Methodology for Cement Manufacturing Application

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Authors' contributions

This work was carried out in collaboration among all authors. Author AKCS carried out the experiment as a final course project, performed the statistical analysis and wrote the first draft of the manuscript. Author ASM managed the study's analysis. Author SCP designed the study and wrote the protocol. All authors read and approved the final manuscript.

Original Research Article	

ABSTRACT

The narrowing between technological and sustainable development comes as one of the main challenges for the scientific environment and the modern company. In this scenario, waste recycling is considered an alternative for preservation of non-renewable natural resources and the environment, as a possibility of reducing energy consumption, carbon dioxide generated in the manufacture of traditional materials, and consequently, an economic advantage. The interrelationship between the steel segment and the civil segment show the opportunity of using the slag generated in the steelmaking by the cement industry. However, one of the challenges of using this co-product as cementitious input is the chloride ion contamination of unknown origin. This research aimed to propose a method to ensure the technical feasibility of using slag generated in steel refining, aiming to eliminate the chloride anion as impurity. Four samples collected from different points of the steelmaking process were studied, applying a wash with distilled water to the non-soluble solid residue, in order to extract the contaminating ion. It was evidenced that, after contact between solid residue and water, in the first wash, the performance presented an efficiency within the average range of 92 to 93%. Thus, after the practice of a simple method of chloride extraction with liquid fluid, the steel slag can be applied without restriction as an alternative material and input in cement production. Achieving the satisfactory result, a figurative prototype was built in order to enable the industrial scale to perform the same procedure performed in the laboratory.

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1. INTRODUCTION

As a result of the dissemination of environmental information, worldwide ecological concern and the growing search for sustainable development alternatives drive companies to invest in action mechanisms to increase waste utilization, avoiding pollution and storage problems due to the accumulation of material and the unbridled exploitation of new natural resources.

In the steel industry it would be no different. According to a survey by the National Confederation of Industry [1], the total generated co-products and direct waste in steel production in Brazil was 19.8 million tons in 2015 and 18.3 million tons in 2016, representing a specific generation close to 600 kg of these materials per ton of crude steel produced.

Also, it cannot be ignored that the implementation of natural resource conservation measures, recycling and the search for new, less polluting technologies in the industry must be within the increasingly restrictive legal standards of production, identification, transportation, treatment and final disposal of industrial waste, in accordance with the Brazilian standard NBR ISO 14.001 [2] and Law n. 12.305/10 establishing the National Policy on Solid Waste [3].

Cement is a material formed by the combination of five essential elements: silicon, iron, calcium, magnesium and aluminum. Its foundation is based on the mixture of these components, which are calcined, transformed into oxides and crushed. Although the chemical composition of steelmaking slag varies greatly, some of its main constituents are metallic iron and calcium and magnesium oxides [4], which makes their use as an input source in the cement factory interesting. In cement manufacturing, water is used in several steps: (a) In the scrap yard - even at a lower volume than the rest of the operation, it is used to lower dust by moistening the scrap as it is broken and crushed by a rotary machine with about 30 hammers, each weighing 180 kg; (b) In melt shop - room temperature water is used to cool oven refractories, ie to exchange heat with pan containing liquid steel; (c) In lamination - water to cool cages in billet lamination. Each cage is cooled as a large volume of water hits the rollers for longer material durability; (d) In cold drawing - or cold lamination, water is used to cool the block of wire drawing machines and also to cool the supports of some welding equipment. Heat is removed from the liquid with a chiller until the temperature remains in the range of 15 to 20°C; (e) In heat treatment thermex - technique used to cool the outer layer of the material, so that it has a better ratio of strength limit and yield limit, that is, to obtain a product with greater load capacity and ductility.

However, despite being a viable alternative material conferring strength and durability characteristics to the final product, there are some drawbacks to the use of steel waste; for example, the concentration of chloride ion (Cl^-) that can contaminate slag. The main external sources of chloride ions are the defrosting salts and seawater. Regardless of their external origin, chlorides penetrate the concrete by transporting water containing ions, by diffusion of ions in water or by absorption. Repeated or prolonged intake may, over time, result in a high concentration of chloride ions on the surface of the armor [5,6,7]. The contamination of cement by chloride affects the structures after their construction, causing serious problems, especially the corrosion of exposed reinforced concrete with fissures, stains, cracks, detachment of concrete pieces and even loss of the resistant section and adhesion, promoting the collapse of the structure or its parts [8,9,10]. The maximum content of Cl^- in cement is 0.15% of its mass, according to NBR 12.655 of the Brazilian Association of Technical Standards [11]. Slag containing excess level becomes unviable for use as cementitious material.

