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(54) **METHOD AND INSTALLATION FOR THE TREATMENT OF A RADIOACTIVE WASTES**

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(57) **ABSTRACT**

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This invention concerns a method and an installation for the treatment of radioactive wastes produced as a consequence of the operation of nuclear power plants with pressurized water reactors and boron reactivity regulation and will take place for the production of substances like borax with environmentally allowed content of radioactive isotopes that contains only the cesium isotopes with maximum total concentration of 800 Bq in one kilogram of borax; calcium, magnesium or calcium-magnesium borates with environmentally allowed content of radioactive isotopes; boron acid solution with environmentally allowed content of radioactive isotopes; sodium hydroxide solution containing only the cesium isotopes with maximum total concentration of 800 Bq in one kilogram sodium hydroxide; radioactive waste containing under 5 g/l of boron acid.

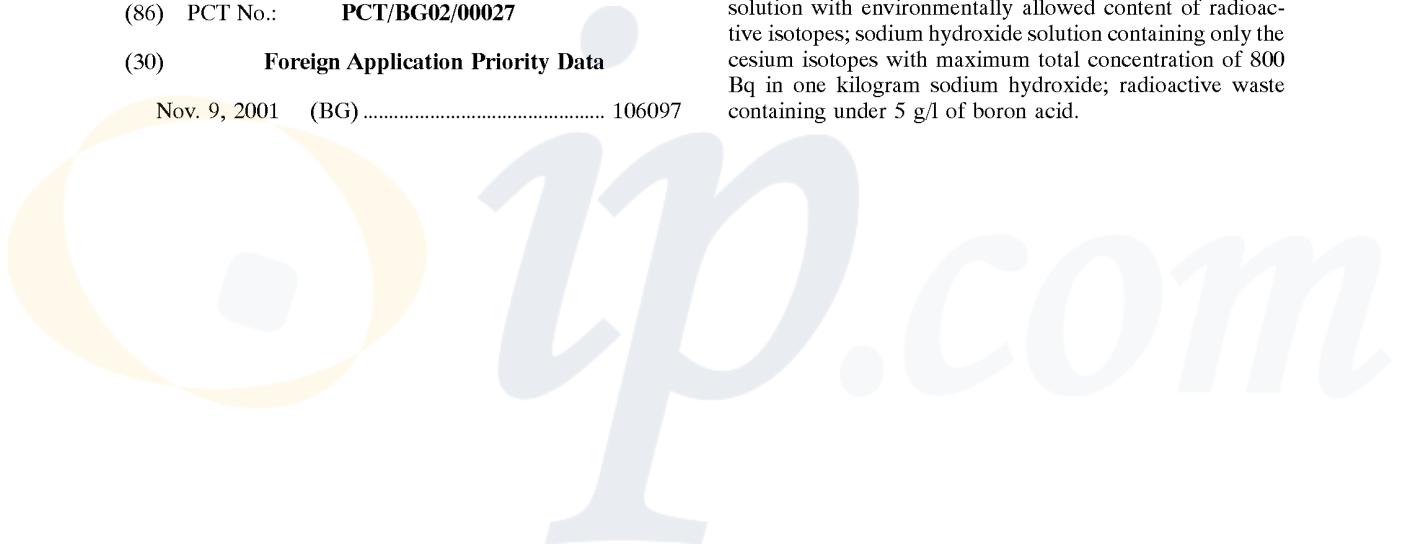
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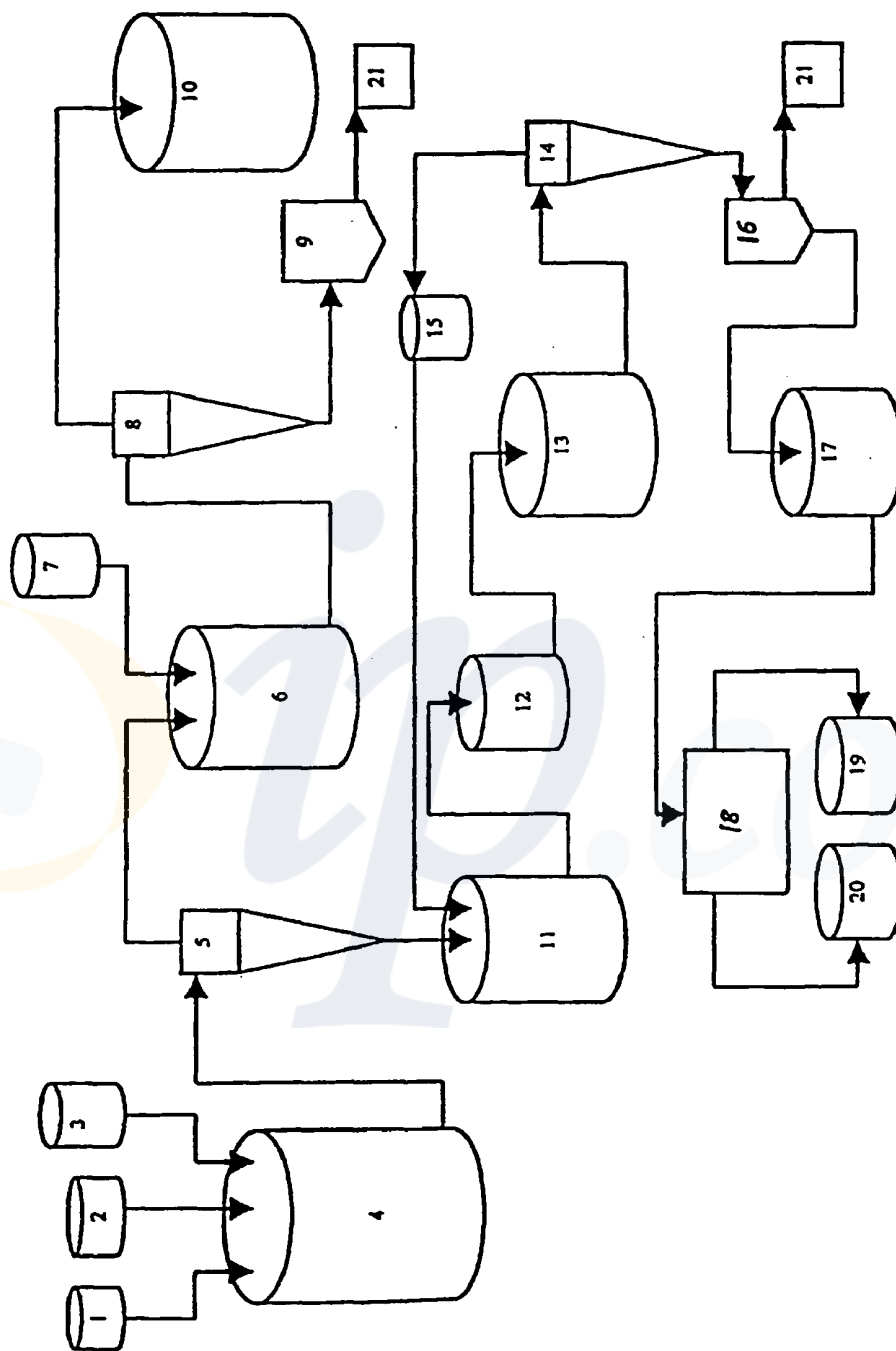


