RESEARCHES REGARDING THE THERMAL BEHAVIOUR OF DIFFERENT CHARGE MIXTURES USED AT SOMETRA A.S., COPSA MICA, ROMANIA

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Abstract
The main problem ISP plants are currently confronted with is linked to the raw materials base, which has suffered a continuous diversification but also a quality regress. In this situation, the maintaining of the procedure’s profitability led to a reconsideration of the conditions imposed to raw materials in the standard technology, especially with regard to the weight of oxides and to the Zn, Pb, Cu, FeO and Si contents in the sintered material.

The author has considered necessary to analyse the main physical-chemical processes and their interdependence with technological factors during sintering.
Changing the weight of certain concentrate types may determine either an improvement or a derangement of the process.

In order to be as close as possible to the real case, several concentrate mixtures, with varying concentrations of Zn, Pb, Cu, Fe, S, SiO₂ and CaO have been analysed and subjected to heat testing:
Several uniform samples (of 50 g each) have been realised. The samples’ thermal behaviour was distinctly described in test bulletins. After these analyses, two mixture types have been selected for the usage in the ISP sintering charge.

1. INTRODUCTION

The improvement of the ISP technology is realised through the diversification of the raw materials base and through the increase of the oxydic materials' weight, resulting in an improvement of the work and environment conditions, in the increase of productivity and in the decrease of the specific energy consumption.

The obtaining of a high-quality product (agglomerate) is conditioned by a high quality of the mining concentrates and of the oxydic materials employed, as well as by the composition of the charge mixture.
Therefore, it is necessary to carry out a complex analysis of the raw materials base and to create possibilities for the combining and preparation of various charge mixtures from different concentrate types.

The paper presents the results of analyses carried out on four categories of charge mixtures and the studies regarding their thermal behaviour.

2. METHODS AND APPARATUSSES FOR THERMAL ANALYSIS

2.1 The differential thermal analysis (DTA)

The differential thermal analysis method allows the studying of phase transformations by means of the recording of time and temperature changes that occur at the uniform heating of a solid material.

From an experimental point of view, the method consists in the heating, under identical conditions, of a test sample and of a thermally inert reference material, continuously and
simultaneously recording the temperature $T$ in the furnace and the temperature difference $\Delta T$ between the test material and the reference material.

The experiments have been carried out with a differential calorimeter, consisting of a furnace, which ensures a constant heating/cooling speed in time. The temperature difference $\Delta T$ is recorded with the help of a device with differential thermocouples, one being positioned in the test sample and the other in the reference material.

The physical transformations and chemical reactions are recorded in a $\Delta T=f(t)$ graph as maximum or minimum values, depending on the processes being exothermal or endothermal.

2.2 Thermogravimetric analysis (TGA)

Thermogravimetry consists in the continuous weighing of a test sample heated at a constant rate, recording the mass variation function of the temperature: $m = f(T)$.

The experimental determinations have been made with the help of thermal scales that allow the automated recording of the mass variation graph function of the sample's temperature. Generally, gravimetric curves offer qualitative information about the studied compounds, quantitative calculations being possible only on horizontal portions of the graph.

2.3. Differential thermogravimetric analysis (DTGA)

In order to expand the applicability of quantitative thermogravimetric analysis also to compounds that do not display a horizontal portion of the TGA curve, the differential curve can be introduced, as graphical expression of the temperature derivative function of the mass changing of the studied compound:

$$f(T) = \frac{dm}{dT}$$ (1)

The graph of the differential thermogravimetric analysis can be drawn with the help of mathematical calculations, based on the data recorded previously for the determination of the thermogravimetric parameters.

3. EXPERIMENTAL DETERMINATIONS

The concentrate types used for charge mixtures subjected to thermal analyses are presented in table 1.

