



Silica removal with sparingly soluble magnesium compounds. Part II



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ABSTRACT

Silica scaling is one of the main bottlenecks in the reuse of papermaking effluents by reverse osmosis. The low hardness of deinking paper mill effluents makes necessary the addition of magnesium compounds to increase silica removal at high pH. Based on the results obtained in Part I, MgO was selected as the most efficient magnesium source. Its efficiency was tested at different dosages (150–10,000 mg/L), pH values (8.2–9.5) and temperatures (25–50 °C) and the optimization of the reaction time was also carried out. Silica removals over 95% were obtained at the 4 pHs and 3 temperatures with MgO dosages over 500 mg/L; however, MgO can only be applied if water temperature is higher than 35 °C, as the dissolution of MgO is limited. Moreover, the analysis of the solids obtained (SEM-EDX and FTIR) showed that the main mechanism for silica removal was co-precipitation of magnesium silicates (forsterite and antigorite) while adsorption was less significant.

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1. Introduction

One alternative to reduce fresh water consumption in the paper industry is the reuse of the final effluent after an extensive treatment, usually involving a final reverse osmosis (RO) stage [1,2]; however, this treatment is not feasible when treating effluents with high silica content, as those typically found in deinking paper mills, due to severe scaling in the membranes. If silica is not previously removed, it is not possible to work on the RO at recoveries higher than 20% [2], thus comprising the economic feasibility of the whole treatment chain. Moreover, there are also stringent limits for silica in the effluents (i.e. 50 mg/L for Finland and Canada) that makes silica removal of a growing interest not only for deinking paper mills but also for other industries even if effluent reuse treatments based on RO membranes are not used [3].

The main origin of the high silica levels in paper mill effluents (50–250 mg/L SiO₂) is the sodium silicate used as process additive [1,3,4]. Due to its great variety of functions, mainly focused on the deinking and bleaching steps, its substitution is very difficult without affecting the quality of the final product [5–7]. Therefore, it has to be removed from the process water. The limitations of silica removal by coagulation at high pH [3,8] and by softening using soluble magnesium compounds [9] motivated the study of sparingly soluble magnesium compounds [10].

In part I of this work, the use of different sparingly soluble magnesium compounds (MgO, Mg(OH)₂, (MgCO₃)₄·Mg(OH)₂·5H₂O) was

studied. At ambient temperature (~20 °C) and 15 min contact time, a maximum 40% silica removal was achieved with the most efficient (MgO). In order to increase dissolved magnesium concentration and thus silica removal, pre-acidification of the slurries of the sparingly soluble magnesium compounds was tested. Results demonstrated this pre-acidification is a competitive approach to increase silica removal. Under the optimal conditions (1500 mg/L dosage, pH = 11.5), 86% silica removal was obtained with both MgO and Mg(OH)₂. Although pre-acidified magnesium compounds increased less the conductivity of the treated water than soluble ones, final conductivity was still high. Therefore, there is a need of generating new knowledge on the direct use of sparingly soluble magnesium compounds to treat high silica loaded waters and the optimal conditions for their application.

In this sense, part II of the article studies the effect of the operational temperature and the contact time on silica removal using MgO, which was the most efficient compound in part I. With this aim, different jar-tests were carried out. Based on the results obtained, the optimal conditions (maximum silica removal and minimum conductivity increase) were selected. An additional novelty of this paper is the elucidation of the mechanism involved in silica removal which is unclear in the literature [11–13].

2. Materials and methods

2.1. Materials

This study was carried out with the effluent of a Spanish paper mill before its discharge to an urban wastewater treatment plant.

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This mill produces newsprint using 100% recovered paper. Table 1 summarizes the main characteristics of the effluent. Dissolved fraction was obtained by filtration through 0.45 μm pore size PTFE membrane filters. Samples were stored at 4 °C during the tests and no sets of trials longer than five days were carried out. MgO, used as magnesium source, and NaOH, used as pH regulator, both analytical grade, were supplied by PANREAC. MgO and NaOH were prepared 10 wt./vol.% on a daily basis.

2.2. Methodology

2.2.1. Optimization of pH, dosage and temperature

First, the treatment was optimized in terms of pH and dosage at ambient temperature (25 °C). MgO was tested at 10 dosages (from 50 to 10,000 mg/L) and at 4 different initial pHs: 8.2 (initial pH of effluent), 9.5, 10.5 and 11.5. These pHs and dosages were selected according to previous studies carried out by the authors with a similar effluent [9,10]. Next, the effect of the temperature on silica removal was studied. In this case, 4 dosages of MgO (150, 250, 500 and 1000 mg/L) were tested at 3 temperatures (25, 35 and 50 °C) without pH regulation.

For these tests a jar-test methodology was used. First, when necessary, the pH of the samples was adjusted by adding NaOH to 200 mL of sample. After 1 min of mixing at 200 rpm, MgO was added and mixed during 24 h at 200 rpm and then the waters were allowed to settle for 1 h. Finally, the clarified waters and its dissolved fraction were characterized. Jar-tests were carried out in a multiposition magnetic stirrer OVAN MultMix Heat D. All trials were carried out by duplicate and the average error between replicates was always around 5%.

