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Boron removal through precipitation softening in presence of ettringite

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ABSTRACT

Boron is frequently present in wastewater from hydrocarbon production, briefly referred as produced water. Boron at high levels is toxic, especially to plants. It makes challenging produced water reuse. State-of-the-art boron removal processes need specific operations resulting in an increase of water treatment train complexity and cost. Among these, we recall reverse osmosis, adsorption on chelating resins and precipitation softening in presence of magnesium in large excess. Ettringite is a calcium-aluminum sulfate hydroxide, $Ca_6Al_2(SO_4)_3(OH)_{12}·26H_2O$, reported as an effective boron adsorbent. The experimentation described in this paper deals to boron removal through precipitation softening in conditions promoting the formation of ettringite. The first-stage-reverse-osmosis permeate from an Italian oil-and-gas site was used as raw water.

Keywords: Ettringite; Water; Boron; Removal; Softening

1. Introduction

The wastewater from hydrocarbon production is briefly referred as produced water. Millions of m^3/d of the latter one must be managed according to the best practices on water resource valorization, environmental protection, and energy production. More than 50% of the total amount is reinjected to maintain an adequate reservoir pressure while the remainder is discharged to surface water bodies or exploited as water resource [1]. Produced water treatment is operated to get requested specifications. It consists into a train of operations able to remove both organic and inorganic contaminants [2]. Precipitation softening is considered among the most common operations. It consists into the removal of the dissolved ions through the formation of the respective poorly soluble carbonates and hydroxides under basic conditions. Both calcium and magnesium salts, main causes of equipment scaling, are removed according to Eqs. (1)–(3) [3]. Calcium carbonate, $CaCO_3$ and magnesium hydroxide $Mg(OH)_2$ have solubility products, S_P expressed as pS_P corresponding to $-\log(S_P)$, of 8.3 and 11.0, respectively [4].

In Eqs. (1)–(3) calcium hydroxide is exemplified as a strong base while calcium bicarbonate, magnesium bicarbonate and magnesium chloride are typical dissolved salts.

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow Mg(OH)_2 + 2CaCO_3 + 2H_2O \quad (1)$$

$$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + 2CaCl_2 \quad (2)$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O \quad (3)$$

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Silica, SiO_2, another cause of equipment scaling, can be removed as well, through adsorption on freshly formed magnesium hydroxide [5].

Like other toxic metal ions, iron can be removed through precipitation softening as hydroxide, $Fe(OH)_3$ with pS_P of 37.0 according to Eq. (4) [4] where ferric chloride is exemplified as a typical dissolved salt. Additionally, ferric hydroxide is an effective adsorbent of poison arsenic acid, H_3AsO_4, another common water contaminant [6].

$$2FeCl_3 + 3Ca(OH)_2 \rightarrow 2Fe(OH)_3 + 3CaCl_2 \quad (4)$$

Precipitation softening is a robust operation: it is based on simple reactor design, inexpensive chemicals and it has virtually no limitations. It is frequently preliminary to other more critical operations (e.g., reverse osmosis, ion-exchange) needed to get the required water specifications. The huge production of caustic sludge to be disposed as a waste is the main drawback.

Boron is an element naturally present in water due to its release from minerals. It is abundant especially in sea water, geothermal water, industrial effluents (e.g., electronic, metallurgical) and produced water. In sea water it can reach units of mg/L while in the latter ones it can reach hundreds of mg/L. It is found in solution mainly in the form of boric acid, $B(OH)_3$, whose weak Lewis acid behavior to form borates, $[B(OH)_4]^-$, is described in Eq. (5) with acidic equilibrium constant, K_A expressed as pK_A corresponding to $-\log(K_A)$, of 9.2 [4].

$$B(OH)_3 + H_2O \leftrightarrow \left[B(OH)_4\right]^- + H^+ \quad (5)$$

Boron is essential for life but if taken in excess it became toxic. For this reason, its level in water is subject to restrictions. According to the recent guidelines of the World Health Organization, WHO, the boron level in potable water must not exceed 2.4 mg/L while the European Union, EU, has established a limit level of 1.0 mg/L. In waters intended for irrigation of sensitive crops, the boron level must be even an order of magnitude lower [7]. Generally, boron removal operations are at the end of the water treatment train. They are based on reverse osmosis or chelating resins whose management is quite critical. Reverse osmosis is operated under basic conditions where the risk of equipment scaling is serious [8]. Chelating resins are quite expensive (about 25 Euro/kg). Furthermore, they need both acidic and basic regeneration due to co-presence of hydroxyl, –OH, and amine functions, $-NH_2$ [9].

