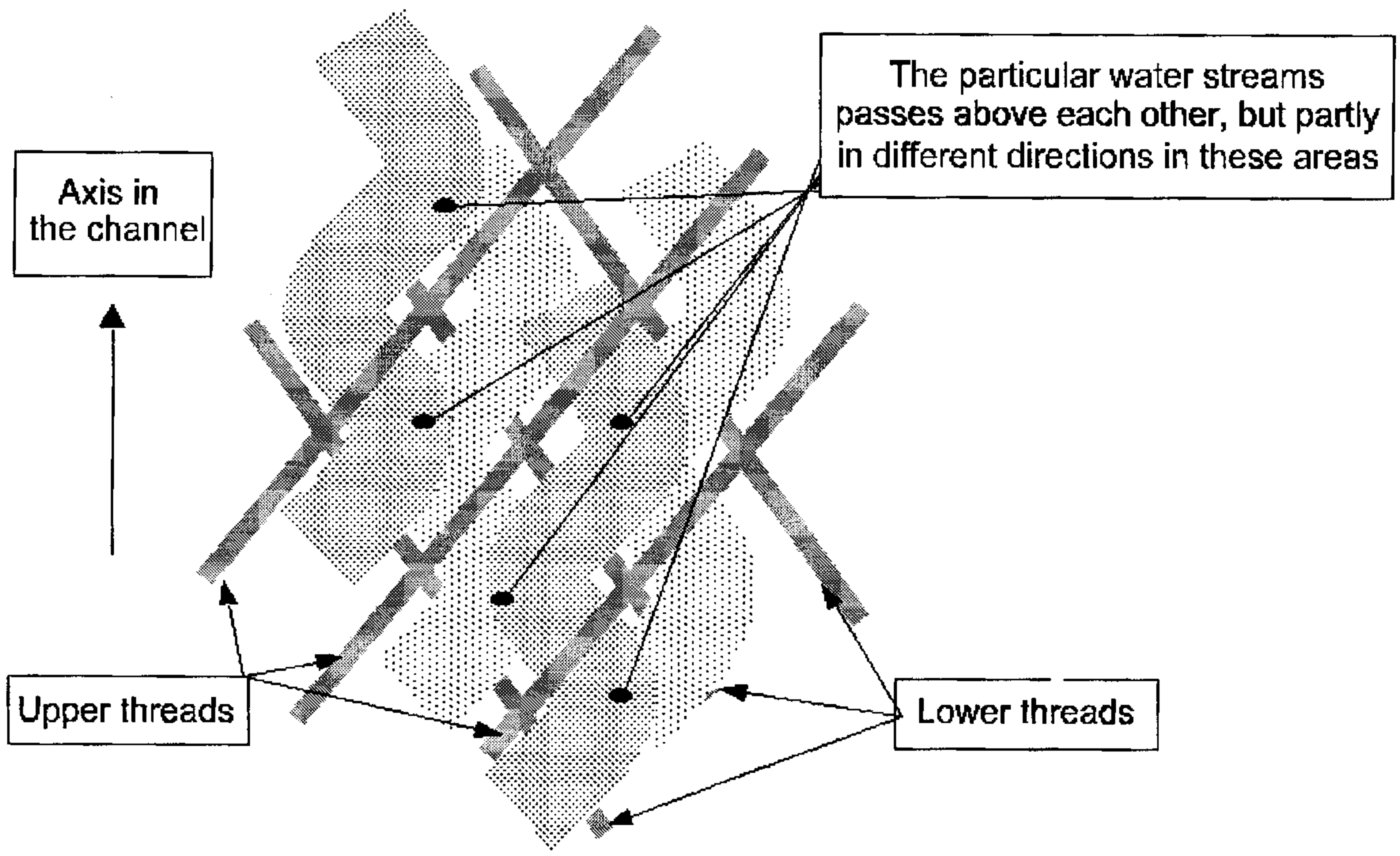


Figure 2.

