Enhancing Molten Sulfur Filtration during Sulfuric Acid Manufacturing for Phosphate Fertilizer Production in Morocco with Cellulose-Based Filter Aids

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Meriem Essakhraoui [1,*], Abdelhamid Nyassi [1], Aziz Boukhair [1], Hajar Bellefqih [2], Nils Haneklaus [3], Hamid Mazouz [4] and Essaid Bilal [2]

[1] Faculty of Sciences, Chouaib Doukkali University, El Jadida 24000, Morocco
[2] École Nationale Supérieure des Mines de Saint Etienne, CNRS UMR EVS, 5600, F42023 Saint Etienne, France
[3] Td-Lab Sustainable Mineral Resources, Universität für Weiterbildung Krems, 3500 Krems, Austria
[4] Division of Research and Innovation (DRI), Mohammed VI Polytechnic University (UM6P), Ben Guerir 43150, Morocco
* Correspondence: messakhraoui@gmail.com

Abstract: The filtration of liquid sulfur is a key operation in the production of sulfuric acid that is used for phosphate fertilizer production in Morocco and elsewhere. The purpose of the filtration process is to remove solid impurities from liquid sulfur, which could clog the sulfur burner spray nozzles, leading to the reduction of the lifetime of the sulfuric acid production unit. The standard life cycle operation for sulfuric acid units is 24 months, while due to clogging, this lifetime can be reduced to less than 18 months, which is obviously a tremendous economic disadvantage. In the liquid sulfur filtration process, a precoat made of diatomaceous earth is usually used. In this work, the performance of a standard diatomaceous earth filter aid was compared to the performance of two commercial, inexpensive, cellulose-based filter aids, namely, FILTER-900 and FILTER-1100, which are distinguished by their respective Dalton numbers (900 Da and 1100 Da). The experiments were realized using an industrial sulfur filtration device, and the results indicated that all three of the filter aids yielded similar performance in terms of the impurity content in the filtered liquid sulfur. The cellulose-based filter aids did, however, show a lower specific filter-aid consumption, accompanied by an increase in operating cycle times from 24 to 72 h. In addition, the use of the cellulose-based filters allowed for the relatively easy removal of the filter cake without damaging the filter cloths (which is often an issue with the diatomaceous earth filter aids). It was further noticed that the filtered liquid sulfur obtained using the cellulose-based filter aids remained uncontaminated by silicate, which is one of the main elements that can result in clogging of the sulfur spray nozzles. The first experimental data presented here are therefore promising, and further industrial tests as well as economic analysis for using cellulose-based filter aids in industrial sulfuric acid production are encouraged.

Keywords: sulfuric acid production; molten sulfur; filter aid; cellulose; diatomaceous earth

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1. Introduction

Sulfuric acid has a crucial role in the production of phosphate fertilizers that are of significant importance to Morocco's economy [1]. Mineral fertilizers are usually produced from wet phosphoric acid (WPA), which is again produced by reacting phosphate ore with sulfuric acid. The attack of one metric tonne (t) of phosphate ore is usually done with 0.6 t concentrated sulfuric acid and generates 0.4 t WPA [2]. In 2021, Morocco produced nearly 10 million t phosphoric acid [3], resulting in a tremendous sulfuric acid consumption. Globally, more than 265 million t sulfuric acid are produced annually. Liquid sulfuric acid is usually produced from solid sulfur. The manufacturing process involves three main steps: the first consists of the combustion of sulfur, followed by the oxidation of sulfur dioxide in the presence of a catalyst, and, finally, the absorption of the resulting sulfur trioxide into sulfuric acid to produce oleum, which is then diluted with water to obtain the desired acid concentration (see Equations (1)–(3)) [4]. All of the steps are exothermic, and modern phosphate fertilizer plants can harvest the resulting energy effectively [5].

$$\text{Combustion}: \ S + O_2 \rightarrow SO_2 \tag{1}$$

$$\text{Conversion}: \ SO_2 + 1/2O_2 \rightarrow SO_3 \tag{2}$$

$$\text{Absorption}: \ SO_3 + H_2O \rightarrow H_2SO_4 \tag{3}$$

The sulfur comes in the form of solidified pellets or flakes that are first melted using low-pressure steam, as shown in Figure 1 [6]. Most of the used natural sulfur contains salt impurities in the ppm (parts per million) levels [7], but elevated levels between 30 ppm and even up to 12,000 ppm have also been measured. Clark [8] reported the impurity limits depicted in Table 1 for industrial sulfur in Canada.

