minerals

Case Report

Ore Processing Technologies Applied to Industrial Waste Decontamination: A Case Study

Hernan Anticoi [1,2,*], Josep Oliva Moncunill [1], Carlos Hoffman Sampaio [1], Rubén Pérez-Álvarez [2] and Beatriz Malagón-Picón [2]

[1] Departament d'Enginyeria Minera, Industrial i TIC, Universitat Politècnica de Catalunya Barcelona Tech, Av. Bases de Manresa 61-63, 08242 Manresa, Spain; josep.oliva@upc.edu (J.O.M.); carlos.hoffmann@upc.edu (C.H.S.)
[2] Grupo de Investigación de Ingeniería Cartográfica y Explotación de Minas, Escuela Politécnica de Ingeniería de Minas y Energía, Universidad de Cantabria, Boulevard Ronda Rufino Peón, 254, Tanos, 39300 Torrelavega, Spain; ruben.perez@unican.es (R.P.-Á.); beatriz.malagon@unican.es (B.M.-P.)
* Correspondence: anticoihf@unican.es

Abstract: The correct management of industrial waste, as well as being an environmental obligation, can also be used as an opportunity to reduce costs in terms of energy and raw material consumption. A large amount of waste sand is generated in foundries with a high content of pollutants adhering to its surface structure. In this study, the material utilized consists of a silicic sand that comes from a casting process, with a thin layer of fixed carbon on the surface of the particles. The objective is to remove this contaminant, in order to have clean sands for use in alternative processes, such as in glass raw material, green concrete, or in the recirculation of these in the same process. The mechanical action that is best for eliminating surface attached contaminants is abrasion. In this regard, two specific devices, commonly used in ore processing operations, were utilized to apply energy in a material in order to reach abrasion by attrition, but with different kinetic approaches: stirring in a slurry media and using a light milling, in both cases reducing the grinding media in order to avoid material fracture. The test performance evaluation is mainly focused on the decontamination efficiency, the sand mass recovery ratio, and the energy consumption. The results show that in all cases, liberation is reachable in different levels at different residence times. We were able to decrease the LOI content from 4% to less than 1%, combined with a near 85% recovery rate of clean sand in the case of stirring. In the case of light milling, the results are even better: the final product reached near 0.5% of LOI content, despite mass flow recovery potentially being less than 80%. Finally, we discuss whether energy consumption is the factor which decides the best alternative. The energy consumed ratio when comparing light milling with stirring is near 9:1, which is a significant amount when taking into account the importance of reducing energy consumption in today's industry due to its economic and environmental impact.

Keywords: mineral processing; attrition; energy optimization; decontamination

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1. Introduction

In recent years, the concept of a circular economy was introduced in the development of mining and industrial activity. Firstly, there are environmental purposes for this: we must reduce the carbon footprint of current processes with new methods by applying innovative technologies. This can also result in an economic opportunity, as we can reduce costs in both energy and raw material consumption, taking advantage of waste that, once treated, can be reinserted into production processes [1,2]. Because of this, the European Commission is making enormous efforts to encourage the implementation of the circular economy through a strategic plan, which involves all industrial and economic sectors to adhere to this new philosophy [3].

This motivates much of the development of this study. A company in the industrial sector in Catalonia, Spain, uses silica sands in its foundry production processes. The waste generated creates significant expenses in waste management, in addition to the cost of replacing these sands for the processes. Regarding the comparative advantages of having an Environmental Management Program (EMP) [4,5], the Polytechnic University of Catalonia (UPC) was commissioned to study the possibility of decontaminating the waste generated with techniques that are typical of mineral processing, and in a second stage, to see about the possibility of recirculating the cleaned material and potentially using it in some other application [6], such as glass raw material [7,8] or green concrete [9]. The benefits can be manifold. In addition to savings on raw material purchases, the costs of waste management [10] and landfill disposal reduction [11] could be significant.

The waste that is normally generated by the foundry industry comes from the raw material of the casting process: molding sand as a binding system and bentonite plus additives as binders [12]. This process also generates residual sands and lumps [13]. Current methods for foundry waste reclamation are divided into two categories: mechanical and thermal approaches [10,14]. Attrition is mentioned as the main method used for surface polishing of contaminated particles through an abrasive medium [15,16]. Attrition is defined as the act of wearing or grinding down by friction [17], generating finer particles by abrasion and fractures [18], in which the surface of the particles is removed. Part of the resulting particles are much smaller than the feed particles, and the other part is similar in size to the feed particles [19]. The grain size reduction also includes a particle shape modification [20]. This phenomenon is even found in natural processes, as we can see on placers, where due to the effects of water or wind, the migration of rocks produces contact between them, and by means of abrasion the minerals are released and settled in sediments tramps [21]. In a laboratory scale, attrition was studied on dolomite by abrasion using scrubbing equipment [22]. Despite attrition being considered an undesirable breakage in industrial processes [23,24], it is widely used for decontamination purposes. There is evidence for the use of attrition for its cleaning efficiency in soil remediation technology, where contaminants can be concentrates in coarse particle surfaces [25]. Under the same principle, [26] studies exist on the effect of attrition time on the carbonate removal of a celestine ore. Thermal methods, on the other hand, are mainly used for core sand recovery, and are identified as efficient but energy intensive [10,27]. It is based on the combustion of the pollutants adhered to the residual sands, applying temperatures in the order of 500–900 °C in order to remove all the organic and carbonaceous material [28]. This method uses heat in rotary kilns, multiple hearth furnaces, or fluidized beds [16]. It is highly efficient to remove the binder dispersed in the material, but the one that is adhered to the particles needs a secondary mechanical treatment, so we reach a technical paradox [10,16].

