

DESCRIPTION

CRYSTALLIZATION REACTOR

5

TECHNICAL FIELD

[0001]

The present invention relates to technology for a crystallization reactor which treats a crystallization target substance such as fluorine or phosphorus as a poorly soluble salt.

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BACKGROUND ART

[0002]

Conventionally, a crystallization method or the like is used as the method for recovering and reusing poorly soluble salts such as calcium fluoride and calcium phosphate. Examples of the crystallization method, for example in the case where fluorine within a fluorine-containing raw water is recovered as calcium fluoride, include a method in which by introducing the fluorine-containing raw water into a reaction tank and then injecting a calcium preparation, the components are reacted, and calcium fluoride is deposited on the surface of seed crystals inside the reaction tank.

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[0003]

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In a conventional crystallization method, either a

fluidized bed crystallization reactor in which a raw water containing a crystallization target substance such as a fluorine-containing raw water is supplied to the reaction tank as an upward flow, and the crystals of poorly soluble salt inside the reaction tank are treated while flowing through the tank (for example, Patent Document 1), or a stirred crystallization reactor in which a stirrer is provided inside the reaction tank, and the crystals of poorly soluble salt inside the reaction tank are treated while being circulated inside the tank under the stirring action of the stirrer (for example, Patent Document 2) or the like is generally used. Usually, a method is employed in which an extraction step of extracting a portion of the poorly soluble salt crystals from the reaction tank once the poorly soluble salt crystals inside the reaction tank have grown to a certain size, and a replenishment step of supplying fresh seed crystals are performed repeatedly, thus enabling the crystals of the poorly soluble salt to be obtained in a continuous manner.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0004]

Patent Document 1: JP 2003-225680 A

Patent Document 2: JP 2008-73589 A

Patent Document 3: JP 2002-292202 A

Patent Document 4: JP 2009-226232 A

Patent Document 5: JP 2010-207755 A

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SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0005]

However, in a crystallization reactor, in order to ensure recovery of the poorly soluble salt in a high yield, it is important that the surface area of the poorly soluble salt crystals and the like inside the reaction tank is kept high, namely, that the particles of the poorly soluble salt crystals inside the reaction tank are maintained at a small particle size. One possible method for maintaining a small particle size (particle size distribution) for the poorly soluble salt crystals inside the reaction tank would be to supply a large amount of seed crystals having a fine particle size distribution to the tank, but increasing the amount of seed crystals supplied results in a corresponding increase in the treatment costs.

[0006]

Accordingly, an object of the present invention is to provide a crystallization reactor that is capable of recovering a poorly soluble salt in high yield without increasing the amount of seed crystals supplied.

MEANS FOR SOLVING THE PROBLEMS

[0007]

(1) A crystallization reactor of the present invention
5 comprises a stirring device having a stirring blade, a
crystallization reaction tank having a crystallization
reaction unit for adding a calcium preparation to a raw water
containing a crystallization target substance and generating
crystals of a poorly soluble salt, and a water supply device
10 for supplying the raw water to the crystallization reaction
unit, wherein an inner peripheral wall which faces an outer
peripheral wall of the crystallization reaction tank is
disposed inside the crystallization reaction tank, a solid-
liquid separation unit which forms an upward flow between the
15 inner and outer peripheral walls and performs a solid-liquid
separation of the crystals and the treated water is provided
inside the crystallization reaction tank, and the water
supply device supplies the raw water to the crystallization
reaction unit intermittently.

20 [0008]

(2) In the crystallization reactor disclosed in (1)
above, it is preferable that the duration of supply of the
raw water during intermittent water supply by the water
supply device is at least $1/2$ but not more than 5 times the
25 retention time in the solid-liquid separation unit, and the

duration for which supply of the raw water is stopped during intermittent water supply by the water supply device is at least $1/5$ but not more than 1 times the retention time in the solid-liquid separation unit.

5 [0009]

(3) In the crystallization reactor disclosed in (1) above, it is more preferable that the duration of supply of the raw water during intermittent water supply by the water supply device is at least 1 times but not more than 24 times
10 the retention time in the solid-liquid separation unit, and the duration for which supply of the raw water is stopped during intermittent water supply by the water supply device is at least $1/4$ but not more than $1/2$ of the retention time in the solid-liquid separation unit.

15 [0010]

(4) In the crystallization reactor disclosed in any one of (1) to (3) above, it is preferable that a discharge port for discharging the treated water is formed in the outer peripheral wall of the crystallization reaction tank in which
20 the solid-liquid separation unit is provided, the top edge of the inner peripheral wall is either located at the same height as the discharge port, or located at a position that is lower than the discharge port but still enables a portion of the treated water to be discharged from the discharge port,
25 and a portion of the treated water inside the solid-liquid

separation unit flows over the top of the inner peripheral wall and is recycled back into the crystallization reaction unit.

5 ADVANTAGES OF THE INVENTION

[0011]

According to the present invention, a poorly soluble salt can be recovered in high yield without increasing the amount of seed crystals supplied.

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BRIEF DESCRIPTION OF THE DRAWINGS

[0012]

FIG. 1 is a schematic view illustrating one example of a crystallization reactor according to an embodiment of the present invention.

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FIG. 2 is a schematic view illustrating one example of the construction of a crystallization reactor of a reference example.

FIG. 3 is a graph illustrating the particle size distribution of crystals inside the crystallization reaction unit of Example 1.

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FIG. 4 is a graph illustrating the particle size distribution of crystals inside the crystallization reaction unit of Example 2.

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FIG. 5 is a graph illustrating the particle size

distribution of crystals inside the crystallization reaction unit of Example 3.

FIG. 6 is a graph illustrating the particle size distribution of crystals inside the crystallization reaction unit of Example 4.

FIG. 7 is a graph illustrating the particle size distribution of crystals inside the crystallization reaction unit of Comparative Example 1.

FIG. 8 is a graph illustrating the particle size distribution of crystals inside the crystallization reaction unit of Comparative Example 2.

FIG. 9 is a graph illustrating the particle size distribution of crystals inside the crystallization reaction unit of Comparative Example 3.

EMBODIMENTS FOR CARRYING OUT THE INVENTION

[0013]

Embodiments of the present invention are described below. These embodiments are merely examples of implementing the present invention, and the present invention is in no way limited by these embodiments.

[0014]

FIG. 1 is a schematic view illustrating one example of a crystallization reactor according to an embodiment of the present invention. As illustrated in FIG. 1, the

crystallization reactor 1 comprises a crystallization
reaction tank 10, a seed crystal silo 12, a calcium
preparation addition line 14 that functions as one example of
an addition device for adding a calcium preparation to the
5 crystallization reaction tank 10, a raw water supply line 16
and a valve 18 that function as one example of an inflow
device for introducing the raw water into the crystallization
reaction tank 10, a seed crystal addition line 20, a treated
water discharge line 22, and a poorly soluble salt discharge
10 line 24.

