INTRODUCTION

Due to its zinc and lead contents, steelmaking dust belongs to technological wastes of considerable environmental noxiousness, but, above all, it is a metal-bearing material that could be reused. Notwithstanding the substantial development of steelmaking dust processing methods, using, either: the rotary-grid furnace (DryIron Process), the multi-hearth furnace (Primuss Process) or other special-design furnaces (such as the VHR, Kawasaki, Ausmelt, Tetronic, Rausmelt, Recumet, Flash Reactor Process and others), investigations aimed at their development and upgrading and searching for new solutions are being intensively carried out [1-4]. The present work undertakes the task of determining the effect of reduced pressure on the potential for intensifying the processes of zinc extraction from steelmaking dust, while using a reducer in the form of graphite and the addition of blast-furnace dust containing 40% of carbon.

The reactions of reduction of main steelmaking dust components, which proceed during the thermal processing of steelmaking dust using carbon, are represented by equations (1-4) below [5-7].

\[
\begin{align*}
\text{ZnO(s)} + \text{C(s)} & \rightarrow \text{Zn(g)} + \text{CO(g)} \\
\text{ZnO·Fe}_2\text{O}_3(s) + 2 \text{C(s)} & \rightarrow \text{Zn(g)} + 2\text{Fe(s)} + 2\text{CO}_2(g) \\
\text{Fe}_2\text{O}_3(s) + \text{C(s)} & \rightarrow 2\text{FeO(s)} + \text{CO}_2(g) \\
\text{PbO(s)} + \text{C(s)} & \rightarrow \text{Pb(1)} + \text{CO(g)}
\end{align*}
\]

Figure 1 shows variation in the standard free enthalpy \(\Delta G^\circ\) at a constant pressure of 1 atm for the reactions of main metal oxides occurring in steelmaking dust with the solid-phase carbon reducer, as calculated using the database of the program FactSage®. The straight lines shown in Figure 1, which represent respective reactions, indicate that the process of reduction of franklinite \(\text{ZnO·Fe}_2\text{O}_3\) with the formation of zinc vapour proceeds at a temperature above 1100 K, while the reduction of \(\text{ZnO}\) takes place at a temperature above 1227 K.
EXPERIMENTAL

Steelmaking dust derived from one of the Polish steelworks producing carbon steels was taken for tests. Its composition is shown in Table 1.

Table 1. Composition of steelmaking dust used in the tests / wt%

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Pb</th>
<th>Zn</th>
<th>FeO</th>
<th>Fe₂O₃</th>
<th>Cl</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2,50</td>
<td>4,00</td>
<td>22,38</td>
<td>1,00</td>
<td>41,51</td>
<td>0,55</td>
<td>3,00</td>
</tr>
</tbody>
</table>

Before proceeding to experimental tests, simulation of the process of steelmaking dust thermal treatment was performed using the computer program FactSage®, which implements the free Gibbs enthalpy minimization method, to determine the thermodynamic conditions of the course of reaction. The calculation was made with the variable values of pressure and temperature and the amount of the reducer used (in the form of blast-furnace dust and graphite). On the basis of the analysis of phase composition of the dust used in the present study, made for the purposes of this work, a sample mass of 100 g was taken, with the following component contents:

13,49 g ZnO + 38,3 g ZnO·Fe₂O₃ + 1,70 g ZnS + 7,85 g Fe₃O₄ + 3,4 g Fe₂O₃ + 11,21 g CaO·Fe₂O₃ + 12,47 g CaO·SiO₂ + 3,4 g PbCl₂ + 1,18 g PbO + 3,2 g NaCl + 1,3 g KCl + 2,5 g C

In the subsequent steps in the salutation, the amount of the reducer was increased, with the reducer being then used in experimental tests. In addition to carbon, the blast-furnace dust brought in also iron oxides and slight amounts of zinc and chlorine to the sample, which were also allowed for in this analysis. Composition of the blast-furnace dust is shown in Table 2.