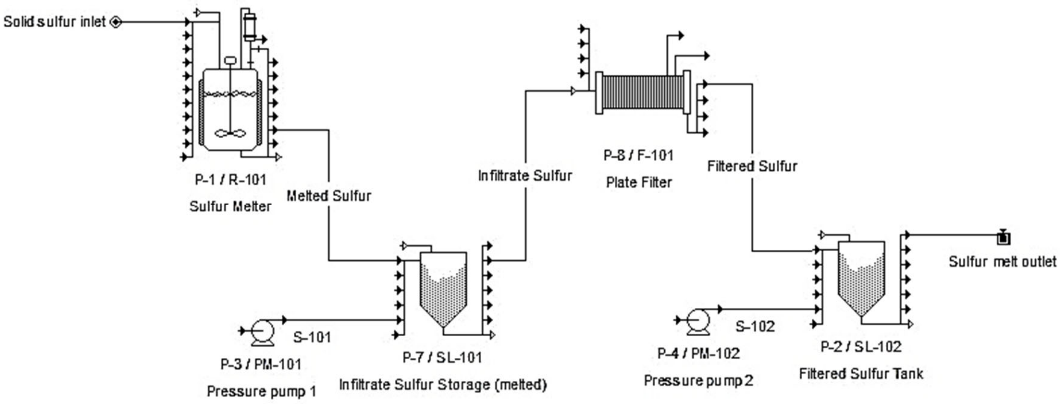

Figure 1. Basic steps of sulfur fusion with filtration for phosphoric acid production in Morocco.

Table 1. Impurity limits of solid sulfur as reported by Clark [8].

Impurities	Specification Limit
Ashes	500 ppm
Carbon	250 ppm
Residual H_2S	0–30 ppm
Arsenic	0.25 ppm
Selenium	1 ppm
Water	1%
Acidity	0.01%
Chloride	50 ppm

The impurities tend to form rubbery or even solid deposits upon heating [9,10]. Furthermore, the relatively large quantities of solid sulfur are generally stored outdoors, and they can thus collect dust as well as dirt from the surrounding environment [11]. To produce the required quality of sulfuric acid, the liquid sulfur that is sent to the burner of the sulfuric acid plant must first undergo a pretreatment or filtration process to remove solid impurities, which are referred to as ashes.

The presence of ashes in the liquid sulfur can plug the sulfur spray nozzles or accumulate in catalyst beds, leading to an increase in pressure and also to shorter operating lifetimes of the equipment, and this results in increased operational costs. Hence, the removal of these solid impurities is crucial to avoid the premature shutdown of a sulfuric acid plant [11]. Several techniques of separation are used for this purpose already. In the beginning, the removal of solids from molten sulfur was performed using settlers, but due to the high viscosity and density of the molten sulfur, the settling rate of the solids in the molten sulfur is relatively slow [11]. Molten sulfur filtration has been adopted in many plants to remove the settlers that proved to be less effective [9,12,13]. In this process, it is common to use horizontal tank-vertical pressure leaf filters made from AISI 316L stainless steel, which are schematically shown in Figure 2. The pressure leaf filters need to be precoated with a filter aid before usage [14]. This filter aid serves to protect the filter cloth from corrosion, prevent fouling of the wires, and improve the later filter cake release [11]. The filter aid must be carefully selected to allow for the highest flow while allowing a reasonable recovery of solid impurities. Bächle et al. [15] provide a useful illustration that shows how the filter aid works.

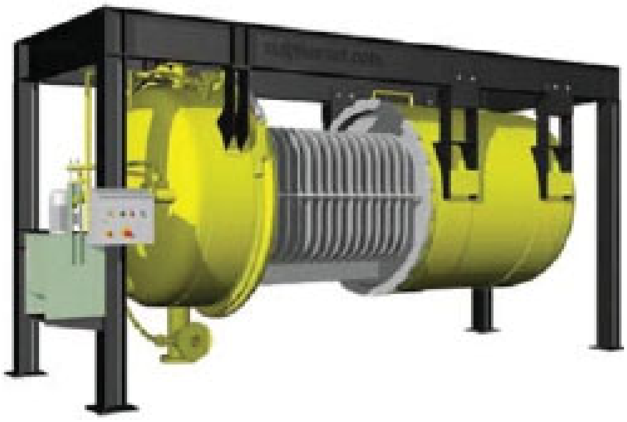

Figure 2. Typical horizontal tank-vertical pressure leaf filter used for molten sulfur filtration [12].

