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Cold Agglomeration of Ultrafine Oxidized Dust (UOD) from Ferromanganese and Silicomanganese Industrial Process

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Abstract: Different wastes are generated in ferromanganese and silicomanganese alloy production. One of them is the ultrafine oxidized dust (UOD) produced in the collection and control of flying dusts in the ferroalloy industry. This waste has fairly high manganese content (20%–40% Mn), making it suitable to be a secondary raw material for the ferromanganese industry. This research proposes a method for the transformation of UOD into a useable raw material. Cold agglomeration is the best option, due to its low energy consumption. Portland cement and refractory cement are compared as suitable candidates in the management of the UOD for their reuse in the electric arc furnace feed.

Keywords: ferroalloys; ferromanganese; silicomanganese; cold agglomeration; Portland cement; calcium aluminate refractory cement

1. Introduction

Manganese has been commonly used since prehistory in different ways, such as in paintings pigmented with manganese dioxide [1], glass-making to add color [2], or in Spartans´ weapons to make them stronger and more effective [3]. Its main use nowadays is as an alloying element (ferromanganese and silicomanganese) for the iron and steelmaking industry [4–7].

The production of ferromanganese is the result of a carbothermic reduction of manganese mineral ores in electric submerged arc furnaces [8]. Manganese oxide ores, reductants (coke and anthracite), and fluxes [1] are used as raw materials [1,9]. These materials (once the charge is calculated) are weighed, transported, and dumped into their respective hoppers that feed the automated mechanism which controls the loading of the furnace.

Once the production cycle is finished and the ores have been reduced in the electric furnace, metal and slag are poured into casting ladles. Due to their density difference, the metal leaves the furnace first, followed by the slag, both being recovered by cascade tapping or skimmer methods [4]. The metal and slag are poured into separate casting yards. During this process, the high temperature of both phases (>1500 °C) causes important manganese losses in the form of metal vapor, due to the higher vapor pressure of manganese (0.01 atm) on the ferroalloy [4,10]. The casting gas is absorbed by an exhaust hood and undergoes pollution control treatment. During transport, it is cooled and oxidized, which causes the appearance of an ultrafine dust containing a high amount of MnO_2. The purification of the captured MnO_2 fines is carried out through a dry treatment, bag filtration. Clogged filters are cleaned by high pressure air injection, collecting the ultrafine dust in storage bags. This ultrafine dust

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waste will from now on be referred to as ultrafine oxidized dust (UOD). Today, UOD is considered a dangerous waste and is sent to an industrial landfill, where it is mixed with other elements, forming an agglomerate—a costly process to prevent the dust particles from being blown away by the wind and the liberation of metals by natural leaching. The amount of UOD is generated in a ratio: 3.8 kg UOD per t of ferroalloy.

One of the processes which has been used in the reuse of the dust generated by the iron and steelmaking industry has been the use of briquettes. In this way, H. Han et al. [11] used briquettes to reuse blast furnace dust. The addition of cement is a common procedure in the recycling of dusts generated in the iron and steelmaking industry; for instance, Kemppainen et al. [12] studied the recycling of fine-sized iron-rich by-products using cement and ground granulated blast furnace slag. Bizhanov et al. [13] studied the application of stiff vacuum extrusion agglomeration technology to manufacture briquettes of manganese ore fines and aspiration dusts to be used in the industrial production of manganese ferroalloys (silicomanganese).

This research pursues the improvement of the current ferromanganese industrial process with the aim of avoiding the generation of UOD waste, but rather transforming the UOD into a material suitable for use in the factory.

2. Materials and Methods

2.1. Raw Materials

The waste called UOD has an extremely fine particle size (<150 µm), and a chemical composition: 27.4% MnO2; 10% C; 9.3% Si; 0.2% P; 0.3% S; 0.04% Ti; 2.3% Fe, making it a medium-low quality Mn raw material, but still suitable for the industrial process.

The objective of this research is to study the viability of UOD cold agglomeration using cement. This requires that the correct physical properties of the feeding material be achieved. The most important property to be achieved was the resistance to degradation at high temperatures in the top of the furnace, a requirement for the product as it recirculates through the process without cracking or powdering after being charged in the furnace when exposed to high temperature [4,5].