Thus, the objectives of this work are to study the efficiency of two mechanical methods used to achieve attrition: stirring and light grinding. In order to control and evaluate the efficiency of the processes, immediate characterization techniques were used, in this case, on the carbonaceous material. The results are compared with the energy consumed for all the equipment tested. The optimum scenario is to get the most uncontaminated particles at the lowest level of energy consumption possible, which will result in important economic savings. However, depending on the best use of the remaining material, various levels of cleaning are acceptable in order not to affect other characteristics of the material under study, such as its shape, size, and degree of recovery in terms of quantity of mass of recovered sands.

2. Material and Methods

The material consists of a wasted mixture of non-porous quartz and roasted additives from a casting process. In terms of size distribution, it is relatively homogeneous granulated sand, with a top size under 1000 μm. The material composition is also bi-modal, with higher contents of silicon and less contents from the remaining calcinated additive—mainly binder, a volatile carbonaceous sea coal additive [29] that is found covering the silicic sand or as free roasted particles. In this study, carbon (C) is considered the target element to be removed, but for monitoring purposes, it is denominated as LOI. This is justified by the extensive use that can be made of the technique known as loss of ignition (LOI) in order to have almost immediate results in the elimination of this target. The relation between organic C and LOI is also presented and evaluated throughout this study.

The activities are structured in order to carry out liberation tests applied to the material and to have the ability to check the performance of each action. The scheme of Figure 1 proposes an experimental protocol: (1) characterization of the initial material in order to know the key points for pollutant liberation, (2) determination of parameters for each separation technique, and finally, (3) results analysis and efficiency evaluation.

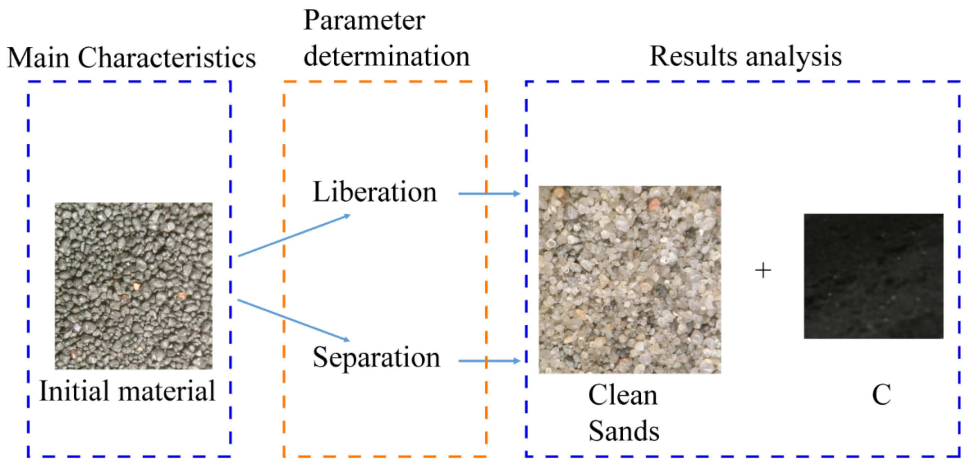

Figure 1. Work strategy scheme to evaluate liberation performance. In an initial stage we have raw material. After liberation and separation, the obtained material is a clean sand plus the removed volatile matter, which is mainly carbon.

In an initial stage, the material is selected using an automatic separator from Laarmann, model LMS-MP10L (Laarmann group, Roermond, the Netherlands). As a way to obtain comparative results, the particle size distribution was determined by means of laser diffraction LS 13 320 Beckman Coulter Particle Size Analyzer (UPC, Manresa, Spain) and standard ASTM sieves [30] using a ro-tap sieve shaker. The target carbon C element was measured using ICP-MS (UPC, Manresa, Spain) from the acid digestion of fused glass beads. Fusion was obtained using lithium or sodium borate. However, in previous studies, a content relation between C and the LOI was established. This technique, loss of ignition (LOI) [31], is used to monitor the whole process. For each test, three representative samples of the material, with a mass of approximately 1 g, were prepared in a crucible of 5 cm radius. The furnace was set at 105 °C to determine the moisture content. After this, the furnace temperature was progressively increased to 505 °C, for 1 h, and then kept burning for 2 h, until the loss of mass was unintelligible. The determined LOI was compared with the total organic carbon (TOC), which was analyzed using a LECO RC612. TOC parameters: oxygen as carrier gas, 3.00 lpm as purge flow, 0.75 lpm as analysis flow, catalyst temp 850 °C. The ratio between both results is also presented in this paper.

To determine the trends of the experimental results, non-linear asymptotic non-convex regressions Equation (1) of the Gauss–Newton type were used through the Minitab@ software. More than 200 iterations were performed, with a tolerance range of 10^{-4}.

$$FC = \Phi_1 + \Phi_2 * e^{\Phi_3 x t} \quad (1)$$

where Φ_1, Φ_2, and Φ_3 are model parameters, and t the experiment time. During simulations, all initial parameters were considered from 1, and the minimum boundaries from −100.

In order to release contaminants by liberation, two mechanical energy applications on the material were studied: attrition by stirring and light milling. The attrition cell [31] consists of an agitator (Figure 2A,B) provided with a stainless steel paddle that rotated at 710 rpm, among other operating conditions (Table 1). Slurry density was about 1.4 g/cm^3, and the solid/liquid ratio used in all tests reached 25%. The liberation of the carbonaceous matter particles was produced by the kinetics generated by the circular movement of the blade, generating collisions between particles and the blade itself. The second technique used in this study was a light milling media device. A laboratory-scale batch drum mill (Figure 2C,D) was used with a reduced ball media charge for the percentage of critical speed (Table 1). The aim is to avoid material breakage by no other effect than abrasion or enhanced inter-particle and grinding media friction, instead of compression or impact [32,33].