Donovan and Barnett [8] previously compared candle and pressure-leaf filter technologies by describing tests with various grades of precoating and additions of body feed, and they recommended conditions for plant filtration of sulfur. In addition, Louie [11] showed that the commonly used filter aids are diatomite and perlite. Diatomite, also known as diatomaceous earth, has been used as a filter aid for nearly a century [16–21]. Sulfuric acid plants usually use diatomite earth as a filter aid, but it is suspected that the high silica content of the inorganic diatomaceous earth can lead, through abrasion, to an early degradation of the filter cloths, so that the sulfur impurities are not properly removed anymore or the units' filter times need to be reduced. In addition, the disposal of the used diatomaceous earth is an issue, as pointed out by Boittelle et al. [22] in their study.

To better understand the impurities present in the molten sulfur, solid samples were recovered from the furnace walls, boiler walls, and gas filters, and they were subsequently analyzed. The accumulation of the impurities at various spots in the sulfuric acid plant revealed high contents of sulfate, calcium, aluminum, and iron, which are shown in Table 2. The source of the calcium is the lime used for neutralization. The other contaminants originate from the addition of the mineral diatomaceous filter aid, which is composed primarily of silica, along with impurities of alumina, iron oxide, and alkaline earth oxides [21].

Table 2. Characterization of solid residues from different locations in the sulfuric acid plant.

	Furnace Wall	**Boiler Wall**	**Gas Filter**
Fe	8.32%	11.46%	10.76%
Al	21.90%	1.42%	1.16%
Mg	1.27%	1.16%	1.27%
Na	2.86%	2.34%	2.74%
Ca	25.03%	26.03%	15.62%
SO_4	7.04%	41.41%	42.09%
Si	6.34%	5.95%	6.18%
Cd	4 ppm	3 ppm	<1 ppm
Cl	33 ppm	27 ppm	29 ppm

The aim of this work is to study a possible substitution of the silica-based diatomaceous earth filter aids with organic cellulose-based filter aids that do not contain silica and other impurities (namely, metals) that could be released into the molten sulfur during filtration. Two types of commercially available, inexpensive, cellulose-based filter aids, FILTER-900 and FILTER-1100, distinguished by the respective molecular weight cutoffs (MWCOs) characterized through the different Dalton numbers (900 and 1100 Da) as well as a diatomite precoat as a control, were used. The focus of the study was on the removal of the impurities present in the molten sulfur. The experiments were conducted with industrial units used in commercial fertilizer production in Morocco.

2. Materials and Methods

In the first set of experiments, three different pre-coating mixtures were prepared from the different filter aids: (1) FILTER-900, (2) FILTER-1100, and (3) diatomaceous earth (control). Approximately 75 kg of each of the different filter aids were used for 24 h while the impurity content of the molten sulfur was monitored after each cycle following ISO 3425–1975 standard [23]. Specifically, the analyses were performed by evaporating the sulfur under an N_2 atmosphere at a temperature of 850–900 °C. The impurity concentration from the different filter aids after each cycle was then reported so that the performance of the different filter aids can be compared. Cellulose-based filter aids were used stirred and unstirred during these experiments to see if this influences the filtration. In total, six filtration cycles were conducted for each of the three filter aids.

In a second set of experiments, the impurity content of the molten sulfur was measured after 24, 48, 72, and 96 h of continuous operation using cellulose-based FILTER-1100 and a control of diatomaceous earth. The second set of experiments was intended to indicate how the two different filter aids compared over a longer period of time. For the second set of experiments, we used approximately 50 kg of each filter aid. In the case of the cellulose-based filter aid (FILTER-1100), the experiments were conducted in an unstirred condition.

The molten sulfur had a temperature of approximately 140 °C during all of the reported experiments.

