

METHOD FOR THE SELECTIVE EXTRACTION OF BORON BY MEANS OF AN ORGANIC SOLVENT FROM SOLUTIONS DERIVED FROM THE ACID ATTACK ON PERMANENT MAGNETS COMPRISING RARE EARTHS

5 FIELD OF THE INVENTION

The invention falls within the general field of boron recycling, originating in particular from used or discarded permanent magnets. More specifically, it concerns a method for solvent extraction of boron contained in a solution resulting from the acid attack of permanent magnets comprising rare earth elements.

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BACKGROUND

The use of rare earth magnets is increasing due to their application in electric vehicle motors, electric scooters, or also wind turbines. The most commonly used rare earth magnets include neodymium-iron-boron (NdFeB) permanent magnets. However, the scarcity of chemical elements constitutive of these magnets and the pollution emitted upon extraction thereof have made their recycling a critical issue.

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Thus, the recovery of rare earths used in the composition of the magnets at the end of their life or still present in the production waste of these magnets, is a determining factor in view of the scarcity of conventional rare earth sources.

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To recover these rare earths, it is essential to separate them from boron during magnet reprocessing operations. The recycling of boron followed by its returning to the market, is thus an important operation. Further, boron being a toxic element, this operation avoids the expensive management of residues which contain it and which are produced during the recycling of magnets.

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Current recycling techniques are essentially based on two processes:

- on the one hand a so-called "short loop" process, in which method the permanent magnets are reduced to a powder, and then directly reformed from this powder,
- on the other hand, a so-called "long loop" process, which consists in the dissolution of the magnets, followed by the separation of the different constituent elements of the magnet.

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The present invention falls within the framework of this second category of process.

To begin with, the recycling starts with the demagnetizing of permanent magnets recovered from end-of-life devices, by heating them to a temperature higher than their Curie temperature.

5 They are then ground into a powder, and then thermally oxidized.

The oxidized powder is then attacked by means of an acid, for example nitric acid, hydrochloric acid, or sulfuric acid, dissolving all or part of the elements.

10 The acid attack solution thus obtained comprises the constituents of permanent magnets, that is, in the case of NdFeB magnets, neodymium, iron, boron, and its traces of other minor constituents, for example other rare earth elements and/or elements such as iron, aluminum cobalt, copper, zinc.

15 From this solution, boron recovery is based on the liquid-liquid extraction technique.

This dissolution method is described, for example, in document WO 96/00698, in which the magnet is oxidized by thermal treatment, then dissolved in a hydrochloric acid solution.

20 On the other hand, there are known from the current state of the art processes in which boron is extracted from aqueous solutions free of rare earths, by means of an organic solvent made of at least one alcohol, or of a diol, diluted in a liquid hydrocarbon mixture.

25 Such a method is for example described in document "*Boron extraction from aqueous medium using novel hydrophobic deep eutectic solvents*", Almustafa et al., 2020, which details the extraction of boron from aqueous solutions originating from wastewater, free of rare earths and iron, by means of eutectic solvents comprising a diol and a monoalcohol.

30 Similarly, in document "*Recovery of boron from unacidified salt lake brine by solvent extraction with 2,2,4-trimethyl-1,3-pentanediol*", Peng et al., 2021, boron extraction is performed from an aqueous solution resulting from brine, free of rare earths and of iron, by means of 2,2,4-trimethyl-1,3-pentanediol.

Such a diol-based extractant system has been applied to magnet reprocessing. After the dissolution, a step of boron extraction which is preceded by a recovery of the rare earths present in the magnet attack solution is described.

- 5 This method is disclosed in document "*Recovery and separation of rare earths and boron from spent Nd-Fe-B magnets*", Liu et al., 2020, which describes boron extraction by means of a solvent made of 2-ethyl-1,3-hexanediol and of sulfonated kerosene, after total precipitation of the rare earths in solution in the form of oxalate.
- 10 This boron extraction method applies to solutions containing no rare earths.

Document "*Separation of fission and corrosion products from boric acid solutions by solvent extraction* ", Narbutt J. et al., 1979, describes a method of liquid-liquid extraction of boric acid dissolved in aqueous solutions resulting from radioactive corrosion and from fission
15 products. It does not concern the extraction of boron originating from used or discarded permanent magnets.

There thus exists a need to develop a method enabling to selectively extract boron from an aqueous solution resulting from the attack of magnets and mainly containing rare earths, with
20 a few traces of other elements.

According to the invention, boron is extracted from an attack solution containing rare earths, which provides a great freedom of choice in processes subsequently implemented to recover and separate rare earths without possible disturbances which would be due to the presence of
25 boron. Indeed, some prior art processes may risk contaminating the rare earths with boron and, further, boric acid has in these solutions a low solubility as compared with rare earth salts, with may limit the parameters of implementation of such processes.

SUMMARY OF THE DISCLOSURE

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The invention, by removing boron, deemed toxic, allows easier management of solid residues which are generated by the recycling of rare earth magnets. It thus contributes more to compliance with environmental constraints.

The invention thus concerns a method of extracting boron contained in an aqueous solution A1 comprising rare earth elements, aqueous solution A1 resulting from the dissolution of a powder of NdFeB magnets, or of machining scrap resulting from the manufacturing of permanent magnets. In the method of the invention, aqueous solution A1 is brought into
 5 contact and mixed with an organic solvent comprising at least one extraction compound made of an alcohol, comprising a chain of from 6 to 18 carbon atoms, aliphatic or aromatic, linear or branched, the contacting and the mixing of aqueous solution A1 and of the organic solvent causing the transfer of boron from said aqueous solution A1 to said organic solvent.

10 The present invention can only be implemented with compounds comprising a number of carbon atoms greater than or equal to 6, or smaller than or equal to 18. Indeed, below 6 carbon atoms, hydrocarbons are gaseous, while above 18 carbon atoms, they are solid waxes or tars.

The steps of contacting and mixing of aqueous solution A1 and the organic solvent cause the
 15 transfer of boron from said aqueous solution A1 to said organic solvent.

"Boron" includes any compound comprising at least one boron atom, present in aqueous or organic phase. For example, boric acid is included in the definition of "boron" according to
 20 the invention.

In the sense of the invention, "alcohol" designates all compounds comprising at least one alcohol function, which includes monoalcohols and diols.

In the present invention, "borate" designates a molecular compound comprising at least one
 25 boron atom and at least one oxygen atom. For example and without this being a limitation, the metaborate BO_2^- and tetraborate $\text{B}_4\text{O}_7^{2-}$ ions are borates.

"Boron salt" includes borate salts. For example and without this being a limitation, sodium metaborate NaBO_2 and sodium tetraborate $\text{Na}_2\text{B}_4\text{O}_7$ are boron salts. Sodium tetraborate
 30 pentahydrate $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ or decahydrate $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, which are also called borax, are boron salts.

Preferably, the extraction compound is selected from the group comprising:

- 1-3 diols, preferably from among 2-ethyl-1,3-hexanediol (EHD), 2-butyl-2-ethylpropane-1,3-diol (BEPD), 2,2,4-trimethyl-1,3-pentanediol (TMPD), 2-chloro-4-(1,1,3,3-tetramethylbutyl)-6-methylol-phenol (CTMP), and their mixtures;
- 5 - monoalcohols of from 6 to 18 carbon atoms, with a branched or linear aliphatic chain, preferably from among 2-ethylhexanol (2-EH), 2-propylheptanol (2-PH), 2-butyloctanol, isodecanol, octanol, and their mixtures.

"1-3 diol" designates a chemical compound which comprises two alcohol functions carried by
 10 two carbon atoms separated from each other by another carbon atom. These compounds are also known as " β -diols".

"Monoalcohol" designates a chemical compound which comprises a single alcohol function.

15 In addition to the extraction compound, the organic solvent may also comprise at least one diluent compound. The diluent compound is preferably formed of a hydrocarbon chain of from 6 to 18 carbon atoms, aliphatic or aromatic.

20 Preferably, the diluent compound is selected from the group comprising: decane and its isomers, dodecane and its isomers, kerosene, toluene, hydrocarbons having from 6 to 18 carbon atoms, aliphatic or aromatic, paraffines, cycloparaffines, and their mixtures. As a diluent compound, Shellsol[®]D70 (aliphatic hydrocarbon), Solvesso[®]150 (aromatic hydrocarbon) can for example be mentioned.

25 Preferably, the diluent compound is a liquid substance having the extraction compound dissolved therein.

According to an embodiment, the organic solvent further comprises a modifier compound, different from the extraction compound. The modifier compound is preferably made of an
 30 alcohol comprising an aliphatic chain of from 6 to 18 carbon atoms.

Preferably, the modifier compound is selected from the group comprising monoalcohols, preferably from among decan-1-ol, octan-1-ol, isodecan-1-ol, hexan-1-ol, dodecan-1-ol, 2-propylheptanol, 2-ethylhexanol, and their mixtures.

- 5 In the sense of the invention, "modifier compound" designates a chemical species other than the extraction compound and the diluent compound, likely to alter certain properties of the organic solvent.

For example, the modifier compound may delay the occurrence of a third phase or aid the
10 decantation of the organic solvent and of the aqueous solution.

It can be dissolved in the diluent compound.

