# WATER MANAGEMENT AND TREATMENT FOR AN ENVIRONMENTALLY FRIENDLY CLOSED CIRCUIT MANUFACTURE

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## ABSTRACT

Water processing and final disposal are key factors for fiber-cement industry since it requires a high consumption of this resource during the production process due to Hatschek (or similar) technology. At the same time, an essential challenge to improve fiber-cement production process is the optimization of water recovery system, which would allow the reuse of this raw material after filtration from the different production points. However, the water process circuit after several filtration cycles begins to get concentrated with several pollutant substances that inhibit the production of fiber-cement products. Total dissolved salts (TDS) and Chemical Oxygen Demand (COD) are of special concern amongst the most detrimental factors for water reusing in fiber-cement production. Therefore, this work presents alternative technologies to keep these parameters within acceptable limits to reuse filtrated water for fiber-cement production. Considering the different applied techniques, water pollutants may be reduced to admissible levels for water recycling through the production line.

## KEYWORDS:

Fiber-cement; water treatment; COD; TDS

## INTRODUCTION

The fiber-cement industry is well established and since its invention in 1895, the product has been successfully used worldwide. For more than 80 years asbestos cement was manufactured using Hatschek technology for the manufacture of thin fiber-cement panels for roofing products as well as façade panels and internal wall elements. Due to the health concerns of asbestos fibers the product has gone through a major change in the redesign of asbestos free mix for replacement technologies since 1975. This also resulted in modifications to the process conditions of the Hatschek machine.

Water treatment and final water disposal is a key factor for fiber-cement industry since it requires a high consumption of this resource during the production process due to Hatschek (or similar) technology. For mixing every component present in fiber-cement formulation (fiber + cement + additives) a large amount of water is needed in order to disperse the fibers, and an excess of water is later removed in order to manufacture the final product.

It became apparent that varied fiber-cement (asbestos free) manufacturers were forced to change processing parameters to adapt to the new technology. Therefore, it was necessary to change the process technology but also the raw materials used, which needed to be adapted due to the very complex product demands in modern fiber-cement production. These included the use of cellulose fibers and other additives. This resulted in significant impacts on processing parameters where, amongst others, flocculants, anti-foaming agent, etc., were now required to stabilize the production process. Also new concerns were related to the use of cellulose pulp which contains lignin and can contaminate the highly alkaline production water by a leaching effect. Not only this aspect, but modern cements for the concrete industry became an issue as well regarding the use of for example fly ash and micro silica. It became very clear that modern fiber-cement factories had to adapt to the

new asbestos free production as the contamination from cellulose pulp, modern cement, flocculant and other additives became a major concern for production water recycling (Khalil and Ward, 1973; Van der Heyden, 2010).

The Hatschek process is a filtration process where the fibre slurry is collected on a rotating sieve. The water passes through the sieve. The fiber-cement product collected on the sieve is subsequently transferred to a felt and thereafter transferred to a rotating drum. After this the "wet green sheet" is cut from the forming drum and the product is manufactured, using varied curing methods. Ideally, the end product should contain the raw materials in the design mix. However, some fine solid particles are lost through the sieve during production and these are returned to the process via recuperation tanks. The function of the recuperator is to collect the solid particles and return these to the machine. A Hatschek machine has more than one recuperator with an overflow system to the second or third recuperator. The second and third recuperators are reasonably clean of solid particles. The solids from the first recuperator are returned to the process and the water from the second and third recuperates is used for mixing water, cellulose preparation, sieve spray, etc. However, due to the fact that the recuperator gradually became contaminated during continuous production because of the dissolved salts and lignin from cellulose and other additives; there is a need to neutralize the recycled water periodically. Traditionally, the fiber-cement industry dumps the excess solid build up and treat the highly alkaline water. However, due to environmental restrictions, which can be different from country to country, the disposal of waste material is not always the same for every factory.

The present work in this paper focuses on the possibility of reusing the effluents after treatment. Although water characterization is not homogeneous for different factories around the globe, the water used in the Hatschek process is gradually polluted after filtration with time. Therefore, it is mandatory to treat the production water in order to keep the process water's pollutants content at low to moderate level. In this sense, this study explores the different alternatives to treat the more problematic effluents, organic matter and dissolved salts, to make viable a longer reuse of the effluent and reach a closed water circuit without water disposal.

## MATERIALS AND METHODS

The water used for the present study was collected from the sedimentation tank after five days of production running from a European fiber-cement plant (Etex Factory in Valladolid, Spain). These sampling conditions are considered as the most unfavorable since water had been recirculated during the whole week of production and collected in the most polluted part of the Hatschek system. Quantitative analysis of metals and anions were performed by Inductively Coupled Plasma Optical Emission Spectrometry and Ionic Chromatography, respectively (**Table 1**). The results obtained, together with the characterization of production water was characterized two more times in order to check pollution levels at different dates, are detailed in Table 2.