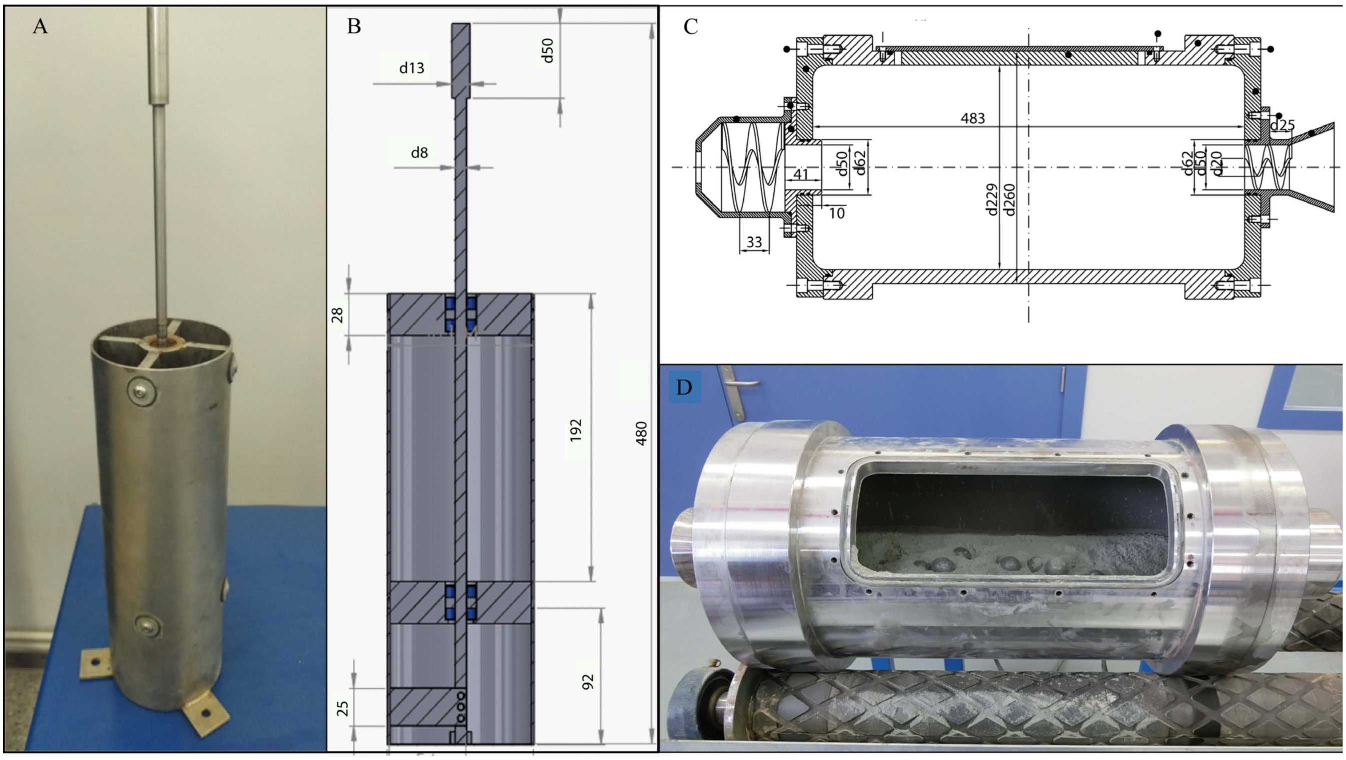

Figure 2. Attrition devices used in this study. (**A**) view of the attrition cell, (**B**) Plot of the attrition cell, (**C**) plot of the tumbling mill , (**D**) view of the tumbling mill.

Table 1. Operative condition of the attrition equipment, batch mill and agitator paddle.

Concept	Light Milling	Stirring	Units
Drum diameter	0.24	0.24	m
Power draw	750	710	W
Critical speed V_C	90	N.A.	rpm
Operative speed	30	710	rpm
Grinding media charge	4	N.A.	kg
Material mass	0.3	0.3	kg
Water	1	1	kg
Solid/water ratio % w/w	30	30	%

N.A.: Not applicable.

Control of the decontamination degree is the key to finding the operational parameters in separation processes. This is why a monitoring strategy was developed for each stage of the process in order to define and evaluate these parameters. The initial material was passed through a physical process of abrasion, at different residence time, by the two previously defined methods: stirring and light milling. The products were subsequently separated into two size phases: the smaller than 90 µm and the coarser ones above this mesh cut size. This size limit was defined in the characterization chapter, and involved the cutoff between particles that are mostly liberated, and those that needed a breakage energy to be released. The split finer phase was characterized, and the coarser particles went to a sink and float test, using a dense media separation solution. In this case, zinc chloride was prepared to achieve a density of 1.7 t/m^3. Each characterized light and dense phase's mass flow values were also determined (Figure 3).