2.2.2. Optimization of the contact time

The optimization of the contact time was carried out at the optimal dosage of MgO (500 mg/L) and at the 4 initial pHs (8.2, 9.5, 10.5 and 11.5) and the 3 temperatures (25, 35 and 50 °C) used previously. In this case, the pH regulator was firstly added to 600 mL of sample and after 1 min mixing, MgO was added. Samples were taken at different time periods and immediately filtered through 0.45 μm PTFE filter to remove the solids present in the water and stop the reaction. These samples were characterized in terms of silica and magnesium concentration. After a number of consecutive samples, with silica concentration approximately constant the experiment ended.

2.3. Analytical methods

The pH was measured using a model GLP 22 (Crison, S.A), according to Standard Method 4500, and the conductivity was

Table 1
Characteristics of the paper mill effluent.

Raw water	
pH	8.2
Conductivity (mS/cm)	2.55
COD (mg/L)	380
Total alkalinity (mg/L CaCO ₃)	721
Total suspended solids (mg/L)	75
Total solids (mg/L)	2050
Turbidity (NTU)	125
Dissolved fraction	
Silica (mg/L SiO ₂)	260
COD (mg/L)	360
Sulfates (mg/L)	250
Calcium (mg/L)	33.9
Magnesium (mg/L)	6.8
Total solids (mg/L)	1975

measured with a model GLP 31 (Crison, S.A.), according to Standard Method 2510 [14]. Alkalinity was measured by titration with sulfuric acid 0.1 N using a pH electrode connected to an automatic titrator, model Compact I (Crison Instruments S.A.) to reach pH 4.5, according to EPA 310.1 method. Total solids and total suspended solids were measured according to the Standard Method 2450 B and 2450 D respectively [14]. Turbidity was measured according to ISO 7027:2001 with a LP 2000-11 nephelometer supplied by Hanna Instruments. Reactive silica was measured by flow analysis and photometric detection through silicomolybdate and reduction to molybdenum blue, using a FIA Compact (MLE GmbH) according to DIN EN ISO 16264 and expressed as mg/L of SiO₂. COD was photometrically measured by the Nanocolor[®] COD 1500 Method from Macherey–Nagel GmbH, according to ISO 15705:2003 in an Aquamate UV–Vis spectrophotometer supplied Thermo Scientific Inc. Calcium and magnesium content were measured using a direct air-acetylene flame atomic absorption method according to ISO-7980:1986 in a SpectraA 220 spectrophotometer supplied by Varian.

Precipitated solids were analyzed by FTIR spectrophotometry and SEM–EDX. The FTIR analyses were carried out in a Nicolet Magna 750 spectrophotometer with a Spectratech IR-Plan Advantage Microscope. Spectra were recorded at 2 cm⁻¹ resolution and 16 scans were taken for both the samples and the background. Samples were prepared with the same amount of sample and KBr, i.e. 0.6 mg of sample and around 250 mg of KBr. Finally, the image analyses of the precipitate particles were carried out in a JEOL JSM-6400 Scanning Electron Microscope (SEM). This SEM is configured with an energy dispersive X-ray analyzer (EDS system) which enables to perform compositional analysis.

3. Results and discussion

3.1. Optimization of the operational conditions

3.1.1. Optimization of pH, dosage and temperature

Fig. 1 shows silica removal rates obtained at 25 °C with different dosages of MgO, at four initial pHs. As observed, silica removals over 95% were obtained at dosages higher than 500 mg/L, independently of the initial pH.

With 50 mg/L of MgO, silica removal was around 20–25% at the 4 pHs. These low removal rates could be attributed to the low dosages of MgO used. Considering silica precipitates as enstatite (MgSiO₃), with molar ratio Si/Mg = 1, the theoretical maximum silica removal rate that could be achieved using 50 mg/L MgO would be 28% which is very close to the obtained results. This maximum

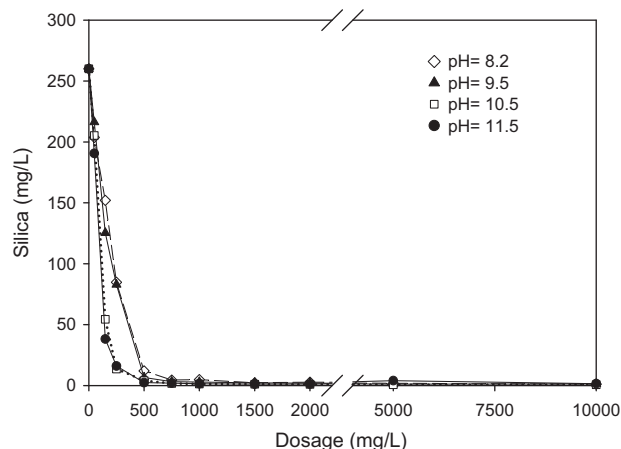


Fig. 1. Silica removal vs. MgO dosage at 25 °C and different initial pHs.

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