**Table 1- Analysis of the chemical elements present in the water.**

| Concentration (mg/l) of metals | | | | |
|---|---|---|---|---|
| Na | K | Mg | Ca | Si |
| 2145 | 8524 | 0.1 | 570 | 0.30 |
| **Fe** | **Cr** | **Zn** | **Ni** | **Al** |
| <0.1 | 0.055 | <0.050 | <0.050 | <0.1 |
| **Mn** | **Cu** | **Sr** | **Ba** | **Li** |
| <0.030 | <0.050 | 6.7 | 0.30 | 9.7 |
| Concentration (mg/l) of anions | | | | |
| $Cl^-$ | $NO^{2-}$ | $NO^{3-}$ | $PO_4^{3-}$ | $SO_4^{2-}$ |
| 523 | 4,9 | <10 | <20 | 11549 |

**Table 2- Properties analysis of the water used in this study.**

| Parameter | pH | e-cond (mS/cm) | COD | TDS | [Ca$^{2+}$] | [K$^+$] | [Na$^+$] | [SO$_4^{2-}$] |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | | | | | (mg/L) | | | |
| February value | 13.45 | 48.7 | 1306 | 30035 | 3810 | 10976 | 2761 | 17347 |
| April value | 13.20 | 50.6 | 1053 | 28655 | 1226 | 9366 | 1493 | 15650 |

From water characterization results, it is possible to see clearly that production water has high conductivity (as conductive as seawater), with values around 50mS/cm in both cases, and elevated TDS concentration of around 30 g/L. As expected from TDS values, most of the dissolved salts are alkali sulfates, that are very soluble and therefore are difficult to remove. Obtained COD values are above 1000mg/L, which are not harmful enough for FC products. However, if the intended final goal is the closure of the water circuit, higher values should be avoided, so COD removal is of major interest. In order to assure that the water employed in this study is representative of the overall companies worldwide, waters from 2 different Brazilian companies were analyzed (Table 3). From Table 3, it is confirmed that the pollutants observed in the studied water are also present in Brazilian waters, being highly alkaline and conductive. The main difference is the reduced COD content in Imbralit water, probably due to the use of bleach cellulosic fibers.

**Table 3- Properties analysis of the water from Brazilian companies.**

| Parameter | pH | e-cond (mS/cm) | COD | TDS | [Ca$^{2+}$] | [K$^+$] | [Na$^+$] | [SO$_4^{2-}$] |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | | | | | (mg/L) | | | |
| Eternit Brazil | 13.35 | 36.86 | 879 | *** | *** | 8420 | 1502 | 9800 |
| Imbralit | 13.60 | 55.25 | 474 | 35431 | 3129 | 9872 | 2144 | 12435 |

## APPLIED TREATMENTS

Regardless the treatment applied, for every procedure, water was previously filtered through a by filter with a porosity size of 45 μm to measure pH and electronic conductivity. Then, water samples of 200 mL were magnetically stirred in Erlenmeyer flasks. Then, every treatment was applied for 45 min. Three different treatments were applied to the waters summarized in Table 2:

1. Chemical sulfate precipitation;
2. Reduction of alkali sulfate by mixing with ethanol;
3. Ionic removal by Ionic Exchange.

### Chemical sulfate precipitation

Governments in next decades will probably control sulfate concentrations in water in a harsher manner. Current recommended levels for sulfate worldwide establishes a maximum value of 1000mg/L, 10 times lower than the sulfate content of the FC production waters. Traditionally, the common method for sulfate precipitation is the chemical addition of lime, to precipitate CaSO$_4$. Since FC production water is saturated in Ca(OH)$_2$ from Portland grains dissolution in water and later precipitation, it is difficult dissolve more Ca(OH)$_2$ so sulfate precipitation is inhibited. Even with Ca(OH)$_2$–free water, the high pH of the water, above the lime solubility limit (around 12.5), would leave insoluble lime in the reactor. In order to make viable sulfate removal by CaSO$_4$ precipitation two different routes, summarized in **Table 4**, were explored.

**Table 4- Alternatives for chemical precipitation of sulfates compounds**

| Reduction of production water pH | Adding soluble Ca compounds |
|---|---|
| Adding $H_2SO_4$ (pH=2.38) | Adding $CaCl_2$ + $NaAlO_2$ |
| Adding $CO_2$ (pH=7.29) | |

**Reduction of alkali sulfate by mixing with ethanol**

The main challenge of alkali sulfate removal is the high solubility of this type of salt in water, with values of 14 g/100 mL and 111 g/L at 20ºC for $NaSO_4$ and $KSO_4$ respectively. Even after partial chemical sulfate precipitation, $K^+$ and $Na^+$ concentrations are hardly decreased, increasing alkalinity over time, which is much undesired. A usual process to sort this problem out is evaporative crystallization, but it requires a high amount of energy, which involves an economic cost in order to vaporize water to saturate the solution and precipitate the salt. One possibility for FC production water could be the addition of an organic solvent to reduce the alkali sulfate solubility. For that, a new ternary system (alkali sulfate + ethanol + water system) is used to promote the precipitation of any alkali sulfate (Urréjola et al., 2011). Contrarily to sodium, the potassium sulfate salt has no coordination water when it is in equilibrium with an aqueous solution or in a solution of water and ethanol, thus the only substance to be transferred between the solid phase and the aqueous is potassium sulfate. After mixing the ternary system in the batch and precipitating, ethanol was evaporated by distillation in a packed distillation column with glass raschig rings.

