

Description

Method for separating radioactive nuclides by means of ceramic filter membranes

5 [0001] The present invention relates to a method for obtaining industrial water or drinking water from water that contains radioactive nuclides.

10 [0002] Water is a precious commodity in many countries, for instance in numerous African and Arabian countries in which complex measures must be taken in order to cover the need for drinking water and industrial water. In Saudi Arabia, for example, considerable amounts of water are extracted from deep wells or provided via seawater desalination plants. A problem, however, is that water from deep wells frequently contains very high fractions of radioactive nuclides and heavy metal salts such as iron and manganese salts. In water from deep wells, in particular the isotopes ^{226}Ra and ^{228}Ra are found, and also ^{228}Th which is bound to the same decay chain. These are formed, in particular, by the decay of naturally occurring uranium. In deep groundwater, 15 the radioactive nuclides are generally either in the form of dissolved ions or are present bound to fine suspended mineral matter.

20 [0003] Deep groundwater is usually purified using reverse osmosis methods, via which the majority of the ionic loading present in the water can be separated off. In order that the reverse osmosis membranes in use are not too severely polluted, usually a plurality of prepurification steps are connected upstream of the reverse osmosis. These are, in particular, filtration steps in which the mentioned suspended particles present in the water and precipitated heavy metal compounds and the radioactive nuclides bound thereto are intended to be separated off. In Saudi Arabia, for this purpose, sand filters weighing tons have been used to date. Such sand filters have diverse disadvantages. 25 They do not achieve their full capacity directly after starting up, but instead they must first be run in with great effort. After some months (generally up to a maximum of 20 months), high amounts of radioactive nuclides have become fixed in the sand filters regularly in such a manner that the filters must be replaced. Regeneration of the filters is not practicable, disposal thereof is problematic solely because of the extremely large 30 amounts of contaminated sand.

[0004] The radium ions or thorium ions contained in the deep groundwater are separated off only inadequately by a sand filter alone. Attempts are therefore made to precipitate out the ions chemically, before the deep groundwater enters into the sand filter. The radioactive precipitate thus produced can then be retained in the sand filter. 35 The most useful variant of the precipitation is the addition of water-soluble barium salts, for example barium chloride. Generally, the deep groundwaters that are to be

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 .

5 [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.

10 [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
15 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
20 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
25 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
30 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.

[0011] Of the two variants cited, relating to the addition of manganese dioxide to the radioactive nuclide-containing water, the first is preferred, that is to say the variant according to which the manganese dioxide is added directly to the water that is to be purified.

5 [0012] Manganese dioxide is particularly suitable that is present as porous precipitate having a particularly large internal surface area (specific surface area $> 350 \text{ m}^2/\text{g}$, determined in accordance with BET). Since manganese dioxide ages and in the process loses porosity, as far as possible it should not be produced until immediately before addition thereof.

10 [0013] Particularly preferably, for this purpose the manganese dioxide used 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. A suitable manganese salt is, for example, manganese sulphate. A suitable oxidizing agent is, for example, potassium permanganate or sodium hypochlorite. It is also possible to adjust the potassium permanganate to be basic, for example using NaOH, and to add the basic potassium permanganate to a slightly acidic manganese sulphate solution. In this manner the stoichiometry of the reaction may be controlled better.

20 [0014] The concentration of manganese dioxide in the water is preferably set to a value in the range between 0.1 and 10 ppm. The optimum value in this case is dependent on the amount of radioactive nuclides present in the water which is to be purified. A great excess of manganese dioxide should be avoided as far as possible, since the manganese dioxide must be separated off again. A slight excess, in contrast, can be advantageous, since in the presence of air, iron and other metal ions present can also be possibly co-adsorbed. However, it is preferred first to separate off the iron, 25 in particular by oxidation, and then to add the manganese dioxide.

[0015] In preferred embodiments, it is possible that the chemical pretreatment of the radioactive nuclide-containing water does not only comprise the mentioned addition of the manganese dioxide. Thus, in particularly preferred embodiments, in addition to the manganese dioxide, a barium salt is also used in the pretreatment. As mentioned at 30 the outset, the barium salt can, e.g., promote the precipitation of radium.

[0016] Furthermore, the addition of further chemicals or of atmospheric oxygen is also conceivable, for example in order to oxidize other metals and metal ions present in the water (e.g. the abovementioned separation of iron by oxidation). In such a measure, generally, also, manganese ions that may also be already present in the water are 35 oxidized. By the oxidation of the manganese ions that are already present in the water, an unwanted excess of manganese dioxide can be produced. This can be avoided by determining the amount of these manganese ions present in the water, and only in

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.

5 **[0017]** Particularly preferably, the membrane used is a microporous membrane.