<table>
<thead>
<tr>
<th>Concentrate type (origin)</th>
<th>Contents [%]</th>
<th>Zn</th>
<th>Pb</th>
<th>Cu</th>
<th>S</th>
<th>Fe</th>
<th>SiO$_2$</th>
<th>CaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc-based EL MOCHITO</td>
<td></td>
<td>52.08</td>
<td>1.48</td>
<td>0.80</td>
<td>30.56</td>
<td>10.26</td>
<td>1.90</td>
<td>1.02</td>
</tr>
<tr>
<td>Zinc-based KASSANDRA</td>
<td></td>
<td>52.37</td>
<td>3.60</td>
<td>0.23</td>
<td>32.56</td>
<td>8.98</td>
<td>0.70</td>
<td>0.79</td>
</tr>
<tr>
<td>Zinc-based TUNISIAN</td>
<td></td>
<td>48.84</td>
<td>4.00</td>
<td>0.32</td>
<td>30.58</td>
<td>5.97</td>
<td>3.02</td>
<td>2.20</td>
</tr>
<tr>
<td>Zinc-based GALMOY</td>
<td></td>
<td>50.75</td>
<td>1.52</td>
<td>0.041</td>
<td>31.68</td>
<td>5.21</td>
<td>2.68</td>
<td>1.42</td>
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<tr>
<td>Zinc-based CERTEJ</td>
<td></td>
<td>32.19</td>
<td>8.95</td>
<td>1.14</td>
<td>33.64</td>
<td>11.43</td>
<td>2.68</td>
<td>1.42</td>
</tr>
<tr>
<td>Collective MRM</td>
<td></td>
<td>46.59</td>
<td>11.25</td>
<td>0.98</td>
<td>27.28</td>
<td>3.16</td>
<td>4.64</td>
<td>1.03</td>
</tr>
<tr>
<td>Collective CANAKKALE</td>
<td></td>
<td>31.96</td>
<td>34.32</td>
<td>0.34</td>
<td>23.43</td>
<td>3.15</td>
<td>3.97</td>
<td>2.20</td>
</tr>
<tr>
<td>Collective BRUNSWICK</td>
<td></td>
<td>31.87</td>
<td>16.68</td>
<td>1.02</td>
<td>31.90</td>
<td>10.49</td>
<td>0.69</td>
<td>1.33</td>
</tr>
<tr>
<td>Lead-based KASSANDRA</td>
<td></td>
<td>5.12</td>
<td>71.06</td>
<td>0.59</td>
<td>16.32</td>
<td>3.16</td>
<td>0.92</td>
<td>0.84</td>
</tr>
</tbody>
</table>
Based on these concentrates, four different samples, A-D, were prepared as concentrate mixtures, each having a mass of 50 g:

**SAMPLE A:**
34% zinc-based EL MOCHITO concentrate  
12% zinc-based KASSANDRA concentrate  
24% zinc-based CERTEJ concentrate  
24% collective CANAKKALE concentrate  
6% lead-based KASSANDRA concentrate

**SAMPLE B:**
34% zinc-based EL MOCHITO concentrate  
12% zinc-based KASSANDRA concentrate  
24% zinc-based CERTEJ concentrate  
30% collective CANAKKALE concentrate

**SAMPLE C:**
42% zinc-based GALMOY concentrate  
18% zinc-based KASSANDRA concentrate  
10% lead-based KASSANDRA concentrate  
10% zinc-based TUNISIAN concentrate  
20% collective BRUNSWICK concentrate

**SAMPLE D:**
38% collective MRM concentrate  
19% zinc-based GALMOY concentrate  
14% zinc-based TUNISIAN concentrate  
10% collective CANAKKALE concentrate  
19% zinc-based CERTEJ concentrate

The chemical composition of these four samples is given in table 2:

<table>
<thead>
<tr>
<th>Concentrate type (origin)</th>
<th>Contents [%]</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zn</td>
<td>Pb</td>
<td>Cu</td>
<td>S</td>
<td>Fe</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Sample A</td>
<td>39.69</td>
<td>15.58</td>
<td>0.69</td>
<td>8.25</td>
<td>28.97</td>
<td>2.38</td>
</tr>
<tr>
<td>Sample B</td>
<td>41.31</td>
<td>13.38</td>
<td>0.68</td>
<td>8.25</td>
<td>29.40</td>
<td>2.56</td>
</tr>
<tr>
<td>Sample C</td>
<td>42.51</td>
<td>12.13</td>
<td>0.35</td>
<td>6.82</td>
<td>30.24</td>
<td>1.76</td>
</tr>
<tr>
<td>Sample D</td>
<td>43.50</td>
<td>10.26</td>
<td>0.68</td>
<td>5.51</td>
<td>29.60</td>
<td>3.60</td>
</tr>
</tbody>
</table>

The thermal behaviour of each sample can be seen in figures 1,2,3 and 4.

4. DISCUSSION OF RESULTS

4.1 Thermal behaviour of sample A

50-395 °C: A mass loss of 0.75% can be noticed, due to the elimination of the sample's humidity and due to the oxidation of organic substances,
395-585 °C: In this domain, an exothermal effect occurs, with a maximum at 445°C due to the oxidation of sulphides, and also a weak endothermal effect at 540°C. The sample's mass loss is of 2.14%.

585-720 °C: Throughout this domain, a mass loss of 2.19% has been recorded, without there being any clearly defined thermal effects, except for a weak endothermal effect at 630°C.

720-1000 °C: The mass loss in this domain is of 3.16%, without clearly defined thermal effects.

Figure 1. Test bulletin indicating the thermal behaviour of sample A
4.2 Thermal behaviour of sample B

50-330 °C: This is a domain in which the heated sample does not display any clear thermal effects and also presents no mass modifications.

330-500 °C: In this temperature domain, an exothermic effect occurs, with a maximum at 360°C occurs, as well as a weak endothermic effect at 480°C. The reactions lead to a mass loss of 2.12%.

500-630 °C: A mass loss of 1.66% appears in a domain in which there appears a slight endothermic effect at 560°C.