In addition to that, EU considers boron as a critical raw material, CRM, for the green energy transition (e.g., it is part of niobium-iron-boron, NdFeB, permanent magnets used in windmill) thus any mining opportunity should be considered [10].

Boron removal through precipitation softening is still a challenge although appreciable results have been reported [11]:

- in presence of a magnesium/boron ratio higher than 10 mol/mol, at industrial scale. Production of gelatinous, hygroscopic sludge has been noticed as a drawback [12]. Like in silica removal, adsorption has been inferred as the boron removal mechanism. Worse removal has been reported adding pre-formed magnesium hydroxide [13];
- in presence of hydrogen peroxide, H_2O_2, at laboratory scale. Formation of poorly soluble calcium perborate, ($CaB_2O_4(OH)_4$), has been inferred as the boron removal mechanism. Better removal has been reported adding barium hydroxide, $Ba(OH)_2$, instead of calcium hydroxide [14];
- in presence of ettringite calcium-aluminum sulfate hydroxide, $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$, at industrial scale [15]. The latter one is an important hydration product of Portland cement and a clay rarely occurring in nature (Fig. 1). It can be obtained from aluminum sulphate hydrate, $Al_2(SO_4)_3\cdot 18H_2O$ and calcium hydroxide [16]. Its structure is composed of $Ca_6[Al_2(OH)_{12}\cdot 24H_2O]^{6+}$ columns lying parallel to the *c*-axis with sulfate, SO_4^{2-}, and water, H_2O, units within inter-column channels. Hydrogen bonds shore up the whole structure [17]. It is quite open allowing mobility of water and ion exchange [18]. Specifically, ettringite exchanges one sulfate with one borate giving the charlesite clay, $Ca_6Al_2(SO_4)_2(B(OH)_4)(OH,O)_{12}\cdot 26H_2O$ of the same group [19]

Ettringite is largely used as Portland cement in waste management at industrial scale [20] while its potential benefits in water treatment are less exploited [11]. In both cases, the operational variables optimization is mainly empirical and kept undisclosed as proprietary know-how. According to that, limited systematic investigation is available [16].

The experimentation described in this paper deals to the removal of boron through precipitation softening. The conditions promoting the formation of ettringite consistent to industrial scale implementation (e.g., simple reactor design, acceptable temperature, pressure and contact time, inexpensive reactants) were adopted. The first stage reverse osmosis permeate from an Italian oil-and-gas site with a still too high boron level was used as raw water. Both boron-rich and oily raw waters were considered to test precipitation softening robustness, as well. Attention was focused on reagent dosing optimization, safe boron-rich solids disposal and boron mining opportunity.

2. Materials and methods

2.1. Raw water

The first stage, reverse osmosis permeate from an Italian oil-and-gas site with specific electrical conductivity, EC, of 400 µS/cm and boron level of 15.2 mg/L, was used as raw water. It was stored as such in 5 L polyethylene, PE, tanks at 4°C.

Both the boron-rich and the oily raw waters were obtained through initial one modification.

The boron-rich raw water was obtained through the addition of Merck Pro Analysis™ boric acid till a boron level of 130.0 mg/L.

The oily raw water was obtained through the addition of 1.0 g/L of a middle-distillate-hydrocarbon cut obtained in the temperature range from 250°C to 350°C.

Before each precipitation softening test the boron level in the raw water was checked as described in Section 2.4 – Physical–chemical characterization.

2.2. Precipitation softening

The precipitation softening tests were run on 0.5 L samples at room temperature and pressure, in a polyethylene reactor, under stirring at 500 1/min to maintain a well dispersed slurry through a Teflon™-coated bar moved by an Ika Basic™ magnetic device.

The following Carlo Erba Reagents RPE™ were added sequentially: aluminum sulfate hydrated and calcium hydroxide till pH of 11.5. Specifically, aluminum sulfate hydrated dosing was referred to the amount needed to form the ettringite able of adsorbing the whole dissolved boron, assuming the stoichiometric ratio borate/ettringite of 1.0 mol/mol [18] (e.g., 906 mg/L of aluminum sulfate hydrated for 15.2 mg/L of dissolved boron). It will be referred as the stoichiometric dose, 1.0X, with NX as N-fold the stoichiometric dose.

