purified also contain sulphate ions. As a result, therefore, for example the radium present in the water can precipitate out after addition of the barium chloride as $Ba(Ra)SO_4$.

[0005] Corresponding procedures may be found, for example, in the patent publications US 4,636,367, US 4,423,007 and US 4,265,861. However, it is disadvantageous that, e.g., barium chloride is toxic and very expensive. In addition, barium ions, in the event of incomplete precipitation, can be carried over to downstream reverse osmosis appliances. High concentrations of barium ions can lead to damage of the reverse osmosis membranes arranged in the appliances.

[0006] The object of the present invention was to improve markedly the long-practiced procedures for removing radioactive nuclides from deep groundwaters.

[0007] This object is achieved by the method having the features of Claim 1 and the plant having the features of Claim 7. Preferred embodiments of the method according to the invention are cited in dependent Claims 2 to 6. The wording of all claims is hereby incorporated by reference in the contents of the present description.

[0008] The method according to the invention serves for obtaining industrial water or drinking water from water that contains radioactive nuclides such as, e.g., the radium and thorium isotopes mentioned at the outset, in particular from radium-containing groundwater. Industrial water, in contrast to drinking water, is not suitable for consumption, but must nevertheless meet defined quality criteria in order that it can be used in the private, commercial or agricultural sectors. Radioactivity in this regard is an exclusion criterion; a contamination limit of 10 pCi/l, caused by radioactive nuclides, should not be exceeded. In some cases, the limiting value is only 5 pCi/l.

[0009] The method according to the invention always comprises the following treatment steps, namely

- a chemical pretreatment of the radioactive nuclide-containing water and
- filtration of the chemically pretreated water.

[0010] The method according to the invention is particularly characterized in that in the context of the chemical pretreatment, manganese dioxide is added to the water and/or manganese dioxide is generated in situ in the water and in that the filtration of the chemically pretreated water proceeds using a ceramic membrane. This combination of features has proved to be particularly advantageous, whereupon it will be considered further in more detail.

dependence thereon establishing the amount of the manganese dioxide that is to be added. The total required amount of manganese dioxide is therefore preferably, firstly, provided by oxidation of manganese ions already present in the water and secondly by the addition of externally synthesized manganese dioxide.

[0017] Particularly preferably, the membrane used is a microporous membrane.

[0018] The ceramic membrane used is particularly preferably a flat membrane plate having internal filtrate outlet channels and an external porous separation layer. Such membranes are described extensively, for example in DE 10 2006 008 453 A1, the contents of which are hereby incorporated by reference into the contents of the present description.

[0019] It is preferred that, for the present method, membrane plates are used in which the pores of the separation layer have a median diameter between 80 nm and 800 nm, in particular between 100 nm and 300 nm.

[0020] Particularly preferably, in the context of the present method, filtration units are used which comprise a plurality of flat membrane plates. Suitable filtration units are described, for example, in DE 10 2006 022 502 A1. Particularly suitable are the filtration units described in WO 2010/015374, which comprise at least two ceramic filter membranes. The contents of WO 2010/015374 A1 are hereby incorporated by reference into the contents of the present description.

[0021] The ceramic filter membrane used is preferably operated at a reduced pressure (100 mbar to 600 mbar reduced pressure are preferred), but variants are also conceivable in which the ceramic filter membranes are operated at a superatmospheric pressure.

[0022] As already mentioned above, in particular the combination of the addition of manganese dioxide to the radioactive nuclide-containing water and the subsequent filtration using a ceramic filter membrane has proved to be particularly advantageous. With a ceramic filter membrane, the actual separation process takes place exclusively at the surface of the membrane, for which reason a special separation layer is frequently also provided as mentioned above. A problem in this case is, however, that the membrane pores situated at the surface can become blocked very rapidly. In practice, although attempts are made to counteract this by regular backwashing, it is not possible to prevent a layer of separated particles and materials from being deposited on the membrane surface, which layer is constantly becoming thicker during use. For this reason, it was not considered to be conceivable to replace the sand filters that weigh tons described at the outset by substantially more compact ceramic membranes. Sand filters, in contrast to ceramic membranes, do not have pores that

Claims

1. Method for obtaining industrial water or drinking water from water that contains radioactive nuclides, in particular from radium-containing groundwater, which comprises

   - a chemical pretreatment of the radioactive nuclide-containing water and
   - filtration of the chemically pretreated water,

   wherein, in the context of the chemical pretreatment, manganese dioxide is added to the water and/or manganese dioxide is generated in situ in the water and wherein the filtration of the chemically pretreated water proceeds using at least one ceramic filter membrane.

2. Method according to Claim 1, characterized in that the manganese dioxide is obtained by oxidation of an aqueous manganese salt solution set to a pH between 4.5 and 9, in particular between 7 and 9, before it is added to the water.

3. Method according to Claim 1 or Claim 2, characterized in that the concentration of manganese dioxide in the radium-containing water is set to a value in the range between 0.1 ppm and 10 ppm.

4. Method according to any one of the preceding claims, characterized in that the radioactive nuclide-containing water is additionally admixed with a water-soluble barium salt in the pretreatment step.

5. Method according to any one of the preceding claims, characterized in that the ceramic filter membrane is a flat membrane plate having internal filtrate outlet channels and an external porous separation layer, wherein the pores of the separation layer preferably have a median diameter between 80 nm and 800 nm, particularly preferably between preferably 100 nm and 300 nm.

6. Method according to any one of the preceding claims, characterized in that, after the filtration of the chemically pretreated water, the filtrate is purified using at least one pressure-driven membrane separation method, wherein the pressure-driven membrane separation method is preferably a reverse osmosis.