[0015]

The raw water supply line 16 from a raw water storage
tank (not shown in the drawing), and the calcium preparation
addition line 14 from a calcium preparation storage tank (not
15 shown in the drawing) are connected to the crystallization
reaction tank 10. Further, the seed crystal addition line 20
is connected between the seed crystal silo 12 and the
crystallization reaction tank 10. Moreover, the treated
water discharge line 22 is connected to a treated water
20 discharge port 21 in the crystallization reaction tank 10,
and the poorly soluble salt discharge line 24 is connected to
a poorly soluble salt discharge port in the crystallization
reaction tank 10.

[0016]

25 A crystallization reaction unit 28 for generating

crystals of a poorly soluble salt, and a solid-liquid separation unit 30 for performing a solid-liquid separation of the poorly soluble salt crystals and the treated water are provided inside the crystallization reaction tank 10. An inner peripheral wall 26 which faces an outer peripheral wall of the crystallization reaction tank 10 is disposed inside the crystallization reaction tank 10, and the space between the outer peripheral wall and the inner peripheral wall 26 functions as the solid-liquid separation unit 30. The inner peripheral wall 26 of the present embodiment is provided inside a prescribed section of the outer peripheral wall of the crystallization reaction tank 10, but the inner peripheral wall 26 may also be provided around the entire inner periphery of the outer peripheral wall.

[0017]

The crystallization reaction unit 28 and the solid-liquid separation unit 30 are separated by the inner peripheral wall 26, but a connection port 32 that interconnects the crystallization reaction unit 28 with the solid-liquid separation unit 30 is formed in a lower section of the inner peripheral wall 26. Further, the aforementioned treated water discharge port 21 is provided in the outer peripheral wall of the crystallization reaction tank 10 where the solid-liquid separation unit 30 is formed, and the treated water discharge line 22 is connected to this treated

water discharge port 21.

[0018]

The crystallization reaction unit 28 of the crystallization reaction tank 10 includes a draft tube 36, and a stirring unit 34 that functions as one example of the stirring device for stirring the fluid inside the crystallization reaction unit 28. The stirring unit 34 comprises a stirring blade 38, and the stirring blade 38 is disposed inside the draft tube 36, and is rotated by the rotational force generated by a motor and transmitted through a stirring shaft.

[0019]

Next is a description of the operation of the crystallization reactor 1 according to the present embodiment.

[0020]

First, the valve 18 of the raw water supply line 16 is opened, and a raw water containing a crystallization target substance such as fluorine or phosphorus (hereafter sometimes referred to as simply "the raw water") is transported through the raw water supply line 16 and into the crystallization reaction unit 28 of the crystallization reaction tank 10. Further, a calcium preparation is added to the crystallization reaction unit 28 through the calcium preparation addition line 14. Moreover, a motor is preferably used to add seed crystals from the seed crystal

silo 12 to the crystallization reaction unit 28 through the seed crystal addition line 20.

[0021]

The crystallization target substance such as the
5 fluorine or phosphorus contained in the raw water reacts with the calcium preparation inside the crystallization reaction unit 28 of the crystallization reaction tank 10, thereby producing calcium fluoride or calcium phosphate (a poorly soluble calcium salt) which is deposited on the surfaces of
10 the seed crystals and generates crystals of the poorly soluble salt (poorly soluble calcium salt).

[0022]

The crystals of the poorly soluble calcium salt such as calcium fluoride or calcium phosphate generated inside the
15 crystallization reaction unit 28 are, for example, periodically extracted from the poorly soluble salt discharge line 24, and discharged outside the system. There are no particular limitations on the method used for extracting the crystals of the poorly soluble calcium salt, and suitable
20 methods include a method in which a slurry pump such as a tube pump is used to extract the crystals of the poorly soluble calcium salt from the crystallization reaction tank 10, and a method in which, as illustrated in FIG. 1, a valve 24a is fitted in the poorly soluble salt discharge line 24,
25 and simple gravity is used to extract the crystals of the

poorly soluble calcium salt from the crystallization reaction tank 10.

[0023]

On the other hand, following the crystallization
5 reaction inside the crystallization reaction unit 28, the treated water flows through the connection port 32 and into the solid-liquid separation unit 30. At this time, a portion of the poorly soluble salt crystals flow into the solid-liquid separation unit 30 together with the treated water,
10 but in the solid-liquid separation unit 30, the treated water following the crystallization reaction forms an upward flow that passes up through the solid-liquid separation unit 30, thereby achieving a solid-liquid separation of the poorly soluble salt crystals contained in the treated water and the
15 treated water. The treated water that has undergone this solid-liquid separation passes through the treated water discharge line 22 and is discharged outside the system as the final treated water of the present embodiment.

[0024]

20 If supply of the raw water to the crystallization reaction unit 28 is continued, then a portion of the crystals of the poorly soluble calcium salt inside the crystallization reaction unit 28 (including poorly soluble calcium salt crystals that were not able to be deposited on seed crystal
25 surfaces) and a portion of the freshly replenished seed

crystals from the seed crystal silo 12 flow into the solid-liquid separation unit 30 together with the treated water generated following the crystallization reaction, and accumulate inside the solid-liquid separation unit 30. Among these crystals and seed crystals, those crystals and seed crystals having a particularly small particle size flow into the solid-liquid separation unit 30 most readily.

Accordingly, as supply of the raw water to the crystallization reaction tank 10 is continued, retention of crystals and seed crystals of small particle size inside the crystallization reaction unit 28 becomes difficult, meaning it becomes impossible to maintain a large surface area per unit of weight of the crystals and seed crystals that exist inside the crystallization reaction unit 28, resulting in a reduction in the recovery rate for the crystals of the poorly soluble calcium salt.

[0025]

Accordingly, in the present embodiment, by supplying the raw water to the crystallization reaction unit 28 intermittently, namely by repeating a water supply step and a step in which water supply is stopped, the recovery rate of crystals of the poorly soluble calcium salt is increased. In the present embodiment, first, supply of the raw water to the crystallization reaction unit 28 is performed, and crystals of the poorly soluble calcium salt are obtained. During this

process, a portion of the obtained crystals of the poorly soluble calcium salt (including seed crystals), and particularly those poorly soluble calcium salt crystals having a small particle size, flow into and accumulate inside the solid-liquid separation unit 30, as described above. However, in the present embodiment, by stopping supply of the raw water to the crystallization reaction tank 10, those crystals of the poorly soluble salt of small particle size that have accumulated inside the solid-liquid separation unit 30 naturally settle, and at least a portion of those crystals and the like are returned to the crystallization reaction unit 28. In order to facilitate the return of the crystals and the like accumulated in the solid-liquid separation unit 30 to the crystallization reaction unit 28, the bottom portion of the solid-liquid separation unit 30 is preferably sloped downward toward the crystallization reaction unit 28.

