Materials recovery from residues of integrated steel making process: experimental investigation on briquettes production

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Keywords: circular economy, crushing test, recycling, residues valorisation.
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Abstract

The recovery of residues from the integrated steel making process and their subsequent re-use inside the production cycle itself represent an exciting challenge, which can have strong economic and environmental implications. The aim of this study was to verify the feasibility of recovering and reusing residues from the steel production process of the ILVA steelworks. In detail, the residues of the steel process were tested in order to produce briquettes to be re-introduced as a ferrous source in the converters during the transformation process of hot metal into steel. For the scope, experimentations were carried out on a pilot briquetting plant; several mixtures, with contents varying between 70 and 80% slag and between 10 and 30% stock-house dust and sludge from steel shop n.2 were tested. As binders, hydrated lime and beet molasses were added in varying amounts. Results showed how each mixture was able to make briquettes of good consistency and integrity. However, the "mixture 2b", consisted of a molasses and hydrated lime content of 8% and 2.7%, respectively, was found to be optimal in terms of crush resistance (CS = 75.33 daN/ briquette) and iron content (29%). The large-scale mass balance of the entire steelworks has made it possible to estimate the potential annual production volume of briquettes as well as the amount of iron to be recovered.

1. Introduction

The circular economy is based on the capacity of an economic system, defined as circular, to self-generate by using renewable sources and optimizing production processes (Bilitewski, 2012).

One of the world's greatest examples of the use of raw materials and energy resources, production of finished products, generation of residues and by-products as well as wastes disposal, is the integrated steel making process (Annunziata Branca *et al.*, 2014). The ILVA plant in Taranto (Apulia Region, Southern Italy) is one of the largest steel factories currently active in Europe for steel production (5-6 t/y), territorial extension (15 km^2) and plant complexity (e.g. n.4 blast furnaces, n.2 steel shops, n.2 hot rolling mills). The recovery of residues from the production process and their subsequent re-use inside the production cycle itself represent an exciting challenge, which can have strong economic and environmental implications.

In this context, the aim of this study was to verify the feasibility of recovering and reusing residues from the steel production process of the ILVA steelworks. In detail, some representative residues of the steel process were tested in order to produce briquettes to be re-introduced as a ferrous source in the converters during the transformation process of hot metal into steel.

2. Materials and methods

The experimental investigation involved the following phases: (i) Identification and quantification of residues to be recovered for briquette production; (ii) Characterisation of residues and binders; (iii) Design of mixes for briquetting pilot tests; (iv) Preparation of materials and (v) mixtures; (vi) Identification of the best mix design; (vii) Chemical and mechanical characterisation of the briquettes obtained by varying the mix design and; (viii) Mass balance at the entire steelworks for the evaluation of the extensibility of the full scale process in the future.

2.1 Identification and quantification of the residues to be recovered

Knowledge of the production processes has made it possible to identify the residues to be recovered. Furthermore, the purpose was that these materials were characterized by large amounts of iron, as shown in Table 1. A residues total production of 520,305 tonnes per year was observed. The largest fraction was BOF slag with a share of 94.2%. The total iron content was variable in the range of 30.7-73.0%.

Table 1. Summary of residues to be sent for material recovery.

Production residue[(a)]	**Fe tot content (%)**	**Amount (ton/y)**
Slag from BOF converters (steel shop n.2)	30.70	490,000
Sludge from gas OG cleaning (steel shop n.2)	73.00	26,000
Dust from dedusting system of Stock-house Blast Furnace 1 (BF n.1)	50.23	4,305
Dust from dedusting system of Stock-house Blast Furnace 2 (BF n.2)	48.50	
Dust from dedusting system of Stock-house Blast Furnace 4 (BF n. 4)	46.69	

[(a)]: The data refer to 2015 year in which the steel production was about 4.7 Mtonnes.

2.2 Residue characterisation

Chemical analyses were carried out according to ISO/TS 16878:2010 test methods for metallic iron, ISO 9035:1989 for iron oxide II, ISO 15350:2010 for total carbon and sulphur, and ISO 12677:2011 for all remaining parameters.

Table 2 showed that BOF slag and dust had a limited moisture content, varying in a narrow range (0.2-0.51%). On the other hand, the moisture content of the sludge averaged 12.2%, in line with the characteristics of a dehydrated sludge (Metcalf & Eddy, 2003).

Among all fractions, sludge from gas OG cleaning (steel shop n.2) showed the highest value of the total iron content, equal to 73%.

Table 2. Characterization of residues and hydrated lime used in briquetting[(a)].