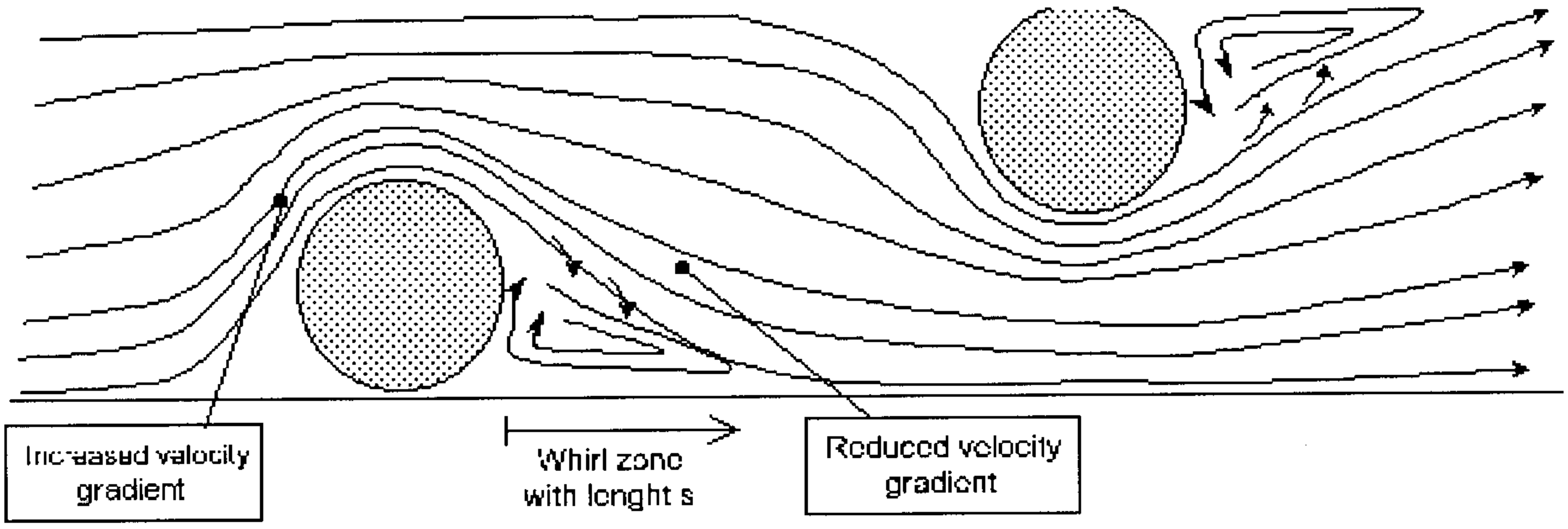


Figure 3.