In a specific embodiment of the invention, the organic solvent comprises:

- 15 - from 10% to 100% of at least one extraction compound,
- from 0% to 90% of at least one diluent compound,
- from 0% to 70% of at least one modifier compound,
by weight relative to the total weight of the organic solvent, the total being equal to 100%.

20 According to an embodiment, the organic solvent comprises at least 5%, or even 20%, or even 30%, or even 40%, or even 50%, of at least one extraction compound. The organic solvent may comprise at most 90%, or even 80%, or even 70%, or even 60% of at least one extraction compound.

25 According to an embodiment, the organic solvent comprises at least 5%, or even 20%, or even 25%, or even 30%, or even 40%, or even 50%, of at least one diluent compound. The organic solvent may comprise at most 95%, or even 80%, or even 70%, or even 60%, or even 55% of at least one diluent compound.

30 According to an embodiment, the organic solvent comprises at least 5%, or even 10%, or even 20%, or even 25%, or even 30%, or even 40%, of at least one modifier compound. The organic solvent may comprise at most 80%, or even 70%, or even 60%, or even 50% of at least one modifier compound.

According to the invention, the organic solvent is brought into contact with the aqueous solution A1 comprising rare earth elements and boron.

According to the invention, this aqueous solution A1 is a solution resulting from the acid
 5 attack of demagnetized neodymium-iron-boron (NdFeB) permanent magnets or from machining scrap resulting from the manufacturing of permanent magnets, reduced to powder and oxidized. Preferably, it has a pH in the range from 0.5 to 3.5.

"Solution resulting from the acid attack of magnets" designates a solution obtained as a result
 10 of the dissolution of a magnet powder, in particular an NdFeB magnet, in a solution of acid, for example nitric acid, hydrochloric acid, or sulfuric acid. This powder results from the demagnetization, grinding, and oxidation of permanent magnets.

"Machining scrap" designates scrap material created on manufacturing of permanent magnets.
 15 It contains the same constituents as the magnets, that is, iron, boron, and rare earth elements.

In particular, one mainly finds, by mass, Nd (from 14% to 26%), then Pr (from 0% to 9%), Dy (from 0% to 6%), Tb (from 0% to 1%), Ce (from 0% to 6%). One does not find Sc, Y, Tm, Yb, Lu, in NdFeB magnets. A typical composition of an NdFeB magnet is for example, by
 20 mass: 65% Fe, 24% Nd, 2.5% Pr, 4.25% Dy, 1% B, 5% Co.

This aqueous solution A1 preferably comprises:

- from 20 to 450 g/L of rare earth elements in the form of dissolved salt,
- from 1 to 9 g/L of boron in the form of boric acid,
- 25 - from 0 to 20 g/L of iron in the form of dissolved salt, and
- from 0 to 5 g/L of metal elements in the form of dissolved salt belonging to the group comprising cobalt, aluminum, zinc, copper, manganese, and nickel.

According to the invention, these rare earth elements are selected from the group comprising:
 30 lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, and their mixtures.

In particular, solution A1 may comprise between 0 g/L and 1 g/L of cobalt, between 0 g/L and 1 g/L of copper, between 0 g/L and 1 g/L of aluminum, and/or between 0 g/L and 0.5 g/L of zinc in the form of dissolved salt.

- 5 In particular, dissolved salts of rare earth elements belong to the group comprising rare earth nitrates, rare earth chlorides, rare earth sulfates, and their mixtures.

Ideally, the method according to the invention thus comprises a step of bringing into contact of the organic solvent and of aqueous solution A1, preferably with a ratio between their
10 respective volumes in the range from 1 to 10.

The contacting and the mixing are implemented in a liquid-liquid extraction device. Preferably, the duration of the mixing is in the range from 1 to 15 minutes, preferably from 3 to 5 minutes.

- 15 The mixing is followed by a separation step performed, for example, by decantation of aqueous solution A1 and of the organic solvent.

The contacting and the mixing are preferably carried out at a temperature in the range from 20°C to 70°C, preferably from 40°C to 60°C.

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A boron-enriched solvent and a boron-depleted aqueous raffinate are thus obtained.

Advantageously, the boron concentration in this solvent is in the range from 1 g/L to 14 g/L.

- 25 The selectivity of the boron extraction is such that the concentrations in rare earths, iron, aluminum, cobalt, copper, and zinc are lower than 10 mg/L therein.

This extraction operation is advantageously performed in counter-current flow over a plurality of stages, in mixer-settler batteries or in agitated or pulsed columns.

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After the boron transfer, the boron concentration in the aqueous raffinate is typically lower than 30 mg/L. This corresponds to a boron extraction rate greater than 95%. The quantities of rare earths, iron, aluminum, cobalt, copper, and zinc exiting in the raffinate are equal to those entering the initial aqueous solution A1. The targeted residual boron content is selected
5 according to environmental constraints.

If need be, the method may be adapted in such a way as to have a boron content lower than 30mg/L in the aqueous solvent.

10 Further, the method comprises, after the boron transfer, a step re-extraction of the boron present in the organic solvent. Preferably, this step of boron re-extraction is carried out by bringing a Brönsted base into contact with said solvent, the base being advantageously selected from the group comprising: NaOH, KOH, LiOH, NH₄OH, and their mixtures. The boron can then be recovered in the form of alkaline borate obtained from these solutions.

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Generally, the base has a concentration in the range from 0.1 to 2 mol/L.

In the sense of the invention, "re-extraction" designates a liquid-liquid extraction enabling to transfer from the organic solvent to an aqueous phase the boron already extracted by means
20 of said solvent.

Here, the boron contained in the organic solvent is transferred to the aqueous phase containing the base. Thus, the recovered solvent is virtually boron-free. Preferably, it has a boron concentration lower than 10 mg/L.

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The method of the invention may further comprise a step of recovery of boron in the form of boron salt from boric acid present in the organic solvent. This boron recovery step comprises the following sub-steps:

- a) bringing into contact of a basic aqueous solution A2 with the organic solvent to extract
30 the boron in the form of solubilized borate into basic aqueous solution A2;
- b) distillation of the borate-laden basic aqueous solution A2 to concentrate the solution, generating a distillate;
- c) crystallization of the borate in the form of hydrated boron salt;

- d) solid-liquid separation of the crystallized hydrated boron salt, generating crystallization mother water;
- e) reintroduction of the distillate and of the crystallization mother water at the step of bringing into contact of basic aqueous solution A2 with the organic solvent.

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The crystallized hydrated boron salt, recovered in solid form, may be re-used in various sectors of industry, for example in the industry of glass (borosilicate glass), of ceramic (boron nitride), of metallurgy (steel flux), or medical products (antiseptics).

- 10 Steps a) to e) are advantageously carried out in a closed loop, to allow the continuous flow of aqueous solutions, for their recycling. In this embodiment, the water introduced into the method flows in a loop therein. Further, the method consumes no additional water than that which is initially introduced and recycled.

- 15 In parallel, all traces of organic solvent present in aqueous phase are entirely recycled and recovered.

This enables to recover, advantageously, more than 99% of the boron contained in the organic solvent. The produced solid borate has, advantageously, a purity higher than 99%.

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Sub-step a)

The organic solvent comprises, at this stage, boric acid at a boron concentration generally in the range from 1 mg/L to 14 g/L, preferably from 1 g/L to 14 g/L.

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Advantageously, basic aqueous solution A2 is prepared by dilution of a concentrated basic solution or by solubilization of a solid basic compound.

- 30 Preferably, it is a solution of NaOH, KOH, LiOH, or NH₄OH. The selection of the base depends on the boron salt to be produced, for instance a NaOH solution will allow the forming of sodium borate. Similarly, a KOH solution will be selected to obtain potassium borate.

Preferably, basic aqueous solution A2 is introduced in a stoichiometric quantity with respect to the quantity of boron salt to be produced

Thus, the number of moles of alkaline or of ammonium added determines the structure of the final product. For example, to produce sodium tetraborate $\text{Na}_2\text{B}_4\text{O}_7$, 0.5 mol. NaOH are introduced for 1 mol. of boron present in the organic solvent. Similarly, 1 mol. NaOH will have to be introduced for 1 mol. of boron to generate sodium metaborate NaBO_2 .

The basic solution is thus not introduced in excess. Thereby, the consumption of alkaline product is decreased.

Advantageously, the ratio of the number of alkaline or ammonium moles of the basic solution to the number of boron moles of the organic solvent is in the range from 0.3 to 1.

During the step of bringing into contact of the aqueous basic solution A2 with the organic solvent, the boric acid present in the solvent is transferred from the organic phase to the aqueous phase. A borate-laden basic aqueous solution is thus obtained.

Sub-step a) of bringing into contact the aqueous basic solution A2 with the organic solvent is, preferably, carried out in a device comprising a plurality of stages, where the organic solvent and the aqueous basic solution A2 flow in opposite directions.

For this purpose, the two liquids are circulated at different flow rates, such that the ratio of the flow rate of the aqueous basic solution to the flow rate of the organic solvent can be in the range from 0.1 to 2, preferably from 0.1 to 1, and more preferably still from 0.1 to 0.5. These flow rate ratios enable to minimize the quantity of water flowing in the method and to optimize the power consumption of the method.

According to a variant, this step is carried out at a temperature in the range from 20°C to 70°C, preferably from 40°C to 60°C. These temperature ranges are optimized for a ratio of the flow rate of the aqueous basic solution to the flow rate of the organic solvent in the range from 0.1 to 2.