7. Plant for removing radioactive nuclides from water, in particular from radium-containing groundwater, comprising

   - at least one container for the chemical pretreatment of the radium-containing water,

- at least one filtration appliance in order to purify the chemically pretreated water by filtration and also optionally
- a device for carrying out a pressure-driven membrane separation method for further treatment of the water purified by filtration,

wherein the at least one container for the chemical pretreatment of the radium-containing water is coupled to storage containers from which manganese dioxide or a manganese salt and an oxidizing agent can be fed into the container for the chemical pretreatment and wherein the filtration appliance is a device comprising at least one ceramic filter membrane.

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purified also contain sulphate ions. As a result, therefore, for example the radium present in the water can precipitate out after addition of the barium chloride as $Ba(Ra)SO_4$.

[0005] Corresponding procedures may be found, for example, in the patent publications US 4,636,367, US 4,423,007 and US 4,265,861. However, it is disadvantageous that, e.g., barium chloride is toxic and very expensive. In addition, barium ions, in the event of incomplete precipitation, can be carried over to down-stream reverse osmosis appliances. High concentrations of barium ions can lead to damage of the reverse osmosis membranes arranged in the appliances.

[0006] The object of the present invention was to improve markedly the long-practiced procedures for removing radioactive nuclides from deep groundwaters.

[0007] This object is achieved by the method having the features of Claim 1 and the plant having the features of Claim 7. Preferred embodiments of the method according to the invention are cited in dependent Claims 2 to 6.

[0008] The method according to the invention serves for obtaining industrial water or drinking water from water that contains radioactive nuclides such as, e.g., the radium and thorium isotopes mentioned at the outset, in particular from radium-containing groundwater. Industrial water, in contrast to drinking water, is not suitable for consumption, but must nevertheless meet defined quality criteria in order that it can be used in the private, commercial or agricultural sectors. Radioactivity in this regard is an exclusion criterion; a contamination limit of 10 pCi/l, caused by radioactive nuclides, should not be exceeded. In some cases, the limiting value is only 5 pCi/l.

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- filtration of the chemically pretreated water.

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[0018] The ceramic membrane used is particularly preferably a flat membrane plate having internal filtrate outlet channels and an external porous separation layer. Such membranes are described extensively, for example in DE 10 2006 008 453 A1.

[0019] It is preferred that, for the present method, membrane plates are used in which the pores of the separation layer have a median diameter between 80 nm and 800 nm, in particular between 100 nm and 300 nm.

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[0021] The ceramic filter membrane used is preferably operated at a reduced pressure (100 mbar to 600 mbar reduced pressure are preferred), but variants are also conceivable in which the ceramic filter membranes are operated at a superatmospheric pressure.

[0022] As already mentioned above, in particular the combination of the addition of manganese dioxide to the radioactive nuclide-containing water and the subsequent filtration using a ceramic filter membrane has proved to be particularly advantageous. With a ceramic filter membrane, the actual separation process takes place exclusively at the surface of the membrane, for which reason a special separation layer is frequently also provided as mentioned above. A problem in this case is, however, that the membrane pores situated at the surface can become blocked very rapidly. In practice, although attempts are made to counteract this by regular backwashing, it is not possible to prevent a layer of separated particles and materials from being deposited on the membrane surface, which layer is constantly becoming thicker during use. For this reason, it was not considered to be conceivable to replace the sand filters that weigh tons described at the outset by substantially more compact ceramic membranes. Sand filters, in contrast to ceramic membranes, do not have pores that

Claims

1. Method for obtaining industrial water or drinking water from water that contains radioactive nuclides, which comprises

   - a chemical pretreatment of the radioactive nuclide-containing water and
   - filtration of the chemically pretreated water,

   wherein, in the context of the chemical pretreatment, manganese dioxide is added to the water and/or manganese dioxide is generated in situ in the water and wherein the filtration of the chemically pretreated water proceeds using at least one ceramic filter membrane.

2. Method according to Claim 1, characterized in that the water that contains radioactive nuclides is radium-containing groundwater.

3. Method according to Claim 1, characterized in that the manganese dioxide is obtained by oxidation of an aqueous manganese salt solution set to a pH between 4.5 and 9, before it is added to the water.

4. Method of claim 3, characterized in that the aqueous manganese salt solution is set to a pH between 7 and 9.

5. Method according to any one of the preceding claims, characterized in that the concentration of manganese dioxide in the radium-containing water is set to a value in the range between 0.1 ppm and 10 ppm.

6. Method according to any one of the preceding claims, characterized in that the radioactive nuclide-containing water is additionally admixed with a water-soluble barium salt in the pretreatment step.

7. Method according to any one of the preceding claims, characterized in that the ceramic filter membrane is a flat membrane plate having internal filtrate outlet channels and an external porous separation layer, wherein the pores of the separation layer have a median diameter between 80 nm and 800 nm.

8. Method according to claim 7, characterized in that the pores of the separation layer have a median diameter between 100 nm and 300 nm.

9. Method according to any one of the preceding claims, characterized in that, after the filtration of the chemically pretreated water, the filtrate is purified using at least one pressure-driven membrane separation method, wherein the pressure-driven membrane separation method is a reverse osmosis.

10. Plant for removing radioactive nuclides from water, comprising

- at least one container for the chemical pretreatment of the radium-containing water,
- at least one filtration appliance in order to purify the chemically pretreated water by filtration and also optionally
- a device for carrying out a pressure-driven membrane separation method for further treatment of the water purified by filtration,

wherein the at least one container for the chemical pretreatment of the radium-containing water is coupled to storage containers from which manganese dioxide or a manganese salt and an oxidizing agent can be fed into the container for the chemical pretreatment and wherein the filtration appliance is a device comprising at least one ceramic filter membrane.

11. Plant of claim 10, characterized in that the water is radium-containing groundwater.