Therefore, the purpose of this work was to characterize steel slag samples, mainly in relation to chloride ion, and investigate the possibility of removal of this anion, so that the waste can be used as input in the cement factory, contributing to the improvement of quality of life, mainly socioeconomic, prioritizing environmental preservation and proposing technological innovations to reuse the waste generated in the steel production process and the viability of an alternative for its reuse.

2. MATERIALS AND METHODS

The test was developed at the Analytical Chemistry Laboratory of the Center for Sciences and Technology of the Catholic University of Pernambuco, Recife, Pernambuco, Brazil, based on a problem that arose in the process of a steel

Table 1. Variation of parameters used in the first step of the experiment

	Volume of distilled water	Shaking time	Temperature
	ml	min	ºC
Reference	50	20	Room
Variation 1	25	20	Room
Variation 2	50	10	Room
Variation 3	15	10	Room
Variation 4	50	20	50
Variation 5	50	20	70
Variation 6	50	10	50

Where: (Room) Distilled water used at laboratory room temperature

Table 2. Variation of parameters used in the second stage of the experiment

	Volume of distilled water	Temperature
	ml	ºC
Variation 1	25	Room
Variation 2	50	Room

Where: (Room) Distilled water used at laboratory room temperature

industry and that consulting available literature did not find an effective answer to this. Hence the research proposal presented here.

Four representative samples of small slag, collected from different points of the steelmaking process, according to NBR 10.007 of the Brazilian Association of Technical Standards [12], were analyzed from stockpiles located in the courtyard of a steel mill located in Recife, Pernambuco, Brazil. The samples were stored in plastic containers, labeled and sent to the Laboratory for chemical characterization. Thereafter, we proceeded to obtain leachate extract (chloride) of solid wastes, based on NBR 10.005 [13].

In the first experimental stage, 3.00 g of the residue was weighed from each of the four samples; then we incorporated 50.0, 25.0 and 15.0 ml of distilled water to the mass (first washing) under agitation at 200 revolutions per minute (rpm) for 20 and 10 minutes, using a shaker table at room temperature (25°C), 50°C and 70°C. The separation between the residue and the extract was done by centrifugation at 3000 rpm. The solid and insoluble part was subjected again to the washing process (second wash), in order to determine how much of the chloride ion had been solubilized in the first percolation (Table 1).

In the 2nd experimental stage, 3.00 g of the residue was weighed from each of the four samples; then we performed vacuum filtration at 50.0 and 25.0 ml of distilled water (first wash);

and soon after, the vacuum filtration process (second wash) was repeated, both at room temperature (25°C).

Finally, the first and second wash solvents of both steps were conducted to determine chloride by precipitation titration, using the Mohr method according to the American Public Health Association [14] and the average efficiency of the process was calculated.

It is noteworthy that the tests were performed in triplicate, where the investigation with water at higher temperatures was employed, since it was considered that the dissolution of most chloride-containing solutes is endothermic, being soluble in hot water in greater proportion than in cold water as suggests [15].

3. RESULTS AND DISCUSSION

Tables 3 and 4 present the results found for the average efficiency of the chloride ion extraction process of the steel residue, facilitating the interpretation of the effectiveness of the tests.

After applying the two experimental steps, it is revealed that the percentage of chloride found in the slag was around 2% by mass, demonstrating its incompatibility for use in the cement industry.

In the first stage of the research (Table 1), in order to investigate the influence of the variables volume, water temperature and shaking time, 168 titrations were performed, always aiming at greater Cl^- extraction.