The pH of the reaction slurry, critical for the formation of ettringite, was measured in double both with the Supelco MQuant™ indicator papers and with the Hanna 9829™ multiparameter probe.

The obtained slurry was stirred for a contact time t of 1.5 h, and finally vacuum-filtered on Nalgene 0.45 µm porous cellulose acetate septa.

The solids were air-dried for 48 h at room temperature and pressure, weighed through a Mettler PE 1600™ analytical balance and sent as powder to leaching and physical–chemical characterization as described in Sections 2.3 and 2.4.

The filtrates underwent physical–chemical characterization, as well.

The whole operational procedure was adopted considering the equipment already available at the oil-and-gas site.

The boron removal, ΔB, was computed considering the difference between the final boron level, B_F, and the initial boron level, B_I, referred to the latter one according to Eq. (6):

$$\Delta B = \frac{\left(B_F - B_I\right)}{B_I} \times 100 \quad (6)$$

2.3. Leaching test

The leaching test was carried on in duplicate on solids from precipitation softening ones with a boron removal higher than 95% [21]. The solids were suspended into deionized water with pH of 7.0 and EC of 15 µS/cm according to a liquid/solid ratio of 10 mL/g. The obtained slurry was shaken in polyethylene bottles at room temperature and pressure, at 15 1/min, for a contact time t of 24 h through a Velp Scientifica Rotax 6.8™ upside-down shaker. Finally, the slurry was vacuum filtered on Nalgene 0.45 µm porous cellulose acetate septa. The obtained liquid and solid underwent the same route reported for precipitation softening ones in Section 2.2.

2.4. Physical–chemical characterization

Both raw waters and filtrate underwent boron quantification through the Hack Lange LCK 307™ optical absorption spectrometry kit based on the Azomethine-H method.

The filtrates underwent aluminum quantification through the Hack Lange LCK 301™ optical absorption spectrometry kit based on the Chromazurol-S method.

In both cases, a Hach Lange DR 5000™ ultraviolet, visible, near-infrared, UV, VIS, NIR, spectrometer was used.

The boron quantification in solids was carried out through optical emission spectroscopy, ICP-OES, on a Thermo Scientific ICAP 6300 Duo™ spectrometer equipped with a plasma torch, calibrated with a Sigma Aldrich single-element standard solution. The solids were previously mineralized through a mixture of Merck Supelco Suprapur™ 67% wt./wt. aqueous nitric acid, HNO_3 and Merck Supelco Suprapur™ 40% wt./wt. aqueous hydrofluoric acid, HF.

The structural characterization of solids was carried out through X-ray diffraction (XRD), on a Panalytical X'Pert Alpha-1Θ/2Θ™ Bragg-Brentano diffractometer using the Cu Kα radiation corresponding to the wavelength, λ of 1.5416 Å with the X-ray tube set to 40 V and 40 mA. The patterns were collected from 5°–90°, 2θ, with step size 0.02° and acquisition time of 15 s for each step. The qualitative crystal phase analysis was carried out through the Hanawalt method using the PDF-2 data base of the International Center of Diffraction Data, ICDD. The full profile analysis was performed using the Rietveld method implemented in the Bruker TOPAS™ software package.

Morphological characterization of solids was carried out through field emission scanning electron microscopy, FESEM, on an ultra-high resolution Jeol JSM 7600F™ Schottky microscope (SEM) with a 5 keV energy beam. The images were collected using secondary electrons signal.

3. Results and discussion

The results from the precipitation softening experimentation are resumed in Table 1.

