Silicomanganese and Ferromanganese Slags Treated with Concentrated Solar Energy †

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Abstract: Solar energy when properly concentrated offers a great potential in high temperature applications as those required in metallurgical processes. Even when concentrated solar energy cannot compete with conventional metallurgical processes, it could find application in the treatment of wastes from these processes. These by-products are characterized by their high metallic contents, which make them interesting as they could be a raw material available in the own factory. Slags are one of these by-products. Slags are most of them disposed in controlled landfill with environmental impact, but also with economic impact associated to the storing costs and the metallic losses. Here we propose the treatment of ferromanganese and silicomanganese slags with concentrated solar energy with the purpose of evaluating the recovery of manganese from these slags.

Keywords: concentrated solar energy; manganese; environment; ferroalloys; slags

1. Introduction

Solar energy has taken growing interest in the last decades with the development of renewable energy sources, and particularly when properly concentrated, this energy source can be used in high temperature applications, as those that can be read in Fernández-González et al., 2018 [1], and, for instance, in our case, we used solar energy in the synthesis of calcium aluminate cement [2] and in the iron metallurgy [3].

Slags are usually recycled in the own process or disposed in controlled landfill [4–8], but they contain significant quantities of metal and recovering it from the slag could be interesting since the economic and environmental point of view. This paper is dedicated to the utilization of concentrated solar energy in synthesizing ferromanganese, and in the treatment of ferromanganese and silicomanganese slags.

2. Materials and Methods

Experiments were carried out in a 1.5 kW vertical axis solar furnace located in Odeillo and belonging to the PROMES-CNRS (Procédés, Matériaux et Énergie Solaire-Centre National de la Recherche Scientifique). The solar furnace is based on that the sun radiation strikes a heliostat, which tracks the sun and reflects the radiation towards a 2 m. in diameter parabolic concentrator (Figure 1). This parabolic concentrator makes solar radiation converge at a focal point of 12–15 mm. in diameter. In this way, solar radiation (700–1100 W/m²) is concentrated by four orders of magnitude. A shutter was used to control the power applied to the sample.
Figure 1. Experimental equipment used in the experiments. Parabolic concentrator and experimental device (right) and heliostat (left).

Mixtures of Fe₂O₃, MnO₂ and carbon (laboratory quality reagents; different carbon excesses, 10, 15, 25 and 40% wt.), were loaded in mullite crucibles of 75 mm in length, 12 mm in width and 8 mm in depth (see in [9] a full description of the same process used in the case of Fe₂O₃ + C mixtures), having as objective synthesizing ferromanganese. A series of thermocouples were located at the bottom of the crucible (outside) to register the temperature (max. temperature >1200 °C). Crucible displaced at a controlled speed below the focal point to treat all the material loaded in the crucible.

Mixtures of ferromanganese and silicomanganese slags (industrial slags, Table 1), some with calcium carbonate to liberate manganese from them, were prepared separately in crucibles of tabular alumina with 55 mm in height, 30 mm in upper diameter, 25 mm in lower diameter and 3 mm in thickness of the crucible walls. The crucible was located below the focal point (15 mm in diameter) and covered with a glass hood to avoid the projections in the parabolic concentrator. Samples comprised four different types of mixtures of slags: ferromanganese (Table 1), silicomanganese (Table 1), ferromanganese with limestone and silicomanganese with limestone. The additions of limestone were performed in an attempt of forming silicates of calcium instead of silicates of manganese and thus liberating manganese from the slag. Initial slags were analyzed through x-ray diffraction, and in the case of FeMn slag it reported glaucochroite ((Ca, Mn)₂SiO₄), gehleneite (Ca₂Al₂SiO₇) and manganosite (MnO), while in the case of SiMn slag it showed gehleneite (Ca₂Al₂SiO₇), kirschsteinite (CaFeSiO₄), melilite (Ca₈Al₆MgSi₅O₂₈) and manganese oxide (IV), in order of abundance.

### Table 1. Chemical composition of the slags (above silicomanganese, and below ferromanganese).

<table>
<thead>
<tr>
<th>Element</th>
<th>O</th>
<th>Mn</th>
<th>Ca</th>
<th>Si</th>
<th>Al</th>
<th>Mg</th>
<th>S</th>
<th>Ba</th>
<th>K</th>
<th>Na</th>
<th>Sr</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc. (%)</td>
<td>37.12</td>
<td>19.02</td>
<td>17.76</td>
<td>12.56</td>
<td>6.569</td>
<td>2.741</td>
<td>1.189</td>
<td>1.084</td>
<td>0.6663</td>
<td>0.5670</td>
<td>0.2544</td>
<td>Balance</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>O</th>
<th>Mn</th>
<th>Ca</th>
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<th>Fe</th>
<th>Na</th>
<th>K</th>
<th>Ba</th>
<th>Ti</th>
<th>S</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc. (%)</td>
<td>33.25</td>
<td>29.39</td>
<td>19.62</td>
<td>11.04</td>
<td>3.228</td>
<td>1.375</td>
<td>0.4204</td>
<td>0.4063</td>
<td>0.3997</td>
<td>0.2761</td>
<td>0.2031</td>
<td>Balance</td>
</tr>
</tbody>
</table>

3. Results

Samples were analyzed using x-ray diffraction technique in powdered materials.