Table 3. Average percentage of chloride extracted after treatment residue / water at first wash

	Volume	Shaking time	Temperature	Average efficiency
	ml	min	ºC	%
Reference	50	20	Room	91,9
Variation 1	25	20	Room	89,2
Variation 2	50	10	Room	92,8
Variation 3	15	10	Room	59,8
Variation 4	50	20	50	93,0
Variation 5	50	20	70	92,7
Variation 6	50	10	50	92,1

Where: (Room) Distilled water used at laboratory room temperature

Table 4. Means of chloride percentage extracted after treatment residue / water in the second wash

	Volume of distilled water	Temperature	Average efficiency
	ml	ºC	%
Variation 1	25	Room	76,4
Variation 2	50	Room	91,7

Where: (Room) Distilled water used at laboratory room temperature

Regarding the temperature parameter, it is noted that the influence of the elevation of the water heat range is not highly significant in relation to the effectiveness of the contaminating ion leaching. Keeping the solvent volume, the waste mass used and the stirring time constant, it can be seen that increasing the temperature results in a 1% increase in process efficiency. That is, the gain is much lower than expected, taking into account the time and energy expenditure to increase the fluid temperature.

As for the agitation time, similarly, its variation did not offer significant change in the percentage degree. Keeping the water portion at 50.0 ml and at room temperature, the efficiency did not change with the agitation interval variation, while for the same volume of solvent at 50°C the efficiency decreased by only 1% with the decrease of homogenization time from 20 to 10 minutes.

Thus, the relevant factor in the use of the method is the volume of water to be used. The best waste/water ratio found was, on average, 3.00 g of solid mass per 50.0 ml of fluid at room temperature. The test presented the best yield in term of extraction, obtaining an average value of 92.4% in the percolation efficiency of the chloride ion. While the test elaborated with the waste/water ratio from 3.00 g to 15.0 ml presented the lowest efficiency (59.8%).

Thus, with the decreasing variation of the waste/water ratio, there is consequently an increase in the absorption of the Cl⁻ anion, with the minimum ratio found at 6%. Therefore, the smaller the volume of water applied, the lower the absorption, indicating a proportional behavior, resulting in an unfeasible process.

Since the gain offered by changing the agitation time and temperature was not significant, the second experimental step was applied, focusing only on water volume variation (Table 4). In this step, a yield similar to the values found with agitation was obtained in the tests performed with the same ideal waste/water ratio as in the first stage. Therefore, after the 48 titrations, it is confirmed that the direct contact between a given solid residue mass and the appropriate volume of water (50.0 ml), in just one wash, allows an excellent chloride removal.

Consequently, it can be seen from this second step that agitation can be removed from the process, and that only contact with water even at room temperature and a slight homogenization is already sufficient to obtain an effective yield, directly impacting the economic improvement of the methodology. There is no restriction regarding the Cl⁻ content after the process, for the application of steel slag in cement production as an alternative material.

Finally, the idealization and construction of the figurative prototype of the washing plant, which will enable the industrial scale to perform the same procedure performed in the laboratory, is represented in Fig. 1.
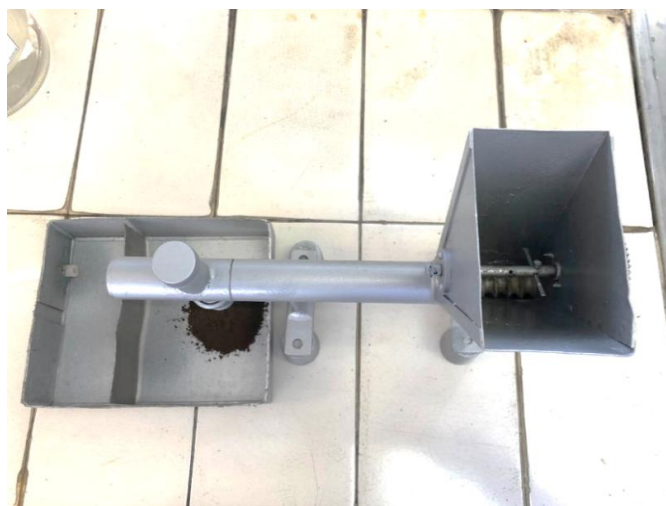
Fig. 1. Prototype developed for slag washing

Solid waste and water are introduced into the mechanism equipped with a rotary shaft (Fig. 1), which in addition to offering a slight homogenization, assists in the mobility of the mixed complex, as well as in combating incrustation. Upon exiting the steel waste mixer, the composition would be arranged in a tank containing a filter mesh responsible for separating the mass from the leachate, functioning as a high mesh sieve, given that the slag particles are very thin. In this way, Cl^- would be extracted with the fluid, while the residue would be free of this contamination.