10 **[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.

15 **[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.

20 **[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.

25 **[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.

30 **[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
35 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

can become blocked, in fact they consist only of a bed of fine sand particles and therefore do not become blocked so readily.

[0023] This problem is able to be countered by using the manganese dioxide mentioned in the chemical pretreatment step for separating off radioactive nuclides.

5 Manganese dioxide is itself porous, in particular if it was produced under the abovementioned conditions. For example, radium ions present in the water that is to be purified can be attached by adsorption in the pores of the added manganese dioxide or on the outer surface thereof. The manganese dioxide is then separated off from the ceramic filter membrane together with these attached ions. Owing to its high inherent
10 porosity, the manganese dioxide layer forming on the surface of the ceramic membrane, however, is more permeable than layers of non-porous substances, and so the ceramic membranes lose efficiency less rapidly and backwashing processes are required less often. A constant high flux results without the ceramic membrane becoming blocked.

15 **[0024]** Owing to the combination of the manganese dioxide addition and the use of a ceramic membrane, frequently results are achieved that are so good that frequently the downstream purification by reverse osmosis that is necessary when sand filters are used can be dispensed with.

[0025] Regardless of the above, it can be preferred that, after the filtration of the
20 chemically pretreated water, the filtrate is further purified using at least one pressure-driven membrane separation method, wherein the pressure-driven membrane separation method is preferably a reverse osmosis. In addition, for example nanofiltration or ultrafiltration can supplement or replace the reverse osmosis.

[0026] It is also possible to mix the water that has been purified by the at least one
25 pressure-driven membrane separation method with water that exits directly from the ceramic membrane.

[0027] The method according to the invention has striking advantages compared with the conventional procedures described at the outset. Firstly, the ceramic membranes used are substantially more compact than the classical sand filters and usually have a
30 markedly higher flux, secondly the problem that generally occurs of the contaminated sand filters that are to be disposed of is avoided. In the context of the present described method, only comparatively small amounts of contaminated manganese dioxide slurries arise, which can be simply disposed of, or optionally even recycled. The filtration using ceramic membranes delivers directly from the start a filtrate without
35 suspended matter and separates off radioactive nuclides, in particular radium, more effectively. The sand filters can only achieve such a quality, if at all, after some weeks

by enrichment effects. In addition, in the case of the sand filters, on backwashing, again MnO_2 and radioactive nuclides are carried over into the filtrate.

[0028] A plant according to the invention for removing radioactive nuclides from water, in particular from radium-containing groundwater, comprises

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- at least one container for the chemical pretreatment of the radioactive nuclide-containing water, and
 - at least one filtration appliance in order to purify the chemically pretreated water by filtration.

10 **[0029]** Optionally it can also comprise a device for carrying out a pressure-driven membrane separation method for further treatment of the water purified by filtration.

15 **[0030]** In this case 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 (which must be able to oxidize the manganese salt to manganese dioxide) can be fed into the container for the chemical pretreatment. The filtration appliance is a device comprising at least one ceramic filter membrane.

20 **[0031]** Containers which are suitable for treating radium-containing water chemically are known to those skilled in the art and need not be described in more detail. The same applies to devices for carrying out pressure-driven membrane separation methods.

[0032] With respect to suitable devices comprising the at least one ceramic filter membrane, reference is made to the abovementioned DE 10 2006 022 502 A1 and WO 2010/015374.

25 **[0033]** In **Fig. 1**, the fundamentals of the method sequence are shown schematically for a preferred embodiment of a method according to the invention. A raw water stream **101** enters into the containers for the chemical pretreatment **102**. Therein, the raw water is first admixed with atmospheric oxygen and the disinfectant chlorine or sodium hypochlorite (e.g. respectively 0.1 to 4 ppm free chlorine), then a manganese dioxide suspension is fed in. After an exposure time, the water admixed with manganese
30 dioxide can be transferred to the filtration tank **103**. Therein, two filtration appliances **104** and **105** are arranged, each of which comprises a plurality of ceramic filter membranes having internal filtrate outlet channels. Here, the manganese dioxide is separated off. The resultant filtrate is then introduced into the reverse osmosis unit **106** and is then purified there. As stated above, however, this is not absolutely necessary.

[0034] Obviously, it is possible that the method according to the invention, in addition to the treatment steps shown in Fig. 1, comprises further purification steps. It can be advantageous, for example, to provide in addition multimedia filters or ion exchangers, in each case dependent on the quality of the water that is to be purified.

Claims

1. Method for obtaining industrial water or drinking water from water that contains radioactive nuclides, in particular from radium-containing groundwater, which comprises
 - 5 • 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
10 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.
- 15 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-
20 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
25 800 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.
- 30 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,

5 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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