Sub-step b)

During sub-step b), the aqueous basic solution A2 comprising the solubilized borate is advantageously submitted to a step of concentration by distillation generating a distillate. This step is carried out at a temperature in the range from 20°C to 110°C, preferably from 30°C to 105°C, and at an absolute pressure in the range from $2 \cdot 10^4$ Pa to 10^5 Pa, preferably. The concentration of the solution enables to obtain a borate-saturated solution.

Sub-step c)

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Crystallization sub-step c) is advantageously carried out by distillation of the borate-concentrated aqueous basic solution A2, or by cooling of the borate-concentrated aqueous basic solution A2.

15 The crystallized solid is then in suspension in the solution. This distillation is implemented to obtain the desired quantity of crystallized solid in suspension. This step is carried out at a temperature in the range from 20°C to 110°C, preferably from 30°C to 105°C, and at an absolute pressure in the range from $2 \cdot 10^4$ Pa to 10^5 Pa, preferably.

20 The temperature at which the distillation is performed determines the degree of hydration of the produced boron salt. For example, for a temperature in the range from 20°C to 60°C, borax decahydrate $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ is obtained. However, borax pentahydrate $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ is obtained for a temperature in the range from 60°C to 100°C.

25 According to another variant of the invention, the crystallization of borate is achieved by cooling of the borate-concentrated aqueous basic solution, so that the solubility of the boron salt in solution decreases. In this case, the solution is cooled according to a temperature gradient from 10°C to 40°C per hour.

30 The borate suspension may be heated to obtain a partial re-solubilization of borate and then submitted to a new cooling to form a borate suspension again, this operation forming a crystallization cycle. Between 1 and 3 crystallization cycles may be carried out, preferably 1 to increase the purity of the crystallized borate.

These two crystallization processes, respectively distillation and cooling, enable to remove solvent traces remaining in the solid to the crystallization mother water.

5 "Solvent traces" designates small quantities of extraction compound, and/or of modifier compound and/or of diluent compound.

Further, the distillation performed during the step of concentration and possibly of crystallization generates a distillate, which generally contains less than 1% by mass of solvent traces.

10 This distillate is advantageously recirculated in the method and/or mixed with the aqueous basic solution A2 during the step of bringing into contact the aqueous basic solution A2 with the organic solvent. Indeed, the distillate dilutes the concentrated basic solution or solubilizes the solid basic compound.

15 After the crystallization step, the borate crystal suspension may be submitted to a maturation suspension, lasting for from 30 minutes to 2 hours, preferably 1 hour. This duration enables the solution to reach a thermodynamic balance.

20 Sub-step d)

According to sub-step d), the crystals of hydrated boron salt are advantageously recovered by carrying out a solid-liquid separation step. Solid-liquid separation methods include, without this being a limitation, distillation, centrifugation, and filtering.

25 Advantageously, the crystallized hydrated boron salt is filtered, generating crystallization mother water. This crystallization mother water may contain less than 1% by mass of solvent traces.

30 The filtering may be performed under vacuum or under a positive pressure in the range from 10^5 to $5 \cdot 10^5$ Pa, preferably 10^5 Pa, or under reduced pressure between 10^4 and $8 \cdot 10^4$ Pa.

Sub-step e)

Advantageously, the crystallization mother water is recirculated in the method during the step of bringing into contact the aqueous basic solution A2 with the organic solvent. It is mixed
5 with the aqueous basic solution A2 during this contacting step.

According to the invention, the solid thus recovered is a hydrated borate, having a formula that may be $\text{NaBO}_2 \cdot y\text{H}_2\text{O}$, $\text{Na}_2\text{B}_4\text{O}_7 \cdot y\text{H}_2\text{O}$, $\text{Na}_2\text{B}_5\text{O}_8 \cdot y\text{H}_2\text{O}$, $\text{Li}_2\text{B}_4\text{O}_7 \cdot y\text{H}_2\text{O}$, $\text{K}_2\text{B}_4\text{O}_7 \cdot y\text{H}_2\text{O}$, or $(\text{NH}_4)_2\text{B}_4\text{O}_7 \cdot y\text{H}_2\text{O}$, where y is in the range from 0 to 11.

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After the solid-liquid separation, the recovered solid may undergo a washing, to wash off any solvent traces.

In this case, the crystallized hydrated boron salt is washed with an aqueous solution and/or
15 with the distillate, resulting from the distillation, generating washing water. This washing water may contain less than 1% by mass of solvent traces.

The washing water is advantageously recirculated in the method during the step of bringing into contact the aqueous basic solution A2 with the organic solvent. It may be mixed with the
20 aqueous basic solution A2 during this contacting step.

Thus, the method according to the invention causes no loss of solvent and enables to obtain a very low residual carbon content, originating from the organic solvent, in the crystallized boron salt.

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The re-use of the distillate, of the crystallization mother water, and/or of the washing water has the advantage of enabling to recover all aqueous flows and all the solvent.

A drying step may be carried out after the washing. In particular, the drying may be performed
30 at a temperature in the range from 50°C to 150°C, at an absolute pressure in the range from 10^4 Pa to 10^5 Pa.

Depending on the drying temperature, hydrated or anhydrous borax will be obtained. For example, a drying temperature in the range from 100°C to 150°C will produce anhydrous borax.

5 BRIEF DESCRIPTION OF THE DRAWINGS

The way in which the invention can be carried out and the resulting advantages will better appear from the following example of embodiment, given as a non-limiting example, in relation with the accompanying drawing.

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Figure 1 is a simplified representation of a battery of four mixers-settlers implementing the method of boron extraction according to a specific embodiment of the invention.

Figure 2 is a simplified representation of the method according to a specific embodiment of the invention.

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DETAILED DESCRIPTION OF THE DRAWINGS

A specific embodiment of the method implemented in a battery of four mixers-settlers is schematized in Figure 1.

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The method is carried out in a device comprising a plurality of stages, where the organic solvent and the aqueous basic solution flow in opposite directions.

In particular, the method may be carried out in a mixer-settler battery or in liquid-liquid extraction columns. The number of stages of these devices is preferably in the range from 3 to 10, preferably from 5 to 7.

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The device of Figure 1 is a mixer-settler battery (e) with four stages (a,b,c,d), of a type known per se. A first stage (a) is fed with an organic solvent laden with boric acid (11) and a borax solution (12) resulting from the recycling of the crystallization mother water and optionally of the washing water.

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Further, an aqueous NaOH solution (13) is fed in counter-current flow to the fourth stage (d).

A distillate (20) obtained during the implementation of the invention is also fed in counter-current flow to the fourth stage (d).

5 The boron-laden organic solvent (11) of the first stage (a) is then transferred to the second stage (b), then to the third stage (c), and eventually to the fourth stage (d), mixed and decanted at each stage.

10 The aqueous phase which feeds the fourth stage (d), consisting of the aqueous NaOH solution (13), is transferred via stages (c), (b), to the first stage (a) where it combines with the borax solution (12), in each stage the aqueous and solvent phases are mixed and decanted.

The aqueous alkaline borate solution (14) is recovered at the output of the first stage (a). The extraction solvent (15) comes out, boron-free, at the fourth stage (d).

15 Referring to Figure 2, the aqueous borate solution (14) coming out of the mixer-settler battery (e) is recovered and processed to crystallize the borate.

20 The aqueous borate solution (14) is first distilled (g) by increasing the temperature and/or by modifying the pressure of the medium to obtain a borate-saturated solution and a distillate (20). The crystallization (h) is then carried out either by distillation generating distillate (20) again, or by cooling, resulting in both cases in the forming of a crystallized borate suspension.

25 Eventually, the boron salt suspension is filtered (i), enabling to recover the crystallization mother water (21) and the crystallized borate (16). If need be, the borate may be washed (j), which generates washing water (22). The distillate (20) is also used to wash the borate.

30 The distillate (20) is re-used to dilute (f) a basic soda-concentrated solution (17) enabling to obtain the aqueous NaOH solution (13), which will be introduced into the mixer-settler battery (e) for the liquid-liquid extraction of boron.

The crystallization mother water (21) and the washing water (22) are mixed to form the borax solution (12) which is reintroduced into the battery (e).

EXAMPLES OF EMBODIMENT OF THE INVENTION

Examples 1 to 21 aim at highlighting different embodiments of the invention. They disclose the basic data used for the implementation of a method of boron extraction according to the invention, in the presence of rare earths in solution.

Example 1: Boron extraction by an EHD/octan-1-ol solvent

In a 50-mL vial, 20 mL of an aqueous solution resulting from the dissolution of a powder of oxidized permanent magnets in nitric acid are introduced, the solution having a 4.5-g/L boron concentration, a 110-g/L neodymium concentration, a 27-g/L praseodymium concentration, a 7-g/L dysprosium concentration, a 3-g/L cerium concentration, and a concentration of other rare earths of less than 1 g/L, for a total 150 g/L of rare earths. The solution has a 2-g/L iron concentration, a 0.5-g/L aluminum concentration, a 0.5-g/L cobalt concentration, a 0.2-g/L copper concentration, and it comprises zinc traces. It has a pH of 2.

The aqueous solution is prepared by demagnetizing neodymium-iron-boron NdFeB permanent magnets, by grinding them into powder and eventually by thermally oxidizing them. The oxidized powder is then dissolved in a nitric acid solution.