3.1. Synthesis of Ferromanganese

Partially reduced iron and manganese oxides were detected. Manganese oxide (II)(MnO) and manganese oxide (II, III) (Mn²⁺Mn³⁺O₄) are the partially reduced manganese oxides as the initial manganese oxide was pyrolusite (MnO₂). Partially reduced iron phases are not typical, but when they appear they do as magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃, which is like a magnetite with vacancies) while the initial iron oxide was in the form of hematite (Fe₂O₃). Typical phases, major components in the quantitative analysis discounting amorphous phases, were iwakiite and jacobsite ((Mn²⁺, Fe²⁺)(Fe³⁺, Mn³⁺):O₄), and the manganese oxides.

3.2. Treatment of Ferromanganese Slag

Calcium carbonate additions were not sufficient to produce any effect in the slag and thus phases identified in one and another type of sample were similar. In this case, as we will see in the case of...
the silicomanganese slags, silicates are the main phase in the slag. Gehlenite (Al₂Ca₂O₇Si),
glaucochroite (CaMn₂⁺SiO₄) and kirschsteinite (CaFeSiO₄) were identified, the same as manganese
oxides (MnO, MnO₂, Mn₃O₄ and Mn²⁺Mn³⁺₂O₄). Other phases identified in these samples were:
brownmillerite (Ca₄(Al, Fe)₂O₁₀), fayalite ((Fe²⁺)₂SiO₄), melilite (Ca₈Al₆MgSi₅O₂₈) and yoshiokaite
(Ca(Al, Si)₂O₄).

3.3. Treatment of Silicomanganese Slag

The same as in the other case, calcium carbonate additions were not sufficient to produce any
effect in the slag and thus phases identified in one and another type of sample were similar. Gehlenite
(Al₂Ca₂O₇Si) and kirschsteinite (CaFeSiO₄) are the main phases. Manganese oxides (MnO, MnO₂ and
Mn²⁺Mn³⁺₂O₄) are also representative in the x-ray diffraction analyses. Other phases identified in the
samples were melilite (Ca₈Al₆MgSi₅O₂₈), manganese aluminate oxide (Mn₂AlO₄) and glaucochroite
(CaMn₂⁺SiO₄).

4. Discussion

Synthesis of ferromanganese: Ferromanganese was not detected during the experiments. Partially reduced mixed manganese and iron oxides are detected, as we found jacobsite and iwakiite
in the samples as main constituents (Mn²⁺, Fe²⁺)(Fe³⁺, Mn³⁺)₂O₄ (substitutions and vacancies as
expressed), while in the initial mixture we had Mn⁴⁺ and Fe⁴⁺. Regarding the Mn and Fe individual
oxides, we found MnO and Mn₃O₄ (Mn²⁺Mn³⁺₂O₄), and Fe₃O₄ (FeOFe₂O₃) and γ-Fe₂O₃ Working under
ambient atmosphere is unfavorable for the reduction reactions (even when using carbon excesses)
because carbon was burned during the process and left the sample without fully reducing the load.
Thermal decomposition allows the partial reduction of the mixture, but neither this method nor the
carbon (nor the combined effects) allows obtaining the ferromanganese (Fe, Mn). Reactions solid-
solid are difficult, and the expected solid-gas (carbon monoxide, Boudouard mechanism) reaction is
minimized because hot gas tends to leave the sample without reducing because of the venetian blind
(shutter) that allows the entrance of air from outside of the building causing circulation of air. The
presence of a glass hood connected to a reducing or inert atmosphere would have been positive for
the obtaining of ferromanganese. Temperature is also problematic, as if the temperature is increased
to maximum values we did not improve the results, but we achieve the melting of the crucible and
the appearance of silicates.

Ferromanganese and silicomanganese slags: Results are not satisfactory, complex silicates are
the main phases identified together with manganese silicates and oxides (these in lower quantities).
Calcium carbonate additions (6 % wt.) did not play role in the treatment of the slags because it should
have destroyed the silicates and liberate Mn. The treatment is also limited by the depth that is possible
to reach (20 mm in depth). Increasing the additions could have improved the results, the same as the
stirring during the process. If Mn would have been transformed into oxide (well-developed and with
proper size), the sample could have been grinded and milled, and manganese oxides could have been
recovered through gravimetric methods. These unfavorable results could make more interesting
alternatively hydrometallurgical processes for manganes residues, as for instance, that used by
Fernández-González et al., in the treatment of anodic lodes and scrapings from the zinc electrolytic
process [10]. Maybe the addition of any reductant reagent or even increasing the quantity of calcium
carbonate (or lime if calcined) would liberate manganese from the silicates present in the slag.
Anyway, and as opposed to the iron by-products where iron can be removed from them through
magnetic methods, manganese should be separated through gravimetric methods, and this requires
a proper development and growth of the manganese phase to obtain it with the proper size for the
gravimetric separation.

5. Conclusions

Concentrated solar thermal was used to obtain of ferromanganese. The lack of reducing
atmosphere impeded the presence of reducing conditions that could have reduced iron and
manganese oxides to obtain ferromanganese. This way, only partially reduced phases, as iwakiite and jacobsite, were detected.

Concentrated solar thermal was also used to treat silicomanganese and ferromanganese slags although with negative results. Manganese was not liberated from the slag as oxide (although oxides were identified) or any other phase. Additions of calcium carbonate were not enough to promote the destruction of manganese silicates and thus liberating this element. Further studies should be necessary to evaluate the possibility of recovering manganese from these slags.

**Author Contributions:** D.F.-G. and L.F.V. conceived and designed the experiments; D.F.-G. performed the experiments; D.F.-G. and L.F.V. analyzed the data; D.F.-G. contributed reagents/materials/analysis tools; D.F.-G. wrote the paper, and J.P.-N. reviewed the paper.

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**References**