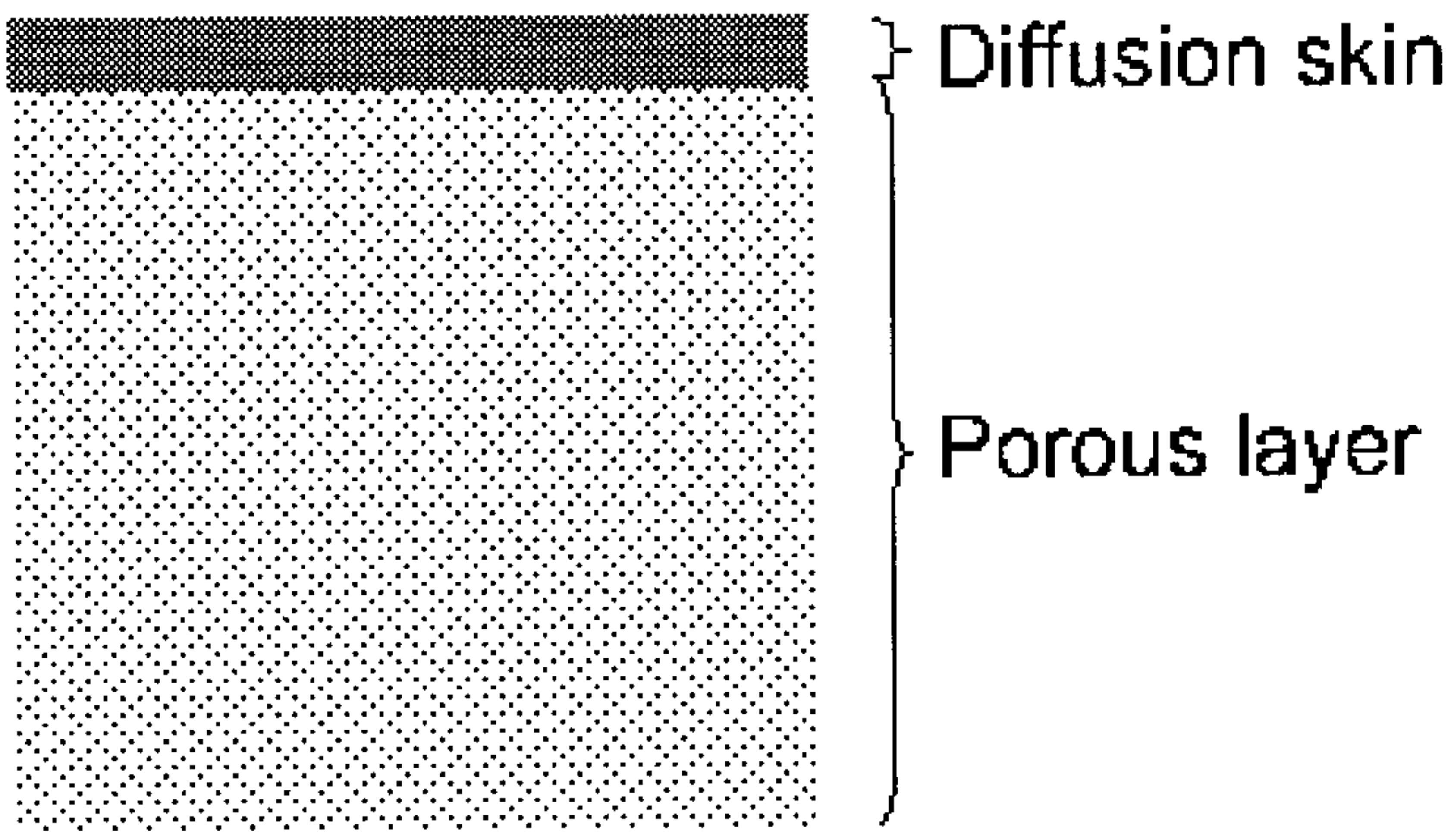


Figure 4

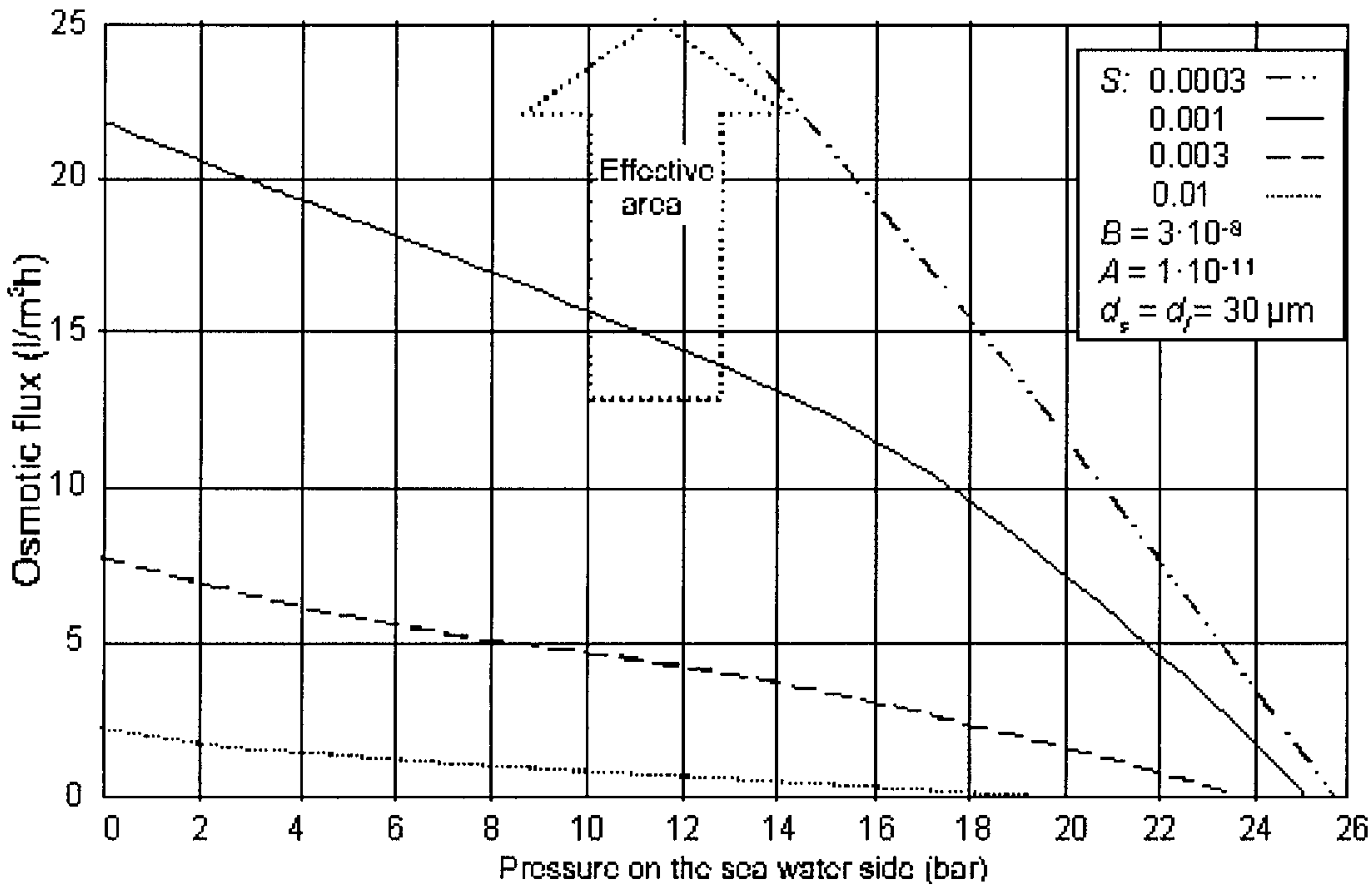


Figure 5