20 mL of organic extraction solvent consisting of 30% by mass of 2-ethyl-1,3-hexanediol (EHD), as an extraction compound, and 70% by mass of octan-1-ol, as a diluent compound, are introduced into this same vial.

The volume ratio between the aqueous phase and the organic phase thus is 1.

The medium is vigorously agitated at 60°C for 15 minutes. After this, the aqueous and organic phases are separated by decantation.

A boron concentration in aqueous phase of 0.25 g/L, in organic phase of 4.25 g/L, and thus a boron partition coefficient equal to 17 are then obtained.

The final concentrations of total rare earths, iron, aluminum, cobalt, copper, and zinc in the solvent are lower than 10 mg/L, whereby the partition coefficient of neodymium is lower than 10^{-4} while the partition coefficient of copper is lower than 0.05.

5 Example 2: Boron extraction by an EHD/octan-1-ol solvent

The extraction method of example 1 is repeated, but by this time introducing into a vial 40 mL of the acid aqueous solution resulting from the dissolution of a powder of oxidized permanent magnets of example 1, and 10 mL of the organic extraction solvent of example 1.

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The volume ratio between the aqueous phase and the organic phase thus is 4.

A partition coefficient of boron equal to 5 is then obtained.

15 The concentrations of total rare earths, iron, aluminum, cobalt, copper, and zinc in the solvent are lower than 10 mg/L, whereby the partition coefficient of neodymium is lower than 10^{-4} while the partition coefficient of copper is lower than 0.05.

Example 3: Boron extraction by an EHD/Solvesso®150/2-EH solvent

20

In a 100-mL vial, 60 mL of an acid aqueous solution resulting from the dissolution of a powder of oxidized permanent magnets in nitric acid are introduced, the solution having a 4.5-g/L boron concentration, a 110-g/L neodymium concentration, a 27-g/L praseodymium concentration, a 7-g/L dysprosium concentration, a 3-g/L cerium concentration, and a concentration of other rare earths of less than 1 g/L, for a total 150 g/L of rare earths. The solution has a 2-g/L iron concentration, a 0.5-g/L aluminum concentration, a 0.5-g/L cobalt concentration, a 0.2-g/L copper concentration, and it comprises zinc traces. It has a pH of 2.

25

10 mL of organic extraction solvent consisting of 30% by mass of 2-ethyl-1,3-hexanediol (EHD) as an extraction compound, 50% by mass of Solvesso®150, as a diluent compound, and 20% by mass of 2-ethylhexanol (2-EH) as a modifier compound are introduced into this same vial.

30

The volume ratio between the aqueous phase and the organic phase thus is 6.

The medium is vigorously agitated at 60°C for 15 minutes. After this, the aqueous and organic phases are separated by decantation.

5

A boron partition coefficient equal to 6 is then obtained.

The concentrations of total rare earths, iron, aluminum, cobalt, copper, and zinc in the solvent are lower than 10 mg/L, so that the partition coefficient of neodymium is lower than 10^{-4} while the partition coefficient of copper is lower than 0.05.

10

Example 4: Boron extraction by an EHD/Solvesso[®] 150/2-EH solvent

The extraction method of example 3 is repeated, by this time introducing into a vial 50 mL of an acid aqueous solution resulting from the dissolution of a powder of oxidized permanent magnets of example 3, and 50 mL of the organic extraction solvent of example 3.

15

The volume ratio between the aqueous phase and the organic phase thus is 1.

A boron partition coefficient equal to 32 is thus obtained.

20

The concentrations of total rare earths, iron, aluminum, cobalt, copper, and zinc in the solvent are lower than 10 mg/L, so that the partition coefficient of neodymium is lower than 10^{-4} while the partition coefficient of copper is lower than 0.05.

25

Example 5: Boron extraction by a TPMD/kerosene/decanol solvent

In a 100-mL vial, 50 mL of an acid aqueous solution resulting from the dissolution of a powder of oxidized permanent magnets in nitric acid, having a 4.5-g/L boron concentration, a 110-g/L neodymium concentration, a 27-g/L praseodymium concentration, 7-g/L dysprosium concentration, a 3-g/L cerium concentration, and a concentration of other rare earths of less than 1 g/L, for a total 150 g/L of rare earths, are introduced. The solution has a 2-g/L iron

30

concentration, a 0.5-g/L aluminum concentration, a 0.5-g/L cobalt concentration, a 0.2-g/L copper concentration, and it comprises zinc traces. It has a pH of 2.

10 mL of organic extraction solvent consisting of 15% by mass of 2,2,4-trimethyl-1,3-pentaediol (TPMD), as an extraction compound, 25% by mass of kerosene, as a diluent compound, and 60% by mass of decanol, as a modifier compound are introduced into this same vial.

The volume ratio between the aqueous phase and the organic phase thus is 5.

10

The medium is vigorously agitated at 60°C for 15 minutes. After this, the aqueous and organic phases are separated by decantation.

A boron partition coefficient equal to 1.7 is then obtained.

15

The concentrations of total rare earths, iron, aluminum, cobalt, copper, and zinc in the solvent are lower than 10 mg/L, so that the partition coefficient of neodymium is lower than 10^{-4} while the partition coefficient of copper is lower than 0.05.

20 Example 6: Boron extraction by a TPMD/kerosene/decanol solvent

The extraction of example 5 is repeated but by this time introducing into a vial 50 mL of the acid aqueous solution resulting from the dissolution of a powder of oxidized permanent magnets of example 5, and 50 mL of the organic extraction solvent of example 5.

25

The volume ratio between the aqueous phase and the organic phase thus is 1.

A boron partition coefficient equal to 18 is then obtained.

30 The concentrations of total rare earths, iron, aluminum, cobalt, copper, and zinc in the solvent are lower than 10 mg/L, so that the partition coefficient of neodymium is lower than 10^{-4} while the partition coefficient of copper is lower than 0.05.

Example 7: Boron extraction by a BEPD/kerosene/decanol solvent

In a 100-mL vial, 50 mL of an acid aqueous solution resulting from the dissolution of a powder of oxidized permanent magnets in nitric acid, having a 4.5-g/L boron concentration, a 110-g/L neodymium concentration, a 27-g/L praseodymium concentration, a 7-g/L dysprosium concentration, a 3-g/L cerium concentration, and a concentration of other rare earths of less than 1 g/L, for a total 150-g/L of rare earths, are introduced. The solution has a 2-g/L iron concentration, a 0.5-g/L aluminum concentration, a 0.5-g/L cobalt concentration, a 0.2-g/L copper concentration and it comprises zinc traces. It has a pH of 2.

10 mL of an organic extraction solvent consisting of 15% by mass of 2-butyl-2-ethylpropane-1,3-diol (BEPD), as an extraction compound, 25% by mass of kerosene as a diluent compound, 60% by mass of decanol, as a modifier compound are introduced into this same vial.

The volume ratio between the aqueous phase and the organic phase thus is 5.

The medium is vigorously agitated at 60°C for 15 minutes. After this, the aqueous and organic phases are separated by decantation.

A boron partition coefficient equal to 1.65 is then obtained.

The concentrations of total rare earths, iron, aluminum, cobalt, copper, and zinc in the solvent are lower than 10 mg/L, so that the partition coefficient of neodymium is lower than 10^{-4} while the partition coefficient of copper is lower than 0.05.

Example 8: Boron extraction by a BEPD/kerosene/decanol solvent

The extraction of example 7 is repeated but by introducing into a vial 50 mL of the acid aqueous solution resulting from the dissolution of a powder of oxidized permanent magnets of example 7, and 50 mL of the organic extraction solvent of example 7.

The volume ratio between the aqueous phase and the organic phase thus is 1.

A boron partition coefficient equal to 2 is then obtained.

The concentrations of total rare earths, iron, aluminum, cobalt, copper, and zinc in the solvent are lower than 10 mg/L, so that the partition coefficient of neodymium is lower than 10^{-4} while
 5 the partition coefficient of copper is lower than 0.05.

Example 9: Boron extraction by a BEPD/kerosene/decanol solvent

In a 200-mL vial, 100 mL of an acid aqueous solution resulting from the dissolution of a
 10 powder of oxidized permanent magnets in sulfuric acid, having a 0.6-g/L boron concentration, a 14.7-g/L neodymium concentration, a 3.6-g/L praseodymium concentration, a 0.9-g/L dysprosium concentration, a 0.4-g/L cerium concentration, and a concentration in other rare earths of less than 0.1 g/L, for a total 20-g/L of rare earths, are introduced. The solution has a 0.25-g/L iron concentration, an aluminum, cobalt, and copper concentration lower than 0.1-g/L and it comprises zinc traces. It has a pH of 2.
 15

10 mL of organic extraction solvent consisting of 15% by mass of 2-butyl-2-ethylpropane-1,3-diol (BEPD), as an extraction compound, 25% by mass of kerosene as a diluent compound, 60% by mass of decanol, as a modifier compound, are introduced into this same vial.
 20

The volume ratio between the aqueous phase and the organic phase thus is 10.

The medium is vigorously agitated at 60°C for 15 minutes. After this, the aqueous and organic phases are separated by decantation.
 25

A boron partition coefficient equal to 1.7 is then obtained.

The concentrations of total rare earths, iron, aluminum, cobalt, copper, and zinc in the solvent are lower than 10 mg/L, so that the partition coefficient of neodymium is lower than $5 \cdot 10^{-4}$
 30 while the partition coefficient of copper is lower than 0.1.