**Ionic removal by Ionic Exchange**

For cation exchange ($Na^+$, $K^+$, $Ca^{2+}$), the Amberlite IR120 Na resin suits the characteristics of the FC production water, which is hard with a $Ca^{2+}$ concentration above 2000mg/L and, at the same time, mineralized. For anion exchange, mainly $SO_4^{2-}$, Amberlite IRA420 Cl resin was employed. After every use, Amberlite IR120 Na resin was regenerated with a $H_2SO_4$ solution in water at 60g/L for 30 min. Amberlite IRA420 Cl resin was regenerated with a NaOH solution of 3% for 30min

## RESULTS AND DISCUSSION

**Chemical sulfate precipitation**
    a)    Reduction of production water pH

With the reduction of the pH, according to Table 5, it is possible to reduce the levels of sulfate up to 14.02% when $CO_2$ is injected into FC water. This treatment makes more soluble $Ca(OH)_2$, precipitating mainly $CaCO_3$ and $CaSO_4$. This is clearly seen from **Figure 1**, where it is possible to observe that the main diffraction peaks match the diffraction planes of both $CaCO_3$ and $CaSO_4$. There is also a decrease of the conductivity of the water. Water before treatment presented a conductivity value of 50.2 mS/cm, so this conductivity reduction is related to the precipitation of compounds and the removal of hydroxyl groups. It is remarkable that the addition of $H_2SO_4$ increases the level of sulfate, although it also reduces conductivity and pH is low to solubilize $Ca(OH)_2$.

**Table 5- Water parameters after the different techniques to reduce water pH.**

| Acidification treatment | $\%[SO_4^{2-}]$ removal | cond (mS/cm) | pH |
|---|---|---|---|
| $H_2SO_4$ addition | -25.7 | 34.7 | 2.38 |
| $CO_2$ addition | 14.0 | 32.3 | 7.29 |

| Lime addition+$CO_2$ treatment | $\%[SO_4^{2-}]$ removal | cond (mS/cm) | pH |
|---|---|---|---|
| 4.2 g/L $Ca(OH)_2$ | 56.8 | 32.4 | 10.33 |
| 5.6 g/L $Ca(OH)_2$ | 39.3 | 34.7 | 11.88 |

Since $CO_2$ addition is effective to reduce pH, lime addition was applied to further decrease sulfate content. Lime addition is effective to remove sulfate ions from water once $CO_2$ is applied, presenting higher sulfate removal efficiency for the lower $Ca(OH)_2$ addition. It is clear that the lower the pH the higher the lime solubility so $CaSO_4$ is easily precipitated. $CO_2$ injection into any reactor is a conventional procedure with little economic impact, though the optimization of the process is necessary. This reduction of pH after filtration becomes an interesting option to remove sulfates from water due to the economy of the method and the decrease of the electrical conductivity achieved. An additional water treatment, by the incorporation of lime to the system, intensifies the removal of $SO_4^{2-}$ without modifying conductivity. The application of this treatment would have a reduced financial impact due to the low cost of lime and the possibility of obtaining a chemical byproduct, $CaSO_4$, with high purity. Since FC water is strongly buffered at high pH, great amount of sulfuric acid is required to acidify the water, so acidification with $H_2SO_4$ is discarded to remove sulfates according to previously exposed.
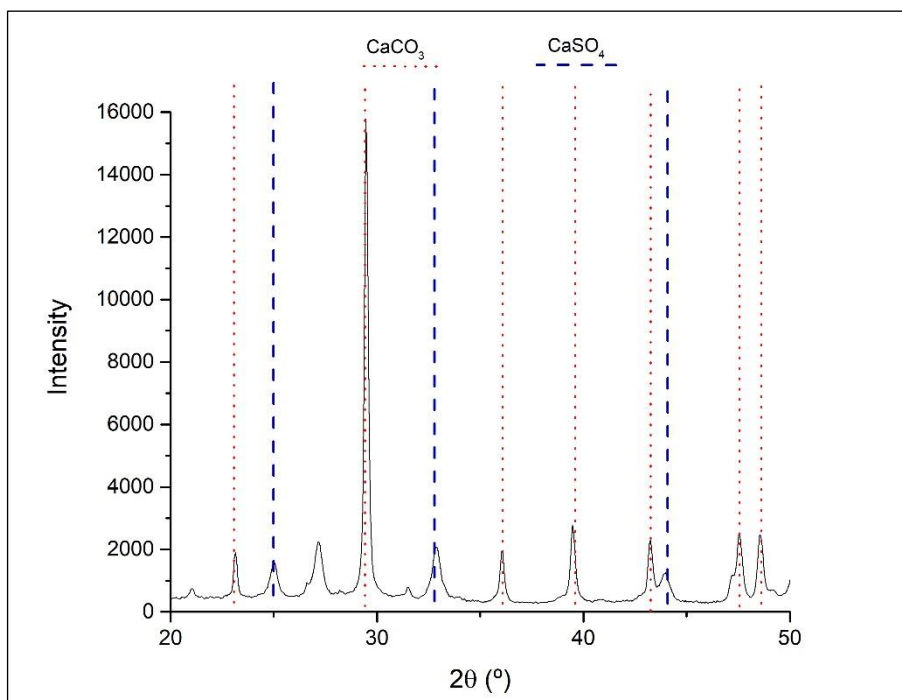