Parameter	Residues characterization (%)				
	Slag from BOF converters (steel shop n.2)	Sludge from gas OG cleaning (steel shop n.2)	Stock-house BF 1 dust	Stock-house BF 2 dust	Stock-house BF 4 dust
Moisture	0.51	12.20	0.30	0.20	0.50
Fe_{tot}	30.70	73.00	50.23	48.50	46.69
FeO	28.55	54.92	2.76	2.23	2.00
Fe metal	0.89	12.81	0.50	0.50	0.39
Fe_2O_3	10.90	11.62	68.04	66.16	63.98
SiO_2	12.31	2.26	6.62	6.51	6.06
Al_2O_3	1.29	0.35	1.42	1.44	1.74
CaO	32.72	7.59	11.62	10.08	8.28
C	0.03	5.81	3.84	8.68	12.58
MgO	6.29	2.83	2.02	1.80	1.39
MnO_2	1.73	0.42	0.24	0.22	0.22
P_2O_5	1.57	0.22	0.14	0.14	0.14
TiO_2	0.32	0.10	0.09	0.10	0.12
S	0.08	0.07	0.11	0.14	0.09

[(a)]: Analysis methods: ISO/TS 16878:2010 for metallic iron, ISO 9035:1989 for ferrous oxide II, ISO 15350:2010 for total carbon and sulphur and ISO 12677:2011 for all remaining parameters.

The blast furnace slag, which represents the largest residual fraction, had a value of 30.7%. Table 2 also showed the characteristics of hydrated lime used as binder in the preparation of mixtures.

Finally, Figure 1 shows the results of the particle size analysis. The residues had different particle size characteristics, dust and sludge had a finer particle size compared to that of the slag, and the dust curves were overlapped.

2.3 Mixture design

Based on the results of preliminary tests and the technical and scientific know-how of ILVA technicians, 5 experimental blends were defined to identify the optimal mix for the briquettes production.

The mixtures were characterised by slag between 70 and 80%, BF stock-house dust between 10 and 30% and sludges OG gas cleaning from the steel shop n.2.

Table 3 showed the compositions of the experimental mixtures tested in the laboratory, both in percentage and absolute terms. Mixture 1 has included BOF slag (60.63%) and stock house dusts (25.98%); 7.09% was made up of beet molasses, while 6.30% was water.

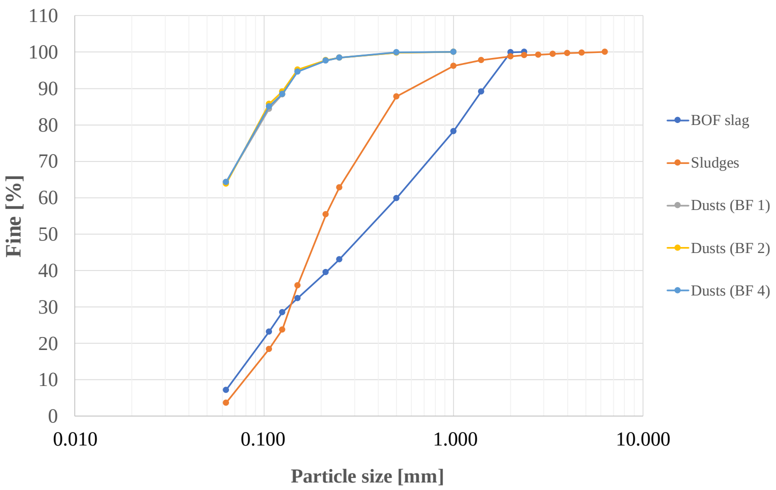


Figure 1. Particle size analysis of residues

Table 3. Mix design for briquetting.

N.	Mixture composition [%]						
	BOF slag	Stock house dusts	BOF Sludges from steel shop 2[a]	Molasses	Water	Hydrated lime	Total
1	60.63	25.98	0.00	7.09	6.30	0.00	100.00
2	65.42	14.02	14.02	4.67	0.00	1.87	100.00
2b	62.50	13.39	13.39	8.04	0.00	2.68	100.00
3	61.95	0.00	26.55	6.19	3.54	1.77	100.00
3b	61.40	0.00	26.32	7.02	3.51	1.75	100.00
4	64.22	18.35	9.17	4.60	1.83	1.83	100.00
4b	63.64	18.18	9.09	5.45	1.82	1.82	100.00
4c	61.40	17.55	8.77	7.02	2.63	2.63	100.00

[a]: OG gas cleaning sludges from steel shop n.2

Mixtures 2 and 2b provided for the use of all three residues; the presence of sludge, characterized by a moisture content of 12.2%, has made the addition of water superfluous. The two mixtures were characterised by different amounts of added binders, higher for the 2b mixture.