Example 10: Boron extraction by a 2-PH/kerosene solvent

In a 100-mL vial, 50 mL of an acid aqueous solution resulting from the dissolution of a powder of oxidized permanent magnets in nitric acid are introduced, the solution having a 4.5-g/L boron concentration, a 110-g/L neodymium concentration, a 27-g/L praseodymium concentration, a 7-g/L dysprosium concentration, a 3-g/L cerium concentration, and a concentration in other rare earths of less than 1 g/L, for a total 150-g/L of rare earths. The solution has a 2-g/L iron concentration, a 0.5-g/L aluminum concentration, a 0.5-g/L cobalt concentration, a 0.2-g/L copper concentration and it comprises zinc traces. It has a pH of 2.

10

10 mL of organic solvent consisting of 60% by mass of 2-propylheptanol (2-PH), as an extraction compound, and 40% by mass of kerosene, as a diluent compound are introduced into this same vial.

15 The volume ratio between the aqueous phase and the organic phase thus is 5.

The medium is vigorously agitated at room temperature for 15 minutes. After this, the aqueous and organic phases are separated by decantation.

20 A boron partition coefficient equal to 0.6 is then obtained.

The concentrations of total rare earths, iron, aluminum, cobalt, copper, and zinc in the solvent are lower than 10 mg/L, so that the partition coefficient of neodymium is lower than 10^{-4} while the partition coefficient of copper is lower than 0.05.

25

Example 11: Boron extraction by a 2-PH/kerosene solvent

The extraction of example 10 is repeated, by however introducing into a vial 50 mL of the acid aqueous solution resulting from the dissolution of a powder of oxidized permanent magnets of example 10, and 50 mL of the organic extraction solvent of example 10.

30

The volume ratio between the aqueous phase and the organic phase thus is 1. A boron partition coefficient equal to 0.6 is then obtained.

The concentrations of total rare earths, iron, aluminum, cobalt, copper, and zinc in the solvent are lower than 10 mg/L, so that the partition coefficient of neodymium is lower than 10^{-4} while the partition coefficient of copper is lower than 0.05.

5 Example 12: Boron extraction by a pure 2-PH solvent

In a 100-mL vial, 50 mL of an acid aqueous solution resulting from the dissolution of a powder of oxidized permanent magnets in nitric acid are introduced, the solution having a 4.5-g/L boron concentration, a 110-g/L neodymium concentration, a 27-g/L praseodymium
10 concentration, a 7-g/L dysprosium concentration, a 3-g/L cerium concentration, and a concentration in other rare earths of less than 1 g/L, for a total 150-g/L of rare earths. The solution has a 2-g/L iron concentration, a 0.5-g/L aluminum concentration, a 0.5-g/L cobalt concentration, a 0.2-g/L copper concentration and it comprises zinc traces. It has a pH of 2.

15 10 mL of organic extraction solvent formed of 100% by mass of 2-propylheptanol (2-PH), as an extraction compound are introduced into this same vial.

The volume ratio between the aqueous phase and the organic phase thus is 5.

20 The medium is vigorously agitated at 60°C for 15 minutes. After this, the aqueous and organic phases are separated by decantation.

A boron partition coefficient equal to 0.56 is then obtained.

25 The concentrations of total rare earths, iron, aluminum, cobalt, copper, and zinc in the solvent are lower than 10 mg/L, so that the partition coefficient of neodymium is lower than 10^{-4} while the partition coefficient of copper is lower than 0.05.

Example 13: Boron extraction by a pure 2-PH solvent

30

The extraction method of example 12 is repeated, by however introducing into a vial 50 mL of the acid aqueous solution resulting from the dissolution of a powder of oxidized permanent magnets of example 12, and 50 mL of the organic extraction solvent of example 12.

The volume ratio between the aqueous phase and the organic phase thus is 1.

A boron partition coefficient equal to 0.58 is then obtained.

- 5 The concentrations of total rare earths, iron, aluminum, cobalt, copper, and zinc in the solvent are lower than 10 mg/L, so that the partition coefficient of neodymium is lower than 10^{-4} while the partition coefficient of copper is lower than 0.05.

Example 14: Boron extraction by a pure 2-PH solvent

10

In a 100-mL vial, 50 mL of an acid aqueous solution resulting from the dissolution of a powder of oxidized permanent magnets in hydrochloric acid are introduced, the solution having a 4.5-g/L boron concentration, a 110-g/L neodymium concentration, a 27-g/L praseodymium concentration, a 7-g/L dysprosium concentration, a 3-g/L cerium concentration, and a
15 concentration in other rare earths of less than 1 g/L, for a total 150-g/L of rare earths. The solution has a 2-g/L iron concentration, a 0.5-g/L aluminum concentration, a 0.5-g/L cobalt concentration, a 0.2-g/L copper concentration and it comprises zinc traces. It has a pH of 2.

50 mL of an organic extraction solvent formed of 100% by mass of 2-propylheptanol (2-PH),
20 as an extraction compound, are introduced into this same vial.

The volume ratio between the aqueous phase and the organic phase thus is 1.

The medium is vigorously agitated at 50°C for 15 minutes. After this, the aqueous and organic
25 phases are separated by decantation.

A boron partition coefficient equal to 0.63 is then obtained.

The concentrations of total rare earths, iron, aluminum, cobalt, copper, and zinc in the solvent
30 are lower than 10 mg/L, so that the partition coefficient of neodymium is lower than 10^{-4} while the partition coefficient of copper is lower than 0.05.

Example 15: Boron extraction by a pure 2-PH solvent

In a 100-mL vial, 50 mL of an acid aqueous solution resulting from the dissolution of a powder of oxidized permanent magnets in sulfuric acid, having a 0.6-g/L boron concentration, a 14.7-g/L neodymium concentration, a 3.6-g/L praseodymium concentration, a 0.9-g/L dysprosium concentration, a 0.4-g/L cerium concentration, and a concentration in other rare earths of less than 0.1 g/L, for a total 20-g/L of rare earths, are introduced. The solution has a 0.25-g/L iron concentration, an aluminum, cobalt, and copper concentration lower than 0.1-g/L and it comprises zinc traces. It has a pH of 2.

50 mL of an organic extraction solvent formed of 100% by mass of 2-propylheptanol (2-PH), as an extraction compound, are introduced into this same vial.

The volume ratio between the aqueous phase and the organic phase thus is 1.

The medium is vigorously agitated at 50°C for 15 minutes. After this, the aqueous and organic phases are separated by decantation.

A boron partition coefficient equal to 0.30 is then obtained.

The concentrations of total rare earths, iron, aluminum, cobalt, copper, and zinc in the solvent are lower than 10 mg/L, so that the partition coefficient of neodymium is lower than 10^{-4} while the partition coefficient of copper is lower than 0.05.

Example 16: Boron extraction by a pure 2-PH solvent from an aqueous solution having a 250-g/L rare earth concentration

In a 100-mL vial, 50 mL of an acid aqueous solution resulting from the dissolution of a powder of oxidized permanent magnets in nitric acid, having a 4.5-g/L boron concentration, a 183-g/L neodymium concentration, a 45-g/L praseodymium concentration, a 12-g/L dysprosium concentration, a 5-g/L cerium concentration, and a concentration in other rare earths of less 5-g/L, for a total 250-g/L of rare earths, are introduced. The solution has a 2-g/L iron

concentration, a 0.5-g/L aluminum concentration, a 0.5-g/L cobalt concentration, a 0.2-g/L copper concentration and comprises zinc traces. It has a pH of 2.

10 mL of an organic extraction solvent formed of 100% by mass of 2-propylheptanol (2-PH),
5 as an extraction compound, are introduced into this same vial.

The volume ratio between the aqueous phase and the organic phase thus is 1.

The medium is vigorously agitated at 60°C for 15 minutes. After this, the mixture is
10 centrifuged, and the aqueous and organic phases are separated by decantation.

A boron partition coefficient equal to 0.65 is then obtained.

The concentrations of total rare earths, iron, aluminum, cobalt, copper, and zinc in the solvent
15 are lower than 10 mg/L, so that the partition coefficient of neodymium is lower than 10^{-4} while the partition coefficient of copper is lower than 0.05.

Example 17: Boron extraction by a pure 2-PH solvent from an aqueous solution having a 350-g/L rare earth concentration

20

In a 100-mL vial, 10 mL of an acid aqueous solution resulting from the dissolution of a powder of oxidized permanent magnets in hydrochloric acid, having a 4.5-g/L boron concentration, a 256-g/L neodymium concentration, a 63-g/L praseodymium concentration, a 17-g/L dysprosium concentration, a 7-g/L cerium concentration, and a concentration in other rare
25 earths of less 7-g/L, for a total 350-g/L of rare earths are introduced. The solution has a 2-g/L iron concentration, a 0.5-g/L aluminum concentration, a 0.5-g/L cobalt concentration, a 0.2-g/L copper concentration and comprises zinc traces. It has a pH of 2.

40 mL of an organic extraction solvent formed of 100% by mass of 2-propylheptanol (2-PH),
30 as an extraction compound, are introduced into this same vial.

The volume ratio between the aqueous phase and the organic phase thus is 0.25.

The medium is vigorously agitated at 60°C for 15 minutes. After this, the mixture is centrifuged, and the aqueous and organic phases are separated by decantation.