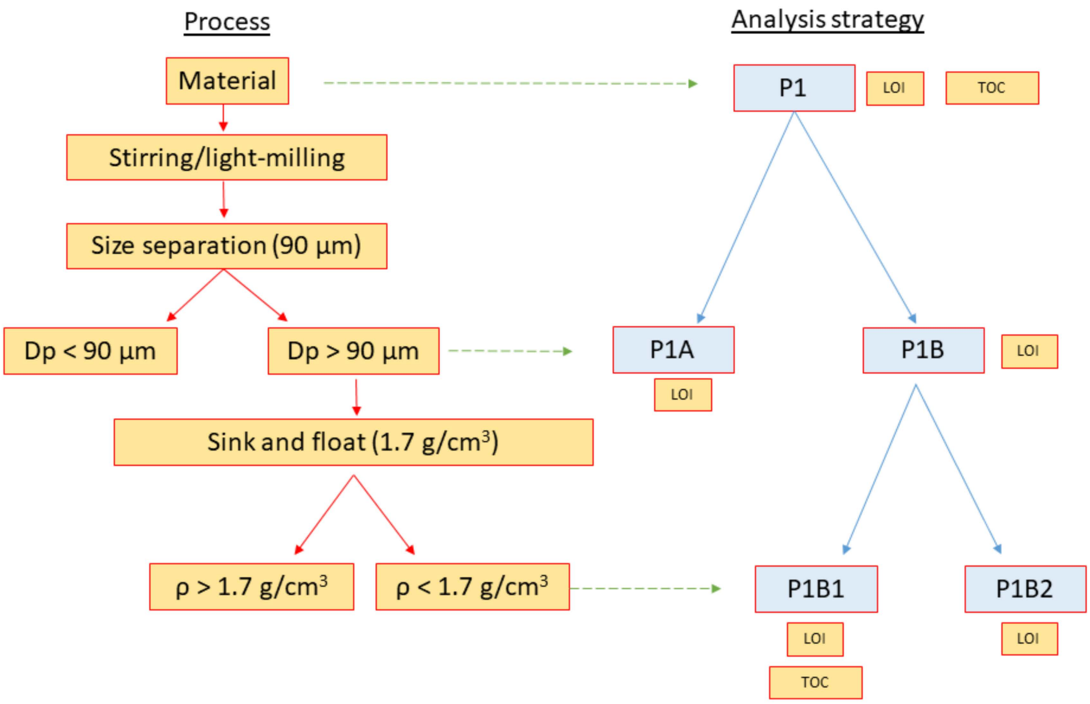

Figure 3. Scheme to obtain liberation of the volatile material contented in the sand, and analysis Scheme.

The energy consumed was the ratio between the times of each experiment, the power of the motors for each piece of equipment, the amount of material processed, and the current measured every second with a standard ammeter [34].

3. Results

3.1. Characterization for Decontamination

A total of 25 tests on the raw material were performed in order to determine the content of LOI, and resulted in an average value of 3.7% (Figure 4), which is consistent with the ICP results, giving nearly 3.9% of C content (Table 2). The overall material composition is interesting in terms of clean sand recovery purposes, thus in case of a highly efficient separation process, an 84% yield of SiO_2 can be recovered from this waste material. The carbon comes from the additives in the smelting process, and it can be seen that the total content of this element, close to 21.47%, coincides with the sum of carbon in the coarse phase and the fines. The aim of this study was to try to clean up this 3.9% of the coarse phase, and to revalue the silica sands (Table 2).

Table 2. Partial result of ICP of the waste material (coarse waste material is the used in this study) and the raw material for foundry purpose.

Element	Waste Material		Raw Material	
	Coarse	Fines	Silicic Sand	Binders
	[%]	[%]	[%]	[%]
O	48.57	39.92	52.23	37.45
Si	35.10	23.57	44.32	21.34
C	3.87	16.50	-	21.47
Others	12.47	20.01	3.45	19.74

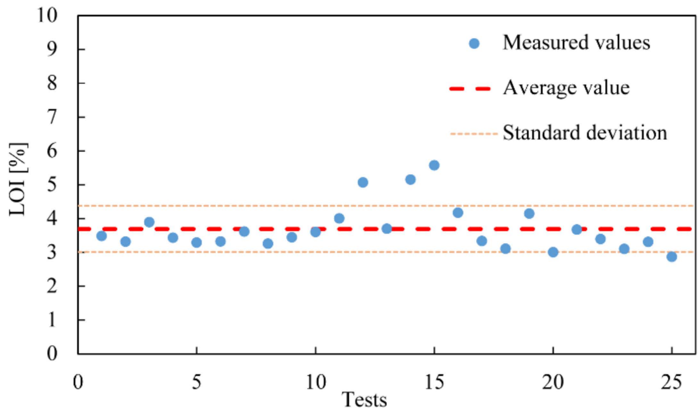

Figure 4. Results of the target waste material in terms of fixed carbon using the LOI technique.

The particle size distribution and the content in LOI (%) that resulted from the raw material characterization is quite interesting, since there is an unusual quantity of mass under 90 µm (Figure 5A) combined with the fact that in finer phases there is a high content of LOI represented by nearly 20%. This fact, plus the high quantity of material on coarser phases (more than 50% of the material population is over 250 µm), gives an opportunity to apply physics methods to clean the sand of contaminants, quantified by the larger content of LOI, especially under the 90 µm cut-point (Figure 5B).

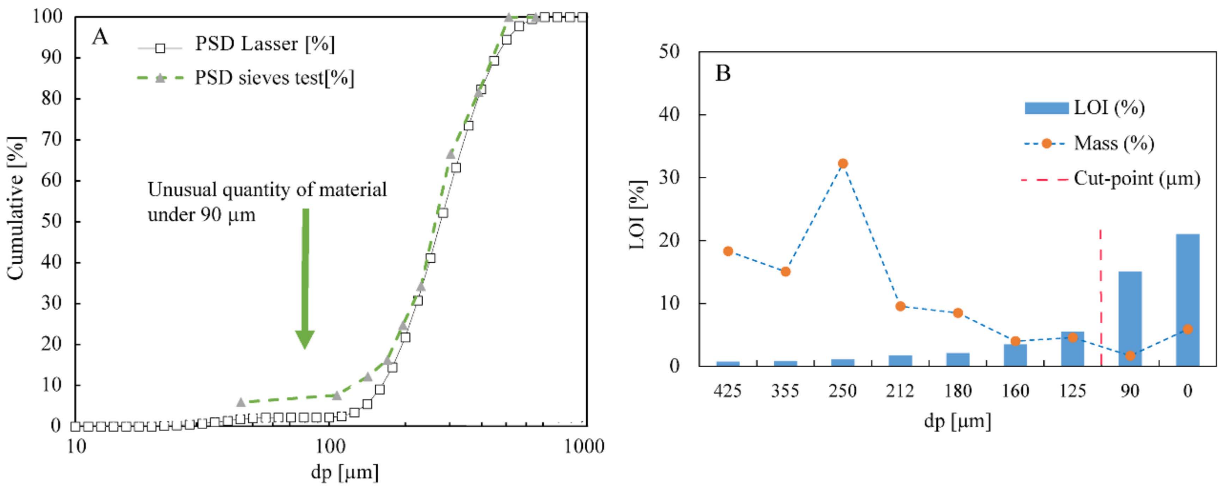

Figure 5. (**A**) Particle size distribution of the initial material resulted from the laser analysis and sieve analysis, where the cumulative mass is plotted against particle diameter, (**B**) LOI (%) content for each particle size range in abscissa.