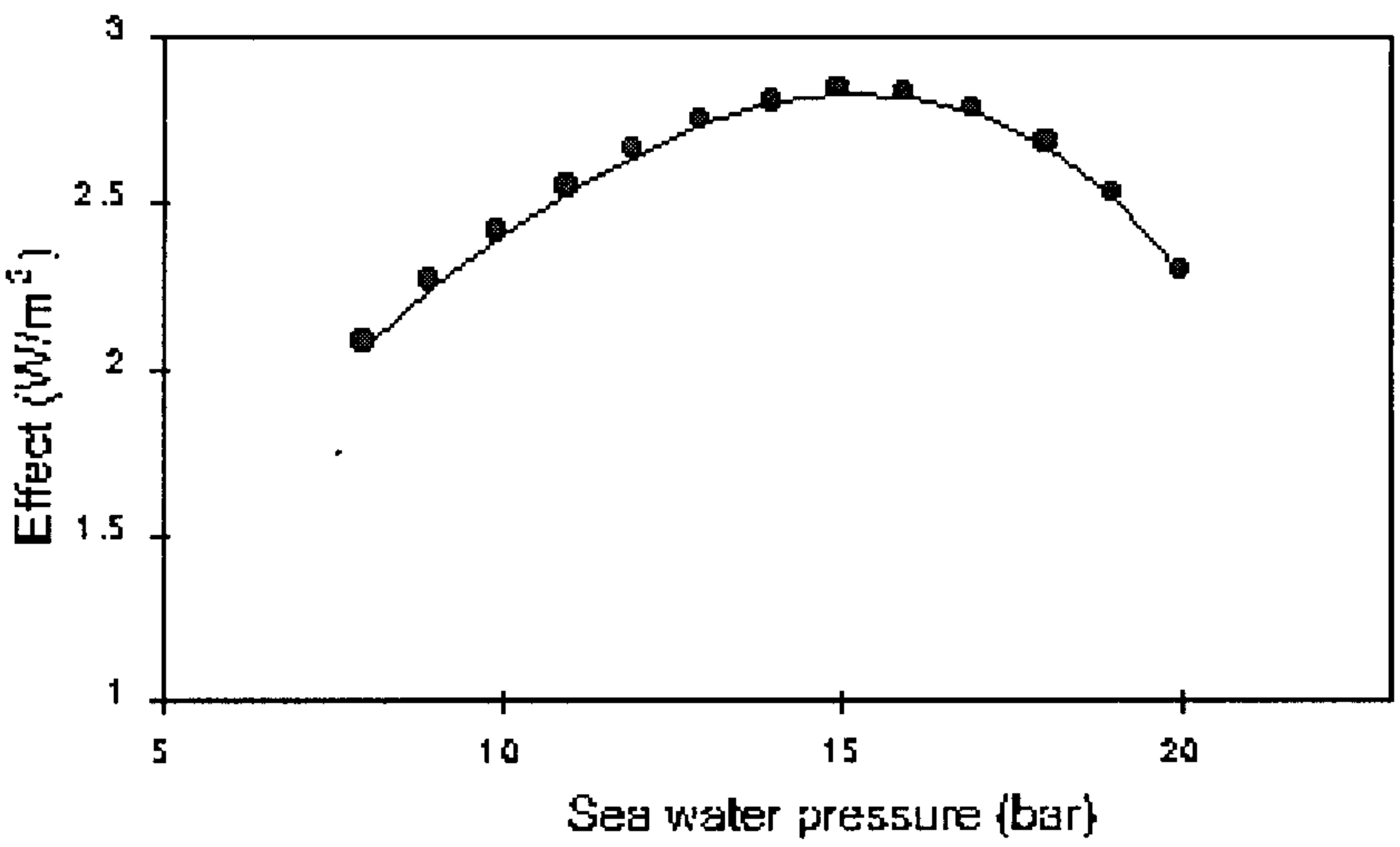


Figure 6

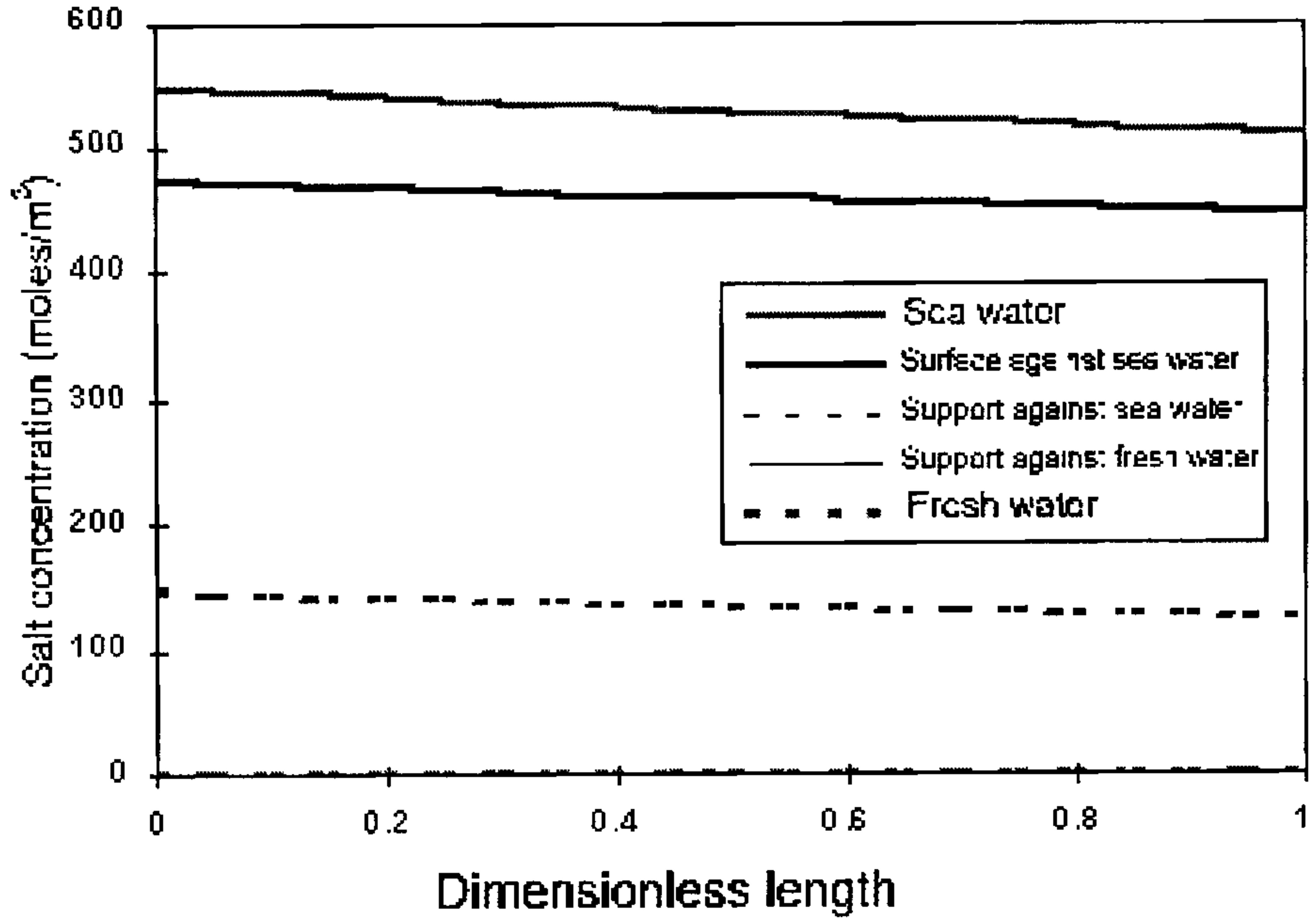