**Figure 1- XRD of the precipitate after $CO_2$ addition to FC water analyzed.**

b)    Use of soluble Ca compounds at pH > 12.5

As expected, sulfate removal by $CaSO_4$ is easily achieved by using a soluble calcium compound. In the case of $CaCl_2$ it is obvious the efficiency of the treatment to reduce $SO_4^{2-}$ anions, increasing the sulfate removal with the increase of $CaCl_2$ concentration in water. This relation is valid until the maximum concentration of $CaSO_4$ is reached, around 1600-2100 mg/L depending on the water characteristics. Once this solubility limit is overcome (over 24 g/L), extra $CaCl_2$ is not effective and, therefore, pointless. It is remarkable that electric conductivity that is strongly related to anion levels in the water stays reasonably constant until a concentration of 24 g/L. The introduction of $Cl^-$ to the water is counterbalanced by the removal of $SO_4^{2-}$. Another remarkable point is that the total organic carbon (TOC) decreases with higher $CaCl_2$ concentrations. When further sulfate removal is intended by the precipitation of ettringite (Aft), monosulfate (AFm) and Firedel's salt, it is possible a complete sulfate removal (Abdel-Wahab and Batchelor, 2002; Almasri et al., 2015) along with a reduction of TOC. It should be noted that these calcium anion-aluminates generates viscous solids that would be filtered easily with the aid of conventional flocculants.

**Table 6- Water characterization of the water after treatment with CaCl$_2$ addition.**

| | Chemical addition (CaCl$_2$) | % [SO$_4^{2-}$] removal | TOC (mg/L) | cond (mS/cm) | |
|---|---|---|---|---|---|
| [1] | 0.25g/L CaCl$_2$ | 1.4 | 217 | 50.4 | |
| [2] | 0.5g/L CaCl$_2$ | 3.8 | 205 | 51.0 | |
| [3] | 1g/L CaCl$_2$ | 10.0 | 196 | 51.6 | |
| [4] | 8g/L CaCl$_2$ | 13.8 | 202 | 52.3 | |
| [5] | 16g/L CaCl$_2$ | 53.3 | 212 | 52.9 | |
| [6] | 24g/L CaCl$_2$ | 82.8 | 168 | 54.9 | |
| [7] | 32g/L CaCl$_2$ | 82.2 | 146 | 63.9 | |
| | **Chemical addition [CaCl$_2$+Ca(OH)$_2$+AlNaO$_2$]** | **% [SO$_4^{2-}$] removal** | **TOC (mg/L)** | **cond (mS/cm)** | **Na$^+$ (mg/L)** |
| [1] + | 21.2 g/L Ca(OH)$_2$ + 8.5g/L AlNaO$_2$ | 69.6 | 255 | 92.7 | 2844 |
| [2] + | 21.2 g/L Ca(OH)$_2$ + 8.5g/L AlNaO$_2$ | 74.5 | 238 | 85.7 | 3027 |
| [3] + | 21.2 g/L Ca(OH)$_2$ + 8.5g/L AlNaO$_2$ | 94.6 | 215 | 86.4 | 4163 |
| [4] + | 18 g/L Ca(OH)$_2$ + 6.6g/L AlNaO$_2$ | 97.8 | 210 | 83.5 | 2955 |
| [5] + | 8.4 g/L Ca(OH)$_2$ + 3.2g/L AlNaO$_2$ | 100.0 | 224 | 68.4 | 2647 |
| [6] + | 3.4 g/L Ca(OH)$_2$ + 1.2 g/L AlNaO$_2$ | 98.5 | 165 | 65.0 | 1815 |
| [7] + | 3.4 g/L Ca(OH)$_2$ + 1.2 g/L AlNaO$_2$ | 96.1 | 155 | 61.3 | 1965 |