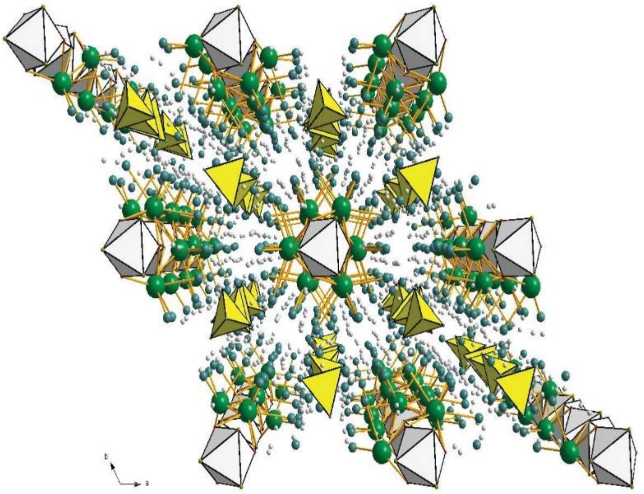

Fig. 1. Crystal structure of ettringite projected onto the (001) plane. Calcium atoms are displayed with ball-and-stick model as green spheres, aluminate octahedral in gray, sulfate tetrahedral, in yellow and hydrogen atoms in light grey. $Ca_6[Al_2(OH)_{12}{\cdot}24H_2O]^{6+}$ arrays are arranged along to the *c*-axis with sulfate and water molecules in the intercolumn channels.

It is evident that the highest boron removal has been obtained with aluminum sulfate hydrated dosing higher than 2.5X. The reason for the excess of reagents is uncertain although it can be inferred that it is due to face competing ions (e.g., hydroxide, OH^-, carbonate, CO_3^{2-}, silicate, SiO_4^{4-}).

Boron removal remains higher than 90% even with the boron-rich raw water, Test X, and above all with the oily raw water, Test Y. According to that, boron removal through precipitation softening can be applied also to concentrates from previous boron removal operations and doesn't suffer presence of dispersed hydrocarbons. It can be also effectively applied to produced water with a minimal pretreatment.

Table 1
Results from tests A-Y. The following data are reported: dosing of aluminum sulfate hydrated, boron removal, ΔB, boron final level, B_F, aluminum final level, Al_F, solid amounts referred to raw water volume

Test (–)	Dosing (–)	ΔB (%)	B_F (mg/L)	Al_F (mg/L)	Solids (g/L)
A	1.0X	–13.1	13.2	4	1.2
B	1.0X	–16.4	12.7	11	2.1
C	2.0X	–45.7	8.3	55	2.8
D	2.0X	–38.7	9.3	1	2.8
E	2.0X	–38.4	9.4	0.4	2.7
F	2.5X	–94.6	0.8	0.2	3.8
G	2.5X	–94.7	0.8	0.4	3.8
H	2.5X	–98.8	1.8	1.8	6.1
I	3.0X	–91.6	1.3	0.04	7.2
J	3.0X	–99.9	0.02	0.04	5.6
K	5.0X	–99.8	0.03	0.03	9.2
L	5.0X	–99.8	0.03	1.4	12.0
X	2.5X	–98.3	2.2	0.5	N.A.
Y	2.5X	–93.6	1.0	0.5	N.A.

N.A., not available.

In many filtrates boron and aluminum levels are close the EU limits for potable water corresponding to 1.0 and 0.2 mg/L, respectively [22].

Structural characterization of solids points to ettringite and calcite, $CaCO_3$, as the most abundant crystal phases as reported in Tables 2 and 3 and exemplified in XRD patterns in Fig. 2. With respect to the nominal primitive hexagonal cell volume value of ettringite, the Rietveld analysis applied to XRD patterns reveals a significative contraction indicating an effective substitution of sulfur atoms by boron ones in the tetrahedral, T–O, sites. The contraction is due to the minor value of the boron covalent radius with respect to the sulfur one, 88.2 and 104.2 pm [23]. Additionally, Fig. 3 confirms that the higher the ettringite content in solid, the higher the boron removal, although a contribution from calcite is reported [24].

High-resolution images of solids from Tests B, H, L are reported in Fig. 4. They show the ettringite typical morphology made by sub-micrometric needle-like crystals

Table 3
Identified crystalline phase formulas for solids from Tests A-L

Phase	Formula
Aragonite	$CaCO_3$
Bassanite	$CaSO_4{\cdot}0.5H_2O$
Calcite	$CaCO_3$
Dolomite	$CaMg(CO_3)_2$
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26(H_2O)$
Gypsum	$CaSO_4{\cdot}2H_2O$
Hydrotalcite	$Mg_4Al_2(OH)_{12}(CO_3){\cdot}3(H_2O)$
Kuzeite	$Ca_3Al_6(OH)_{18}(SO_4)_{1.5}{\cdot}9(H_2O)$
Portlandite	$Ca(OH)_2$
Talc	$Mg_3Si_4O_{10}(OH)_2$
Vaterite	$CaCO_3$

