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# Process water management and the organic matter issue

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## Abstract

The deterioration of the quality of fiber cement industry process water, due to organic matter (OM) accumulation, is a rising concern, especially for closed circuit methods. This study focused on the OM contamination by evaluating: i) the effect of OM on the fiber cement production process and final product; ii) the origin of the OM contamination and iii) the variability of OM contamination during a production cycle. The effects of OM in the production process and in the final product were evaluated by a hydration test applied to the Portland cement and a bending test applied to the fiber cement production in lab scale using processing water with different OM contents from three different industries. The origin of the OM contamination was evaluated by leaching tests with different waters (pH wise) and cellulose pulps with different lignin content. Finally, the process water from the production cycle of three different industries were analyzed. Increasing the OM content (up to 1700 mgCOD/L) in the water has shown to slow down hydration reactions in 1.3 h and to reduce the bending resistance of fiber cement composites (modulus of rupture 27% lower) in comparison to the reference. The origin of contamination is mainly related to the leaching of the cellulose pulp during refining process, which was evidenced by the leaching tests. Using water with lower pH, pulps with lower lignin content and lowering the retention time in the tanks that store refined pulp (< 6 h) can therefore be effective routines for reduction of OM contamination. The temporal profile of OM contamination during production cycle varies from one industry to another and the knowledge of this profile is essential to decide when the treatment to OM removal should be applied.

## KEYWORDS:

Fiber cement, leaching effect, water contamination, closed cycle, water reuse.

## INTRODUCTION

In the fiber cement industry, a large amount of water is needed in order to disperse the fibers and the matrix ingredients in the formulation of the composites. In the Hatschek process, after mixing the components, the excess of water is removed enabling reuse of water in a closed circuit.

During continuous production process in closed circuit, the water gradually becomes contaminated, because of the dissolved salts (inorganic), lignin from cellulose (organic) and other additives, resulting in the necessity of periodically neutralization of the recycled water, in order to maintain the quality of the final product and the efficiency of the process. The neutralization of the inorganic contamination of process water was already evaluated in previous study (MÁRMOL et al., 2018). However, to the best of our knowledge, there are no open access studies relating the influence of organic matter (OM) content in process water on fiber cement production or evaluating the necessity or importance of neutralization of this contaminant.

The presence of OM in the water used in the manufacturing of the fiber cement is a possible source of problems to the quality of the final product. Studies in cement hydration have shown that the presence of organic compounds in the water do not promote fundamental changes in the products of hydration, however it affects the speed of the reaction (KHALIL; WARD, 1973; GOVIN et al., 2005; GOVIN; PESCHARD; GUYONNET, 2006; LI et al., 2018). This would interfere undoubtedly in the fiber-cement production process and in the final product. Thus, this is a subject of great interest to the industries and a gap to be addressed. The focus of the present study was to fulfill this gap and make a thorough evaluation of the problem assessing some of the main factors of particular significance in water reuse projects, such as the reclaimed water quality and the process water characteristics (METCALF & EDDY, 2003). This comprises the origin of contamination and the changes of those characteristics during production process.

Due to the complexity of the subject, this study was carried out in two parts. The first one, approaching the origin of the contamination and the effect of contamination in the final product, is presented in the present paper. The second part focuses in the evaluation of treatment alternatives and will be also presented in a separate paper entitled: "*Fiber cement process water treatment for organic matter removal*". Three Brazilian fiber cement industries were involved in the present research, not only supplying process water and raw material, but also crucially contributing with information and knowledge in the fiber cement production process.

## MATERIALS AND METHODS

The OM contamination was covered in three different research lines: i) the effect of OM on the fiber cement production process and final product; ii) the origin of the OM contamination and iii) the variability of OM contamination during a Hatschek production cycle.

The effects of OM in the production process and in the final product were evaluated by a hydration test applied to the Portland cement and a bending test applied to composites manufactured in lab scale. The origin of the OM contamination was evaluated by leaching tests with different waters (pH wise) and cellulose pulps with different lignin content. The process waters from the production cycle of three different industries were analyzed to observe temporal profile of OM contamination during production process.

### *Cement hydration test*

Three different waters were used in the cement hydration test. Deionized water (D), process water (P), took from one of the partner industries and this same process water with higher OM content (P+). The characteristics of the three different waters are given in Table 1.