3. Results and Discussion

Figure 3 shows the impurity or ash concentration after 24 h of continuous molten sulfur filtration. In total six experiments à 24 h were conducted for each of the three filter aids indicated by the numbers (1–6) in Figure 3. It can be seen that the results of both of the cellulose-based filter aids (FILTER-900 and FILTER-1100) are comparable to the results of the diatomaceous earth filter aid that is currently used in industrial production. The cellulose-based filter aid FILTER-1100 showed the best performance among all three different filter aids, especially if FILTER-900 and FILTER-1100 are compared with each other directly, and this is not surprising since the higher Dalton number of FILTER-1100 already indicates a finer mesh that would most likely result in better filtration results. For FILTER-1100, the unstirred filter aid resulted in slightly better results than the stirred one, while for FILTER-900, the results suggest the opposite trend. However, for FILTER-1100, particularly, it can be noted that the difference between the stirred and unstirred filter aid were negligible.

Figure 4 shows that substituting the traditional diatomaceous earth filter aid with a new cellulose-based filter aid (FILTER-1100) can result in similar or even better filtration results. It is also noteworthy that the overall amount of utilized filter aid was reduced by one third from the former 75 kg per cycle (approximately) to the current 50 kg per cycle (approximately).

The cellulose-based filter aid is less dense than the conventional diatomaceous earth filter aid, and this allows the formation of thicker pre-layers with appropriate pipes that promote the flow of liquid sulfur through these pre-layers. Moreover, the elasticity of the cellulose-based filter aid allows for more efficient filtration, even at lower specific consumption. These observations are supported by Dinand et al. and their previous experiments [24].

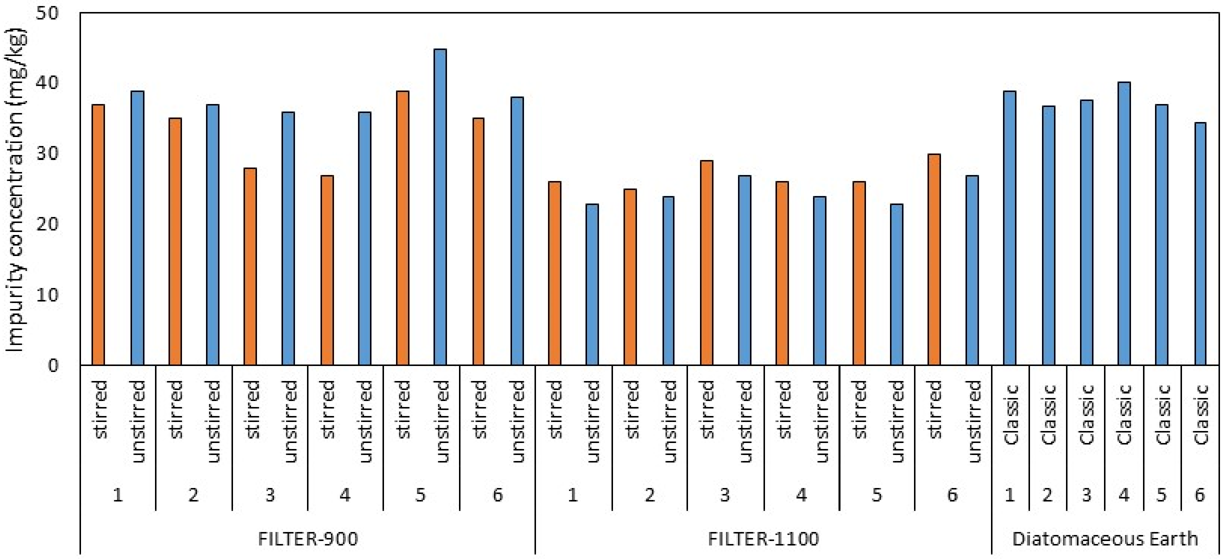

Figure 3. Molten sulfur impurity content using different filter aids (cellulose-based FILTER-900 and FILTER-1100 as well as a diatomaceous earth control) after 24 h of continuous operation. Experiments have been repeated six times (numbers 1–6) for each filter aid.