On the other side, there is a neat increase of conductivity for the higher AlNaO$_2$ concentrations. This increase is related to the higher amount of Na$^+$ in the water after solution and precipitation of Al$^{3+}$. For additions with high content in AlNaO$_2$ (8.5 g/L), samples with lower Na$^+$ content display conductivity values above values for samples with higher Na concentrations, since lower Na levels are related to lesser Al$^{3+}$, SO$_4^{2-}$, (OH)$^-$ and Cl$^-$ precipitation, so water is more ionic charged. The addition of CaCl$_2$ is attractive due to the low-price of this compound in the case any FC company had the possibility of later remove chloride with a different technology. Thus, conductivity would remain at lower values even allowing the total replacement of sulfate by the addition of a soluble compound able to release Al$^{+3}$. Though it is out of the topic of this research, the precipitation of salts in the form of AFt and AFm may be explored in order to recycle these compounds in the composition of the matrix of FC cement products

**Reduction of alkali sulfate by mixing with ethanol**

After adding ethanol to the fiber-cement water in different concentration by volume, ranging from 10 to 40%, a clear removal of sulfate from water was produced (Figure 2). As it was expected, alkali solubility decreases and, thus, sulfate precipitation is easier to occur. As the ternary system (water + ethanol + alkali sulfate) introduces a great amount of organic compounds, it is necessary to evaporate ethanol from the system. It is important to notice that a compromise solution is required to apply the treatment, given that the larger ethanol concentration in the system increases both the sulfate removal efficiency and the volume of liquid to evaporate. Water before treatment and after ethanol treatment (40% by volume) and later evaporation was characterized. Table 7 shows that [K$^+$] is reduced in almost 85%, while Na$^+$ content is reduced in approximately 20%, because of the hydrous form in which sodium sulfate is presented. The SO$_4^{2-}$ and K$^+$ reduction is produced along with a significant reduction of pH and electrical conductivity, leaving water parameters under acceptable values to be reused for fiber-cement production.
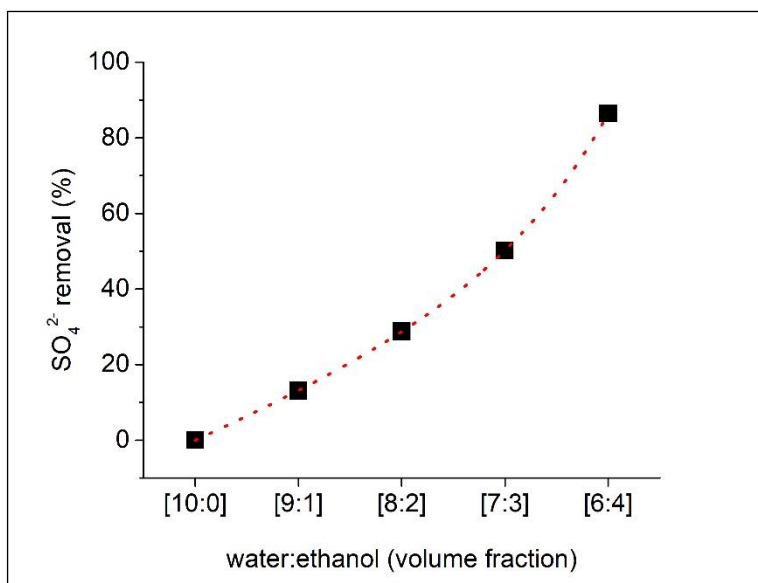
**Figure 2- Trend of sulphate removal for different ethanol concentrations in water.**

**Table 7- Water characterization before treatment with ethanol and after treatment and vaporization**

| Water | $K^+$ | $Na^+$ | $Ca^{2+}$ | TOC | pH | cond |
|---|---|---|---|---|---|---|
| | | | concentration (mg/L) | | | |
| As received | 9366 | 1494 | 610 | 218 | 13.2 | 51.9 |
| 6:4 by volume | 1462 | 1246 | 143 | 270 | 12.8 | 29.3 |