**Table 1 - The OM content was measured as Chemical Oxygen Demand (COD).**

| *Water type* | *Code* | *COD (mg/L)* | *pH* | *Conductivity (mS/cm)* |
|---|---|---|---|---|
| ***Deionized*** | D | 0 | 6.4 | $9 \times 10^{-3}$ |
| ***Process*** | P | 918 | 12.6 | 28.8 |
| ***Process with higher OM content*** | P+ | 1778 | 12.3 | 28.7 |

The OM content of P+ was increased by leaching of cellulose pulp (Kappa 100). The leaching process will be further explained in the present work. The hydration heat of cement paste was tested using an eight-channel micro-heat instrument (TAM-Air). Portland cement CP-ARI (ABNT NBR 16697:2018, equivalent to Type III – ASTM C150) was used in the hydration test with the three different waters with different OM content (Table 1: D, P and P+). Glass ampoules containing ~3.9 g of a cement paste with 50% water and 50% cement were placed in the TAM-Air to monitoring the heat released during hydration process. The test lasted for 7 days, however, after the 3rd day there were no detectable changes in the heat of the samples.

***Bending test***

Fiber cement composites were manufactured in lab scale with the same three different waters used in the cement hydration test (D, P and P+). The pads of the composites of (200 × 200) $mm^2$ and around 6 mm thick were prepared in laboratory scale using a vacuum dewatering box followed by pressing technique described elsewhere (MÁRMOL et al., 2013)

The formulation used in composites preparation was (in proportion of the total solid mass): cement CP-ARI (equivalent to Type III ASTM) (64%), limestone (31.1%), cellulose pulp (3.5%), synthetic fiber (1.4%). The solids were mixed in a proportion of 7.6 water/cement by mass. Each composite was sealed wet in a plastic bag to proceed with thermic cure for 10 days. The bending test was performed with all the specimens according to the RILEM draft recommendation (Testing Methods for Fibre Reinforced Cement-Based Composites) in a universal testing machine Emic DL-30000 equipped with 1 kN load cell. A four-point bending configuration was applied for the determination of the values of modulus of rupture (MOR), limit of proportionality (LOP) and specific energy (SE).

***Leaching test***

The leaching test consisted in simulating the refining (or beating) process in a laboratory scale. Three different waters (deionized water, alkaline water and process water) and two different cellulose pulps with different lignin content (Kappa 100 and Kappa 30) were applied. The use of deionized water simulates an optimum operational situation, that is, no organic or inorganic contamination in the process water. The alkaline water (deionized water with pH 12 due to NaOH addition) was used to observe the role of pH, on leaching process. The process water was tested to simulate a situation closer to the industry reality (OM content of 1025 mg/L).

The test was held by grinding for 5 min the two different pulps with the three different waters in a lab scale (2 L) blender. After grinding, the mix water + pulp was put under mixing (140 rpm) at controlled temperature of 50°C for 24 h. This condition simulates the tanks where the pulp is kept after refining in the industries, before its use in the production process. The leaching was monitored by measuring the OM content (COD basis) in the water with 1, 3, 6, 12 and 24 h of contact between water and pulp.

***Temporal OM content profile test***

To observe if there were changes in the organic matter content in the process water during a production cycle, temporal profiles were performed. Thus, samples of the process water were taken during two production cycles to industries 1 and 3 and one production cycle to industry 2. During the cycle the water is continuously recirculated in the system, what delimitates a cycle is the interruption of the production for machines cleaning.

## RESULTS

### *Cement hydration test*

Figure 1 shows the first 12 h of hydration reaction. The reaction of cement occurs right after contact with water and it can be observed in the first minutes of test (Phase I). Even though a properly study of this phase of reaction demands mixing of water and cement inside the calorimeter (which was not the case), in the presented graphic, it can be perceived that a greater heat flow was liberated when deionized water (D) was used, comparatively to the use of both process water (P and P+). This indicates that a greater ions dissolution occurs when "clean" water is used.

After Phase I, the rate of the reaction drops and Phase II (dormant period) begins. In this stage the cement concrete stays in the plastic state, which is important for workability and transportation (ABBAS; MAJDI, 2017). Finally, in Phase III, the cement hydration and heat liberation takes place. In Figure 2, it could be noticed that when P+ was used, the hydration process occurred at a lower rate and that when deionized water was used, the rate of reaction was slightly superior to the reaction with process water.  That means the OM had a retarding effect on hydration process, and that the greater the OM content the slower the reaction will be. The retarding effect of OM in the hydration process was already related in previous studies. Components like esters (LI et al., 2018), carboxylic acids (GOVIN et al., 2005) and lignosulfonates and glucose (MILESTONE, 1979) have a retarder effect on the hydration of Portland cement.

