Foundry sand recycling in the troughs of blast furnaces: a technical note

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Abstract

The foundry sand agglomerated with alkaline phenolic resin, used for the manufacture of molds, was found to be a residue which is able to be recycled, minimizing the costs of disposal and the environmental impact. This paper analyzes the thermomechanical regeneration and leaching processes and also assesses the influence of additives on the improvement of the mechanical properties of the sands. Besides, the industrial experiments carried out at CSN aiming at the foundry sand recycling in the covering of the blast furnace troughs are presented.

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1. Introduction

The requirements of environmental laws led many foundries to increase their costs for disposing molding sands in the specialized landfills. The foundry sector generates several types of residues, including the ones from the foundry sands agglomerated with phenolic resins. Aiming at decreasing as much as possible the effects of environmental degradation, the thermal, the wet and the additive methods for the reclaimed foundry sands were investigated. However, it was found necessary to understand firstly the degradation mechanism of the sands and to identify the key factors of this process.

Recycling studies for the application of this residue at CSN’s works were also carried out, avoiding therefore the disposal costs, as well as decreasing the raw material costs.

The concern about the environmental impact of solid residues generated at the Brazilian producing units has been increasing considerably. Several Brazilian industries are adopting a system of environmental management, aiming at the ISO 14,000 certification. The Brazilian federal environmental laws are under voting process in the Congress, whereas some states and cities have been already enforcing their laws dealing with this subject, turning out to be one of the factors responsible for the ecological consciousness of the Brazilian producing sector.

This growing awareness of ecology has been increasing the production costs in items such as disposals according to the laws, treatments of residues, monitoring, transportation and occasional fines. On the other hand, the recycling reduces the purchasing costs of raw materials.

At the foundries, sand is one of the main source of residues, as normally big amounts of sand are consumed for the production of molds and males. Sand is used by means of different processes: green molding, shell, no-bake, hot box, cold box and others. Each one of them presents its own particularities and advantages in relation to the needs of the products. The types of residues generated and the recovering processes also present particularities.

CSN’s foundry once used furanic resin in most of their cast pieces. The residues were satisfactorily recycled by means of a mechanical process. However, this high-cost agglomerating system presented limitations in relation to its hot mechanical resistance, besides problems in terms of toxicity to the operators. When phenolic resin was implemented, some of the aforementioned problems were surpassed. On the other hand, another hindrance was created: the low recycling ability of this product.
1.1. The recycling ability of foundry sands

Several recycling methods for foundry sands have been published [1–4], such as the mechanical recovering, the wet, the thermal and the thermomechanical processes. The statement of Couture [5] represents well the problem of recycling foundry sands: “Do your own test. Whatever works for the neighbor foundry may not work for yours”. This statement relies upon the several manufacturing processes of foundry molds and the several requirements for the raw materials and agglomerating systems.

The sands agglomerated with organic binders require more severe processes and more complex equipment for the foundry sand recycling, as these binders require a more demanding raw material specification [6]. The sand/alkaline phenolic resin system is included within this consideration, once its reclaim presents serious complications, as well as the recycling of the regenerated sand.

The literature proposes for the foundry sand agglomerated with alkaline phenolic resin the mechanical cleaning and the thermal processes. However, these are quite controversial processes, as they present problems in the point of view of recovering the original sand properties. In the mechanical cleaning a big deviation of particle size distribution occurs, as well as the process is inefficient, with a low level of cleanness. On the other hand, the recycling by calcination involves a high energy cost, besides being ineffective in recovering the initial sand properties.

CSN’s foundry regenerates 1930 metric tons of sand per month, from the green sand, cold cure and shell molding processes, giving rise to 761 metric tons of residues. In this way, CSN undertook once again a joint R & D project with the Multidisciplinary Center for the Development of Ceramic Materials. In this project, the existing processes were investigated and new processes were developed to re-establish the sand properties, assessing the application of the produced residue, avoiding therefore the environmental problems and reducing costs with disposal and raw materials.