[0026]

It was generally thought that an operation such as supplying the water intermittently would make it difficult to operate the reactor in a stable manner while maintaining a good recovery rate of the poorly soluble salt crystals, but if the reactor configuration of the present embodiment is employed, and the raw water is supplied intermittently while operating the reactor, then when the supply of the raw water is restarted, because crystals and the like of the poorly

soluble calcium salt of small particle size are retained inside the crystallization reaction unit 28, the surface area per unit of weight of the crystals and the like of the poorly soluble calcium salt inside the crystallization reaction unit

5 28 increases, and the recovery rate of the poorly soluble salt crystals can be increased, without increasing the amount of seed crystals replenished from the seed crystal silo 12.

In the present embodiment, the duration of supply of the raw water and the duration for which supply of the raw water is

10 stopped may be set appropriately to ensure a satisfactory time for generating crystals of the poorly soluble calcium salt and a satisfactory time for achieving natural settling of the crystals and the like retained inside the solid-liquid separation unit 30, and the duration of supply of the raw

15 water and the duration for which the water supply is stopped are preferably set in accordance with the conditions described below.

[0027]

First, the valve 18 of the raw water supply line 16 is

20 opened, and the raw water is supplied to the crystallization reaction unit 28 such that the duration of the supply of the raw water to the crystallization reaction unit 28 is at least $1/2$ but not more than 5 times the retention time in the solid-liquid separation unit 30. Subsequently, the valve 18

25 of the raw water supply line 16 is closed, and the supply of

the raw water to the crystallization reaction unit 28 is stopped so that the duration for which the supply of the raw water to the crystallization reaction unit 28 is stopped is at least 1/5 but not more than 1 times the retention time in the solid-liquid separation unit 30. As a result, sufficient time can be provided for the crystals and the like of the poorly soluble calcium salt of small particle size to settle down inside the crystallization reaction unit 28, and because these crystals are retained inside the crystallization reaction unit 28, the recovery rate for the crystals of the poorly soluble calcium salt can be increased. Because it is mainly crystals of small particle size of 50 μm or less that are retained in a larger number inside the crystallization reaction unit 28, the recovery rate of the poorly soluble calcium salt crystals can be further improved. If the assumption were made that all of the particles inside the reactor were of the same size, then the surface area per particle increases in proportion with the square of the particle diameter, but the number of particles per unit of weight increases in inverse proportion with the cube of the particle diameter. Consequently, the surface area per unit of weight increases in inverse proportion with (particle diameter)³/(particle diameter)² = particle diameter, and therefore by starting and stopping supply of the raw water in accordance with the conditions of the present embodiment, and

increasing the amount of crystals and the like of the poorly soluble calcium salt of small particle size inside the crystallization reaction unit 28, the surface area per unit of weight of the crystals inside the crystallization reaction unit 28 can be increased dramatically, enabling a large improvement in the recovery rate for the poorly soluble salt crystals. Here, the retention time in the solid-liquid separation unit 30 is the retention time of the raw water introduced into the crystallization reaction tank 10, and is represented by the value obtained by dividing the volume of the solid-liquid separation unit 30 by the flow rate of the raw water introduced into the crystallization reaction tank 10. The opening and closing of the valve 18 of the present embodiment may be performed manually or automatically.

[0028]

If the duration of supply of the raw water to the crystallization reaction unit 28 is less than $1/2$ of the retention time in the solid-liquid separation unit 30, then the duration of water supply is too short, the amount of water that can be treated by the reactor decreases, and the efficiency of the recovery of the poorly soluble calcium salt crystals may deteriorate. Further, if the duration of supply of the raw water to the crystallization reaction unit 28 exceeds 5 times the retention time in the solid-liquid separation unit 30, then a large amount of crystals and the

like of the poorly soluble calcium salt of small particle size are discharged from the system, and an adequate amount of the crystals of small particle size may not be able to be retained inside the crystallization reaction unit 28, making it difficult to improve the recovery rate for the poorly soluble calcium salt crystals. If the duration for which the supply of the raw water to the crystallization reaction unit 28 is stopped is less than $1/5$ of the retention time in the solid-liquid separation unit 30, then the crystals of small particle size that have accumulated inside the solid-liquid separation unit 30 are not able to be completely returned to the crystallization reaction unit 28, meaning an adequate amount of the crystals of small particle size may not be able to be retained inside the crystallization reaction unit 28, making it difficult to improve the recovery rate for the poorly soluble calcium salt crystals. Further, if the duration for which the supply of the raw water to the crystallization reaction unit 28 is stopped exceeds 1 times the retention time in the solid-liquid separation unit 30, then the stoppage time is overly long, the amount of water that can be treated by the reactor decreases, and the efficiency of the recovery of the poorly soluble calcium salt crystals may deteriorate.

[0029]

Next, consideration is given to those very fine crystals

and the like of the poorly soluble calcium salt which do not separate from the treated water in the solid-liquid separation unit 30, but rather pass through together with the treated water.

5 [0030]

For example, crystals among the replenished seed crystals which have an overly small particle size, and very fine particles of crystals and the like of the poorly soluble calcium salt that have not been deposited on the surfaces of the seed crystals do not separate in the solid-liquid separation unit 30, but rather flow upward with the treated water under the action of the upward flow, and are discharged outside the system. Generally, these discharged very fine particles are not recovered and are simply disposed of as a sludge, but if these discharged very fine particles were able to be grown to a size that enabled solid-liquid separation, then the amount of sludge generated could be reduced, and the amount of fresh seed crystals supplied could also be reduced. Conventionally, in order to grow these very fine particles that are discharged with the treated water to a particle size that enables solid-liquid separation, methods have been proposed in which the very fine particles within the treated water are returned to the crystallization reaction unit (for example, see JP 2002-292202 A, JP 2009-226232 A and JP 2010-207755 A).

[0031]

In the present embodiment, as shown in the crystallization reactor 1 illustrated in FIG. 1, the top edge of the inner peripheral wall 26 that separates the solid-liquid separation unit 30 and the crystallization reaction unit 28 is set at either the same height as the treated water discharge port 21, or at a position that is lower than the treated water discharge port 21 but still enables a portion of the treated water to be discharged from the treated water discharge port 21.

