Exploitation of steel slags in clay bricks

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Abstract

The feasibility of steel slag recycling in bricks was assessed through laboratory trials on three different typologies of wastes and clay bodies. The use of slag, previously ground below 3 mm, is substantially possible for additions of 2-3\% without particular hindrances of technological nature. Additions of up to 5-6\% seem to be practicable, even though with a porosity increase and a deterioration of the mechanical properties of both unfired and fired products. Larger amounts of slag are decidedly inadvisable for the changes in the chemical and physical characteristics of products.

1 Introduction

The disposal and exploitation of steel production residues are still unresolved problems, not only because of the large quantities involved (over 2 million tons a year in Italy alone), but also because of the variety of waste materials produced, that come from different processing phases (melt scrorification, dust abatement, etc.) and depending on the technology (electric arc furnaces, crown furnaces, etc) and the type of steel (common, stainless, special) have different chemical and physical properties [1-2]. To date, current know-how has not yet found solutions that may effectively be applied to the steelworks sector, and that would allow for a true recovery of the waste products, that are now mainly dump to disposal sites.

Previous studies concerned the potential use of steel slags have been only applied to cementitious material [3-5]. The aim of this research has been basically to assess the feasibility of recycling steel slags in brick production. The
slag from the processing of common steel has been selected as it offers the best re-use potential, because it is the most abundant residue produced by the steel works and also because it does not contain large quantities of heavy metals such as chromium, nickel or molybdenum [1-2].

2 Materials and methods

Slag samples from three different steelworks, referred to as D, O and V respectively, have been taken into consideration together with three clay bodies from brickworks, located near the steelworks (M, S and F respectively). Clay/slag mixes (matching D+M, O+S, V+F) were designed up 10% wt of waste added. Slag was preliminarily ground by jaw crushing and hammer milling below 3 mm. Slag and clay samples were characterised determining: chemical composition (XRF-WDS, ICP-OES, ASTM E 1019); phase composition (XRPD, TGA-DTA); bulk density (ASTM C 329); particle size distribution (ASTM C 325, ASTM C 958). The technological behaviour was assessed by simulating the brickmaking process on a laboratory scale, by pan milling, extrusion, drying and firing, and the following characterisations: moisture content (ASTM C 324); plasticity with Atterberg limits (CNR-UNI 10013); hygroscopicity [6]; drying and firing shrinkage (ASTM C 326); dry and fired bend strength (ISO 10545-4); drying sensitivity according to the Bigot curve [7], thermodilatometric analysis (TDA); water absorption and saturation coefficient (UNI 8942-3); open porosity, bulk density and apparent specific weight (ASTM C 373); efflorescence (UNI 8942-3); analysis of the water soluble components by means of ICP-OES (EN 772-5).

3 Results and discussion

3.1 Chemico-physical characteristics of slags

The slags are made up of irregular, very dense (3.7–4.0 g/cm³) and bubbly fragments from 1 to 10 cm in size. The chemical composition is characterised by high iron oxide (34-40%) and calcium oxide (18-27%) contents (Table 1).

Slag is to a large extent amorphous, being wustite (FeO) the main crystalline phase together with, in decreasing order of abundance: larnite (Ca₂SiO₄), lime (CaO) and traces of periclase (MgO) and magnesioferrite (MgFe₂O₄).

The thermal behaviour of the slag shows a gradual in mass increase up to 1000 °C that may be explained as oxidation of FeO to Fe₂O₃.

3.2 Technological behaviour of clay/slag mixes

Very different clay mixtures were chosen, in terms of both the chemico-mineralogical and granulometric characteristics [8].
3.2.1 Behaviour during shaping

The mixing and moulding of the raw materials did not lead to particular problems, even with 10% of slag. The presence of waste had a similar effect on all three body types: the higher the slag percentage, the lower the optimum water content for extrusion. Furthermore, there was a plasticity increase from the slag-free clay to bodies containing 5% or 6%; this trend is generally inverted in the mix with 10% of waste.

In any case, the variations are modest, and do not compromise the shaping behaviour of the bodies, which nearly always fall within the “optimum” field for extrusion [9], irrespective of the addition of steelwork residues.