Figure 1

METHOD AND INSTALLATION FOR THE TREATMENT OF A RADIOACTIVE WASTES

TECHNICAL AREA

[0001] The present invention relates to a method and an installation for the treatment of radioactive wastes resulting from the operation of nuclear power plants with pressurized water reactors using boron reactivity regulation and is destined for the yielding of products like borax, calcium-magnesium borates, boron acid and sodium hydroxide solution with allowed content of radioactive isotopes suitable for multiple use and for comprehensive environmental protection.

BACKGROUND OF THE INVENTION

[0002] It is known a method for the treatment of radioactive waste water (BG 32683) that is first converted to an almost dry salt and thereafter treated with alcohols with longer carbon chain. At the treatment of boron acid-containing salts with alcohols begin an esterification of the boron acid and alcohol. The ester so obtained is treated by high temperature (above 100° C.) distillation until boron acid is produced.

[0003] The main shortcoming of this method is that all the processes are running at high temperatures, using longer carbon chain alcohol and applying ester distillation of boron acid with large heat energy consumption. Basically this process is very complicated and labor consuming.

[0004] It is known also a method is known (BG 51265A) for the treatment of radioactive wastes until the obtaining boron acid containing radionuclides with environmentally friendly concentration. The method consists of several stages—concentration of radioactive wastes with different indications of pH—lower than 4.5 and higher than 8.5, and thereafter mixing the concentrates. Under appropriate temperature regime the radioactive waste containing boron acid in concentration of 15-20 g/l and borax in environmentally admissible radioactive isotopes concentration is produced, which is no more a radioactive waste. Boron acid solution is obtained from the borax by means of a suitable technology—ion-exchanging or electro dialysis.