630-1000 °C: In this temperature range, no clearly defined thermal effects are recorded and the mass decreases by 2.04%.

Figure 2. The thermal behaviour of sample B
4.3 Thermal behaviour of sample C

50-395°C: In this temperature range, a dehydration and oxidation of the sample's organic substances can be remarked. A mass loss of 0.88% is recorded.

395-650°C: This is a domain with two exothermal peaks at 435°C and 585°C due to the oxidation of sulphides. The processes lead to a mass reduction by 5.17%.

650-810°C: In this temperature range, no clearly defined thermal effects are recorded and the mass increases by 0.53%.

810-1000°C: The thermal effects are not clearly defined in this temperature range. The process unfolds with a mass loss of about 3.48%. This behaviour can be ascribed to the decomposition of carbonates present in the sample.

Figure 3. The thermal behaviour of sample C
4.4 Thermal behaviour of sample D

50-300 °C: This temperature range corresponds to the dehydration and oxidation of the sample's organic substances can be remarked. The mass loss is of 0.75%.

300-650 °C: In this temperature domain, a significant mass decrease of 5.54% can be observed. There is an exothermal effect with a maximum at 410 °C, followed by a less pronounced endothermal effect at 580 °C.

650-760 °C: A domain without a clearly outlined thermal effect and a mass increase of 0.66%.

760-1000 °C: In this temperature range, no clearly defined thermal effects are recorded and the mass decreases by 3.62%.

Figure 4. The thermal behaviour of sample D

5. CONCLUSIONS

The study of the four samples' behaviour during heating in oxidant atmosphere, carried out with the differential thermal analysis and differential thermogravimetric analysis methods, has
indicated that the linear oxidation products up to 700-750°C are the sulphides, oxides appearing as reaction by-products, while at higher temperatures the oxidation occurs with a direct formation of oxides. During the agglomerative roasting process, the burning front advances vertically uniform, so that in the depth of the charge layer, the temperature varies between very broad limits.

As a consequence, the forming of sulphides is inevitable, but at the burning front, where the temperature surpasses 1100°C, these decompose so that the sulphide contents in the final agglomerate is very low.

For the study of the concentrate mixtures' behaviour, two types of mixtures have been formed: samples A, B and C are composed mostly of zinc-based concentrates and a collective concentrate, while sample D is composed of selective zinc-based concentrates and collective concentrates. The samples' composition takes into account the restrictions imposed by the ISP technology.

The analysis of the thermal curves has allowed to determine the ignition temperature, the exothermal peak and the maximal mass loss for each studied mixture (table 3).

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mixture A</td>
<td>395</td>
<td>445</td>
<td>2.14</td>
<td>395-585°C</td>
</tr>
<tr>
<td>2</td>
<td>Mixture B</td>
<td>330</td>
<td>360</td>
<td>2.12</td>
<td>330-500°C</td>
</tr>
<tr>
<td>3</td>
<td>Mixture C</td>
<td>395</td>
<td>435</td>
<td>5.17</td>
<td>395-650°C</td>
</tr>
<tr>
<td>4</td>
<td>Mixture D</td>
<td>300</td>
<td>410</td>
<td>5.54</td>
<td>300-650°C</td>
</tr>
</tbody>
</table>

For sample B, as compared to sample A, the weight of collective concentrate has increased from 24% to 34% at the expense of the lead-based concentrate, which led to a decrease of the ignition temperature and of the first exothermal peak from 395 to 330°C and from 445 to 360°C, respectively, the mass loss in the two cases being almost the same.

In mixture C, other zinc-based concentrates (Galmoy and Tunisian) have been used instead of the Peruvian one. A significant mass loss of 5.17% can be noticed between 395-650°C, with two exothermal peaks, due to the sulphides' oxidation.

Mixture D is composed of two collective concentrates (or even three, as the Certej-type, zinc-based concentrate is closer to the composition of a collective one) and of two zinc-based concentrates with very good thermal characteristics. Here there can be noticed also a significant mass loss of 5.54% between 395-650°C, due to the sulphides' oxidation.

In conclusion, for a good thermal behaviour, it is recommendable to realise the agglomerate charge of 2-3 zinc-based concentrates (e.g. Tunisian and Galmoy) and of 2-3 types of collective concentrates (MRM, Canakkale, Certej). This mixture ensures a constant advance of the burning and oxidation front and of the sintering front, as well as a temperature that is adequate for the forming of a high-quality agglomerate.

BIBLIOGRAPHY

1. BALAZS B. Report at the Imperial Smelting Process Conference, Cracow, Poland, 2002
2. BALAZS B. Report at the Imperial Smelting Process Conference, Harima, Japan, 2000
5. NEMES, T. Tehnologia materialelor. Publishing House of the University of Sibiu, 2004
6. *** Standards and quality files for products and byproducts. Sometra SA, Copsa Mica, 2001