3.2.2 Drying behaviour

The effect of the slag is more or less the same for all the clay types examined. In particular, with an increasing percentage of slag there is:

- a significant drop of drying shrinkage;
- a decrease of mechanical resistance;
- a clear reduction of hygroscopicity;
- a tendency to increase the drying sensitivity and to extend the shrinkage phase with weight loss in the body DM and OS, vice versa in the mix VF.

The slag, therefore, seems to have a positive effect during drying, which is seen in the reduction of shrinkage and hygroscopicity, which in part is balanced by a longer shrinkage phase with weight loss. In any case, the recorded variations are not conspicuous, but all fall into the range that is normally accepted by the brickworks [10-11].
3.2.3 Firing behaviour

The thermodilatometric curves (Fig. 1) show that:

i) the addition of up to 2% slag to a relatively coarse-grained body and with a moderate carbonate content (M) does not bring about considerable variations, whereas the addition of 5% slag leads to an increase of shrinkage, that is basically connected with the greater contraction that takes place during the interval of about 800-900 °C. The mixture containing 10% waste expands in an anomalous manner between 600 and 800 °C and, as a result, at the end of firing shrinks less than the waste-free clay;
ii) in a carbonate rich and fine-grained body (S), the addition of up to 6% of slag leads to a regular increase of shrinkage, tied mainly to a volume reduction between about 800 and 900 °C. The presence of 10% of steel slag provokes a turnaround in this trend, and this high temperature contraction does not rise further; 

iii) the slag brings about a less evident effect on the fine-grained clay with a low carbonate content (F): the thermodilatometric curves of the slag free and the 10% bodies are practically overlapped. Modest additions of waste seem to promote a lower expansion rate during heating or a slightly greater contraction between 800 and 900 °C.

3.3 Properties of fired bricks

The results of the characterisation of the fired products are summed up in table 2. The presence of slag does not have a great influence on the firing shrinkage, which, depending on the type of clay may decrease (DM), increase (OS) or not vary in an appreciable manner (VF), in any case remaining within values (at the most 0.7 cm/m) that are highly tolerable in industrial practice [12-13].

The greater the quantity of slag, the lower the mechanical resistance. However, it is possible to remark that in the mixture DM and VF the modulus of rupture decreases only slightly with addition of up to 5-6%; on the other hand in the batch OS the bending strength lowers regularly and quite rapidly with additions of up to 6% of slag, and this tend to stabilise. In any case, all materials containing 2-3% of slag have values that are greater than 100 kg/cm², that easily fall into the national standards [14]. The water absorption systematically increases with the slag percentage, being the max increment up to 2% in the carbonate-rich body.

Notwithstanding the porosity augment, there is an increase of bulk density, though it is not proportional to the quantity of waste.

The apparent specific weight, that is the density of the pore-free ceramic material, shows a peculiar trend: it remains more or less constant, or it may even decrease, despite the addition of up to 6% of slag; the effect of the latter is seen clearly only when the content is of 10%. The saturation coefficient does not vary significantly.

The influence of steel slag on the efflorescence phenomenon is modest and in many case absolutely negligible. This situation reflects the quantity and quality of the soluble salts and their variations induced by the addition of slag (Table 3). The total amount of soluble salts is around 0.2-0.3% of the total soluble salts, which are in line with the values recorded in the best quality bricks [8, 15]. The effect of the addition of steel slag is appreciable only for soluble calcium and sulphate, also as a result of the CaO and sulphur supplied by the slag; the Ca²⁺ e SO₄²⁻ variations, in any case, are limited and depend upon the type of clay. The other elements are below 0.01%. All the soluble salt values fall below the risk threshold for medium-high efflorescence [16].

In particular, the hexavalent chromium is ≤ 0.001%, even in bricks containing 10% of slag.
Table 2. Variation of the firing behaviour of the bodies: firing shrinkage ($S_f$), modulus of rupture (MOR), water absorption (E), saturation coefficient ($C_s$), open porosity (P), apparent specific weight (T) and bulk density (B); avrge = average; std dev = standard deviation (n=1).