Table 2
Identified crystalline phase amounts referred to raw water volume for solids from Tests A-L. –, not detected

Test (–)	Aragonite (g/L)	Bassanite (g/L)	Calcite (g/L)	Dolomite (g/L)	Ettringite (g/L)	Gypsum (g/L)	Hydrotalcite (g/L)	Kuzeite (g/L)	Portlandite (g/L)	Talc (g/L)	Vaterite (g/L)
A	0.1	–	0.5	–	0.3	–	0.3	0.1	0.0	0.2	0.0
B	–	–	1.1	0.1	0.9	–	–	–	–	–	–
C	–	–	0.8	–	1.8	0.2	–	–	–	–	–
D	0.1	–	1.5	–	1.1	0.1	–	–	–	–	–
E	0.1	–	0.9	–	1.6	0.1	–	–	–	–	–
F	–	–	0.9	–	2.9	–	–	–	–	–	–
G	–	–	0.9	–	2.7	0.1	–	–	–	–	–
H	–	–	1.0	–	5.1	–	–	–	–	–	–
I	–	–	1.4	–	3.4	–	0.4	–	1.1	–	0.4
J	–	0.3	0.4	–	4.8	0.1	–	–	–	–	–
K	–	–	0.6	–	8.3	0.3	–	–	–	–	–
L	–	–	1.5	–	10.5	–	–	–	–	–	–

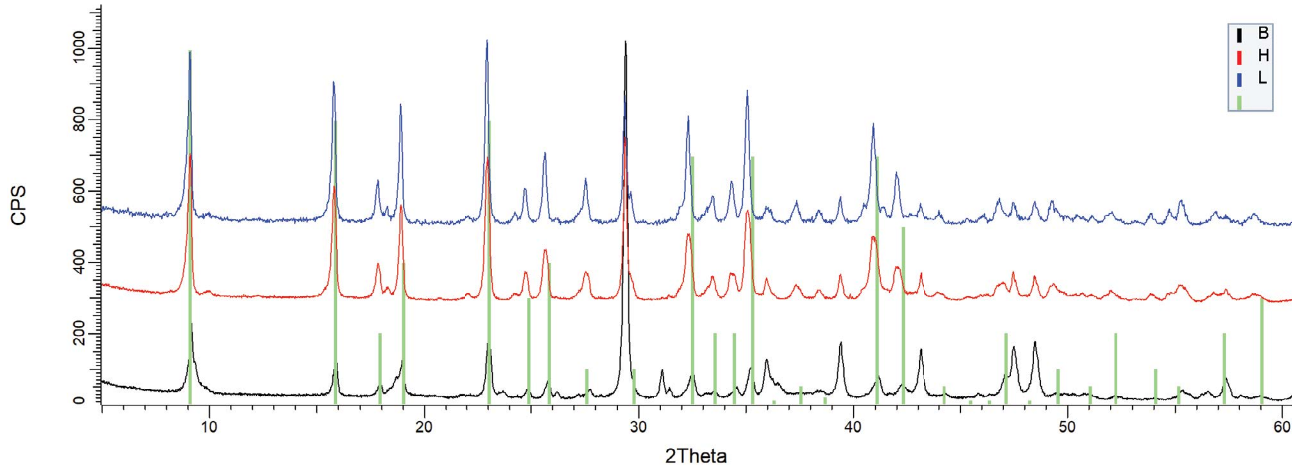

Fig. 2. X-ray diffraction patterns as count per s, CPS, of solids from Tests B, H, L (respectively, from bottom to top). Ettringite lines are sketched by bars.