3.2. Attrition by Stirring

The material under energy application of attrition by stirring is presented in Figure 6. The result of the separation process by size as a first step, and then by sink and float, which takes advantage of the density differences (Figure 6A), is clean sand. The blue points show how the amount of LOI decreases over time, highlighting a rapid decrease in tests with a short stirring time, but with a trend towards a steady-state condition. The stabilization point starts on 12 min reaching near 0.8% LOI. The amount of recovered mass is also remarkable, being around 90% of the total mass. The case of fine rejection represents the separation by size difference criterion of the first stage (Figure 6B). Particles under 90 µm have a great variability on LOI content, however, they are always above 10%, and their mass amount averages less than 2%.

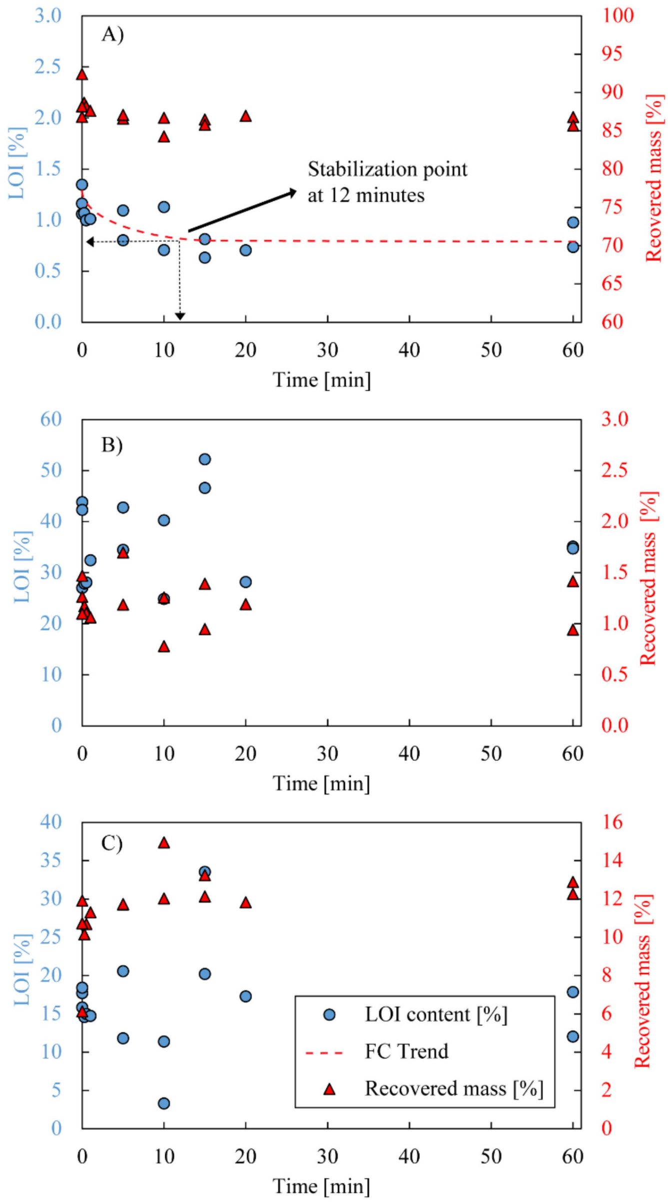

Figure 6. (**A**) Clean sands, (**B**) fines wasted material, (**C**) light wasted material.

Sink and float concentrates near 12% of the initial mass, with no trend apparent through the observed time. The average LOI value is near 20% (Figure 6C).

The stabilization time was obtained according to the model, the parameters of which are shown in Table 2. Firstly, within the exponential is the constant Φ_3. This becomes more negative as time increases, therefore the second factor tends to zero as time passes. As the first factor is independent of the exponential, the minimum value of the predicted LOI can only reach that corresponding to Φ_1. This value is consistent with the experimental values found, which reach near 0.8% LOI. According to the model data, this value starts to be stable after 12 min of stirring, therefore, it agrees with the experimental results. This stabilization point is corroborated through the regression performed on the LOI results, the modelling of which is shown through the parameters in Table 3. On the other hand, no clear trends are observed in the distribution of LOI content in the respective residues of the stirring processes. The main reason for this variation could be the representativeness of the tested samples.

Table 3. Non-lineal regression for obtained results of LOI from Figures 6A and 7A.