By XRD diffraction performed on the precipitate after filtration is possible to confirm that the main compound obtained is $K_2SO_4$. By semi-quantitative analysis with (X'Pert High Score Plus V.4.5), it is calculated that nearly 85% of the total precipitated material belongs to this salt. The rest of the components are sodium sulfate: thenardite ($Na_2SO_4$) and mirabilite ($Na_2SO_4 \cdot 10H_2O$). In addition, $CaSO_4$ and some minor traces of $CaCO_3$ are present in alignment with $K_2SO_4$. The addition of ethanol to FC water after initial filtration may awake some interest for factories in areas with large ethanol production at reduced cost. The major inconvenience of this process comes with the addition of organic compound, $C_2H_6O$, that may interfere in the cement properties and consequently in the properties of fiber-cement products. Nevertheless, a conventional distillation process removes almost all ethanol content from the water, so the inconvenience becomes an energetic matter to evaporate ethanol. The great advantage of this technique is the possibility of precipitating a solid with elevated content in $K_2SO_4$ that is prominently valuable as fertilizer, compensating the issue of the extra energy demand of this method.
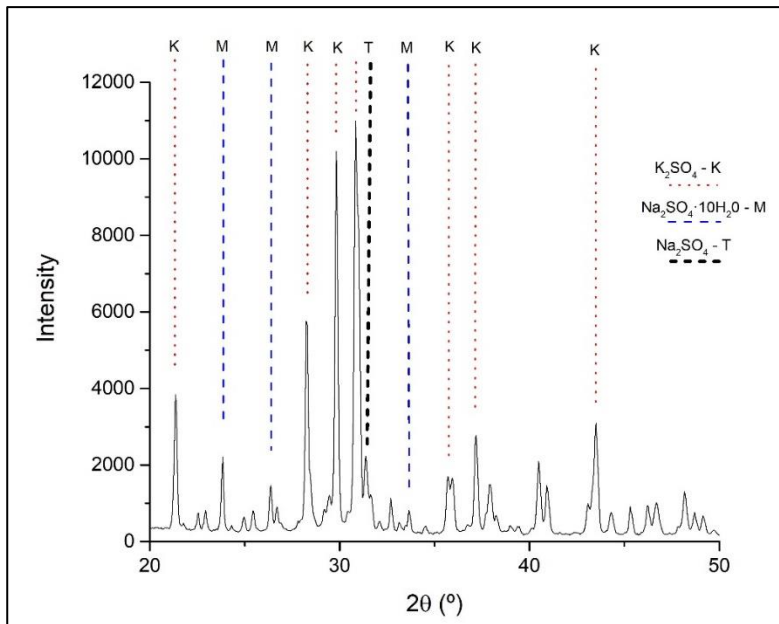
**Figure 3- X-ray diffractogram of the precipitate obtained after treatment with ethanol and latter filtration.**

## Ionic removal by Ionic Exchange (IET)

In order to test ionic removal by ionic exchange under different pH conditions, FC water pH was tested: (1) as received, pH > 13); (2) after adding $CO_2$, pH = 7.5 and (3) acidified with $H_2SO_4$, pH =4 .2. **Table 8** displays water characterization for every initial pH conditions before IET. In addition, in order to test the efficiency of the treatment for every pH condition, 3 ionic resin concentrations were used after activation as $H^+$ and $OH^-$ forms and, thus, test the viability of recycling the resins: low (10-20% v.t.), medium (20-40% v.t.) and medium (30-60% v.t.). The most remarkable fact is that the reduction of pH, either using $CO_2$ or $H_2SO_4$, decreases the amount of Na+ in the water even before any treatment. Thus, since the addition of $CO_2$ to reduce pH also results in the reduction of $Na^+$, this parameter has to be taken into account to analyze the efficacy of the process.

**Table 8- Water parameters before Ionic Exchange Treatment.**

| | concentration (mg/L) | | | | | |
|---|---|---|---|---|---|---|
| initial water condition | K+ | Na+ | $SO_4^{2-}$ | TOC | pH | cond (mS/cm) |
| As received (pH > 13) | 9366 | 1494 | 14455 | 218 | 13.2 | 50.6 |
| Adding $CO_2$ (pH = 7.5) | 8895 | 862 | 11333 | 146 | 7.5 | 32.3 |
| Acidified with $H_2SO_4$ (pH = 4.2) | 8921 | 848 | 15843 | 168 | 4.2 | 34.7 |

Results of samples 1 to 9 in Table 9 summarize water characterization after treatment with cationic resins that was intended to remove alkalis from the water. For $K^+$ and $Na^+$ removal, the efficiency of the treatment increases with the higher resin dosage, where samples with initial pH values of 13 and 7.5 present the lower alkali concentration for every resin dosage. Samples with pH = 7.5 do not present significantly lower values compared with water with pH = 13, so it is concluded that for alkali removal pH reduction leads to no improvement of the treatment. Even only regarding [$Na^+$], samples without previous pH reduction show similar values compared with samples with initial pH = 7.5 in spite of the $Na^+$ reduction experienced by the water just adding $CO_2$ to the system. Samples with initial pH = 4.2, besides the lower efficiency to remove sulfate, present higher electric conductivity as the addition of $H_2SO_4$ introduces more ionic charges to the water. However, the acidification of the water promotes a greater removal of organic matter for any resin dosage. **Table 9** also exhibits a reduction in

TOC content for every treatment with cationic resin. The use of cationic resins to remove alkalis from FC water proves to be efficient, even at the lowest dosage tested with a reduction of both alkalis to 50-60% of the initial values in factory conditions. This single treatment results into an improvement of the factory environmental conditions, avoiding the exposure of the workforce to highly concentrated alkaline waters.