[0032]

Because the water level in the crystallization reaction unit 28 is generally the same height as the treated water discharge port 21, positioning the top edge of the inner peripheral wall 26 at the same height as the treated water discharge port 21 or at a position lower than that height would cause the crystals and the like of the poorly soluble calcium salt inside the crystallization reaction unit 28 to flow across the top of the inner peripheral wall 26 and into the solid-liquid separation unit 30. However, in the crystallization reactor 1 of the present embodiment, because the reactor is operated in a state of high crystal concentration in order to maintain a high crystal surface area inside the crystallization reaction unit 28, the specific gravity per unit of volume of the fluid inside the

crystallization reaction unit 28 tends to be higher than the specific gravity of the fluid inside the solid-liquid separation unit 30. When a difference in specific gravity is generated between the crystallization reaction unit 28 and the solid-liquid separation unit 30 in this manner, a water level difference develops between the crystallization reaction unit 28 and the solid-liquid separation unit 30. This difference in water level may be a difference of several meters depending on the size and the like of the reactor. Accordingly, if the position of the top edge of the inner peripheral wall 26 is lowered in the present embodiment in the manner described above, then a portion of the treated water inside the solid-liquid separation unit 30 is able to be returned to the crystallization reaction unit 28 without the raw water inside the crystallization reaction unit 28 flowing over into the solid-liquid separation unit 30. As a result, the very fine particles contained in the treated water (including crystals of the poorly soluble calcium salt and seed crystals) can be recycled back into the crystallization reaction unit 28 without using any powered instruments, meaning the particle size distribution of the poorly soluble calcium salt crystals and seed crystals inside the crystallization reaction unit 28 can be kept small. As a result, the recovery rate for the crystals of the poorly soluble calcium salt can be further improved.

[0033]

Next is a description of other conditions and the like associated with the crystallization reactor 1 of the present embodiment.

5 [0034]

In the present embodiment, the point of addition (or injection point) of the calcium preparation and the raw water to the crystallization reaction unit 28 is preferably in the vicinity of the stirring blade 38. By adding the calcium
10 preparation and the raw water in locations in the vicinity of the stirring blade 38, the calcium preparation and the raw water are dispersed immediately upon introduction into the crystallization reaction unit 28, and the calcium preparation concentration and the concentration of the crystallization
15 target substance such as fluorine or phosphorus drop rapidly. As a result, direct deposition of poorly soluble salt that has formed into the liquid is minimized, and the crystallization target substance (such as fluorine or phosphorus) in the liquid can be gradually collected as
20 poorly soluble salt crystals on the seed crystals inside the crystallization reaction unit 28.

[0035]

In the present embodiment, the draft tube 36 is preferably installed so that the stirring blade 38 of the
25 stirring unit 34 is positioned inside the tube. At this time,

the stirring blade 38 is preferably a blade that forms a downward flow. By installing the draft tube 36 in this manner, a downward flow directed toward the bottom of the tube is generated, and a zone having a comparatively high diffusion flow velocity is formed. As a result, the raw water and the calcium preparation and the like can be dispersed more rapidly, and because regions having localized high concentrations of the raw water or the calcium preparation do not contact one another, direction generation of poorly soluble calcium salt particles is suppressed.

[0036]

Furthermore, by installing the draft tube 36 and the stirring blade 38 in the manner described above, a gentle upward flow zone is formed around the outer periphery of the tube. In this zone, the particles are classified such that those particles of small particle size rise up along the outside surface of the tube, and also re-enter the inside of the tube from the top edge of the tube, thereby being recycled into the vicinity of the injection points for the raw water and the calcium preparation, and the stirring zone positioned beneath the injection points. These crystals of small particle size act as nuclei that promote the crystallization reaction, and therefore the recovery rate for the poorly soluble salt crystals can be improved.

[0037]

Moreover, crystals which have grown larger as a result of the crystallization reaction are unable to rise up under the action of the upward flow around the outer periphery of the tube, and because they are also unable to settle downward and re-enter the inside of the draft tube 36, destruction of the grown crystals as a result of collision with the stirring blade 38 can be prevented, which also contributes to an improvement in the recovery rate for the poorly soluble salt crystals.

[0038]

In the present embodiment, an acid or alkali is preferably added as needed to the crystallization reaction unit 28 to adjust the pH of the crystallization reaction liquid in the crystallization reaction unit 28 to a value within a range from 0.8 to 3, and more preferably within a range from 1 to 1.5. By adding an acid or alkali so that operation of the crystallization reaction unit 28 is conducted at a pH within a range from 0.8 to 3, the concentration of the crystallization target substance such as fluorine or phosphorus within the treated water can be reduced.

[0039]

In the present embodiment, the raw water containing the crystallization target substance such as fluorine or phosphorus may be raw water derived from any source, provided

it contains fluorine or phosphorus or the like that can be removed by a crystallization treatment, and examples include raw water discharged from electronics industries including semiconductor-related industries, electric power generation facilities, and aluminum industries, but this is not an exhaustive list.

[0040]

The fluorine or phosphorus or the like that represents the crystallization target substance may exist in the raw water in any state, provided it can be crystallized by a crystallization reaction. From the viewpoint of existing in solution in the raw water, the crystallization target substance is preferably in an ionized state.

[0041]

Examples of the calcium preparation used in the present embodiment include calcium chloride and calcium hydroxide. The form in which the calcium preparation is added may be a finely powdered state or a slurry-like state.

[0042]

The amount of the calcium preparation introduced into the reactor should provide a chemical equivalence of calcium that is typically 0.8 to 2 times or 1 to 2 times, and preferably 1 to 1.2 times, the amount of fluorine or phosphorus. If the chemical equivalent amount of calcium is more than 2 times the chemical equivalent amount of the

fluorine or phosphorus in the raw water, then the calcium fluoride or calcium phosphate is less likely to be deposited on the seed crystals and more likely to form as very fine particles, meaning the treated water may sometimes contain
5 calcium fluoride or calcium phosphate, whereas if the chemical equivalent amount of calcium is less than 0.8 times, then the proportion of fluorine or phosphorus in the raw water that is not converted to calcium fluoride or calcium phosphate increases, meaning the treated water may contain
10 fluorine or phosphorus.

[0043]

In the present embodiment, seed crystals may or may not already exist in the crystallization reaction unit 28 prior to the addition of the raw water and the calcium preparation
15 to the crystallization reaction unit 28. In order to achieve a stable treatment, it is preferable that seed crystals already exist in the crystallization reaction unit 28.

[0044]

Any material may be selected for the seed crystals,
20 provided the material enables the deposition of formed crystals of the poorly soluble calcium salt on the surface of the seed crystals, and examples of suitable materials include filter sand, activated carbon, particles containing oxides of metal elements, such as zircon sand, garnet sand and
25 sakurundum (product name, manufactured by Japan Carlit Co.,

Ltd.), and particles containing poorly soluble calcium salts formed by deposition in a crystallization reaction, but this is not an exhaustive list. From the viewpoint of obtaining a higher purity poorly soluble salt in the form of pellets or the like, particles containing poorly soluble salts formed by deposition in a crystallization reaction are preferred.

Examples of these particles containing poorly soluble calcium salts formed by deposition in a crystallization reaction include fluorite and the like in those cases where calcium fluoride is to be deposited, and rock phosphate and the like in those cases where calcium phosphate is to be deposited.

[0045]

From the viewpoint of achieving a favorable crystallization reaction, the flow rate of the raw water supplied to the crystallization reaction unit 28 is preferably set so that the retention time is within a range from 1 to 4 hours, and more preferably from 2 to 4 hours.