Gauss-Newton Algorithm	Parameters		
	Φ_1	Φ_2	Φ_3
Stirring	0.7819	0.3212	−0.1951
Light milling	0.5243	0.6335	−0.1679

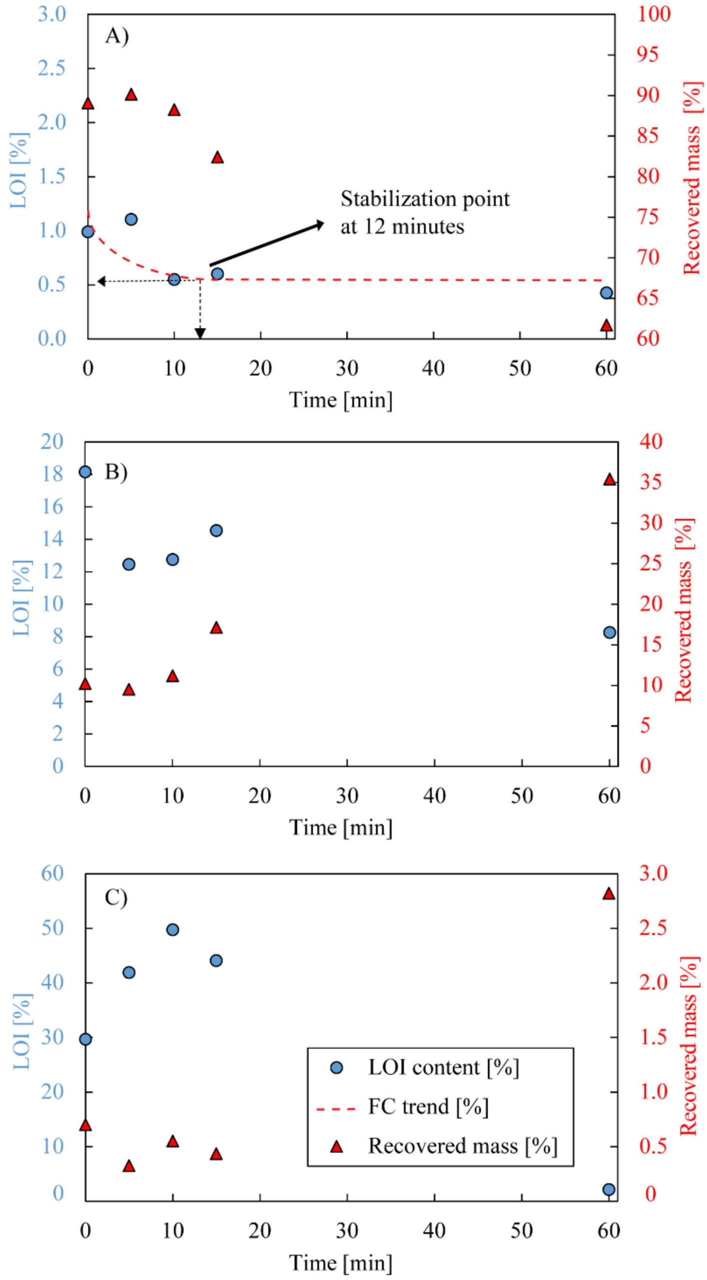

Figure 7. (**A**) Clean sand, (**B**) fines wasted material, (**C**) light wasted material.

In general terms, the recovery of the clean sand is above 85% by mass, and LOI content achieved is below 1% from minute 5. According to Figure 6A, lengthening the stirring time does not lead at lower LOI values, thus representing an unnecessary action.

Rejects (fine and light phases) represent approximately 12% by mass with relatively high LOI percentages (15% fine rejection and 30–40% sink rejection).

3.3. Attrition by Light Milling

Light milling is a somewhat more aggressive mechanical action on the particles, with the aim of generating greater contact between particles, creating an abrasive medium. The operating conditions of the light milling were manipulated in order to avoid fragmentation, something typical of grinding, using a ball load ratio of 40:3 (gr grinding media/gr material) (Table 1), well below the standard [34]. Another action that enhances abrasion is the application of lower impact energy, reducing the cascade effect of the grinding medium, with a percentage of the speed that is also lower than is usual in a typical grinding. Table 1 shows that the operating rotational speed is 30% of the critical speed. In standard grinding conditions, this value usually reaches 60–65%.

Clean sand reduces the amount of LOI quite considerably after 12 min residence time (Figure 7A), stabilized to near 0.5% LOI (which is consistent with the model parameters obtained by regression, Table 2). However, the turning point of this mechanical action is determined by the amount of mass recovered: from minute 15, this value is below 85%, and as longer abrasion times are reached, fragmentation occurs, which is not desirable.

The fine rejection below 90 µm maintains a stable LOI content, close to 12%, but in accordance with clean sands, the number of finer particles increases considerably as they are kept in the mill. The fragmentation effect is verified over time (Figure 7B).

Sink rejection after dense media separation maintains a stable high LOI content, close to 45%, with a relatively low amount of mass. An unwanted inflection point is seen at minute 60, with an increase in mass, but with low LOI values (Figure 7C).

4. Discussion

Carbonaceous matter decontamination is seen to be effective for both mechanical attrition methods of stirring and light milling. However, in both cases it is indirectly evaluated using the LOI technique. In the case of stirring, it takes at least 12 min to reach stabilization near 0.8% LOI, while in the case of light milling, with only one minute of residence time, the LOI content is below 1% (Figure 8B–D). This is consistent with a previous study [22], where a pronounced change in cleaning behavior is observed from a 12 min residence time. This residence time depends on the type of pollutants. There are cases where more than 60 min of agitation were needed to clean molding sands using similar techniques [35]. The key point in this case is achieved by the recovery of clean sands. Although the objective of this study was to reduce the amount of carbon in the waste, it is interesting to maintain constant sand characteristics, i.e., to avoid comminution. By reducing the LOI with light milling, over time, fragmentation also occurs, and subsequent lower recovery of sands in terms of mass. This fact is evident from minute 10 (Figure 8A–C). This phenomenon was also observed with potash, with a similar trend in particle size reduction [36]. This can be very beneficial in terms of pollutant release [37], but can hinder the reuse of the sands by changing their particle size [38].