A commonly-used cement in agglomerating tests is Portland cement [14], generally used in metallurgy as a binding agent for manganese fines [15] or mixtures of raw materials that include coke and dust from the ferromanganese industrial process [16]. However, some tests have shown a poorer resistance of the product when subjected to high temperatures (above 700 °C) [17]. For that reason, in the present research, two different cements were tested and compared to determine which one has better resistance to degradation when exposed to high temperatures (<1000 °C):

1. Portland cement (Tudela Veguín III/A 42.5 N/SR). (Chemical composition: 6% C3A; 18% C3A + C4AF; 3.9% CaCO3; 43.4% slag; 1.52% SO3; and 0.23% unsolvable residue)
2. Calcium aluminate refractory cement SECAR 71 Kerneos Inc. (Madrid, 28020, Spain) (Chemical composition: >68.1% Al_2O_3; <31% CaO; <0.8% SiO_2; and <0.4% Fe_2O_3).

2.2. Test for the Determination of the Optimal Mixture

An optimal mixture was determined after testing different samples of product by varying the proportions of UOD and cement (Portland or refractory). Every mixture was first kneaded, then subjected to a range of high temperatures, and finally tested for degradation using a method based on the Coke Strength after Reduction test used for cokes (CSR) [9] and the TUMBLER assay used for testing iron ores [18].

A suitable kneading was achieved by using a laboratory sigma kneading machine. The optimal mixture obtained was an easy to handle dough that would finally achieve a briquette without cracks after curing. A standard amount of 500 g of UOD was used, and different proportions of cement (5%, 10%, and 15%) were added, observed, and compared. The amount of water was determined by pouring water into the mixture until the fluency of the mixture was correct. The amount of water ranged between 22% and 25%, depending on the type of binding agent.

Once the consistency of the mixture was adequate, it was placed in temperature-resistant silicone molds (10.5 × 6 × 3 cm^3) and stored at room temperature (20 °C) for 96 h to ensure an appropriate mechanical strength [19]. Thirty briquettes were manufactured, 15 using Portland cement (five briquettes for each percentage of binding agent: 5%, 10%, and 15%) and 15 using calcium aluminate refractory cement (five briquettes for each percentage of binding agent: 5%, 10%, and 15%).

Removing the briquettes from their molds was an easy operation, as the samples contracted while curing. Cracking was observed by visual inspection of the samples with 5% of Portland cement (Figure 1). On the contrary, mixtures with 10% and 15% Portland cement dried and showed no signs of cracking. All briquettes manufactured using refractory cement solidified without cracks.

Figure 1. Sample showing cracks (5% Portland cement).

A muffle furnace with controlled atmosphere was used to simulate the conditions on the top of the furnace (less than 1200 °C and reducing atmosphere). Each briquette was cut and heated up to one of the following temperatures: 20 °C, 430 °C, 530 °C, 580 °C, 680 °C, and 780 °C in the presence of coal products. After 30 min, briquettes were slowly cooled inside the oven.

Briquette degradation resistance was determined after heating and cooling. The equipment used to produce degradation was composed of a metallic cylinder 69 cm long and 13 cm diameter, which rotated longitudinally around the center of the tube at a fixed rotation speed of 24 rpm, controlled by a frequency-regulated motor.

At the end of each test, the material was removed from the cylinder. Large pieces (+10 mm) were separated from the material passing the mesh (generated dust) by using a 10 mm sieve. The amount of material passing through the sieve determined the degradability of the briquette. It is expressed as a percentage of the weight of the sample tested. In addition, the percentage of the large pieces of material (over 10 mm) was determined and used as the complementary value. The reference test is the resistance to degradability of material only processed at room temperature (20 °C).

Results showed similar behavior pattern in both samples of 10% and 15% Portland cement (Table 1).

Table 1. Optimal percentage of Portland cement.

	5%			10%			15%	
***t* (min)**	**% >10 mm**	***T* (°C)**	***t* (min)**	**% >10 mm**	***T* (°C)**	***t* (min)**	**% >10 mm**	***T* (°C)**
15	0	25	15	73.6	25	15	75.0	25
15	0	450	15	47.0	450	15	65.0	450
15	0	515	15	16.0	515	15	38.0	515
15	0	650	15	20.0	650	15	36.0	650
15	0	780	15	3.6	780	15	13.0	780

The optimal parameters for making the briquettes using Portland cement were:

1. 15% Portland cement
2. 500 g UOD
3. Water: 25% of the cement–UOD mixture

Comparing results adding a 10% and a 15% of Portland cement, it can be assumed that higher amounts of the binding agent show a better performance; however, it also increases the economic cost. For that reason, 10% of Portland cement was selected as the optimal percentage of binding agent.