[0005] A shortcoming of this method is the obtaining of the radioactive waste contains 15-20 g/l non-radioactive boron acid, subject to a long-term storage. The final product contains non-radioactive acid, which fills the large capacities in the radioactive waste storage facilities, reduces the concrete matrix strength and allows radioactive isotopes, washing away from the matrix in case of radioactive waste cementation method application.

SUMMARY OF THE INVENTION

[0006] An object of the present invention is to establish a method and an installation for the treatment of liquid radioactive wastes, enabling the preparation of the radioactive wastes for a long-term storage with a minimum non-radioactive boron acid content and the production of environmentally harmless materials appropriate for further use.

[0007] The solution of this problem can be found through a method, by which after the separated collection of acid and alkali radioactive wastes, the separated concentration of radioactive wastes is brought with pH above 8.5 until

reaching a concentration of boron acid from 35 to 200 g/l—on the one hand, and on the other hand—of radioactive wastes with pH under 6.0 not free of boron acid, until the total salt content reaches levels between 400 and 500 g/l. Then the concentrates are mixed in ratio from 0.5:1 to 1:2 based on recalculated values of contained in the wastes gram-equivalent ratio of sodium hydroxide to boron acid. These ratios lead to the achieving of mixture pH from 8.0 to 10.1. If necessary additional pH corrective additives are being used—for example nitrogen acid or other acid, sodium carbonate or sodium hydroxide. The borax separation process runs under these conditions and the boron acid concentration in the mother solution reaches 20-25 g/l. The separate borax crystals are dissolved and filtered so that the joint salt depositions be separated. From refined solution the borax recrystallises with content of radioactive isotopes that allow its storage in standard chemical storage conditions, e.g. radiologically safe for the environment.

[0008] Subsequently the borax crystals filtration process part of the obtained substance at a concentration of 20-25 g/l may be used, or the solution with the same concentration may be prepared from separate borax crystals for treatment by electro dialysis until boron acid solutions in concentration from 0.1 to 60 g/l and sodium hydroxide in concentration up to 150 g/l are obtained. The assembly for electro dialysis operates by means of heat-resistant membranes and electrical current 0.2 to 45 A with voltage from 5.0 to 55 V.

[0009] The base part of the produced radioactive waste (filtrate) containing boron acid in concentration of 20-25 g/l is treated by salts of alkaline-earth metals in which process a non dissolvable borates are obtained. This reaction produces radioactive waste—filtrate containing 2-4 g/l of boron acid.

[0010] As an alkaline-earth metals calcium and magnesium salts or their mixtures are used.

[0011] The substances obtained through this radioactive waste refining method according to this invention are as follows:

[0012] Borax with environmentally allowed content of radioactive isotopes including only cesium isotopes with maximum total concentration of 800 Bq per kilogram borax;

[0013] Calcium, magnesium or calcium-magnesium borates with allowed for the environment content of radioactive isotopes;

[0014] Boron acid solution with environmentally allowed content of radioactive isotopes;

[0015] Sodium hydroxide solution containing only the isotopes of cesium in maximum total concentration of 800 Bq per kilogram sodium hydroxide.

[0016] Radioactive waste containing under 5 g/l boron acid;

[0017] The method according to the present invention was realized with an installation for the treatment of a radioactive waste.

[0018] This installation includes reactor-homogenizer, fed by reservoirs for radioactive wastes connected to it, with pH under 5.5 and pH above 5.5, as well as reservoir for pH correction additives.

[0019] The reactor-homogenizer is also connected with the crystal borax phase separator and liquid radioactive waste containing 20-25 g/l boron acid.

[0020] The liquid radioactive waste runs to a mixer-settling tank that is connected in its upper part with a reservoir for feeding with alkaline-earth metals salt solutions and in its lower part with separator for alkaline-earth borates. From the last the crystal phase of these alkaline-earth borates are subject to rectification in separator and after that feeds the packing unit. The liquid radioactive waste containing 2-4 g/l boron salts feeds the treated radioactive waste reservoir.