The content of fixed carbon detected by the technique LOI is closely related to the carbon quantity present in the studied material. Average LOI v/s C ratio is around a 1.1/1. That is, at the detected amounts of LOI, there should be a lower amount of C. The total organic carbon (TOC) is consistent. In just a few points FC percentages match with the TOC. The rest of them accomplish this LOI/C ratio. This is an entirely acceptable difference, since in other types of results, even higher ratios are achieved between these two techniques [39,40].

In addition, the release of C is reaffirmed for both attrition processes, and indicates a satisfactory reduction of C in the case of stirring (Figure 9A), where in all cases, the C content is below 1%. It is also observed that no greater mechanical energy is needed, even in light milling, which reduces a significative amount of C (Figure 9B). Light milling would be necessary if the carbon reduction requirement were higher. In this study, it is not considered necessary, since efficiency reaches near 86% of sand decontamination.

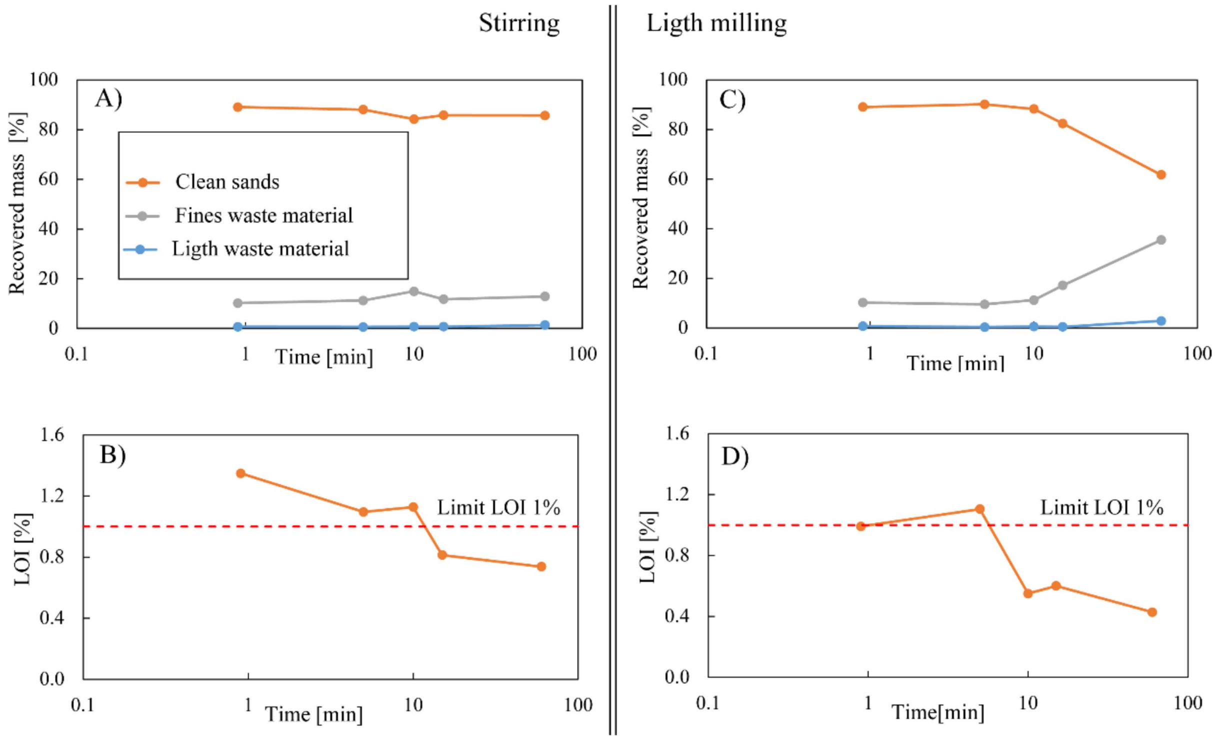

Figure 8. Comparative results of the liberation test. (**A**) Recovered mass using stirring, (**B**) LOI reduction using stirring, (**C**) recovered mass using light milling, (**D**) LOI reduction using light milling.

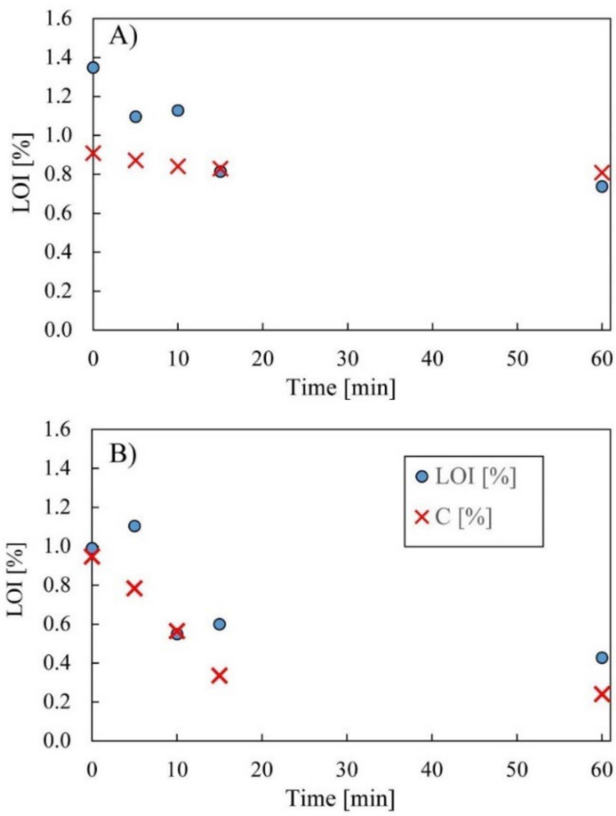

Figure 9. (**A**) Clean sands from stirring process, (**B**) clean sands from light milling.