The idea is to perform the washing using the effluent itself generated in the steel production process, so that it is free of chloride.

In routes already made for steel synthesis, about 98% of this mostly cooling water is reused in the process itself. Extraction of the slag chloride would be another alternative for reusing the fluid and enabling a possibility of reuse of the residue. Even charged with oxides, due to contact with the material (iron and steel), the effluent can participate in the proposed washing methodology, as long as it is not contaminated by the Cl^- anion.

Finally, the extract that would not have incorporated aggravating chloride content would be destined to the plant's internal treatment plant in order to improve the condition of the water to be reused in the steel production process and subsequent release, while the solid waste would be free of contamination and without restriction as to its use as cementitious input.

4. CONCLUSION

Given the results obtained it can be concluded that the factor that acts in a relevant way in the use of the method is the volume of water to be used. The best ratio between residue/water found was, on average, 3.00 g of solid mass to 50.0 ml of fluid at room temperature, presenting an efficiency within the average range of 92 to 93%. Therefore, after the practice of a simple method, steel slag can be applied as an alternative material and input in cement production, being used within the legal composition.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. CNI. National Confederation of Industry. The steel industry in Brazil: Brazil Steel Institute. Brasilia: CNI; 2017.
2. ABNT. Brazilian Association of Technical Standards. ABNT NBR 12.655: Portland cement concrete - preparation, control and receiving - procedure. Rio de Janeiro: ABNT; 2015.
3. BRAZIL. Law n. 12,305 of August 2, 2010. Establishes the National Policy on Solid Waste; amends Law 9605 of February 12, 1998; and makes other arrangements. Official Gazette: Brasilia, August 2; 2010.
4. Arrivabene LF. Addition of waste from the granite industry in BOF steel slag aiming

its use in cement production. Thesis (Doctorate in Metallurgy and Materials) - Postgraduate Program in Metallurgy and Materials, University of São Paulo, São Paulo. 2012;165.

5.   Neville AM. Concrete properties. 5. Ed. Porto Alegre: Bookman. 2016;888.

6.   Theiss AF. Evaluation of concrete steel corrosion with the addition of migratory corrosion inhibitor in the face of chloride ion action. Postgraduate in Civil Engineering, University of Santa Catarina (Master). 2019;120.

7.   Saints LAML. Determinants of steel consumption: A panel data analysis. Course Conclusion Paper (Undergraduate) - Undergraduate Course in Economic Sciences, Federal University of Juiz de Fora, Governador Valadares. 2018;28.

8.   Ferreira PRR. Analysis of chloride corrosion induction in reinforced concrete with the addition of crushed brick residue from accelerated tests. Postgraduate in Civil Engineering, Federal University of Pernambuco (Master). 2015;229.

9.   Gartner N, Kosec T, Legat A. The efficiency of a corrosion inhibitor on steel in a simulated concrete environment. Materials Chemistry and Physics. 2016;184:31-40.

10.   Torres AS. Chloride corrosion in reinforced concrete structures: A meta-analysis. Thesis (Doctorate in Civil Engineering), Federal University of Rio Grande do Sul, Porto Alegre. 2011;170.

11.   ABNT. Brazilian Association of Technical Standards. ISO 14.001: Environmental management systems - Requirements with guidelines for use. Rio de Janeiro: ABNT; 2015.
Available:https://edisciplinas.usp.br/pluginfile.php/3203062/mod_folder/content/0/NBR ISO14001.pdf?forcedownload=1
(Accessed on: 09 Oct. 2019)

12.   ABNT. Brazilian Association of Technical Standards. ABNT NBR 10.007: Sampling of solid waste. Rio de Janeiro: ABNT; 2004.

13.   ABNT. Brazilian Association of Technical Standards. ABNT NBR 10.005: Procedure for obtaining leached extract from solid waste. Rio de Janeiro: ABNT; 2004.

14.   APHA, AWWA, WEF. Standard methods for the examination of water and wastewater. 22. Ed. Washington: American Association of Public Health, APHA; 2012.

15.   Oliveira IMF, Silva MJSF, Tófani SFB. Fundamentals of analytical chemistry: Factors that affect the solubility of precipitates. Minas Gerais: UFMG; 2009.
Available:http://www.ufjf.br/quimicaead/files/2013/05/FQAnalitica_Aula11.pdf
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