**Table 9- Water characterization after Ionic Exchange Treatment**

| Sample Nº | Initial pH | Resin type | Resin dosage (% v.t.) | concentration (mg/L) | | | TOC | pH | cond (mS/cm) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $K^+$ | $Na^+$ | $SO_4^{2-}$ | | | |
| Cationic resin treatment | | | | | | | | | |
| 1 | 13 | $Na^+$ | 10 | 3942 | 497 | * | 121 | 1.8 | 25.1 |
| 2 | 7.5 | $Na^+$ | 10 | 3943 | 490 | * | 117 | 1.7 | 27.9 |
| 3 | 4.2 | $Na^+$ | 10 | 4760 | 563 | * | 110 | 1.3 | 45.2 |
| 4 | 13 | $Na^+$ | 20 | 2273 | 333 | * | 96 | 1.2 | 38.6 |
| 5 | 7.5 | $Na^+$ | 20 | 1987 | 295 | * | 96 | 1.2 | 38.4 |
| 6 | 4.2 | $Na^+$ | 20 | 2683 | 374 | * | 95 | 1.0 | 59.2 |
| 7 | 13 | $Na^+$ | 30 | 1331 | 223 | * | 82 | 1.1 | 47.1 |
| 8 | 7.5 | $Na^+$ | 30 | 1359 | 229 | * | 99 | 1.1 | 46.1 |
| 9 | 4.2 | $Na^+$ | 30 | 1785 | 276 | * | 83 | 0.9 | 67.3 |
| Anionic resin treatment | | | | | | | | | |
| 10 | 13 | $Cl^-$ | 10 | * | * | 10639 | 134 | 13.1 | 55.3 |
| 11 | 7.5 | $Cl^-$ | 10 | * | * | 7632 | 105 | 9.8 | 31.4 |
| 12 | 4.2 | $Cl^-$ | 10 | * | * | 10639 | 125 | 12.5 | 37.3 |
| 13 | 13 | $Cl^-$ | 20 | * | * | 3931 | 123 | 13.2 | 61.3 |
| 14 | 7.5 | $Cl^-$ | 20 | * | * | 8673 | 70 | 10.7 | 31.9 |
| 15 | 4.2 | $Cl^-$ | 20 | * | * | 9483 | 106 | 12.7 | 42 |
| 16 | 13 | $Cl^-$ | 30 | * | * | 1849 | 90 | 13.2 | 63.8 |
| 17 | 7.5 | $Cl^-$ | 30 | * | * | 10408 | 81 | 12.3 | 34.9 |
| 18 | 4.2 | $Cl^-$ | 30 | * | * | 8326 | 110 | 12.9 | 46.4 |

The use of anionic resin aims essentially to reduce the sulfate levels from water. In this sense, higher removal efficiency occurs for treatments with higher resin dosage when initial pH value is high (> 13) and acidified with $H_2SO_4$ (pH = 4.2). However, as previously stated, the dissolution of the $H_2SO_4$ used for pH reduction generates more $SO_4^{2-}$, which reduces the efficiency of the treatment under these conditions. The reduction of sulfate levels is more notorious when treatment is applied in waters with no changes in initial pH, where the concentration is diminished up to 26, 73 and 87 % for a resin dosage of 10, 20 and 30% respectively. Contrary to what happens with cationic resin (**Table 9**), samples with $CO_2$ seem to be less effective for higher resin dosage. This loss of effectiveness may be related to the affinity of the resin with charges from organic matter in the water, since TOC content is cut down up to 52% for a dosage of 20% v.t., so that samples with reduced initial pH by CO2 addition present lowest TOC values after treatment with anionic resin. Similar effects as noticed for IET with cationic resins take place for anionic resins, as TOC values are lower for any treatment condition.

**Different treatments combination**

The idea after all the water treatments considered in this study is that ionic exchange (IET) is the only treatment able to reduce all the contaminants levels ($K^+$, $Na^+$, $SO_4^{2-}$ and organic matter). However, IET by itself is neither as effective as it would be combined with any other possible treatment nor a definitive solution. It has to be taken into account that anionic exchange viability relies on the capacity of regeneration of the resins, which demands additional chemical regenerants that are gradually polluted with ions removed from water, which must be treated before discharge. Besides, some of the treatments explored in this study showed higher efficiency to decrease sulfate levels and in a cheaper way. The benefit of using precipitation treatments is the simplicity of their implementation and the lower cost compared to other advanced water treatment methods. In a close water circuit, it is only necessary a sedimentation sector with a filtration system to integrate this technique. Probably, the foremost inconvenience of using precipitation treatment is the generation of solid waste that is necessary to be properly either treated before dumped or disposed in controlled landfills.