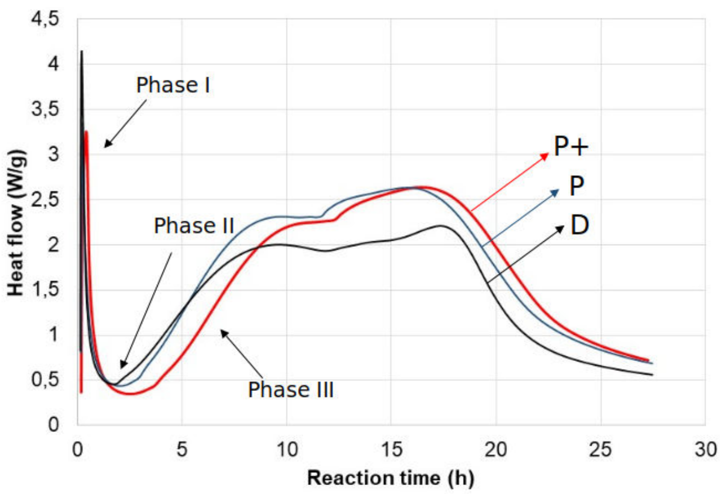


**Figure 1 - Heat flow of hydration reactions (D: deionized water; P: process water and P+: process water with higher OM content).**

### *Bending test*

The specimens manufactured with process water with higher OM content (P+) presented stratification. The higher OM content in P+ hindered the incorporation of cellulose pulp to the fiber cement mixture, and a layer of fiber could be seen in the composites (Figure 2A-C).

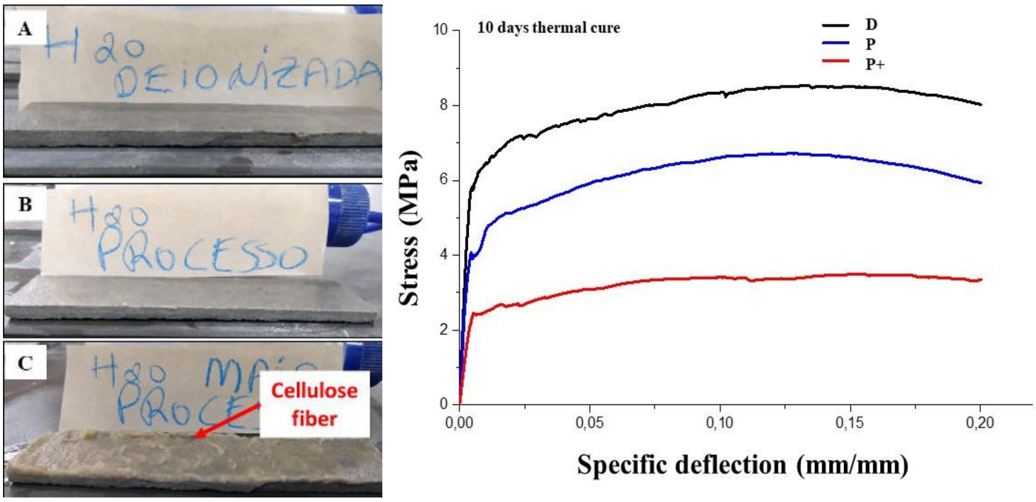


**Figure 2 - Specimens manufactured with (A) Deionized water – D, (B) Process water – P, and (C) Process water with higher OM content – P+. Right-hand graphic: Stress versus specific deflection curves.**

Figure 3D shows typical stress versus specific deflection curves of the composites manufactured with the three different types of water (D, P and P+). Significant differences can be observed between the composites made with different waters. The stress the composites made with P+ could endure before deformation is about 30% of the stress supported by composites made with D and 50% of the composites made with P.

These results demonstrate that the OM content in the water used in the manufacture of fiber cement composites has a significant influence on the physical and mechanical properties of the final product. They also indicate that the grater the OM content, the greater the losses in bending strength. At the OM content of ~1700 mgCOD/L, the stratification of composites occurs, which implies that there is a minimum quality requirement (process water OM content limit) to be accomplished. Thus, the monitoring of OM content in water is of great importance to control the quality of fiber cement final product and also to predict when treatment of process water to remove OM is required.