Mixtures 3 and 3b has included BOF slag and BOF sludges; although the presence of sludge, it was decided to increase the water content of the mixture by adding 3.5% water. With the same hydrated lime (around 1.75%), the two mixtures differed in the molasses content of 6.19% and 7.02% for mixtures 2 and 2b, respectively.

Finally, mixtures 4, 4b and 4c were an alternative to mixtures 2 and 2b, as they all use the three available residues. However, they were characterized by the presence of additional water in the mixture (1.82-2.63%) and by different amount of the binders.

Molasses is a brown liquid obtained by the process of producing sugar as a by-product (separation by centrifugation) and, for the purposes of this study, has been used as a binder to give a good degree of cohesion to the briquettes once produced. In addition, as the molasses dries, it tends to solidify, making the briquette more compact.

2.4 Materials preparation

As the granulometry of the BOF slag was heterogeneous, in order to achieve a good yield of the experimental briquettes, it was necessary to carry out a series of operations of volumetric reduction and sieving in order to obtain a residue with an average size ≤ 2 mm. In detail (Fig. 2), the following steps were carried out: manual material selection in order to exclude any unbreakable lumps, coarse grinding using a blade mill (Retsch mechanical crusher model BB 300 Mangan) in order to obtain a material size ≤ 25 mm, fine grinding with the same mill used previously to obtain a material size ≤ 5 mm and manual sieving with certified sieves (Giuliani series DIN1171), with a mesh opening of 2.80/2.36/2.00 mm (in order to obtain a material size ≤ 2 mm). The material thus obtained had an average moisture content of 0.51%, which was too low to allow a good experimental mixture to be obtained. Thus, a quantity of water equal to 13.6% of the weight of the briquettes was subsequently added to the fine BOF slag; water and slag were rested for at least 24 hours.

BOF sludge from steel shop n. 2 had a very fine grain size of 0.3 mm averagely (Fig. 2); contrary to the slag, it was not necessary to proceed with the various phases of manual grinding and sieving. The average moisture content of 12.20% (Tab. 2) made wetting unnecessary.

The dust from the stock-house dedusting systems of BF 1-2-4 had a very fine particle size of 0.1 mm averagely (Fig. 2). For this reason, it was not necessary to carry out the various stages of manual grinding and sieving.