A boron partition coefficient equal to 2.46 is then obtained.

5

The concentrations of total rare earths, iron, aluminum, cobalt, copper, and zinc in the solvent are lower than 10 mg/L, so that the partition coefficient of neodymium is lower than 10^{-4} while the partition coefficient of copper is lower than 0.05.

10 Example 18: Boron extraction by a pure 2-PH solvent from an aqueous solution having a 400-g/L rare earth concentration

In a 100-mL vial, 50 mL of an acid aqueous solution resulting from the dissolution of a powder of oxidized permanent magnets nitric acid, having a 4.5-g/L boron concentration, a 293-g/L neodymium concentration, a 72-g/L praseodymium concentration, a 19-g/L dysprosium concentration, a 8-g/L cerium concentration, and a concentration in other rare earths of less than 8 g/L for a total 400 g/L of rare earths, are introduced. The solution has a 2-g/L iron concentration, a 0.5-g/L aluminum concentration, a 0.5-g/L cobalt concentration, a 0.2-g/L copper concentration and it comprises zinc traces. It has a pH of 2.

20

50 mL of an organic extraction solvent formed of 100% by mass of 2-propylheptanol (2-PH), as an extraction compound are introduced into this same vial.

The volume ratio between the aqueous phase and the organic phase thus is 1.

25

The medium is vigorously agitated at 60°C for 15 minutes. After this, the aqueous and organic phases are separated by decantation.

A boron partition coefficient equal to 3 is then obtained.

30

The concentrations of total rare earths, iron, aluminum, cobalt, copper, and zinc in the solvent are lower than 10 mg/L, so that the partition coefficient of neodymium is lower than 10^{-4} while the partition coefficient of copper is lower than 0.05.

Example 19 hereafter shows the advantage of operating on rare earth concentrated solutions. Example 20 gives an example of operation in a mixer-settler battery comprising boron extraction and solvent recycling.

5 Example 19: Boron extraction by a pure 2-PH solvent

The solubility of boron in attack solutions is limit, and to benefit from this concentration effect (examples 13, 16, 18), the extraction should be carried out in two steps, first on the attack solution at approximately 150 g/L of rare earths, and then on the partially boron-depleted
10 solution reconcentrated at approximately 400 g/L.

In a reactor, one introduces at a 50°C temperature:

- 300 mL of an organic solvent formed of pure 2-propylheptanol, as an extraction compound;
- 15 - 75 mL of an aqueous solution resulting from the dissolution of a powder of oxidized permanent magnets, the solution having a 4.5-g/L boron concentration, a 110-g/L neodymium concentration, a 27g/L praseodymium concentration, a 7-g/L dysprosium concentration, a 3g/L cerium concentration, and a concentration in other rare earths of less than 1 g/L for a total 150 g/L of rare earths, a 2-g/L iron concentration, a 0.5-g/L
20 aluminum concentration, a 0.5-g/L cobalt concentration, a 0.2-g/L copper concentration and comprising zinc traces. It has a pH of 2.

After a 15-mn mixing and decantation of the phases, one recovers:

- 300 mL of an organic solvent having a 0.8-g/L boron concentration.
- 25 - 75 mL of an aqueous phase comprising rare earths, the solution having a 1.27-g/L boron concentration, a 110-g/L neodymium concentration, a 27g/L praseodymium concentration, a 7-g/L dysprosium concentration, a 3-g/L cerium concentration, and a concentration in other rare earths of less than 1 g/L for a total 150-g/L of rare earths, a 1-g/L iron concentration, a 0.5-g/L aluminum concentration, a 0.5-g/L cobalt concentration
30 and comprising zinc traces.

The boron extraction rate for this first step is 71.1%.

In a second step, the previous aqueous phase is concentrated by distillation to obtain a 400-g/L rare earth concentration, that is, a 3.40-g/L boron concentration, a 293-g/L neodymium concentration, a 72-g/L praseodymium concentration, a 19-g/L dysprosium concentration, a 8-g/L cerium concentration, and a concentration in other rare earths of less than 3 g/L, a 2.6-g/L iron concentration, a 1.3-g/L aluminum concentration, a 1.3-g/L cobalt concentration and comprising zinc traces and a 28-mL solution volume.

Then, in a second reactor, one introduces at a 50°C temperature:

- 56 mL of an organic solvent formed of pure 2-propylheptanol, as an extraction compound;
- 28 mL of the previously-obtained concentrated solution

One recovers:

- 56 mL of an organic solvent having a 1.37-g/L boron concentration.
- 28 mL of an aqueous phase comprising rare earths, the solution having a 0.62-g/L boron concentration, a 293-g/L neodymium concentration, a 72-g/L praseodymium concentration, a 19-g/L dysprosium concentration, a 8-g/L cerium concentration, and a concentration in other rare earths of less than 3 g/L, a 2.6-g/L iron concentration, a 1.3-g/L aluminum concentration, a 1.3-g/L cobalt concentration and comprising zinc traces.

With this sequence of extraction-concentration-extraction operations, the aqueous phase has been fully depleted of boron and the general extraction rate with respect to the initial solution is 95%.

Example 20: Boron extraction by a BEPD/kerosene/decanol solvent in a mixer-settler battery

This example is an embodiment of the invention implemented in a counter-current extraction battery.

- a) Placing into contact of an aqueous solution and of an organic solvent

In a battery of six mixers-settlers operating in counter-current flow, at a 50°C temperature, one introduces:

- at stage 1: an organic solvent at a 145 mL/h flow rate, the solvent being formed of 15% by mass of BEPD, as an extraction compound, 25% by mass of kerosene, as a diluent compound, and 60% by mass of decanol, as a modifier compound;
- at stage 5: an acid aqueous solution resulting from the dissolution of a powder of oxidized permanent magnets, at a 145-mL/h flow rate, the solution having a 4.60-g/L boron concentration, a 110-g/L neodymium concentration, a 25-g/L praseodymium concentration, a 6-g/L dysprosium concentration, a 3-g/L cerium concentration, and a concentration in other rare earths of less than 1 g/L, for a total 137-g/L of rare earths. The solution has a 1-g/L iron concentration, a 0.5-g/L aluminum concentration, a 0.5-g/L cobalt concentration, and it comprises zinc traces. It has a pH of 1.5.
- at stage 6: water at a 7-mL/h flow rate.

One recovers:

- at stage 1: an aqueous raffinate of rare earths at a 152-mL/h flow rate, the raffinate having a 16-mg/L boron concentration, a 131-g/L rare earth concentration, a 0.95-g/L iron concentration, a 0.48-g/L aluminum concentration, a 0.48-g/L cobalt concentration and comprising zinc traces;
- at stage 6: a boron-laden organic solvent at a 145-mL/h flow rate, the solvent having a 4.58-g/L boron concentration.

The boron extraction rate thus is 99.6%. This rate corresponds to the mass of boron recovered in the solvent to the total boron mass introduced in the feed.

The method enables to transfer the most part of the boron initially contained in the aqueous solution to the organic solvent.

The aqueous raffinate thus obtained comprises a quantity of boron lower than 30 mg/L.

Rare earths, iron, and other impurities are not present in the solvent, they are recovered in the aqueous raffinate.

b) Re-extraction of boron from the boron-laden solvent

In a second battery of four mixers-settlers operating in counter-current flow, at a 50°C temperature, one feeds:

- 5 - at stage 1: the organic boron-laden solvent, recovered at the output of stage 6 during the previous step of bringing into contact, at a 145-mL/h flow rate, the solvent formed of 15% by mass of BEPD, 25% by mass of kerosene, 60% by mass of decanol, and having a 4.58-g/L boron concentration;
- 10 - at stage 4: an aqueous NaOH solution, at a 79-mL/h flow rate, the solution having a 0.40-mol/L concentration.

One recovers:

- at stage 1: a basic solution, at a 79-mL/h flow rate, having a 8.35-g/L boron concentration and a 9.2-g/L sodium concentration, that is, a 0.52 sodium boron molar ratio;
- 15 - at stage 4: an organic solvent, at a 145-mL/h flow rate, the solvent having a 30-mg/L boron concentration.

The boron re-extraction rate is 99.3%. This rate corresponds to the mass of boron recovered in the basic solution to the mass of boron contained in the laden organic solvent.

20

The boron recovery rate is 98.9%. This rate corresponds to the mass of boron recovered in the basic solution to the mass of boron contained in the acid aqueous solution resulting from the dissolution of a magnet powder (that is, the boron mass introduced in the method).

- 25 The solvent thus regenerated has a low boron concentration, lower than 30 mg/L, it is recycled upon extraction.

Example 21: Boron regeneration from an organic solvent laden with boric acid and comprising BEPD

30

In a battery of five mixers-settlers operating in counter-current flow, at a 50°C temperature, one feeds:

- at stage 1: an organic solvent made of 15% by mass of 2-butyl-2-ethylpropane-1,3-diol (BEPD), of 25% by mass of kerosene, and of 60% by mass of decan-1-ol, the boron concentration of the solvent being 4.40 g/L, with a 100-L/h flow rate;
- at stage 5: a NaOH solution with a 9.40-g/L sodium concentration, with a 50-L/h flow rate.

One recovers:

- at stage 1: an aqueous borate solution with a 8.78-g/L boron concentration, and with a 9.40-g/L sodium concentration, with 0.1% by mass of BEPD, with a 50-L/h flow rate.
- at stage 5: an organic solvent having a residual boron concentration lower than 0.01 g/L, with a 100-L/h flow rate.