However, the mixing in laboratory condition and the absence of flocculants influence the homogeneity of the manufactured composites and play an important role in their performance. In real conditions, in the industrial facilities, the difference in those properties may be mitigated by the use of better equipment for mixing and flocculants.

***Leaching test***

In Figure 3, pulp kappa 100 promoted greater increment on the COD regardless the water was used, comparatively to pulp kappa 30. The lower lignin content on the pulp kappa 30 promotes lower increment of OM (measured as COD) on the water, so the use of bleached pulps should be considered to lower the contamination of water with OM.

With deionized water the increment in COD occurs mainly in the grinding, demonstrating lower leaching potential, and indicating that the quality of the water used in the refining process could significantly reduce the OM contamination. Regarding the alkali and the process water, both resulted higher leaching effect, and if the initial COD of process water is ignored, the alkaline water resulted higher leaching potential. The pH seems to play an important role in the extraction of OM from cellulose to the water. Thus, if the pH of process water is neutralized, possibly lower leaching effect would be observed.

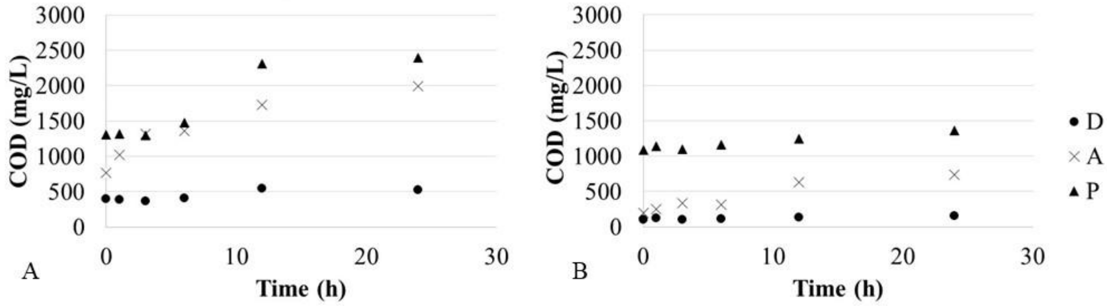


**Figure 3 – Chemical oxygen demand (COD) temporal profile during leaching test. (A) Pulp kappa 100 with higher lignin content and (B) Pulp kappa 30 with lower lignin content. (D: Deionized water; A: Alkaline water and P: Process water)**

Another factor to be considered in the leaching test is the time of contact between pulp and water. In Figure 3, it is possible to observe (mostly with pulp kappa 100) that greater increase in COD occurs after the first 6 h of contact. This demonstrates that keeping short period contact between water and pulp is an important strategy to diminish water contamination with OM and that if the contact between water and pulp is greater than 6h, the monitoring of the OM content in water is even more important.

***Temporal OM content profile test***

Understanding the temporal profile of the OM in the process water is important to determinate at what point of the production process the treatment of the water should be applied. Figures 4, 5 and 6 show the temporal profile of the COD content of the process water in the different industries, partners in this research.

Industry 1 had similar behavior on COD content in both cycles, the average COD content of the process water was (1061 ± 85) mg/L and no cumulative increment of OM over time was observed (Figure 4). Industry 2 presented a lower OM content at the beginning of the cycle (468 mg/L) which increased over time, reaching 935 mg/L of COD at the end of the cycle (Figure 5). In the Industry 3, both cycles had no significant increase in the OM content during time, average COD content of (872 ± 96) mg/L, even though on the last day of one of the cycles there was a drop in the COD content (Figure 6).

The process water COD content temporal profile was different for different industries. This must be due to differences in production process and raw material use, such as a greater replenishment of water, for example, or the use of pulps with lower lignin content.

The differences observed between industries temporal COD profile (mainly industry 2) demonstrates that each industry has its own particularities and that even though a single method of water management could be applied to all facilities, due to similarities in the composition of process water, the timing to apply the treatment may be the different. In industries 1 and 3, for example, the treatment could be applied at any time during the cycle while for industry 2 the critical point, where treatment should be considered, is after 5 days of recirculating the water.