The effect of different amounts of the calcium aluminate refractory cement was studied, and the same conclusions were reached. No significant difference exists between behavior patterns when using 10% or 15% of refractory cement. Furthermore, behavior patterns change when examining the samples using 5% refractory cement (Table 2).

Table 2. Optimal percentage of refractory cement.

	5%			**10%**			**15%**	
***t* (min)**	**% > 10 mm**	***T* (°C)**	***t* (min)**	**% > 10 mm**	***T* (°C)**	***t* (min)**	**% > 10 mm**	***T* (°C)**
15	41.8	25	15	55.1	25	15	73.6	25
15	21.6	450	15	32.4	450	15	25	450
15	13.4	515	15	30	515	15	21	515
15	11.3	650	15	50	650	15	52	650
15	8	780	15	80	780	15	72	780

The optimal parameters for making the briquettes using refractory cement were:

1. 10% Refractory cement
2. 500 g UOD
3. Water: 22% of the cement–UOD mixture

2.3. Test for the Determination of the Briquettes' Degradability Using Portland and Refractory Cement

Once the optimal percentages of binding agent (Portland cement and refractory cement) and water were determined, 32 briquettes were manufactured using the parameters previously described (16 using Portland cement and 16 using refractory cement).

After curing, briquettes manufactured using the same type of binding agent were matched in pairs and heated following the guidelines described above up to one of the following temperatures: 20 °C, 430 °C, 530 °C, 580 °C, 680 °C, 780 °C, and 1100 °C. Briquettes were consecutively cut into pieces and scattered in two samples. Each sample was weighted and placed into the equipment designed for the degradation test. Two test times were established: 15 and 30 min. One sample was tested for 15 min and the second one for 30 min. CSR test used for coke characterization was carried out in an I-type drum (no lifters) and subjected to 600 revolutions in 30 min. For this reason, the assay for testing briquettes was developed at 24 rpm for 30 min. Moreover, it was decided to develop another assay for 15 min in order to observe the effect of time on briquettes' degradability. Once the test ended, the cylinder was emptied, separating both large pieces and the dust generated during the test with a 10 mm sieve, as explained above. This same procedure was equally applied to the briquettes manufactured with Portland cement and the briquettes manufactured with the calcium aluminate refractory cement.

3. Results and Discussion

Results from both assays (using Portland cement and using refractory cement) were plotted so that a visual interpretation could be made. It is important to highlight that the path between consecutive points cannot be assured to be a straight line; however, it is the better way to illustrate the behavior pattern.

For briquettes manufactured using Portland cement as binding agent, it was observed during the 15 min test that when the temperature increased, the degradation resistance decreased. The same pattern was observed during the 30 min test; however, results showed a higher degradation due to the longer test time employed. It is necessary to highlight that tests with samples heated above 800 °C were not performed due to their total degradation.

In both tests, it was observed that the degradation resistance loss follows a negative linear tendency, as shown in Figure 2.

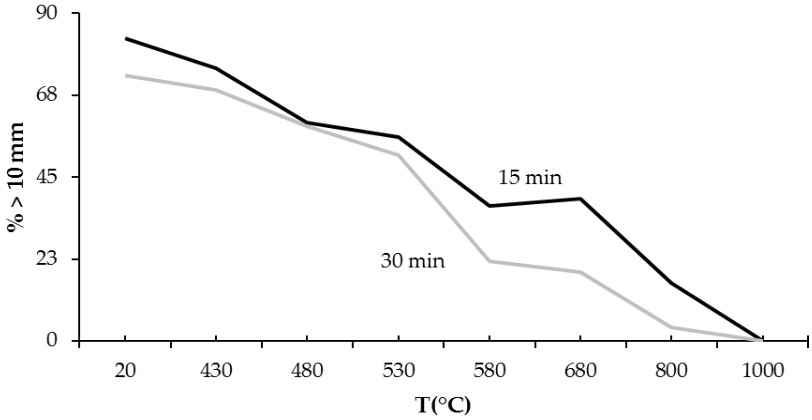

Figure 2. Degradation resistance loss as a function of temperature (Portland cement).

The same test was carried out using the briquettes manufactured with calcium aluminate refractory cement.