2. Experimental methodology

For this study, samples of recovered and regenerated sands were used. Due to differences in cycles and in the history of the materials, two lots of 480 kg for each type of sand were collected in CSN’s industrial foundry. The recovered sand is characterized by the presence of fines, whereas in the regenerated sand these fines were removed during the process.

A preliminary analysis was made including the composition and particle size distribution, which contributed to the evaluation of the studied cleaning processes.

2.1. Thermomechanical regeneration

Firstly the thermogravimetric and thermodifferential analyses of the recovered and regenerated sands were carried out, with the goal of defining the temperature of the calcination process, aiming at optimizing the conditions of the thermal treatment.

Later, the recovered and regenerated sands were submitted to calcination in a rotary kiln with controlled atmosphere. The sand temperature, the burner flame and the combustion products were monitored in order to optimize the temperature and the time of the calcination process. The system used is schematically shown in Fig. 1. After the calcination the changes in the sand particle size distribution were assessed.

With the objective of evaluating the influence of the heating rate of the calcination process on the sand degradation (generation of fines) due to thermal shocks, simulations were carried out under different heating rates. An amount of 5 kg of regenerated sand was heated up to 450° C, under different heating rates (450, 225, 112.5° C/h). The influence of these rates on the degradation of the material was assessed taking into account the change in the sand particle size distribution.

The efficiency of the calcination process in the recovery of the initial properties of these sands was evaluated by characterizing the compressing resistance of samples, taken before and after the calcination. Cylindrical Ø50 mm × 50 mm samples were agglomerated with catalyzed phenolic resin, according to the standards of the CSN’s Foundry Sand Laboratory. The sands were cured and had their compressing mechanical resistance tested.

2.2. The leaching process

The compressing resistance results of the calcined sands demonstrated that the thermomechanical treatment was not effective in regenerating the initial sand properties. One alternative found for the recycling of the foundry sand was the leaching in an aqueous or acidic medium. Several sand samples, taken before and after the calcination, were submitted to leaching, during different times, with variable amounts of water, in closed circuit and under a constant water flow rate.
Fig. 2. Simulation scheme for the laboratorial recovering of the foundry sands.

These samples were agglomerated with alkaline phenolic resin and were submitted to compressing resistance tests.

2.3. Use of additives

Silane addition. Several additives were tested with the purpose of improving the mechanical properties of the sands. Samples of silanes—coupling agent of silica—were obtained from supplier C: C1, amine; C2, epoxy; C3, urea.

Firstly the appropriated silane was selected, i.e., the one with the highest affinity with the alkaline phenolic resin, what was defined by means of compressing resistance tests, performed with different curing times. After the selection of the silane class, its amount was optimized, by varying the percentage of silane added to the sand (0.1, 0.25, 0.5 and 1.0%).

Other additives. A sucrose-based solution (additive from supplier A) and an inorganic additive (supplier B) were added to the regenerated sand during the calcination process. The purpose of the additions was to reduce as most as possible the deleterious effects related to the residual alkali contents of the sand, originated from the alkaline phenolic resin. The calcination was performed in a rotary kiln, at the 450–550 °C temperature range, for 1 h.

These different samples were agglomerated again with alkaline phenolic resin for the manufacture of Ø50 mm × 50 mm cylindrical samples, which were later submitted to compressing resistance tests, with different curing times.

2.4. Surface quality of the grains and the mechanical properties of the sands

Laboratorial recovering simulations were carried out with the purpose of assessing the influence of the surface quality of the grains on the mechanical resistance of the foundry sands agglomerated with alkaline phenolic resin. These tests involved the preparation of molds with 100% of new sand (reference parameter), being used samples from suppliers D and E.

The tested sands presented subangular grains and 45/50 AFS modulus. The solubility, chemical composition, pH, mechanical resistance in all phases (Fig. 2) were evaluated.