Figure 7

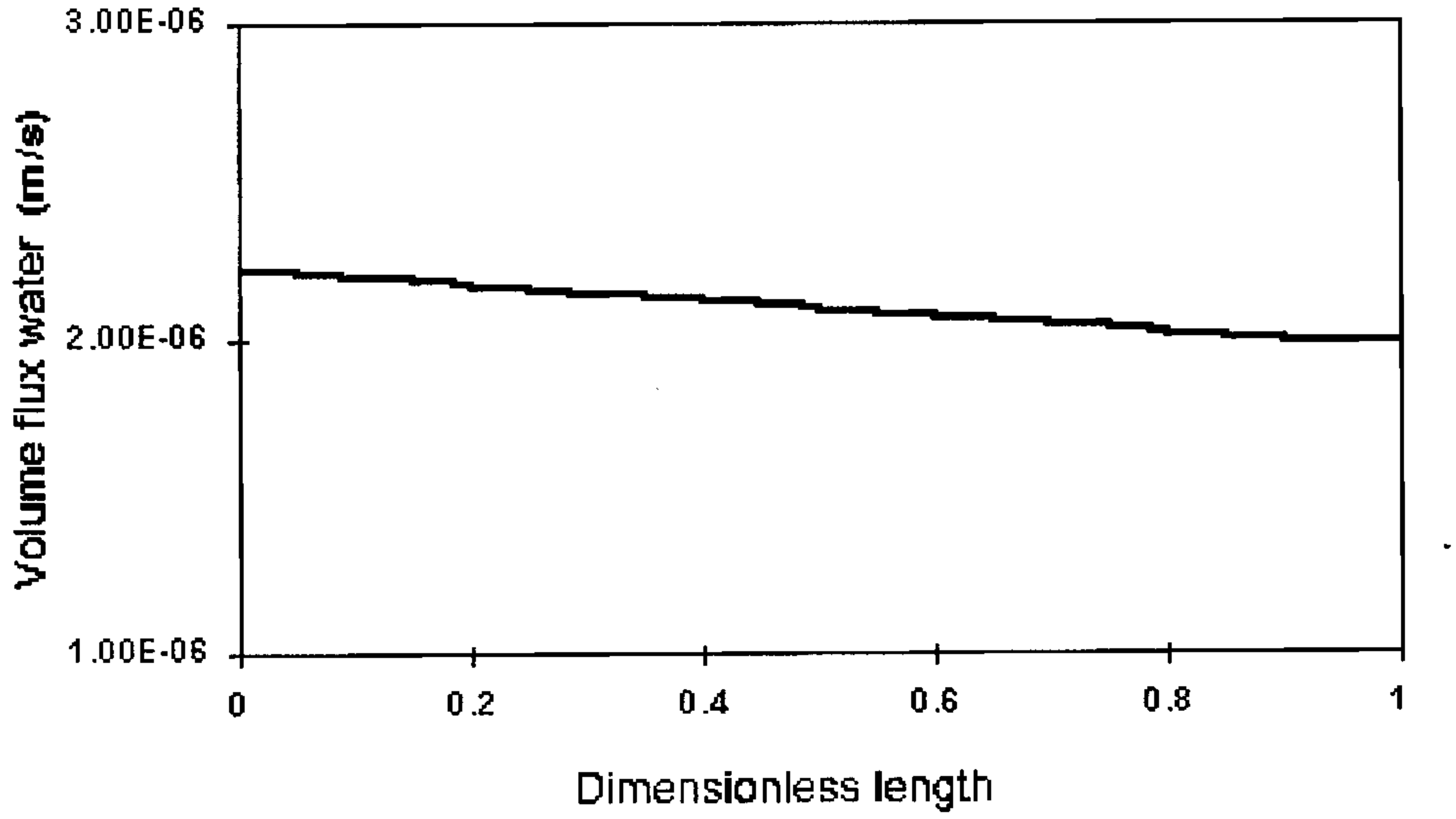


Figure 8

Brackish water
SP
PRESSURE EXCHANGER
WATER FILTER
Sea water
MEMBRANE MODULES
TURBINE
Brackish water
SF
WATER FILTER
Fresh water rest
Fresh water