[0021] The other product—crystal phase of borax produced by the separator connected with the reactor-homogenizer feeds and is dissolved into a buffer reservoir for the borax solution, passes through filter and is transported to reactor and separator. After that recrystallized borax feeds the separator and the mother solution is collected in a reservoir and is returned in the interim buffer borax solution reservoir.

[0022] One part of the recrystallized borax from separator feeds the packing unit and the other part feeds the reservoir for dissolving once again and after that feeds the electro-dialysis assembly where solutions of boron acid and sodium hydroxide are produced.

[0023] The advantages of this method and the installation for radioactive waste treatment according to the present invention consist in the following:

[0024] suitable to use products are being obtained from the radioactive wastes-borax, calcium-magnesium borates, solution of boron acid and sodium hydroxide with environmentally allowed content of radioactive isotopes;

[0025] the radioactive waste for a long-term storage obtained in result of this method and installation contains very small quantities of boron acid, e.g. does not take large spaces in the radioactive waste storage area with non-radioactive products.

[0026] The present invention is explained by the attached technical scheme of the treatment installation for radioactive waste resulted from the operation of nuclear power plants—**FIG. 1.**

[0027] Marks Explanation Sheet

[0028] The installation consist of the following equipment:

[0029] 1—reservoir for radioactive wastes with pH under 5.5

[0030] 2—reservoir for radioactive wastes with pH above 5.5

[0031] 3—reservoir for correctional additives for pH adjustment

[0032] 4—reactor-homogenizer

[0033] 5—borax crystal phase and liquid radioactive waste separator

[0034] 6—mixer-settling tank

[0035] 7—reservoir for solutions of alkaline-earth metals salts

[0036] 8—borate (calcium and magnesium) separator

[0037] 9—separator

[0038] 10—reservoir for treated radioactive wastes with boron salts concentration about 2-4 g/l.

[0039] 11—buffer reservoir for borax solution

[0040] 12—filter

[0041] 13—reactor-crystallizer

[0042] 14—recrystallized borax separator

[0043] 15—interim reservoir

[0044] 16—borax separator

[0045] 17—reservoir for dissolving of recrystallized borax

[0046] 18—electrodialysis assembly

[0047] 19—boron acid solution reservoir

[0048] 20—sodium hydroxide solution reservoir

[0049] 21—packing unit

[0050] The installation operates as follows:

[0051] Radioactive waste with pH under 5.5 from the reservoir 1 and radioactive waste with pH above 5.5 from the reservoir 2 are mixed in reactor-homogenizer 4 with additives from reservoir 3. In result of interaction, the borax is produced in separator 5. The borax crystal phase is transferred and dissolved in buffer reservoir 11, filtered by the filter 12, transported to the reactor-crystallizer 13 and is transferred in recrystallized borax separator 14. Then it feeds separator 16 for borax separation and is packed in packing unit 21. The mother solution from separator 14 is collected in the reservoir 15 and feeds the buffer reservoir 11 one more time.

[0052] The liquid radioactive waste after borax separation from separator 5 is transported to mixer-settling tank 6 where it mixes with alkaline-earth salts solutions from reservoir 7. After that the borate compounds are being separated in separator 8 and refined in the separator 9 and are packed in packing unit 21. The so obtained in settling tank 6 liquid radioactive waste containing boron salts form 2 to 4 g/l through separator 8 feeds the treated radioactive wastes reservoir 10 for storage.

[0053] Recrystallized borax from separator 16 after dissolving in reservoir 17 feeds the electro-dialysis assembly 18. After that in the reservoir 19 boron acid solutions with concentration up to 60 g/l and in reservoir 20—solutions of sodium hydroxide with concentrations up to 150 g/l are produced.

EXAMPLE FOR IMPLEMENTATION OF THE INVENTION

[0054] The present invention is illustrated by, but is no means limited to the following examples.

Example 1

[0055] A 1 liter radioactive waste with pH 8.0 containing 35 g/l boron acid (boron salts) is mixed with radioactive waste with pH 10.1 until the mixture reaches pH 9.1. Then the borax hard crystal phase separation to the other residual part of liquid radioactive waste 9.0 milliliters solution of calcium nitrate is added in concentration of 900 g/l. The so obtained non-dissolvable calcium borate is separated from the mixture and liquid radioactive waste is subjected to concentration until the waste reaches concentration 2.2 g/l boron acid. Separated calcium borates are subjected several times to washing with water and are separated as not radioactive product. From the separated and recrystallized borax a solution is prepared with concentration 20 g/l and subjected to electro dialysis. In the electro dialysis assembly heat-resistant membranes and a current of 0.35 amperes and voltage 5.2 Volts are used. The obtained products are: boron acid solution in concentration of 10 g/l and sodium hydroxide solution in concentration of 1.5 g/l.