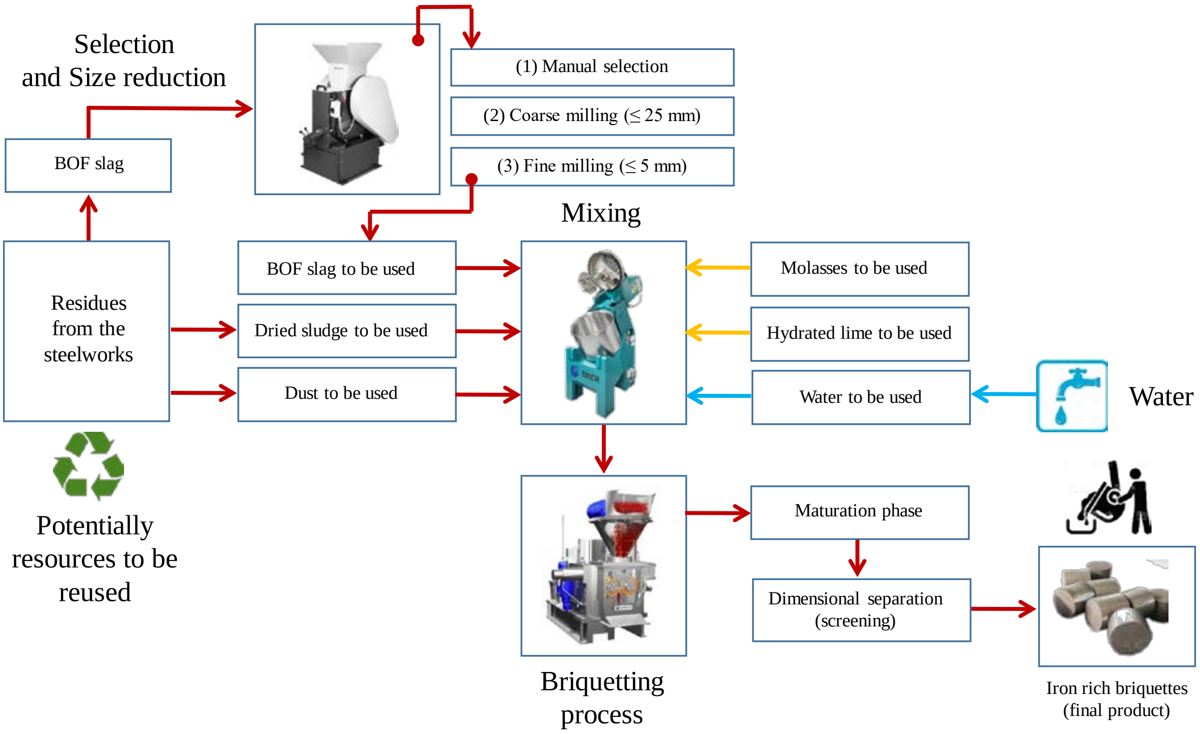


Figure 2. Steps of the briquette production at pilot plant in ILVA.

2.5 Mixture preparation

The preparation of the blends consisted of 5 main steps. In the first (Phase 1), the selected materials were fed individually into the mini Eirich mixing disc through the grate on the top. Once the filling of each material was finished, the mixer was closed and started, by means of the special lever, in order to allow a first homogenization of the partial mixture with a constant rotation speed equal to 24 rpm (Phase 2).

Once all the materials were filled, they were reunited at the centre of the mixer and then closed again to restart the disc for another brief mixing for about 2 minutes (Phase 3). The homogenous mixture obtained in this way, after mixing, was taken from the mini Eirich, placed in a special container with a known weight, and weighed on the Mettler Toledo SB S001 balance (resolution equal to 0.1g, capacity 8.1 kg) (Phase 4).

The dosage of the binders (hydrated lime and/or molasses) and water was the last step of the preparation phase of the mixtures and takes place after the mixing phase in the mini Eirich disc (Phase 5); the addition of the binders was followed by a further phase of manual mixing in order to allow the hydrated lime and/or molasses to distribute evenly within the mix.

2.6 Full scale briquetting test

The briquetting test involved the use of the Kompaktor Hutt CS25 compacting machine, capable of using 5 kg of mix per single test (Fig. 3).

This machine essentially consisted of (i) a mixture loading system equipped with a vacuum for the possible production of powders, (ii) a screw for the transfer of the mixture from the loading opening to the processing mechanism, (iii) two rotating disks each equipped with a series of pockets to contain the mixture, (iv) a pneumatic system acting on the 2 rotating disks by applying the compression force necessary to join the two halves of the briquettes contained in the cells, (v) a compartment to collect the briquettes produced and (vi) an electrical control panel and safety systems on the machine (start/stop buttons, speed adjustment, magnetic end stops).

The mechanism for the formation of the briquettes was mechanical; the material moved by the auger was collected in the cavities of the two antagonistic wheels which, through their movement, applied a compression force to the material, forming the briquette which was subsequently released.

(a) (b) (c)

Figure 3. Details of the equipment used: (a) Retsch mechanical crusher model BB 300 Mangan; (b) Mini Mixer – Eirich; (c) Kompaktor Hutt briquetting machine model CS25.

The briquettes obtained from each test were taken from the appropriate collection compartment, weighed on the Mettler Toledo SB S001 balance and then, in order to allow them to mature, placed in the electro-ventilated stove (Binder model FED-115) for 16 hours at a temperature of 105°C.

2.7 Mechanical strength tests

For the purposes of this experimentation, a crushing test was carried out using experimental briquettes. Furthermore, as there was no specific technical standard for briquettes at international level, it was referred to ISO 4700:2015 "Iron ore pellets for blast furnace and direct reduction feedstocks - Determination of crushing strength".

The test was carried out by placing a sample of material inside two metal plates through which the sample was subjected to a constant pressure. Operationally, the material was placed in the centre of the bottom plate and a load of at least 10 kN applied at a rate between 10 mm/min and 20 mm/min for the duration of the test. The test was considered to have been completed in the following cases: (i) The value of the applied load reached 50% or less of the maximum recorded value; (ii) The gap between the two platters was reduced to 50% of the initial average diameter of the sample being tested. In both cases, the compressive strength or CS (Crushing Strength) was represented by the maximum load value recorded during the test.