3. Results and discussion

Cleaning by calcination. The thermogravimetric and thermodifferential analyses in the samples of regenerated and recovered sands (Fig. 3) showed that the mass loss, originated from the decomposition of the phenolic resin, essentially occurs at the 450–550 °C temperature range. Higher calcining temperatures mean unnecessary energy expenses, besides leading to a more intense formation of agglomerates. This agglomeration arises from the sintering mechanism through the formation of a liquid phase, formed by means of the reaction between the residual sodium and potassium and the fine silica grains.

Fig. 3. Thermogravimetric and thermodifferential analyses of the recovered sand.
Fig. 4 presents the heating curves of the recovered and regenerated sands, which were observed during the simulations at different heating rates.

The particle size distributions, related to before and after calcinations, are represented by the curves presented in Figs. 5 and 6 for the recovered and regenerated sands, respectively. These results showed that the recovered sand, as well as the regenerated sand presented an increase in the coarse fraction (above 0.5 mm) and a reduction in the fine fraction (below 0.15 mm). This evidences the agglomeration effect of the fine sand during the calcination process, which is probably associated to the reaction of the residual alkalies, from the phenolic resin (Na and K), with the fine silica grains, leading to the formation of a liquid phase and grain agglomeration.

The thermogravimetric and thermodifferential analyses of the recovered and regenerated sands, performed after the calcination (Fig. 7), evidenced the efficiency of this process. After the calcination, no further mass losses were verified. However, the results of compressing resistance of the regenerated sand agglomerated with alkaline phenolic resin (Fig. 8) showed that the calcination process is not efficient,
Fig. 5. Particle size distribution of the recovered sand, before and after the calcination carried out according to the several calcination curves.

regarding the regeneration of the initial properties of the material.

According to the obtained results, the calcination process significantly degrades the mechanical properties of the sand. This is probably due to the reaction of triacetine with the agglomerating alkaline solution of phenol–formaldehyde, once the salts originated from such reaction adhere to the surface of the sand grains, reducing therefore the agglomerating capacity.

Cleaning by leaching. The chemical composition, the solubility and compressing resistance of the regenerated and calcined samples, before and after leaching in an acid or aqueous medium, are shown in Table 1. It should be taken into account that the lower limit for the compressing resistance of the sands, established by the CSN’s foundry is 1.24 MPa.

It can be observed that there are no meaningful differences regarding the chemical composition of the regenerated and calcined sands, before and after leaching in potable water and in an acidic medium. However, the compressing resistance of the resin agglomerated sand, after leaching in an acidic medium (1.86 MPa) is much higher than the ones from other cleaning processes used. This fact shows that the degradation of the mechanical properties of the sands is directly associated to the solubility of the formed products and not to the residual concentration of the alkalies (Na and K).

Fig. 6. Particle size distribution of the regenerated sand, before and after the calcination carried out according to the several calcination curves.

Fig. 7. Thermogravimetric and thermodifferential analyses of the recovered and regenerated sands after calcination at 450°C: (a) recovered sand; (b) regenerated sand.

Fig. 8. Compressing resistance of the regenerated foundry sands, after calcination at 450°C.
Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>Elements</th>
<th>SiO₂ (%)</th>
<th>Na₂O (%)</th>
<th>K₂O (%)</th>
<th>Solubility</th>
<th>Compressing resistance (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>New (supplier E)</td>
<td></td>
<td>97.717</td>
<td>0.049</td>
<td>0.016</td>
<td>a</td>
<td>2.34</td>
</tr>
<tr>
<td>Regenerated</td>
<td></td>
<td>86.313</td>
<td>0.062</td>
<td>0.022</td>
<td>b</td>
<td>0.85</td>
</tr>
<tr>
<td>Regenerated calcined</td>
<td></td>
<td>81.735</td>
<td>0.079</td>
<td>0.028</td>
<td>c</td>
<td>0.24</td>
</tr>
<tr>
<td>Regenerated washed</td>
<td></td>
<td>88.446</td>
<td>0.047</td>
<td>0.029</td>
<td>c</td>
<td>0.22</td>
</tr>
<tr>
<td>Regenerated acid washed</td>
<td></td>
<td>88.328</td>
<td>0.043</td>
<td>0.027</td>
<td>a</td>
<td>1.86</td>
</tr>
</tbody>
</table>

*Low qualitative solubility scale.