[0046]

From the viewpoint of enabling favorable solid-liquid separation to be performed, the flow velocity (LV) of the treated water flowing through the solid-liquid separation unit 30 is preferably within a range from 0.1 to 2.0 m/h, and more preferably within a range from 0.2 to 1.0 m/h.

[0047]

FIG. 2 is a schematic view illustrating one example of

the construction of a crystallization reactor of a reference example. The crystallization reactor 100 illustrated in FIG. 2 comprises a crystallization reaction tank 110, a seed crystal silo 112, a calcium preparation addition line 114 that functions as one example of an addition device for adding a calcium preparation to the crystallization reaction tank 110, a raw water supply line 116 that functions as one example of an inflow device for introducing the raw water into the crystallization reaction tank 110, a seed crystal addition line 118, a treated water discharge line 120, and a poorly soluble salt discharge line 122.

[0048]

The raw water supply line 116 from a raw water storage tank (not shown in the drawing), and the calcium preparation addition line 114 from a calcium preparation storage tank (not shown in the drawing) are connected to the crystallization reaction tank 110. Further, the seed crystal addition line 118 is connected between the seed crystal silo 112 and the crystallization reaction tank 110. Moreover, the treated water discharge line 120 is connected to a treated water discharge port 111 in the crystallization reaction tank 110, and the poorly soluble salt discharge line 122 is connected to a poorly soluble salt discharge port in the crystallization reaction tank 110.

[0049]

A crystallization reaction unit 126 for generating crystals of a poorly soluble salt, and a solid-liquid separation unit 128 for performing a solid-liquid separation of the poorly soluble salt crystals and the treated water are provided inside the crystallization reaction tank 110. An inner peripheral wall 124 which faces an outer peripheral wall of the crystallization reaction tank 110 is disposed inside the crystallization reaction tank 110, and the space between the outer peripheral wall and the inner peripheral wall 124 functions as the solid-liquid separation unit 128. The inner peripheral wall 124 of the present embodiment is provided inside a prescribed section of the outer peripheral wall of the crystallization reaction tank 110, but the inner peripheral wall 124 may also be provided around the entire inner periphery of the outer peripheral wall.

[0050]

The crystallization reaction unit 126 and the solid-liquid separation unit 128 are separated by the inner peripheral wall 124, but a connection port 130 that interconnects the crystallization reaction unit 126 and the solid-liquid separation unit 128 is formed in a lower section of the inner peripheral wall 124. Further, the aforementioned treated water discharge port 111 is provided in the outer peripheral wall of the crystallization reaction tank 110 where the solid-liquid separation unit 128 is formed,

and the treated water discharge line 120 is connected to this treated water discharge port 111.

[0051]

Furthermore, the top edge of the inner peripheral wall 124 that separates the solid-liquid separation unit 128 and the crystallization reaction unit 126 is set at either the same height as the treated water discharge port 111, or at a position that is lower than the treated water discharge port 111 but still enables a portion of the treated water to be discharged from the treated water discharge port 111.

[0052]

The crystallization reaction unit 126 of the crystallization reaction tank 110 includes a draft tube 134, and a stirring unit 132 that functions as one example of the stirring device for stirring the fluid inside the crystallization reaction unit 126. The stirring unit 132 comprises a stirring blade 136, and the stirring blade 136 is disposed inside the draft tube 134, and is rotated by the rotational force generated by a motor and transmitted through a stirring shaft.

[0053]

Next is a description of the operation of the crystallization reactor 100 according to this embodiment.

[0054]

First, a raw water containing a crystallization target

substance such as fluorine or phosphorus (hereafter also sometimes referred to as simply "the raw water") is transported through the raw water supply line 116 and into the crystallization reaction unit 126. Further, a calcium preparation is added to the crystallization reaction unit 126 through the calcium preparation addition line 114. Moreover, a motor is preferably used to add seed crystals from the seed crystal silo 112 to the crystallization reaction unit 126 through the seed crystal addition line 118.

[0055]

The crystallization target substance such as the fluorine or phosphorus contained in the raw water reacts with the calcium preparation inside the crystallization reaction unit 126 of the crystallization reaction tank 110, thereby producing calcium fluoride or calcium phosphate (a poorly soluble calcium salt) which is deposited on the surfaces of the seed crystals and generates crystals of the poorly soluble salt (poorly soluble calcium salt).

[0056]

The crystals of the poorly soluble calcium salt such as calcium fluoride or calcium phosphate generated inside the crystallization reaction unit 126 are, for example, periodically extracted from the poorly soluble salt discharge line 122, and discharged outside the system. There are no particular limitations on the method used for extracting the

crystals of the poorly soluble calcium salt, and suitable methods include a method in which a slurry pump such as a tube pump is used to extract the crystals of the poorly soluble calcium salt from the crystallization reaction tank 110, and a method in which, as illustrated in FIG. 2, a valve 122a is fitted in the poorly soluble salt discharge line 122, and simple gravity is used to extract the crystals of the poorly soluble calcium salt from the crystallization reaction tank 110.

[0057]

On the other hand, following the crystallization reaction inside the crystallization reaction unit 126, the treated water flows through the connection port 130 and into the solid-liquid separation unit 128. At this time, a portion of the poorly soluble salt crystals flow into the solid-liquid separation unit 128 together with the treated water, but in the solid-liquid separation unit 128, the treated water following the crystallization reaction forms an upward flow that passes up through the solid-liquid separation unit 128, thereby achieving a solid-liquid separation of the poorly soluble salt crystals contained in the treated water and the treated water. The treated water that has undergone this solid-liquid separation passes through the treated water discharge line 120 and is discharged outside the system as the final treated water of

this embodiment.

[0058]

However, crystals among the replenished seed crystals which have an overly small particle size, and very fine particles of crystals and the like of the poorly soluble calcium salt that have not been deposited on the surfaces of the seed crystals do not separate in the solid-liquid separation unit 128, but rather flow upward with the treated water under the action of the upward flow, and are discharged outside the system. Generally, these discharged very fine particles are not recovered and are simply disposed of as a sludge, but if these discharged very fine particles were able to be grown to a size that enabled solid-liquid separation, then the amount of sludge generated could be reduced, and the amount of fresh seed crystals supplied could also be reduced. Conventionally, in order to grow these very fine particles that are discharged with the treated water to a particle size that enables solid-liquid separation, methods have been proposed in which the very fine particles within the treated water are returned to the crystallization reaction unit (for example, see JP 2002-292202 A, JP 2009-226232 A and JP 2010-207755 A).

[0059]

In the present embodiment, as shown in the crystallization reactor 100 illustrated in FIG. 2, the top

edge of the inner peripheral wall 124 that separates the solid-liquid separation unit 128 and the crystallization reaction unit 126 is set at either the same height as the treated water discharge port 111, or at a position that is lower than the treated water discharge port 111 but still enables a portion of the treated water to be discharged from the treated water discharge port 111.