This test involved the use of n. 3 briquettes of each mixture; for each briquette the CS index value was determined using the RB 1000 press. The loading unit consisted of a disc with appropriate housings in which the briquettes to be tested were placed. Once all 3 briquettes had been placed inside the appropriate housings, the disc rotated and, after detecting the presence of the briquette by means of a sensor, the sample was placed under the mobile cylinder which exerted the axial compression force. The value of the compressive force varied from 1 daN to 1.000 daN with application speeds ranging from 5, 10, 15 or 20 mm/min.

The test began with a force application of 1 daN and it was continuously increased until the breaking condition of the tested sample was reached. The final CS value (expressed in daN/ briquette) was obtained as the arithmetic average of the tests performed on the samples of the same experimental mixture.

2.8 Identification of the optimal mixture

The optimal mixture was the one which maximizes both the value of mechanical resistance (CS index) and the iron content to be recovered. In order to accurately identify the optimal mixture, the multi-criteria analysis methodology reported in De Feo *et al.* (2018, 2008) was adopted. In particular, the construction of the composite indicator (indicated preference index, PI) provided for the assignment of equal weight to the two considered criteria (average CS index, iron content).

3. Results and discussion

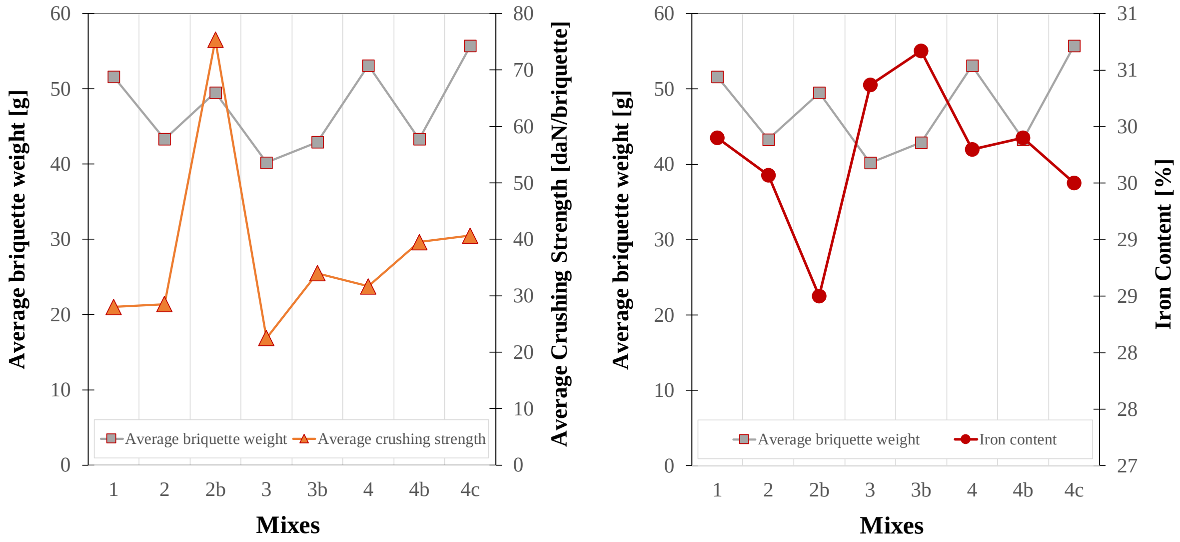
3.1 Mechanical characterisation of the briquettes

The mixtures tested all allowed the briquettes formation characterized by a good consistency and integrity. From a visual point of view, the 2b mixture was the most suitable; the material of the briquette was, in fact, composed of granular particles. Each briquette had an average length of 4,30 cm, an average width of 3,50 cm and a height of 3,00 cm. The weight of the single briquette varied in the range 40.2-55.7 g (Fig. 4).

Once made and matured at a constant temperature of 105° C, the briquettes were subjected to the crushing test performed in accordance with ISO 4700:2015.

In order to ensure the representativeness of the obtained results, the test was carried out on a sample of three selected briquettes of each mixture, chosen from those with the best appearance and total surface integrity. In the case of 2b, due to the significantly higher average CS value compared to the average of the other mixtures, the test was repeated a second time with 3 more briquettes. As six values were available, the outliers (68, 123 and 135 daN) were excluded; the three with a similar value (71, 77, 77 daN) were considered in order to determine the average value of the CS (75,33 daN).

The experimental results (Fig. 4a) showed a better resistance to crushing for mixtures 2b, 4b and 4c with values of 75.33 daN, 39.60 daN and 40.67 daN respectively; these mixtures were characterized by the presence of all three residues used for experimentation.



(a) (b)

Figure 4. (a) Average crushing strength and (b) iron content of the mixtures investigated.