Thus, 99.8% of the boron present in the extraction solvent is recovered.

The concentrations and flow rates are detailed in Table 1.

Table 1

	Input		Output	
	Stage 1	Stage 5	Stage 1	Stage 5
	Solvent	NaOH solution	Aqueous borate solution	Solvent
[B] (g/L)	4.40	/	8.78	0.01
[Na] (g/L)	/	9.40	9.40	/
BEPD % by mass	15	/	0.1	15
Flow rate (L/h)	100	50	50	100

Example 22: Crystallization of sodium tetraborate pentahydrate or borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$) from a sodium tetraborate solution

4.7 L of aqueous borax solution, that is, 4.8 kg, are obtained after extraction of the boron from
 5 of an organic extraction solvent made of BEPD, of kerosene, and of decan-1-ol, and from of a soda solution.

The aqueous solution has a 8.78-g/L boron concentration, a 9.40-g/L sodium concentration. It comprises 0.1% by mass of BEPD, that is, 4.8 g of residual BEPD.

- 10 The crystallization of borax pentahydrate from the aqueous solution is performed according to the following steps:
- i. distillation of the aqueous solution at 100°C to obtain 0.7 kg of solution, with a boron concentration of 6.0% by mass (approximately 60 g/L) and 4.1 kg of distillate;
 - ii. cooling of the obtained solution from 100°C to 65°C for one hour to crystallize the borax
 15 pentahydrate;
 - iii. maturation of the crystals for one hour at 65°C, resulting in the forming of a borax pentahydrate suspension;
 - iv. filtering of the borax pentahydrate suspension under a 10^5 Pa positive pressure;
 - v. washing of the boron salt with 110 g of distilled water at 5°C;
 - 20 vi. drying of the boron salt in a ventilated stove at 65°C to a constant mass.

One obtains:

- 0.55 kg of crystallization mother water comprising 3.8% by mass of boron and comprising less than 50 ppm of solvent;
- 25 - 4.1 kg of distillate comprising 0.12% by mass of BEPD, that is, 4.8 g of BEPD
- 130 g of washing water comprising 3.6% by mass of boron;
- 106 g of borax pentahydrate with a purity higher than 99.8%;
- less than 350 mg/kg of residual organic carbon in the borax;
- 24 g of borax pentahydrate impregnation water.

Among the 41.3 g of boron contained in the initial aqueous solution, 15.7 g are recovered in the form of borax pentahydrate. Thus, 38% of the boron initially contained in the aqueous phase is crystallized. The 62% of borate contained in the mother water are recycled at the step of placing into contact of the organic boron-laden solvent and the aqueous basic solution.

5

The same result can be obtained by distilling the boron-laden solution at 65°C under a reduced pressure, in the range from 10^4 Pa to 7.10^4 Pa, to have 106 g of borax pentahydrate in suspension before filtering.

- 10 The 4.1 kg of distillate contain more than 99% of the BEPD extraction compound from the solvent initially soluble in aqueous phase. The distillate is recycled for the production of the aqueous basic solution.

- 15 Borax decahydrate can be obtained with the same method, by concentrating the initial aqueous solution under vacuum at 60°C, and by cooling it at 5°C within one hour before filtering. The masses are detailed in Table 2.

Table 2

	Input		Output			
	Mother solution	Washing water	Crystallization mother water	Distillate	Washing water	Borax
Mass (g)	4,800	110	550	4,100	130	106
B mass (g)	41.27	/	20.90	/	4.63	15.74
BEPD mass (g)	4.8	/	/	4.8	/	

Example 23: Boron regeneration from a solvent based on 2-propylheptanol (2PH) laden with boric acid

In a battery of six mixers-settlers operating in counter-current flow, at a 50°C temperature,
5 one feeds:

- at stage 1: an organic solvent comprising an extraction compound made of pure 2-propylheptanol, the boron concentration in the solvent being 1.5 g/L, with a 100-L/h flow rate;
- at stage 6: a NaOH solution with a 12.28-g/L sodium concentration, with a 10-L/h flow rate.

One recovers:

- at stage 1: an aqueous borate solution with a 14.9-g/L boron concentration, a 12.28-g/L sodium concentration, and a 70-mg/L 2-propylheptanol concentration, with a 10-L/h flow rate. The Na/B molar ratio is 0.39.
- at stage 6: a solvent having a residual boron concentration lower than 0.01 g/L, with a 100-L/h flow rate.

Thus, 99.3% of the boron present in the extraction solvent is recovered.

The concentrations, flow rates, and masses are detailed in Table 3.

Table 3

	Input		Output	
	Stage 1	Stage 6	Stage 1	Stage 6
	Solvent	NaOH solution	Aqueous borate solution	Solvent
[B] (g/L)	1.5	/	14.9	0.01
[Na] (g/L)	/	12.28	12.28	/
2PH (mg/L)	/	/	70	/
Flow rate (L/h)	100	10	10	100

Example 24: Borax pentahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$) recovery from BEPD

In a battery of five mixers-settlers operating in counter-current flow, at a 50°C temperature, one feeds:

- 5 - at stage 1: an organic solvent made of 15% by mass of BEPD, 25% by mass of kerosene and 60% by mass of decan-1-ol, the solvent has a 3.52-g/L boron concentration and it is introduced with a 576-L/h flow rate and a borax solution with a 39.7-g/L boron concentration and a 42.3-g/L sodium concentration, resulting from the recycling of the crystallization mother water of the produced borax described hereafter, with a 39.6-L/h
10 flow rate.
- at stage 5: an NaOH solution with a 11.5-g/L sodium concentration introduced at a 187.8-L/h flow rate. This solution is made of 3.76 kg of solid NaOH and 187.8 L of distillate.

One recovers:

- 15 - at stage 1: an aqueous solution having a 15.4-g/L boron concentration, a 16,4-g/L sodium concentration and comprising 0.1% by mass of solvent, with a 233.3-L/h flow rate since the conversion of the boric acid into borax generates 5.9 L of water. Molar ratio Na/B is 0.5, that is, the stoichiometry of the tetraborate ion $\text{Na}_2\text{B}_4\text{O}_7$;
- at stage 5: a solvent having a boron concentration lower than 0.01-g/L, with a 576-L/h
20 flow rate.

Thus, 99.7% of the boron present in the extraction solvent is recovered.

The crystallization of borax pentahydrate from the aqueous solution recovered at stage 1 is
25 performed according to the following steps:

- i. distillation of the aqueous solution recovered at stage 1 under vacuum at 65°C, during which the borax pentahydrate precipitates, to obtain a solution with a total boron concentration (solid boron and solubilized boron) of 73.1 g/L and a 77.9-g/L sodium concentration, with a 49.2-L/h flow rate and 187.8 L/h of distillate;
- 30 ii. maturation of the crystals for one hour, resulting in the forming of a borax pentahydrate suspension;
- iii. filtering of the borax pentahydrate suspension under a 10^5 Pa positive pressure;
- iv. drying of the boron salt in a ventilated stove at 65°C to a constant mass.

One obtains:

- 187.8 L/h of distillate containing 0.12% of solvent, which will be recycled towards the battery;
 - 39.6 L/h of crystallization mother water having a 39.7-g/L boron concentration and a 42.3-g/L sodium concentration;
 - 14.4 kg/h of borax pentahydrate comprising 5% by mass of water, that is, 13.7 kg/h of borax pentahydrate, with less than 50 ppm of BEPD, that is, less than 0.035 g/kg of residual organic carbon.
- The obtained borax pentahydrate is pure at more than 99.8%.

The crystallization mother water contains 44% of the total boron.

The distillate contains all the solvent soluble in aqueous phase contained in the boron solution recovered at stage 1.

The concentrations and flow rates of the liquid-liquid extraction and of the crystallization are detailed in tables 4 and 5.

Table 4

Liquid-liquid boron re-extraction					
	Input			Output	
	Stage 1		Stage 6	Stage 1	Stage 6
	Solvent	Borate solution	NaOH solution	Aqueous borax pentahydrate solution	Solvent
[B] (g/L)	3.52	39.7	/	15.4	0,01
[Na] (g/L)	/	42.3	11.5	16.4	/
BEPD (% by mass)	15	/	/	0.1	15
Flow rate (L/h)	576	39.6	187.8	233.3	576

Table 5

Borax crystallization				
	Input	Output		
	Mother solution	Crystallization mother water	Distillate	Borax
Flow rate	233.3 L/h	39.6 L/h	187.8 L/h	13.6 kg/h
[B] (g/L)	15.4	39.7	/	/
[Na] (g/L)	16.4	42.3	/	/
B mass (g/h)	3,593	1,572	/	2,021
BEPD mass (g/h)	233	/	233	/

Example 25: Recovery of borax pentahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$) from 2-propylheptanol

- 5 In a battery of five mixers-settlers operating in counter-current flow, at a 50°C temperature, one feeds:
- at stage 1: an organic solvent made of 2-propylheptanol, with a 1.5 g/L boron concentration, it is introduced with a 1,352-L/h flow rate and a borax solution with a 39.7-g/L boron concentration and a 42.3-g/L sodium concentration resulting from the recycling of the crystallization mother water of the produced borax described hereafter, with a 39.6-L/h flow rate.
 - at stage 5: an NaOH solution with a 11.5-g/L sodium concentration introduced at a 187.8-L/h flow rate. This solution is made of 3.76 kg of solid NaOH and 187.8 L of distillate.