Given the impossibility of analyzing any trend in the results of the fixed carbon content in the waste flows of the processes described (Figure 6B,C and Figure 7B,C), an attempt was made to organize the percentage content of this pollutant with respect to the total (Figure 10). It can be observed that with stirring (Figure 10A), the decrease of carbonaceous matter is plausible as time of the experiment increases, but its redistribution in the fine and light fluxes is not reciprocal. The lack of fragmentation itself may explain this phenomenon, and may simply favor regrouping by flocculation of the pollutants. In the case of light grinding, this is confirmed by the fact that most of the contaminants are concentrated in the finer phases, and for this reason it is possible to attribute this behavior to the trend observed in Figure 10B.

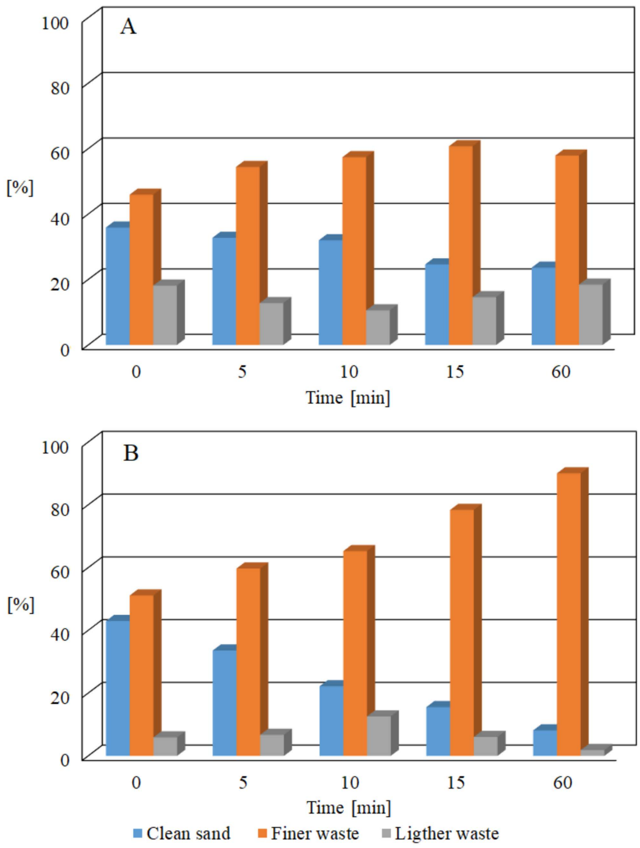

Figure 10. Contaminants distribution depending on process type. (**A**) By stirring (**B**), by light milling.

In energetic terms, the decontamination performance was evaluated for both cases of mechanical action. Table 4 shows the energy used in a 15 min residence time under stirring and light milling. The C reduction and mass recovered in light milling is remarkable in both cases, but there is a larger difference in the energy consumption, where light milling uses 9.1 kWh/t, compared with the 1.5 kWh/t used by stirring. The energy consumed is relevant to the need to obtain liberation by sample size reduction, and is consistent with these purposes [36,41], but an optimal result can be achieved without the need to grind the material.

Table 4. Energy consumption for both attrition mechanism performed in this study.

Concept	Units	Stirring	Light Milling
Recovered clean sand	%	85.5	82.4
C	%	0.8	0.3
Energy consumption	kWh/t	1.5	9.1

The case presented represents the best performance of each mechanical attrition method. Figure 11 shows how, depending on a specific case, efficiency varied on each device. To obtain 0.8% C content by stirring is impossible, regardless of the energy used. On the other hand, with light milling, there is a gap in which it is possible to obtain less than 0.8% C and even reach near 0.4% of C decontamination in a narrow energy range. Thus, there are many alternatives, depending on the permissible limit for a given application of the obtained material.

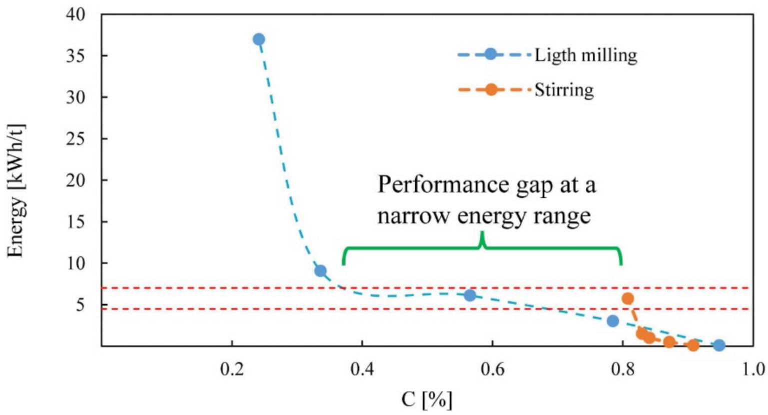

Figure 11. Overall energy consumption along time for each attrition mechanism.

5. Conclusions

Foundry waste sand can be treated by means of two types of mechanical attrition. On the one hand, it can be done by means of stirring, reducing the former waste with 3.8% to 0.8% LOI, which means near 78% contamination removal. On the other hand, with light milling, with which better decontamination efficiency is achieved, reaching near 0.5% LOI content, but with exaggerated energy consumption.

In view of this, intermediate points were found where similar efficiencies are achieved in terms of decontamination and mass of sand recovered, but with lower energy use, in the case of stirring. However, depending on the further application of the cleaned material, light milling could represent a great option to increase contaminants removal at a narrow energy gap; but it should be studied in more detail to determine the suitable properties of the remaining sand so that it can be profitable in other applications, such as a ceramic or vitrics/clinker raw material. It must be considered that for longer residence time by light milling, the energy consumption increases as comminution phenomenon also occurs, changing sand properties from the particle size perspective.

This study, which is in a preliminary phase, also provides the basis for future actions, in which the best industrial-scale separation methods for this type of material can be determined. Finally, the separated carbon fractions can be considered for energy purposes in order to minimize waste generation as much as possible.

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