The 2b mixture, which had the best resistance to crushing, was the one with the highest percentage of molasses (8.04%), a high content of hydrated lime (2.68%) and no additional water (except for the water related to the humidity of the materials used).

The mixtures with the lowest crush resistance were 3 and 1, with values of 22.5 and 28.0 daN respectively; they were biphasic as they were characterised by the absence stock-house dust collection systems of blast furnaces 1-2-4 and OG gas dedusting sludges from the steelworks, respectively. Mixture 3, with the lowest resistance to crushing (22.50 daN), was characterised by the absence of stock-house dust and, on the other hand, had the highest percentage content of OG gas dedusting sludges from the steelworks 2 (26.55 %).

The test of resistance to crushing, as previously specified, was carried out by applying an axial compression force to the briquettes that induced, as it increased, the breakage of the sample. In this regard, the 2b mixture underwent breakage along the direction of the force applied (Fig. 5); in fact, the two half of the briquette had very clean and regular separating surfaces.

Such a breakage was found for mixtures characterised by high CS values. In contrast, mixtures with lower values than the CS strength index had fragment fractures with irregular breaking surfaces; fractures also generated a significant formation of fine fractions, as in the case of mixture 3.

3.2 Chemical characterisation of the briquettes

A first chemical characterization of all used residues, binders and drinking water was carried out to evaluate the presence of substances in such concentrations that they could conferred some dangerousness. Having also excluded the formation of organic micropollutants or other inorganic compounds (because of the fact that the process of preparation of the briquettes is cold), it was proceeded with the analysis of the average iron content of the briquettes.

In this regard, it was observed that the iron content varied between 28.50% of the 2b mixture and 29.90% of the 1 and 4b mixtures (Fig. 4b).

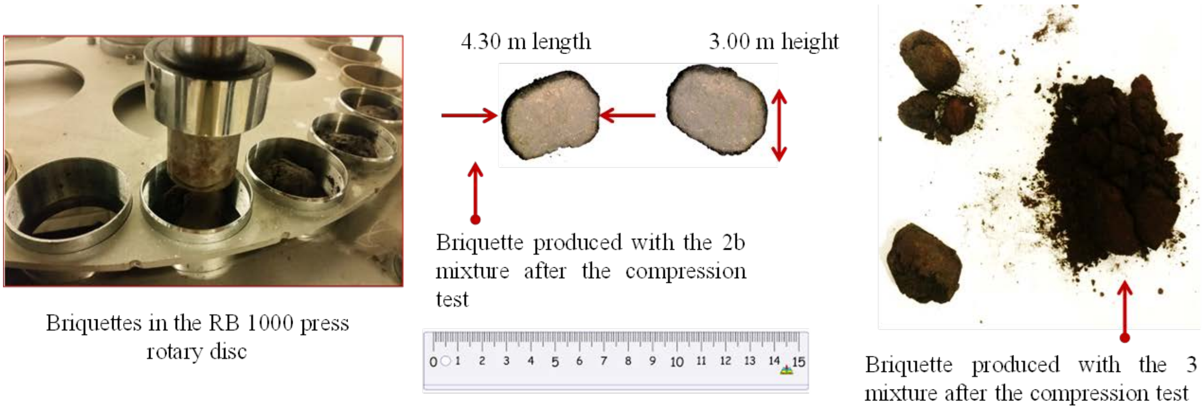


Figure 5. Consistency and geometry of the briquettes produced with the mixtures 2b and 3 after the crushing test.

3.3 Identification of the optimal mixture and mass balance

The application of the multi-criteria analysis methodology (De Feo *et al.*, 2018) made it possible to identify the 2b mixture as the optimal mixture, characterized by the higher value of the composite indicator (Fig. 6). This mixture was the best, mediating between the aspects of mechanical resistance to crushing and iron content.