Example 2

[0056] One liter of radioactive waste with pH 10.0 containing 200 g/l boron acid (boron salts) are mixed with radioactive waste with pH 4.0 until the mixture reaches pH 8.2. After borax separation as a hard crystal phase to residual liquid radioactive waste, 9.4 milliliters of magnesium-chloride solution is added in concentration of 500 g/l. The then obtained dissolvable magnesium borates are separated from the mixture and the liquid radioactive waste is concentrated to a 3.4 g/l boron acid.

[0057] Separated borax is set to recrystallisation and from refined borax a solution is prepared with concentration 25 g/l which is treated by electro dialysis means of heat-resistant membranes and current of 45 Amperes and voltage 55 Volts. The obtained products are: boron acid solution in concentration 59 g/l and sodium hydroxide solution in concentration 150 g/l.

1. A method for treatment of radioactive waste resulting from the operation of nuclear power plants with pressurized water reactors and boron reactivity regulation including separated collecting of acids that do not contain boron salts and alkali that contain boron salts radioactive spent waters, separate concentration of liquid radioactive wastes with pH under 5.5 and pH above 5.5, that can be characterized with the fact that radioactive wastes containing boron acid are concentrated at pH above 5.5 until reaching of boron acid from 35 to 200 g/l and radioactive wastes with pH under 5.5 and do not contain boron acid are concentrated until reaching of total salt content of 400 g/l to 500 g/l, after that concentrates are mixed in ratio of recalculated containing in the wastes gram-equivalents sodium hydroxide to boron acid from 0.5:1 to 1:2, which ratio leads to producing of mixture

with pH from 8.0 to 10.1 from which a boron crystallization process is introduced followed by filtering, washing, recrystallization and liberation of crystal borax radioactively harmless to the environment on the one hand and on the other hand liberation of filtrate containing 20-25 g/l of boron acid, a part of which is mixed with alkaline-earth metals salts in which process non-solvable, radioactively harmless to the environment borates of alkaline-earth metals are liberated and liquid radioactive waste containing 2-4 g/l boron acid and the other part of the filtrate with content of 20-25 g/l boron acid and borax solution with the same content of boron acid is treated by electro dialysis until sodium hydroxide production with concentration up to 150 g/l and solution of boron acid in concentration up to maximum 60 g/l.

2. A method according to claim 1 that can be characterized by the fact that as alkaline salts—earth metals calcium and/or magnesium salts and/or their mixtures are used.

3. A method according to claim 1 is characterized by the fact, that electro dialysis solution of borax is implemented by using heat-resistant membranes with a current of 0.2 to 45 Amperes and voltage from 5.0 to 55 Volts.

4. Installation for treatment of radioactive wastes resulted from the operation of nuclear power plants that consist of reactor-homogenizer fed from connected to them reservoirs for radioactive wastes with pH under 5.5, and pH above 5.5 as well as a reservoir for pH correcting additives, separator for the crystal borax phase and liquid radioactive waste, characterized by the fact that liquid radioactive waste containing 20-25 g/l boron acid separated by separator (5) feeds the mixer-settling tank (6) to which upper part is connected reservoir (7) for feeding of alkaline-earth metal salt solutions and in its lower part the mixer-settling tank (6) is connected to borate separator (8) from which the borate crystal phase of alkaline-earth borates runs for refining in the separator (9) and after that feeds the packing unit (21), and liquid radioactive waste containing 2-4 g/l of boron salts feeds the reservoir (10) for treated radioactive wastes, and on the other hand the borax crystal phase that goes out from the separator (5) feeds and dissolves in the reservoir (11), is filtered through filter (12), transported to reactor (13) and separator (14) from which recrystallized borax feeds the separator (16), the mother solution is collected into the interim reservoir (15) and is returned to the buffer reservoir (11) and one part of recrystallized borax from separator (10) feeds the packing unit (21) and the another part of recrystallized borax goes for dissolving in the reservoir (17) or here is submitted solution of borax from the reactor (13) also after that the solved borax feeds the electro dialysis assembly (18) from which after electro dialysis is submitted boron acid solution in the reservoir (19) and sodium hydroxide solution in the reservoir (20).

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