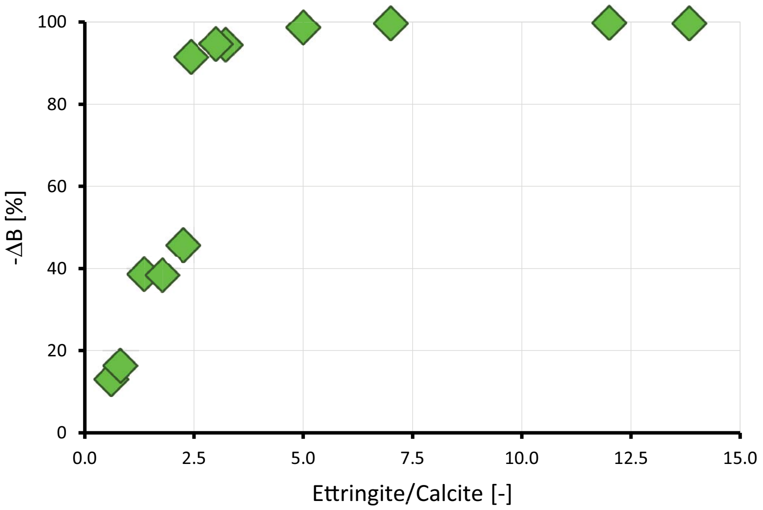

Fig. 3. Effect of ettringite/calcite ratio in solids on boron removal, ΔB.

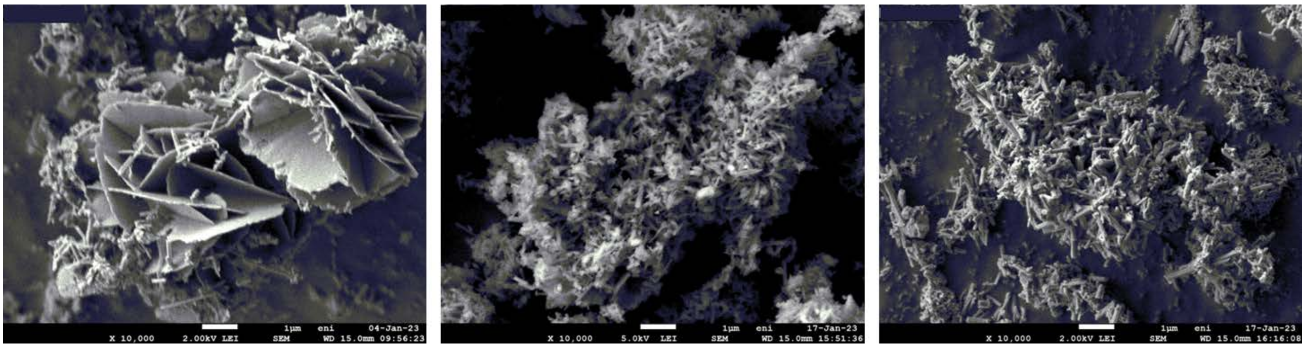

Fig. 4. High-resolution images of solids from Tests B, H, L.

grouped together to get greater uniform micrometric aggregates. In the solid from Test B this morphology is mixed to plate-like calcite crystals. Changes are evident as ettringite become more abundant and only big aggregates of needle-like crystals can be observed in solids from Tests H, L.

Boron level of 33 mg/L affects the filtrate from leaching test. According to that, careful boron-rich solids landfilling must be considered (e.g., dilution with inert materials).

Boron release is not due to ettringite collapse: X-ray diffraction pattern doesn't change after the leaching test despite the pH drop from 11.5 to 8.0 (data not reported). Competition with other dissolved ions (e.g., hydroxide, carbonate, silicate, sulfate) can be inferred as the cause of borate release.

Boron-rich solids addition to building materials has been considered as an alternative option although both potential advantages (e.g., decrease of red brick firing temperature) [25] and disadvantages (e.g., decrease in cement mechanical strength) [26] need additional investigation.

On the other hand, boron-rich solid cannot be considered an exploitable boron source: it contains 0.3% wt./wt. of boron, slightly less than theoretical 0.7 wt./wt. % from the charlesite formula, and markedly less than 15.0% wt./wt. in state-of-the-art minerals [27].

4. Conclusion

Precipitation softening in presence of ettringite has proven to be an effective operation for boron removal from pre-treated produced water containing till 130.0 mg/L of boron, although a 2.5X reagent excess must be considered.

Boron removal higher than 94.0% has been obtained with only minor interferences from dispersed hydrocarbons.

Obtained solids must be disposed carefully due to potential boron release in leachate.

Their addition to building materials has been considered as an alternative option.

On the other hand, boron-rich solids cannot be considered an exploitable boron source: it contains 0.3% wt./wt. of boron, markedly less than 15.0% wt./wt. in state-of-the-art minerals.

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