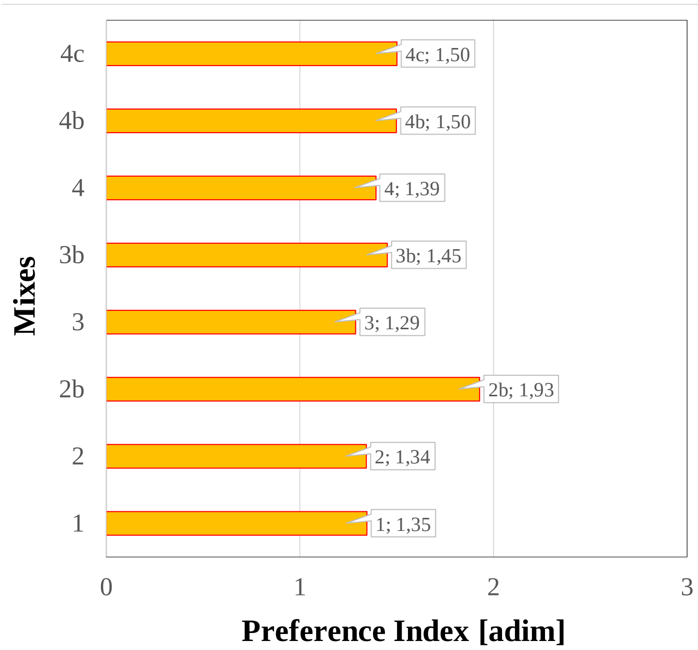


Figure 6. Identification of the most performing mixture in terms of average crushing strength and iron content according to the multi-criteria analysis methodology.

The optimal mixture was subsequently characterized from the chemical point of view; the results are shown in Table 4.

The chemical characterization of the briquettes produced with the 2b mixture confirmed the absence of metals in significant concentrations, as already highlighted by the preliminary characterization of the individual residues constituting the mixture. This further strengthened the hypothesis of re-use within the production cycle.

In view of the chemical analyses carried out, taking into account the production capacity of the ILVA Taranto and the average volumes of BOF slag produced in the steel shop, it was possible to estimate the quantity of residues (BOF slag, stock-house dust and BOF sludge from steel shop n.2) and iron recoverable each year. In the case of the optimal mixture (2b), a mass balance of the entire ILVA production capacity was carried out (Fig. 7).

Table 4. Chemical characterisation of the best mixture (Mix 2b).

Parameter	**Unit**	**Value**
Antimony (Sb)	mg/kg	< 1.4
Arsenic (As)	mg/kg	< 1.4
Barium (Ba)	mg/kg	60
Beryllium (Be)	mg/kg	< 1.4
Cadmium (Cd)	mg/kg	< 1.4
Chromium VI (Cr VI)	mg/kg	< 0.10
Chromium as total (Cr tot)	mg/kg	500
Mercury (Hg)	mg/kg	< 0.14
Molybdenum (Mo)	mg/kg	< 1.4
Nickel (Ni)	mg/kg	9
Lead (Pb)	mg/kg	100
Copper (Cu)	mg/kg	11
Selenium (Se)	mg/kg	< 1.4
Thallium (Tl)	mg/kg	< 1.4
Tellurium (Te)	mg/kg	< 1.4
Vanadium (V)	mg/kg	360
Zinc (Zn)	mg/kg	400
Tin (Sn)	mg/kg	< 1.4
Cobalt (Co)	mg/kg	< 1.4