[0060]

Because the water level in the crystallization reaction unit 126 is generally the same height as the treated water discharge port 111, positioning the top edge of the inner peripheral wall 124 at the same height as the treated water discharge port 111 or at a position lower than that height would cause the crystals and the like of the poorly soluble calcium salt inside the crystallization reaction unit 126 to flow across the top of the inner peripheral wall 124 and into the solid-liquid separation unit 128. However, in those cases where crystals of calcium fluoride or calcium phosphate are obtained, the specific gravity per unit of volume of the fluid inside the crystallization reaction unit 126 tends to be higher than the specific gravity of the fluid inside the solid-liquid separation unit 128. For example, in the case where crystals of calcium fluoride are obtained, the weight inside the crystallization reaction unit 126 per 1 L of raw water containing the crystals may be as high as 2.0 kg/L. In

contrast, the specific gravity inside the solid-liquid separation unit 128 is, at most, about 1.0 kg/L to 1.2 kg/L.

[0061]

When a difference in specific gravity is generated
5 between the crystallization reaction unit 126 and the solid-liquid separation unit 128 in this manner, a water level difference develops between the crystallization reaction unit 126 and the solid-liquid separation unit 128. Accordingly, if the position of the top edge of the inner peripheral wall
10 124 is lowered in the present embodiment in the manner described above, then a portion of the treated water inside the solid-liquid separation unit 128 is able to be returned to the crystallization reaction unit 126 without the raw water inside the crystallization reaction unit 126 flowing
15 over into the solid-liquid separation unit 128. As a result, the very fine particles contained in the treated water (including crystals of the poorly soluble calcium salt and seed crystals) can be recycled back into the crystallization reaction unit 126 without using any powered instruments,
20 meaning the particle size distribution of the poorly soluble calcium salt crystals and seed crystals inside the crystallization reaction unit 126 can be kept small. As a result, the recovery rate for the crystals of the poorly soluble calcium salt can be further improved.

25 [0062]

Next is a description of other conditions and the like associated with the crystallization reactor 100 of the present embodiment.

[0063]

5 The raw water containing the crystallization target substance in the present embodiment is a raw water containing fluorine or phosphorus that is removed by crystallization. However, the raw water may be derived from any source, provided it contains fluorine or phosphorus, and examples
10 include raw water discharged from electronics industries including semiconductor-related industries, electric power generation facilities, and aluminum industries, but this is not an exhaustive list.

[0064]

15 The fluorine or phosphorus or the like that represents the crystallization target substance may exist in the raw water in any state, provided it can be crystallized by a crystallization reaction. From the viewpoint of existing in solution in the raw water, the crystallization target
20 substance is preferably in an ionized state.

[0065]

In the present embodiment, the point of addition (or injection point) of the calcium preparation and the raw water to the crystallization reaction unit 126 is preferably in the
25 vicinity of the stirring blade 136. By adding the calcium

preparation and the raw water in locations in the vicinity of the stirring blade 136, the calcium preparation and the raw water are dispersed immediately upon introduction into the crystallization reaction unit 126, and the calcium

5 preparation concentration and the concentration of the fluorine or phosphorus drop rapidly. As a result, direct deposition of poorly soluble salt that has formed into the liquid is minimized, and the fluorine or phosphorus in the liquid can be gradually collected as poorly soluble salt
10 crystals on the seed crystals inside the crystallization reaction unit 126.

[0066]

In the present embodiment, the draft tube 134 is preferably installed so that the stirring blade 136 of the
15 stirring unit 132 is positioned inside the tube. At this time, the stirring blade 136 is preferably a blade that forms a downward flow. By installing the draft tube 134 in this manner, a downward flow directed toward the bottom of the tube is generated, and a zone having a comparatively high
20 diffusion flow velocity is formed. As a result, the raw water and the calcium preparation and the like can be dispersed more rapidly, and because regions having localized high concentrations of the raw water or the calcium
preparation do not contact one another, direction generation
25 of poorly soluble calcium salt particles is suppressed.

[0067]

Furthermore, by installing the draft tube 134 and the stirring blade 136 in the manner described above, a gentle upward flow zone is formed around the outer periphery of the tube. In this zone, the particles are classified such that those particles of small particle size rise up along the outside surface of the tube, and also re-enter the inside of the tube from the top edge of the tube, thereby being recycled into the vicinity of the injection points for the raw water and the calcium preparation, and the stirring zone positioned beneath the injection points. These crystals of small particle size act as nuclei that promote the crystallization reaction, and therefore the recovery rate for the poorly soluble salt crystals can be improved.

[0068]

Moreover, crystals which have grown larger as a result of the crystallization reaction are unable to rise up under the action of the upward flow around the outer periphery of the tube, and because they are also unable to settle downward and re-enter the inside of the draft tube 134, destruction of the grown crystals as a result of collision with the stirring blade 136 can be prevented, which also contributes to an improvement in the recovery rate for the poorly soluble salt crystals.

[0069]

In the present embodiment, an acid or alkali is preferably added as needed to the crystallization reaction tank 110 to adjust the pH of the crystallization reaction liquid in the crystallization reaction unit 126 to a value within a range from 0.8 to 3, and more preferably within a range from 1 to 1.5. By adding an acid or alkali so that operation of the crystallization reaction unit 126 is conducted at a pH within a range from 0.8 to 3, the concentration of the crystallization target substance such as fluorine or phosphorus within the treated water can be reduced.

[0070]

Examples of the calcium preparation used in the present embodiment include calcium chloride and calcium hydroxide. The form in which the calcium preparation is added may be a finely powdered state or a slurry-like state.

[0071]

The amount of the calcium preparation introduced into the reactor should provide a chemical equivalence of calcium that is typically 0.8 to 2 times or 1 to 2 times, and preferably 1 to 1.2 times, the amount of fluorine or phosphorus. If the chemical equivalent amount of calcium is more than 2 times the chemical equivalent amount of the fluorine or phosphorus in the raw water, then the calcium fluoride or calcium phosphate is less likely to be deposited

on the seed crystals and more likely to form as very fine particles, meaning the treated water may sometimes contain calcium fluoride or calcium phosphate, whereas if the chemical equivalent amount of calcium is less than 0.8 times, then the proportion of fluorine or phosphorus in the raw water that is not converted to calcium fluoride or calcium phosphate increases, meaning the treated water may contain fluorine or phosphorus.

[0072]

In the present embodiment, seed crystals may or may not already exist in the crystallization reaction unit 126 prior to the addition of the raw water and the calcium preparation to the crystallization reaction unit 126. In order to achieve a stable treatment, it is preferable that seed crystals already exist in the crystallization reaction unit 126.

[0073]

Any material may be selected for the seed crystals, provided the material enables the deposition of formed crystals of the poorly soluble calcium salt on the surface of the seed crystals, and examples of suitable materials include filter sand, activated carbon, particles containing oxides of metal elements, such as zircon sand, garnet sand and sakurundum (product name, manufactured by Japan Carlit Co., Ltd.), and particles containing poorly soluble calcium salts

formed by deposition in a crystallization reaction, but this is not an exhaustive list. From the viewpoint of obtaining a higher purity poorly soluble salt in the form of pellets or the like, particles containing poorly soluble salts formed by deposition in a crystallization reaction are preferred.