*Medium qualitative solubility scale.

*High qualitative solubility scale.

As the solubility increases, a decrease in the mechanical resistance of the regenerated sand, agglomerated with phenolic resin, is verified (Table 1). This can be explained by the presence of soluble salts formed during the thermal treatment of the resin that impair the re-agglomeration of the resin.

Fig. 9 presents the results of compressing resistance of regenerated sand, agglomerated with alkaline phenolic resin, after several leaching processes. It is noticed that the higher the leaching times and the water flow rates (preferentially running water), the higher is the recovery of the initial sand properties. The leaching time and the water flow rate can be reduced in the case of previously calcined sands. In this case, the resin decomposition and the formation of soluble salts of sodium and potassium make easier the regeneration of the initial sand properties.

The leaching process was shown to be efficient in relation to the regeneration of the initial sand properties. It should be emphasized that high compressing resistance values were obtained (2 MPa) in the regenerated sands, without previous calcination. In this case, the salts of the alkaline metals or the alkalies dissociated from the resin adhered to the grain surfaces and reacted with the acid, forming easily separated salts.

Utilization of silanes. In the compressing resistance tests of the regenerated sands, to which were added 1% of the commercially available silane classes (amine, urea and epoxy), it was verified that for short curing times, the amine silane presented the best result. However, when the cure took 24 h the results were similar for all the different classes tests. As a result of these data, the amine class was selected to be used.

As it was shown in Fig. 10, the addition of 0.25 wt.% of amine silane to the regenerated sand produced the best result of compression resistance after 24 h of cure (2.41 MPa), being 2.5 times higher than the one obtained with a sand without silane addition.

Taking into account that the lower limit for the compressing resistance allowed by CSN’s foundry is 1.24 MPa, it is observed that the addition of only 0.1% of silane is enough to satisfy the process requirements.

The coupling or the anchoring between the alkaline phenolic resin and the silica grains, through silane bridges, significantly improves the mechanical properties of the foundry sands, canceling the deleterious effect of the alkaline salts deposited over the sand surface.

Calcination additives. The addition of a sucrose-based solution (supplier A) to the regenerated sand during the calcination process did not present the expected results.

Fig. 9. Compressing resistance of the regenerated sands, before and after calcination, leached in potable water and in an acidic medium.

Fig. 10. Compressing resistance of a sand regenerated with the addition of different amounts of amine silane.
According to supplier A, the sugar present in the solution would seize the deleterious agents during calcination and would improve the mechanical properties of the sand. The tests, however, proved the inefficiency of this additive.

On the other hand, the use of inorganic additives during the calcination processes gave rise to high values of compression resistance (1.79 MPa), after 24 h of cure. However, these additives require the use of fluidized bed ovens, which, by means of the gas flow drag out the fine particles, requiring the use of high-cost anti-polluting equipment.

The improvement of the mechanical properties of the sand is explained by the action of the additives, which react with the alkaline metals (Na and K) from the salts present on the surface of the grains.

Surface quality of the sand grains. Taking into account the lower limit of 1.24 MPa for the compression resistance, the sands from suppliers D and E can be recovered only once, according to the results of laboratory simulations carried out (Fig. 11).

However, the compressing resistance results of the sand from supplier D were better than the sand from supplier E, due to the better surface quality of the silica grains. Fig. 12 presents the morphology of the grains of new sands from suppliers D and E.

The cracks present in the grains of new sands from supplier E, originated from its comminution process, are retention points for the alkaline phenolic resin, rendering more difficult for its removal and so influencing the regeneration process (Fig. 13). The medium and fine fractions of sand E, after the first recovering cycle, present residual traces of
resin on these cracks. Otherwise, the smooth grains of better surface quality do not present resin residues.