Table 2. Composition of blast-furnace dust used in the tests / wt%

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Pb</th>
<th>Zn</th>
<th>FeO</th>
<th>Fe₂O₃</th>
<th>Cl</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40,23</td>
<td>0,03</td>
<td>0,44</td>
<td>5,32</td>
<td>44,04</td>
<td>2,64</td>
<td>0,36</td>
</tr>
</tbody>
</table>

Before proceeding to the experimental tests proper, the reaction chamber was purged with argon several times in order to create a non-oxidizing atmosphere. In the reduced pressure tests, the assumed pressure inside the furnace chamber was achieved by using a vacuum pump, and then the heating of the furnace was started, while maintaining a constant pressure value at the preset level during the process. The value of pressure was recorded continuously as the temperature increased. After attaining a specified temperature, the sample was held in steady conditions (pressure, temperature) for 30 minutes.

RESULTS AND DISCUSSION

Figures 2 to 5 represent the degree of zinc removal obtained in the experimental tests using the reducer in the form of graphite and blast-furnace dust, as dependent on the pressure in the furnace reaction chamber at constant temperature, in relation to the degree of zinc removal, as determined from the computer simulation carried out. In the majority of cases analyzed, a high level of agreement between the thermodynamic calculations and the experimental results was achieved, which indicates the usefulness of such analysis in the planning of tests in real conditions. Before carrying out experimen-
tests with the addition of the reducer, a series of tests were performed in the identical conditions without reducer addition, whereby it was demonstrated that the amount of carbon contained in the dust was too low to achieve the adequate degree of reduction of zinc compounds. The highest removal degree of 34.45 % and 21.18 % was achieved under atmospheric pressure conditions at a temperature of 1473 K and in vacuum ($p=1\times10^{-3}$ MPa) at a temperature of 1373 K, respectively, which means at the same time that the process of zinc removal from the dust without the reducer is heavily restricted.

Figures 2 to 3 show the effect of temperature and the amount of the reducer used on the potential for zinc removal from the dust. With increasing addition of the reducer, a higher zinc removal degree was achieved. According to Figure 2, under atmospheric pressure conditions and using a 10 % addition of carbon in the form of graphite, a dust zinc removal degree of 80.59 % at a temperature of 1373 K, and 95.80 % at 1473 K can be achieved.

Blast-furnace dust used as the reducer allows an almost complete removal of zinc from the dust. With the use of a 25 % addition of blast-furnace dust, a zinc removal degree of 93.80 % and 99.50 % was achieved at a temperature of 1373 K and 1473 K, respectively, and at a pressure of 0.1MPa.

The results obtained under atmospheric pressure conditions show that zinc can be satisfactorily removed from the dust with the use of a 10 % addition of graphite and a 25 % addition of blast-furnace dust at a temperature of 1473 K. Figures 4 and 5 show the effect of reduced pressure on the intensification of the zinc compounds reduction process at the variable amount of the reducer used and temperature. According to the testing results obtained, the application reduced pressure offers a possibility for removing zinc at a lower temperature compared to atmospheric pressure conditions with the same amount of reducer used. By adding carbon in the amount of 7.5 % of the dust mass, 98.62 % of zinc can be removed at 1373 K, compared to 70.37 % in atmospheric pressure conditions.

In the case of using blast-furnace dust, a high zinc removal degree was obtained at a temperature of 1273 K (with a 20 % addition, the zinc removal degree was 94.43 %). At the same temperature with the use of a 10 % graphite addition, the maximum zinc removal degree
amounted to 65.78%. At the process temperature of 1373 K, even using the smallest of the blast-furnace dust additions considered (i.e. the 15% addition), an almost complete removal of zinc from the dust was obtained.

This means that, at this temperature and under a negative pressure of $1 \times 10^{-3}$ MPa, further increasing the blast-furnace dust addition does not enhance the zinc removal degree.

**CONCLUSION**

On the basis of the investigation carried out it has been found that graphite and blast-furnace dust can be efficient reducers of zinc compounds occurring in steelmaking dust. Reduced pressure intensifies the process of zinc removal from steelmaking dust, while reducing the temperature and the amount of reducer necessary for the respective reduction reactions to proceed efficiently. Computer simulation of processes occurring during the thermal treatment of dust, performed using the program FactSage®, can be an effective tool in most cases for the planning of experimental tests (only for graphite, Figures 2 and 4, discrepancies are high). It is result from these discrepancies that graphite is not suitable reducer with regard on its structure and in comparison with the blast furnace dusts. The expected process outcome has been largely reflected in the results of tests carried out in real conditions.

**REFERENCES**


*Note: Language consultant Czeslaw Grochowina, Czestochowa, Poland.*