In order to determine the optimal treatment, there are many factors to contemplate such as local administrative regulations, raw materials and equipment availability, FC water conditions and desired water quality after treatment. Considering all these conditions there is not unique technical answer to treat FC water, so a combination of different procedures seems the ideal solution. Figure 4 summarizes the different alternatives tested and their efficiency for each pollutant removal. The diagram displays warmer colors for higher efficiency in the reduction of the pollutants and darker colors for negative performance of the treatment.
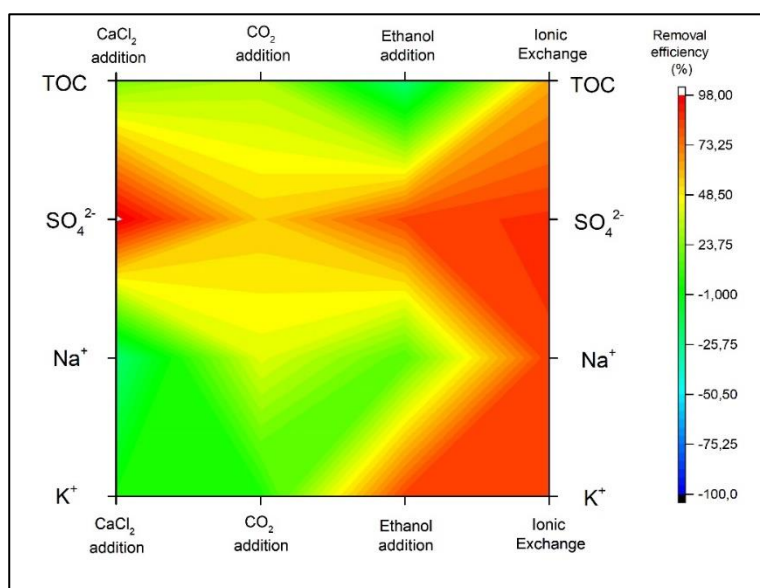


**Figure 4- Diagram of the removal efficiency of every treatment for every pollutant studied with a possible adjustment of the treatment combination.**

It is possible to optimize a combined treatment by averaging and weighting every independent treatment. Figure 4 shows the diagram set following the order in which each treatment has been presented in the present study, which is only illustrative and far from the optimal. An accurate setting of the diagram should include all the factors that are conditioning the treatment selection, both technically and economically. However, just attending to the efficiency of each treatment, it is possible to adjust the diagram in order to obtain a larger warm area. As it was noted earlier, IET would be enough to treat FC, although the addition of $CaCl_2$ promotes sulfate precipitation in a more efficient way. A possible multi-stage treatment would be:
1. $CO_2$ injection (reduction of $Na^+$, $SO_4^{2-}$ and TOC);
2. Precipitation with $CaCl_2$ (further decrease of $SO_4^{2-}$ and slight increase of $Na^+$ and $Cl^-$);
3. IET (cationic resin for reduction of $Na^+$ and $K^+$ and anionic resin for further decrease of $Na^+$ and removal of $Cl^-$ introduced by $CaCl_2$).

## CONCLUSIONS

In view of the results obtained, a promising development is observed to treat FC process waters. These advances still have a great margin for improvement, especially when it comes to implementing them at an industrial level, given the singularities of each company. Therefore, there is the possibility of deepening and giving continuity to the present study so that the water treatment systems are applied successfully. In addition, a couple of key remarks are drawn:

1. Despite the constraints of this study, according to the achieved results, it is possible to develop a technology for the treatment of the FC process water. Thus, water contaminants may be kept at reduced values so equipment maintenance, product quality and water disposal are carried out in a more efficient way. With this study is proven that with simple water treatment techniques, such as $CO_2$ injection and chemical precipitation, sulfate and organic matter may be decreased along with pH and conductivity reduction. Moreover, when techniques that are more advanced are employed, e.g. ionic exchange, pollutants levels are further lessened to values with little interference on water quality for either FC production or human exposure.
2. Depending on the conditions of each company, it would be necessary to address various aspects, such as economic viability and local legislations (health and safety, environmental, filtrated material dumping). In this sense, it is particularly noteworthy the use of ethanol to precipitate alkali sulfate since this technique may be of special interest in regions like Brazil where this organic solvent in largely produced.

Consequently, financial reports and previous implementation in pilot-scale or testing lines are recommended before implementation on an industrial basis in order to offer a customized solution.

### Recommendations for future work

In this study, basic techniques have been explored that allow, on the one hand, the water treatment with the minimum economic impact, and on the other hand, its implementation in the simplest possible way. More restrictive laws, not only from the point of view of the discharge of wastewater, but of the restriction of water usage, would make the production of FC is uncompetitive compared to other types of materials. Therefore, it is necessary to look for alternative treatments that allow the use of water through a closed circuit, thus avoiding the absolute discharge of water. Additionally, the implantation of more sophisticated techniques not studied in this work could be evaluated, like reverse osmosis, ultrafiltration or membrane distillation.

Obtaining a closed water system, which allows the process water to be reused indefinitely, would lead to an increase in the content of organic matter. These high values of organic matter have not been contemplated in the present study given the current conditions of the water used by the industry. However, advanced oxidation techniques could be explored as ozone treatment, $TiO_2$ photocatalysis, photo-Fenton process and electro-oxidation technology in order to remove organic matter in combination with the treatments presented here.

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