Examples of these particles containing poorly soluble calcium salts formed by deposition in a crystallization reaction include fluorite and the like in those cases where calcium fluoride is to be deposited, and rock phosphate and the like in those cases where calcium phosphate is to be deposited.

EXAMPLES

[0074]

The present invention is described below in further detail using a series of examples and comparative examples, but the present invention is in no way limited by the following examples.

[0075]

(Example 1)

In Example 1, the crystallization reactor illustrated in FIG. 1 was used, and calcium fluoride was recovered from a fluorine-containing raw water under the conditions described below.

[0076]

<Crystallization reactor>

Size of crystallization reaction unit: 130 L (440 mmφ × 880 mmH)

Size of solid-liquid separation unit: 230 L (440 × 590 × 880 mmH)

5 <Test conditions>

Fluorine-containing raw water flow rate: 50 L/h

Fluorine concentration of fluorine-containing raw water: 10,000 mg/L

Calcium preparation: solution containing a 10% slurry of slaked lime dissolved in hydrochloric acid

pH of crystallization reaction unit: pH 2 (adjusted by adding NaOH)

Initial amount of seed crystals in crystallization reaction unit: 20 kg (no subsequent replenishment of seed crystals)

Slurry concentration inside crystallization reaction unit: 30 to 35 v/v% (extracted as appropriate from poorly soluble salt discharge line)

[0077]

20 The retention time in the solid-liquid separation unit in Example 1 was 4.6 h (230(L)/50(L/h)), and the retention time in the crystallization reaction unit was 2.6 h.

[0078]

In Example 1, after supplying the raw water to the crystallization reaction unit for 9.2 hours, supply of the

raw water was stopped for 2.3 hours. This water supply step and this step in which water supply was stopped were repeated until the water supply time reached 400 hours. The flow velocity (LV) of the treated water flowing through the solid-liquid separation unit during water supply was 0.2 m/h. The test was performed using a configuration in which a portion of the treated water in the solid-liquid separation unit was not returned to the crystallization reaction unit.

[0079]

10 (Example 2)

In Example 2, with the exception of supplying the raw water to the crystallization reaction unit for 4.6 hours, and then stopping the supply of raw water for 1.15 hours, testing was conducted under the same conditions as Example 1.

15 [0080]

(Example 3)

In Example 3, with the exception of supplying the raw water to the crystallization reaction unit for 4.6 hours, and then stopping the supply of raw water for 2.3 hours, testing was conducted under the same conditions as Example 1.

[0081]

(Example 4)

In Example 4, a crystallization reactor was used in which the size of the solid-liquid separation unit had been altered to 23 L (440 × 60 × 880 mmH). Further, in Example 4,

the raw water was supplied to the crystallization reaction unit for 0.46 hours, and the supply of raw water was then stopped for 0.23 hours. This water supply step and this step in which water supply was stopped were repeated until the water supply time reached 400 hours. The flow velocity (LV) of the treated water flowing through the solid-liquid separation unit during water supply was 2.0 m/h.

[0082]

(Example 5)

In Example 5, with the exception of supplying the raw water to the crystallization reaction unit for 18.4 hours, and then stopping the supply of raw water for 2.3 hours, testing was conducted under the same conditions as Example 1.

[0083]

(Comparative Example 1)

In Comparative Example 1, with the exception of not stopping the supply of raw water, but rather supplying the raw water continuously to the crystallization reaction unit for 400 hours, testing was conducted under the same conditions as Example 1. The flow velocity (LV) of the treated water flowing through the solid-liquid separation unit during water supply was 0.2 m/h.

[0084]

(Comparative Example 2)

In Comparative Example 2, with the exceptions of using a

crystallization reactor in which the size of the solid-liquid separation unit had been altered to 23 L (440 × 60 × 880 mmH), and not stopping the supply of raw water, but rather supplying the raw water continuously to the crystallization reaction unit for 400 hours, testing was conducted under the same conditions as Example 1. The flow velocity (LV) of the treated water flowing through the solid-liquid separation unit during water supply was 2.0 m/h.

[0085]

10 Table 1 summarizes the flow velocity of the treated water in the solid-liquid separation unit, the duration of supply of the raw water to the crystallization reaction unit, the duration for which supply of the raw water was stopped, and the recovery rate for calcium fluoride after 400 hours of
15 water supply for each of Examples 1 to 5 and Comparative Examples 1 and 2.

[0086]

[Table 1]

	Solid-liquid separation unit LV	Total water supply time	Duration of water supply	Duration for which water supply was stopped	Ratio of duration of water supply relative to retention time in solid- liquid separation unit	Ratio of duration for which water supply was stopped relative to retention time in solid- liquid separation unit	Fluorine recovery rate after 400 hours
units	m/h	h	h	h	times	times	%
Example 1	0.2	400	9.2	2.3	2	1/2	80
Example 2	0.2		4.6	1.15	1	1/4	75
Example 3	0.2		4.6	2.3	1	1/2	95
Example 4	2.0		0.46	0.23	1	1/2	90
Example 5	0.2		18.4	2.3	4	1/2	75
Comparative Example 1	0.2		400	0	-	-	65
Comparative Example 2	2.0		400	0	-	-	50

5 [0087]

(Example 6)

In Example 6, a crystallization reactor was used in which the top edge of the inner peripheral wall of the crystallization reactor illustrated in FIG. 1 was set to the same height as the treated water discharge line, and with the exception of returning a portion of the treated water from the solid-liquid separation unit to the crystallization reaction unit, testing was conducted under the same conditions as Example 1.

[0088]

(Example 7)

In Example 7, with the exception of supplying the raw water to the crystallization reaction unit for 4.6 hours, and then stopping the supply of raw water for 2.3 hours, testing was conducted under the same conditions as Example 6.

[0089]

(Comparative Example 3)

In Comparative Example 3, with the exceptions of using a crystallization reactor in which the top edge of the inner peripheral wall of the crystallization reactor illustrated in FIG. 2 was set to the same height as the treated water discharge line, and not stopping the supply of raw water, but rather supplying the raw water continuously to the crystallization reaction unit for 400 hours, testing was conducted under the same conditions as Example 5.

[0090]

Table 2 summarizes the flow velocity of the treated water in the solid-liquid separation unit, the duration of supply of the raw water to the crystallization reaction unit, the duration for which supply of the raw water was stopped, and the recovery rate for calcium fluoride after 400 hours of water supply for each of Examples 6 and 7 and Comparative Example 3.