<table>
<thead>
<tr>
<th>Cycle</th>
<th>940 °C</th>
<th>1000 °C</th>
<th>930 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DM0</td>
<td>DM2</td>
<td>DM5</td>
</tr>
<tr>
<td>Slag (% wt)</td>
<td>0</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>$S_f$ (cm$^3$)</td>
<td>0.6</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>std dev</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>MOR (kg/cm$^3$)</td>
<td>103</td>
<td>95</td>
<td>94</td>
</tr>
<tr>
<td>std dev</td>
<td>5</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>E (%)</td>
<td>16.1</td>
<td>16.6</td>
<td>17.3</td>
</tr>
<tr>
<td>std dev</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>$C_s$ (adim.)</td>
<td>31.8</td>
<td>30.7</td>
<td>31.7</td>
</tr>
<tr>
<td>std dev</td>
<td>0.3</td>
<td>0.2</td>
<td>0.5</td>
</tr>
<tr>
<td>P (%)</td>
<td>2.65</td>
<td>2.61</td>
<td>2.65</td>
</tr>
<tr>
<td>std dev</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>T (adim.)</td>
<td>1.806</td>
<td>1.812</td>
<td>1.809</td>
</tr>
<tr>
<td>std dev</td>
<td>0.002</td>
<td>0.001</td>
<td>0.009</td>
</tr>
</tbody>
</table>

This is considerably important, as the not negligible concentrations of chromium oxide present in the clay/slag mixture (up to 0.2%) and the not particularly high firing temperatures of the DM and VF bricks, could have favoured the formation of soluble chromium [17].

4 Conclusions

The presence of slag has the following effects on technological behaviour of clay bodies:

a) no significant variations during extrusion; the plasticity of the bodies remains constant, whilst the quantity of water decreases slightly. The most important limit during body preparation are the slag granulometry, which is needed to be reduced to less than 3 mm, and its magnetic susceptibility;
Table 3. Chemical composition of the soluble salts (% weight).

<table>
<thead>
<tr>
<th>% wt</th>
<th>DM0</th>
<th>DM10</th>
<th>OS0</th>
<th>OS10</th>
<th>VF0</th>
<th>VF10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na+</td>
<td>0.004</td>
<td>0.003</td>
<td>0.004</td>
<td>0.003</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>K+</td>
<td>0.004</td>
<td>0.004</td>
<td>0.007</td>
<td>0.006</td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td>Mg2+</td>
<td>0.002</td>
<td>&lt;0.001</td>
<td>0.001</td>
<td>&lt;0.001</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>Ca2+</td>
<td>0.137</td>
<td>0.086</td>
<td>0.197</td>
<td>0.144</td>
<td>0.067</td>
<td>0.078</td>
</tr>
<tr>
<td>Mn2+</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Fe3+</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>SO42-</td>
<td>0.204</td>
<td>0.121</td>
<td>0.017</td>
<td>0.021</td>
<td>0.029</td>
<td>0.023</td>
</tr>
<tr>
<td>CrO42-</td>
<td>0.001</td>
<td>0.002</td>
<td>&lt;0.001</td>
<td>0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

b) the drying process seems to be facilitated by the presence of slag, with a reduction of shrinkage and hygroscopicity. The most significant limit is the considerable drop in the mechanical resistance of dry bricks, even if the values remain rather high in the more plastic bodies;

c) during firing there are moderate variations: the presence of slag mainly promotes a porosity increase and, for 10% waste, even in bulk density and in apparent specific weight. The main limits consist in a decrease of mechanical strength, which however is modest with slag addition of 2-3%;

d) the presence of slag does not affect efflorescence and soluble salts to a considerable extent. Firing seems to ensure that the slag is rendered practically totally inert, and in particular there is no hexavalent chromium.

In any case it is important to underline that the slag must be preliminarily ground to particle size < 2-3 mm. Slag may increase the wear on the pan mills in proportion to its granulometry and percentage. In conclusion the introduction of previously ground steel slag in clay bricks seems to be:

- feasible for additions of 2-3%, without particular obstacles of a technological nature;
- practicable for additions of 5-6%, though with a porosity increase and a deterioration of the mechanical properties of unfired and fired bricks; these effects vary upon the type of clay and in many case could be intolerable;
- inadvisable for additions of 10% or more, due to the combination of the variations in the physical and mechanical characteristics of products.

References