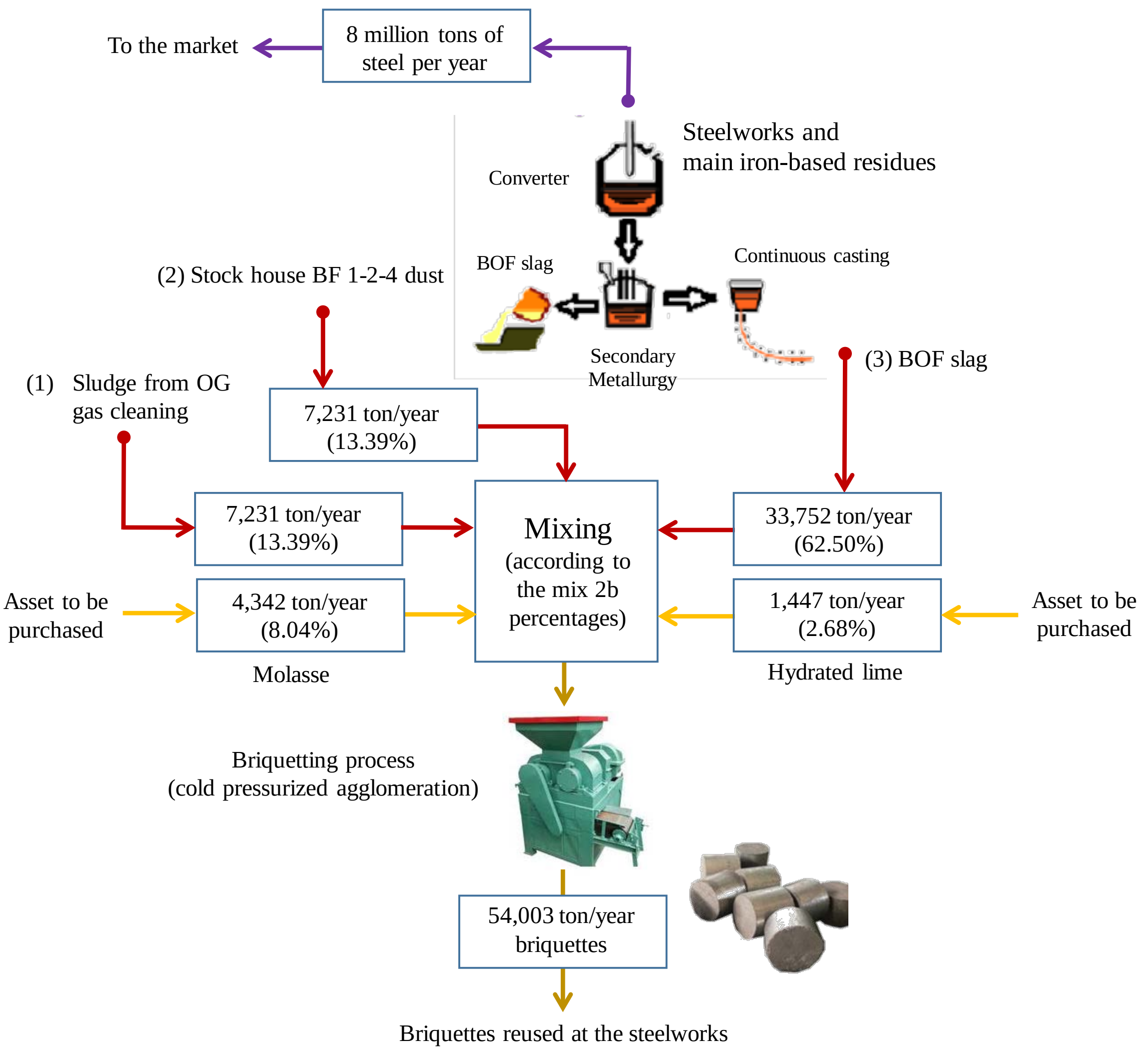


Figure 7. Mass balance at the ILVA Taranto steelworks based on the hypothetic use of briquetting with a 2b mixture.

The results obtained showed a recovery of 48,214 tonnes of residues per year, on the basis of the quantities of BOF residues equivalent to an annual steel production of the plant of Euro 8 million. The volume of the 2b mixture was 54,003 tonnes. The recovery of iron equivalent was estimated at 15,391 tonnes per year.

Moreover, in light of the historical production data for briquettes at the above plant (117,926 tons/y for 2012 and 60,663 tons/y for 2013), the production volume of the 2b mixture previously indicated was in line with the capacity of the briquettes production plant at ILVA, thus confirming the hypothesis of future production start-up.

4. Conclusions

The study aimed at verifying the technical feasibility of recovering steel production process residues such as BOF slag, dust from BF stock-house dedusting systems and sludge from OG gas cleaning. These residues were used for the production of briquettes to be re-introduced as cold fillers into basic oxygen converters during the transformation process of hot metal into steel.

The experimentation, carried out on a pilot briquetting plant, involved the testing of various experimental mixtures, with contents varying between 70 and 80% BOF slag and between 10 and 30% stock-house dust and OG gas sludge from steel shop n. 2. As binders, hydrated lime and beet molasses were added in varying amounts.

The obtained results showed how each mixture was able to make briquettes of good consistency and integrity. However, the 2b mixture was found to be optimal in terms of crush resistance (CS = 75.33 daN/ briquette) and iron content (29%). The 2b mixture consisted of a molasses and hydrated lime content of 8% and 2.7%, respectively.

The large-scale mass balance of the entire steelworks has made it possible to estimate the potential annual recovery of about 48,200 tons of residues and the potential annual production volume of briquettes at about 54,000 tons, having assumed steel production of 8 million tons per year. The recovery of iron was found to be about 15,400 tons per year.

The chemical characterization of the briquettes produced with the 2b mixture confirmed the absence of significant concentrations of metals, strengthening the possibility of re-use in the production cycle.

In short, the process under investigation had the potential to reduce both the volume of raw materials to be purchased entering the production cycle and the volume of residues that could become wastes, with a consequent reduction in environmental impacts and operating costs. Moreover, the tested process could have been an economic potential if the briquettes, once industrially tested, were sold to other steelworks.

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