One recovers:

- at stage 1: an aqueous solution with a 15.4-g/L boron concentration, a 16.4-g/L sodium concentration, and comprising 70 ppm by mass of solvent, with a 233.3-L/h flow rate since the conversion of boric acid into borax generates 5.9 L of water. The Na/B molar ratio is 0.5;
- at stage 5: a solvent having a boron concentration lower than 0.01 g/L, with a 1,352-L/h flow rate.

Thus, 99.3% of the boron present in the extraction solvent is recovered.

The crystallization of borax pentahydrate from the aqueous solution recovered at stage 1 is performed according to the following steps:

- i. distillation of the aqueous solution recovered at stage 1 under vacuum at 65°C, during which the borax pentahydrate precipitates, to obtain a solution with a 73.1-g/L total boron concentration (solid boron and solubilized boron) and a 77.9-g/L sodium concentration, with a 49.2-L/h flow rate and of 187.8 L/h of distillate;
- ii. maturation of the crystals for one hour resulting in the forming of a borax pentahydrate suspension;
- iii. filtering of the borax pentahydrate suspension under a 10^5 Pa pressure;
- iv. drying of the boron salt in a ventilated stove at 65°C to a constant mass.

One obtains:

- 187.8 L/h of distillate containing 87 ppm of solvent, which will be recycled towards the battery;
- 39.6 L/h of crystallization mother water having a 39.7-g/L boron concentration and a 42.3-g/L sodium concentration;
- 14.4 kg/h of borax pentahydrate comprising 5% by mass of water, that is, 13.7 kg/h of borax pentahydrate with less than 50 ppm of 2PH, that is, less than 0.037 g/kg of residual organic carbon.

The obtained borax pentahydrate has a purity higher than 99.8%. The crystallization mother water contains 44% of the total boron.

The distillate contains all the solvent soluble in aqueous phase contained in the boron solution recovered at stage 1.

The concentrations and flow rates of the liquid-liquid extraction and of the crystallization are detailed in tables 6 and 7.

Table 6

Liquid-liquid boron re-extraction					
	Input			Output	
	Stage 1		Stage 6	Stage 1	Stage 6
	Solvent	Borate solution	NaOH solution	Aqueous borax pentahydrate solution	Solvent
[B] (g/L)	1.5	39.7	/	15.4	0.01
[Na] (g/L)	/	42.3	11.5	16.4	/
2PH (mg/L)	/	/	/	70	/
Flow rate (L/h)	1,352	39.6	187.8	233.3	576

Table 7

Borax crystallization				
	Input	Output		
	Mother solution	Crystallization mother water	Distillate	Borax
Flow rate	233.3 L/h	39.6 L/h	187.8 L/h	13.6 kg/h
[B] (g/L)	15.4	39.7	/	
[Na] (g/L)	16.4	42.3	/	
B mass (g/h)	3,593	1,572	/	2,021
2PH mass (g/h)	16	/	16	

Lithium, potassium, and ammonium tetraborates as well as sodium tetraborate decahydrate can be formed by using the method according to the invention.

5 The solubility of these salts in water being different from that of sodium tetraborate pentahydrate, the quantities of distillate, mother water, and boron salt produced during the crystallization vary accordingly.

CLAIMS

1. A method of extracting boron contained in an aqueous solution A1 comprising rare earth elements, aqueous solution A1 resulting from the dissolution of a powder of NdFeB magnets or of machining scrap resulting from the manufacturing of permanent magnets, in which method said aqueous solution A1 is brought into contact and mixed with an organic solvent, said organic solvent comprising at least one extraction compound made of an alcohol, comprising a chain of from 6 to 18 carbon atoms, aliphatic or aromatic, linear or branched, the contacting and the mixing of aqueous solution A1 and of the organic solvent causing the transfer of boron from said aqueous solution A1 to said organic solvent.
2. The method of extracting boron according to claim 1, wherein the extraction compound is selected from the group comprising:
- 1-3 diols, preferably from among 2-ethyl-1,3-hexanediol (EHD), 2-butyl-2-ethylpropane-1,3-diol (BEPD), 2,2,4-trimethyl-1,3-pentanediol (TMPD), 2-chloro-4-(1,1,3,3-tetramethylbutyl)-6-methylol-phenol (CTMP), and their mixtures;
 - monoalcohols of from 6 to 18 carbon atoms, with a branched or linear aliphatic chain, preferably from among 2-ethylhexanol (2-EH), 2-propylheptanol (2-PH), 2-butyloctanol, isodecanol, octanol, and their mixtures.
3. The method of extracting boron according to claim 1 or 2, wherein the organic solvent further comprises at least one diluent compound formed of a hydrocarbon chain of from 6 to 18 carbon atoms, aliphatic or aromatic.
4. The method of extracting boron according to claim 3, wherein the diluent compound is selected from the group comprising: decane and its isomers, dodecane and its isomers, kerosene, toluene, hydrocarbons having between 6 and 18 carbon atoms, aliphatic or aromatics, and their mixtures.

5. The method of extracting boron according to any of claims 1 to 4, wherein the organic solvent further comprises a modifier compound different from the extraction compound, the modifier compound being made of an alcohol comprising an aliphatic chain of from 6 to 18 carbon atoms.
- 5
6. The method of extracting boron according to claim 5, wherein the modifier compound is selected from the group comprising monoalcohols, preferably from among decan-1-ol, octan-1-ol, isodecan-1-ol, hexan-1-ol, dodecan-1-ol, 2-propylheptanol, 2-ethylhexanol, and their mixtures.
- 10
7. The method of extracting boron according to any of claims 1 to 6, wherein the organic solvent comprises:
- from 10% to 100% of at least one extraction compound,
 - from 0% to 90% of at least one diluent compound,
 - 15 - from 0% to 70% of at least one modifier compound,
- by weight with respect to the total weight of the organic solvent, the total being equal to 100%.
8. The method of extracting boron according to any of claims 1 to 7, wherein aqueous solution A1 comprises:
- 20
- from 20 to 450 g/L of rare earth elements in the form of dissolved salt,
 - from 1 to 9 g/L of boron in the form of boric acid,
 - from 0 to 20 g/L of iron in the form of dissolved salt, and
 - from 0 to 5 g/L of metal elements belonging to the group comprising cobalt,
 - 25 aluminum, zinc, copper, manganese, and nickel.
9. The method of extracting method according to any of claims 1 to 8, wherein the dissolved salts of rare earth elements belong to the group comprising rare earth nitrates, rare earth chlorides, rare earth sulfates, and their mixtures.
- 30

10. The method of extracting boron according to any of claims 1 to 9, wherein the contacting and the mixing are carried out at a temperature in the range from 20°C to 70°C, preferably from 40°C to 60°C.
- 5 11. The method of extracting boron according to any of claims 1 to 10, wherein the method further comprises, after the boron transfer, a step of re-extraction of the boron present in the organic solvent.
- 10 12. The method of extracting boron according to claim 11, wherein the boron re-extraction is performed by bringing a Brönsted base into contact with said solvent, the base being selected from the group comprising: NaOH, KOH, LiOH, NH₄OH, and their mixtures.
- 15 13. The method of extracting boron according to any of claims 1 to 12, further comprising a step of recovery of boron in the form of boron salt from boric acid present in the organic solvent, said step of boron recovery comprising the following sub-steps:
- a) bringing into contact of an aqueous basic solution A2 with said organic solvent to extract the boron in the form of solubilized borate into the aqueous basic solution A2;
- 20 b) distillation of the borate-laden aqueous basic solution A2 to concentrate said solution, generating a distillate;
- c) crystallization of the borate in the form of hydrated boron salt;
- d) solid-liquid separation of the crystallized hydrated boron salt, generating crystallization mother water;
- 25 e) re-introduction of the distillate and of the crystallization mother water at the step of bringing into contact of the aqueous basic solution A2 with said organic solvent.
14. The method of extracting boron according to claim 13, wherein the crystallization of borate is achieved by distillation of the borate-concentrated aqueous basic solution A2, or by cooling of the borate-concentrated aqueous basic solution A2.

15. The method of extracting boron according to claim 13 or 14, wherein the contacting of the aqueous basic solution A2 with the organic solvent is performed in a device comprising a plurality of stages, where the organic solvent and the aqueous basic solution A2 flow in opposite directions.
- 5 16. The method of extracting boron according to any of claims 13 to 15, wherein the aqueous basic solution A2 is prepared by dilution of concentrated basic solution or by solubilization of a solid basic compound.
- 10 17. The method of extracting boron according to claim 16, wherein the distillate dilutes the concentrated basic solution or solubilizes the solid basic compound.
- 15 18. The method of extracting boron according to any of claims 13 to 17, wherein the aqueous basic solution A2 is introduced in a stoichiometric quantity with respect to the quantity of boron salt to be produced.
19. The method of extracting boron according to any of claims 13 to 18, wherein the crystallized hydrated boron salt is washed with an aqueous solution and/or with the distillate, generating washing water.
- 20 20. The method of extracting boron according to claim 19, wherein the washing water is recirculated in the method, during the step of bringing into contact of the aqueous basic solution A2 with the organic solvent.