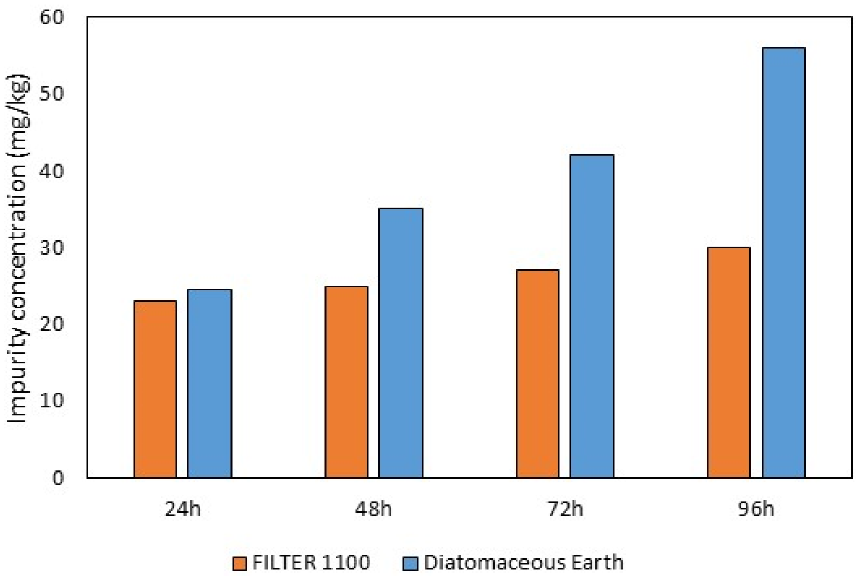

Figure 4. The ash content (AC) according to the specific consumption and the cycle time.

In the case of the cycle time, the performance of the filtration using cellulose-based FILTER-1100 for 72 h is comparable to using diatomaceous earth for 24 h. In other words, even after tripling the length of the filtration cycle, the amount of impurities in the molten sulfur is comparable. Only after 72 h does the impurity content raise to critical levels when FILTER-1100 is used, and, even then, a much smoother increase can be observed. The results thus indicate that the filtration cycle time can be increased from 24 h to 72 h if the diatomaceous earth filter aid is replaced with cellulose-based Filter-1100 while keeping the impurity level in the molten sulfur constant. It is noteworthy that if slightly cleaner sulfur is used, the filtration cycle time may be further increased.

Each filtration cycle is followed by a cleaning operation. In fact, the cleaning operation is complicated when using diatomaceous earth. The pre-coat and solids must be removed from the filter leaves using wooden sticks, which if they are not carefully used, can damage the filter leaves. The large-scale experiments conducted for this study clearly showed that the cellulose-based filter aids can be removed much easier. In fact, in most cases, the filter aid and solids fell out automatically when opening the filters so that potential damage to the filter leaves can probably be largely mitigated if a cellulose-based filter material is used. This will most certainly have to be investigated in industrial application.

We further strongly suggest considering the issue of disposing of the filter aid. It was already pointed out that Boittelle et al. [22] essentially searched for an alternative to diatomaceous earth filter aids because of disposal problems associated with the used filter aid. There are numerous investigations into utilizing a used diatomaceous earth filter aid in construction [25,26]. In comparison, disposal of cellulose-based filter aids that are biodegradable seems to be a much easier process.

4. Conclusions

At the moment, diatomaceous earth is one of the most commonly used filter aids for molten sulfur filtration in Morocco and elsewhere. In this work, we compared the results of a commonly used diatomaceous earth filter aid with that of two cellulose-based filter aids (FILTER-900 and FILTER-1100). The results of this work suggest that using the cellulose-based filter aids does not negatively affect the impurity content of the molten sulfur. Indeed, it was shown that FILTER-1100 can even outperform the diatomaceous earth filter aid, and, so, the filtration cycle time could theoretically be tripled while keeping the impurity content in the molten sulfur constant. The experiments described here were conducted with industrial equipment, and, though very promising, further commercial testing is still strongly suggested. The results are encouraging, though, and besides showing excellent filtration qualities, we believe that the disposal of the used cellulose-based filter material will be much easier than the disposal of the used diatomaceous earth filter aid. In addition, the experiments indicate that cleaning the filters after each filtration cycle, which is a rather tedious task if diatomaceous earth is used as a filter aid, is much easier with cellulose-based filter material, and so the risk of damaging the filter leaves can be reduced. We again recommend further industrial testing to verify the preliminary results presented here.

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