[0091]

[Table 2]

	Solid-liquid separation unit LV	Total water supply time	Duration of water supply	Duration for which water supply was stopped	Ratio of duration of water supply relative to retention time in solid- liquid separation unit	Ratio of duration for which water supply was stopped relative to retention time in solid- liquid separation unit	Fluorine recovery rate after 400 hours
units	m/h	h	h	h	times	times	%
Example 6	0.2	400	9.2	2.3	2	1/2	95
Example 7	0.2		4.6	2.3	1	1/2	96
Comparative Example 3	0.2		400	0	-	-	93

[0092]

FIG. 3 is a graph illustrating the particle size
5 distribution of crystals inside the crystallization reaction
unit of Example 1, FIG. 4 is a graph illustrating the
particle size distribution of crystals inside the
crystallization reaction unit of Example 2, FIG. 5 is a graph
illustrating the particle size distribution of crystals
10 inside the crystallization reaction unit of Example 3, FIG. 6
is a graph illustrating the particle size distribution of
crystals inside the crystallization reaction unit of Example
4, FIG. 7 is a graph illustrating the particle size
distribution of crystals inside the crystallization reaction
15 unit of Comparative Example 1, FIG. 8 is a graph illustrating
the particle size distribution of crystals inside the
crystallization reaction unit of Comparative Example 2, and

FIG. 9 is a graph illustrating the particle size distribution of crystals inside the crystallization reaction unit of Comparative Example 3. The particle size distribution of the crystals inside each of the crystallization reaction units was measured by measuring the particle size distribution inside the crystallization reaction unit after 400 hours of water supply using a particle size distribution analyzer (LS230, manufactured by Beckman Coulter, Inc.).

[0093]

In Comparative Example 1, in which calcium fluoride was recovered by continuous supply of the raw water and without replenishing the seed crystals, it is evident from the results shown in FIG. 7 and Table 1 that a large number of crystals with a particle size of 100 μm or greater existed inside the crystallization reaction unit, and the recovery rate was a low value of 65%. Further, in Comparative Example 2, in which the flow velocity of the treated water in the solid-liquid separation unit was increased to 2.0 m/h, it is evident from the results shown in FIG. 8 and Table 1 that a large number of crystals with a particle size of 125 μm or greater existed inside the crystallization reaction unit, and the recovery rate was an even lower value of 50%. In contrast, in the Examples, in which supply of the raw water was conducted intermittently, and specifically in Examples 1 to 5, in which supply of the raw water was conducted for a

duration of at least 1/2 but not more than 5 times the retention time in the solid-liquid separation unit, and supply of the raw water was then stopped for a duration of at least 1/5 but not more than 1 times the retention time in the solid-liquid separation unit, it is evident from the results shown in FIGS. 3 to 6 and Table 1 that a large number of crystals with a particle size of 100 μm or less existed inside the crystallization reaction unit, and a recovery rate of at least 75% that was significantly higher than the recovery rates in Comparative Examples 1 and 2 was able to be obtained. In particular, in Example 3 in which the supply of the raw water was conducted for a duration of 1 times the retention time in the solid-liquid separation unit, and supply of the raw water was then stopped for a duration of 1/2 of the retention time in the solid-liquid separation unit, and in Example 4 in which the supply of the raw water was conducted for a duration of 1 times the retention time in the solid-liquid separation unit, and supply of the raw water was then stopped for a duration of 1/2 of the retention time in the solid-liquid separation unit, it is evident from the results shown in FIG. 5, FIG. 6 and Table 1 that crystals with a particle size of 50 μm or less existed inside the crystallization reaction unit, and a recovery rate of at least 90% that was higher than the recovery rates in Examples 1 and 2 was able to be obtained. In other words, by

conducting the supply of the raw water for a duration of 1
times the retention time in the solid-liquid separation unit,
and stopping supply of the raw water for a duration of 1/2 of
the retention time in the solid-liquid separation unit,

5 crystals of a finer particle size were able to be retained
inside the crystallization reaction unit, and the recovery
rate for the calcium fluoride was able to be further improved.

[0094]

As is evident from the results of Table 2, in Examples 6
10 and 7 in which the supply of the raw water was conducted
intermittently, and a portion of the treated water inside the
solid-liquid separation unit flowed over the top of the inner
peripheral wall and was recycled back into the
crystallization reaction unit, the recovery rate was able to
15 be further improved to a value of 95% or greater.

REFERENCE SIGNS LIST

[0095]

1,100: Crystallization reactor
20 10, 100: Crystallization reaction tank
12, 112: Seed crystal silo
14, 114: Calcium preparation addition line
16, 116: Raw water supply line
18, 24a, 122a: Valve
25 20, 118: Seed crystal addition line

- 21, 111: Treated water discharge port
- 22, 120: Treated water discharge line
- 24, 122: Poorly soluble salt discharge line
- 26, 124: Inner peripheral wall
- 5 28, 126: Crystallization reaction unit
- 30, 128: Solid-liquid separation unit
- 32, 130: Connection port
- 34, 132: Stirring unit
- 36, 134: Draft tube
- 10 38, 136: Stirring blade

CLAIMS

1. A crystallization reactor comprising a stirring device having a stirring blade, a crystallization reaction tank having a crystallization reaction unit for adding a calcium preparation to a raw water containing a crystallization target substance and generating crystals of a poorly soluble salt, and a water supply device for supplying the raw water to the crystallization reaction unit, wherein

an inner peripheral wall which faces an outer peripheral wall of the crystallization reaction tank is disposed inside the crystallization reaction tank, a solid-liquid separation unit which forms an upward flow between the inner and outer peripheral walls and performs a solid-liquid separation of the crystals and the treated water is provided inside the crystallization reaction tank, and

the water supply device supplies the raw water to the crystallization reaction unit intermittently.

2. The crystallization reactor according to Claim 1, wherein a duration of supply of the raw water during intermittent water supply by the water supply device is at least $1/2$ but not more than 5 times a retention time in the solid-liquid separation unit, and a duration for which supply of the raw water is stopped during intermittent water supply

by the water supply device is at least $1/5$ but not more than 1 times the retention time in the solid-liquid separation unit.

5 3. The crystallization reactor according to Claim 1, wherein a duration of supply of the raw water during intermittent water supply by the water supply device is at least 1 times but not more than 4 times a retention time in the solid-liquid separation unit, and a duration for which
10 supply of the raw water is stopped during intermittent water supply by the water supply device is at least $1/4$ but not more than $1/2$ of the retention time in the solid-liquid separation unit.

15 4. The crystallization reactor according to any one of Claims 1 to 3, wherein a discharge port for discharging the treated water is formed in an outer peripheral wall of the crystallization reaction tank in which the solid-liquid separation unit is provided,

20 a top edge of the inner peripheral wall is either located at the same height as the discharge port, or located at a position that is lower than the discharge port but still enables a portion of the treated water to be discharged from the discharge port, and a portion of the treated water inside
25 the solid-liquid separation unit flows over the top of the

inner peripheral wall and is recycled back into the crystallization reaction unit.