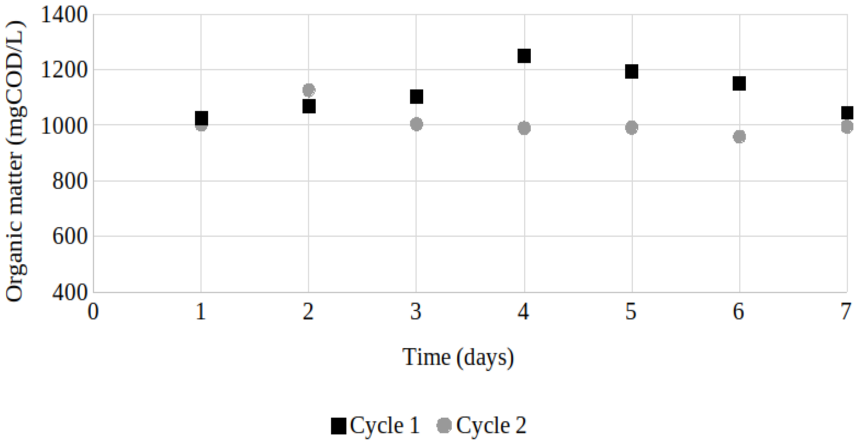


**Figure 4 – Temporal profile of COD content during two cycles - process water of Industry 1.**

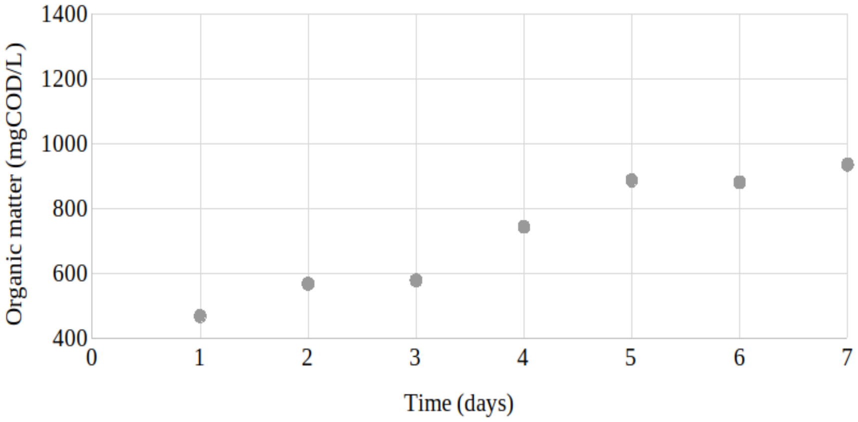


**Figure 5 - Temporal profile of COD content - process water of Industry 2.**

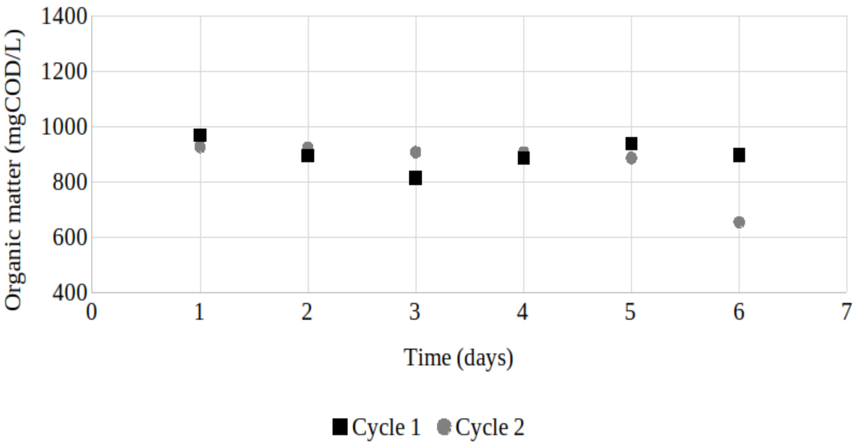


**Figure 6 - Temporal profile of COD content during two cycles - process water of Industry 3.**

## CONCLUSIONS

The presence of OM in the water slows down the cement hydration reactions and increasing OM contents in the process water imply losses in the mechanical performance of final product. The leaching effect in the refining pulp process has a significant contribution to contamination of the process water with OM. Using pulps with lower lignin content, clean water (mainly pH neutrality wise) and reducing contact time between water and pulp, decreases the OM process water contamination. The temporal OM contamination profile was different depending on the industry evaluated, this result shows that to each industry there will be a different time when treatment will be required. Thus, monitoring OM contamination is a key issue to the establishment of a treatment alternative.

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