Microanalyses from the cracked grain region, performed by means of electron microprobe (Fig. 14), identified the presence of the elements Na, K and C, confirming the presence of the phenolic resin. These residual alkalies (Na and K) promote the agglomeration of the fine fraction of the sand during the calcination process through the formation of a liquid phase.

Fig. 15 shows the necking mechanism for the silica grains of the fine silica fraction, after the second recovering cycle, characterizing the phenomenon of sintering through liquid phase.

At the high temperatures of the foundry process, these alkalies react with silica, forming a liquid phase, which leads to a partial sintering of the fine fraction. This explains the weight percentage reduction of the fine fraction (below 0.15 mm), after the calcination process (Figs. 5 and 6).

EDS microanalyses of the necking region (Fig. 16) showed the presence of Na, K, Si and O, confirming the aforementioned statement.

3.1. Industrial recycling tests

The several cleaning processes studied for the foundry sand imply in additional costs and changes in the foundry process, and should be carefully assessed. By this reason, new recycling alternatives within the own industry that do not need big investments, neither in material nor in new equipment, were looked for.

Fig. 14. EDS microanalyses from the cracked region of a grain from sand E, after the third recovering cycle (sample prepared with gold coating).

Fig. 15. Micrographs of the fine fraction of sand E, after the second cycle of recovering, showing the necking of the silica grains.
3.2. Covering of the blast furnaces’ troughs

Nowadays the troughs of CSN’s blast furnaces are covered with a 1:3 blend of washed sand and clay, homogenized in a grinding mill. This covering material has the purpose of making easier the removal and the cleaning of the pig iron projected at the beginning of the tapping (Fig. 17).

The main properties that this covering material must display, in order to allow its application, are elevated refractoriness, the ability to avoid the adherence of the pig iron on the border of the trough and a good compactability.

The blend of foundry reject sand and clay, in a 2:1 volume ratio reached the necessary compactability, but some deficiencies were observed regarding the adherence and the fluidity of the blend, which were later easily overcome. The main problem faced, however, was the foundry reject sand contamination with metal. The presence of metallic scrap can harm the millstones, with risks for this equipment. This problem was solved by means of the sieving of the recycled sand. In the period from May to October 1998 about 700 metric tons of foundry sand were recycled in the covering of the troughs of the blast furnaces.

4. Conclusions

- The calcination of foundry sand, at the range from 450 to 550 °C, is sufficient to remove the phenol originated from the resin. The calcinations performed at higher temperatures, besides increasing the energy consumption, result in a partial agglomeration of the fine fraction. The residual alkalies from the alkaline phenolic resin react with the fine silica grains, forming a liquid phase product.
- The calcination process at moderate temperatures (450–550 °C), either using inorganic calcination additives or coupling additives or associated with the leaching process is effective in terms of regenerating the initial properties of the foundry sands.
- The degradation of the mechanical properties of the foundry sand as a result of the regenerating cycles is due to the adherence and the accumulation alkaline salts on the surface of the silica grains, what reduces the agglomerating capacity of the process.
- The water leaching process is efficient for the regeneration of the initial properties of the previously calcined sands. The calcination process decomposes the resin and forms soluble sodium and potassium salts, making therefore easier the leaching process.
- The leaching in an acid medium was the most efficient solution in terms of regenerating the initial properties of the foundry sands. The sands that were not calcined presented high values of compressing resistance, after being leached in an acid medium. As the sand was not calcined, the alkaline salts and/or alkalies dissociated from the resin and adhered to the surface of the grains, reacted with the acids, forming compounds that do not pose problems under the environmental point of view.
- The utilization of both silica anchoring additives, based on amine silanes, and inorganic calcination additives was shown to be efficient in the regeneration of the mechanical properties of the foundry sands. However, the additional costs derived from these processes must be carefully assessed.
- The mechanical properties of the sands are influenced by the surface quality of the grains. The cracks are anchoring points for the alkaline phenolic resin, rendering more difficult its removal. The accumulation of the resin and its salts presents as consequence the degradation of the mechanical properties, creating the need of a new sand make-up of into the system.
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