During the 15 min test, irregular degradation behavior was observed in the briquettes. The resistance decreased as the temperature increased to 430 °C. Then, a slight increase in degradation resistance was observed up to 530 °C. From that moment on, briquettes showed a degradation resistance increase to 1000 °C. During the 30 min test, briquettes revealed the same behavior pattern as was observed in the 15 min test. The only difference was that during the 30 min test, the degradability was greater than in the other, as a consequence of the longer duration of the test.

Degradation resistance using refractory cement is shown in Figure 3.

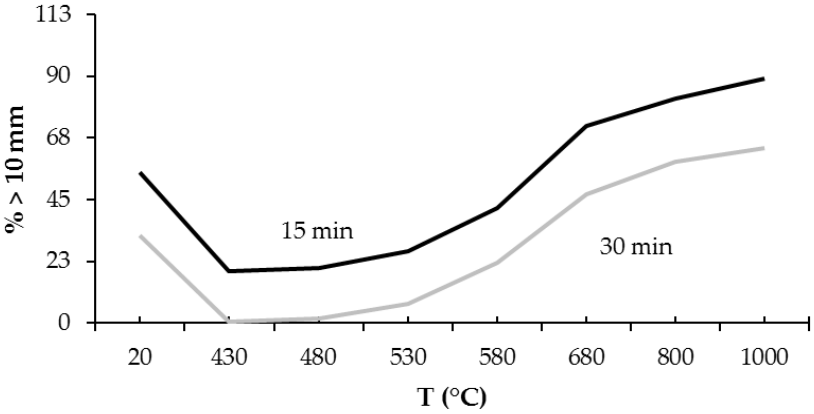

Figure 3. Degradation resistance loss as a function of temperature (refractory cement).

Briquettes manufactured with Portland cement exhibited a continuous degradation behavior when heated, as temperature increased. A direct relationship between temperature and resistance loss was observed, reaching complete degradation when temperature is 800 °C. This degradation resistance loss can be explained from a chemical composition point of view. On one hand, the tri-calcium silicate (which is a metastable phase at room temperature) in the Portland cement composition suffers decomposition when cement is heated below 1300 °C. As a consequence, tri-calcium silicate turns into di-calcium silicate and calcium oxide, showing an allotropic transformation that implies an important volume change when temperature is between 725 °C and 1420 °C [20].

Briquettes manufactured with the calcium aluminate refractory cement exhibit better degradation resistance when heated at high temperatures. This behavior is due to the lack of calcium silicate in the chemical composition of refractory cement. The test revealed a positive relationship between temperature and degradation resistance, though there is a minor resistance loss when approaching 500 °C due to dehydration that causes hydraulic agglomeration loss. The degradation resistance improves afterwards as a consequence of some thermal reactions between dehydration products and aggregates when reaching 800 °C. As a consequence, chemical bonds appear through ceramic links, allowing a rebound of the mechanical resistance.

4. Conclusions

Ultrafine oxidized dust (UOD) is nowadays catalogued in ferromanganese and silicomanganese plants as an industrial waste with high costs associated to landfill deposition and inertization. In this research study, a cold agglomeration process using Portland cement and calcium aluminate refractory cement was studied. The aim of this research was the transformation of UOD into a suitable secondary raw material for the ferromanganese industry and the development of a standard test to characterize the prepared material as temperature increases, simulating its behavior entering the furnace. Both objectives were successfully achieved.

A combination of the Coke Strength after Reduction test (CSR) and the TUMBLER test seems to be a suitable method for the degradation determination of cold agglomerates.

The use of Portland cement as an agglomerating agent does not provide good results. Best performance is reached at room temperature and at temperatures below 500–600 °C, decreasing drastically when heated above. This is due to the decomposition of tri-calcium silicate and the allotropic changes that cause volume variation with increasing temperature. However, it must be highlighted that some authors found that when extrusion techniques (vibropressing and stiff vacuum) are used, Portland cement provides better results.

The use of refractory cement allows briquettes with better degradation resistance at temperatures over 600 °C to be obtained. Moreover, degradation resistance increases with temperature. It is concluded that refractory cement is a successful agglomerating agent for UOD to be recycled in the electric furnace and transformed into a secondary raw material for the ferromanganese industry.

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Author Contributions: Luis Felipe Verdeja designed the work and supervised the experiments. María Ordiales and Daniel Fernández-González performed the resistance tests at different temperatures and wrote the manuscript. Juan Iglesias determined the amount of binding agent needed. José Sancho-Gorostiaga helped writing the draft manuscript. Alberto Fuentes provided the residual material to develop the experiments.

Conflicts of Interest: The authors declare no conflict of interest.

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