ALTERNATIVE IRON MAKING TECHNOLOGIES

INTRODUCTION

The steel industry has been greatly restructured, is much more competitive and is going through a technological revolution driven by capital requirements, shortages in raw materials such as coke and low residual scrap, environmental concerns and very important customer demands. It is very important to know if production technologies are still appropriate in present and which are the new processes that have to be developed in order to meet the future needs of steel market 1, 2, 3 and 4. The steel manufacturing process is highly capital intensive in relationship to the added value to the input materials. Direct iron making using coals and iron ores directly will eliminate the need for coking coals, coke making and agglomeration and address the need to reduce capital and environmental concerns 2, 3. Society continues to press the industry to reduce emissions and recycle more waste materials. Consequently, processes that recycle blast furnace and steel making dust and have lower emissions than conventional coke making and sintering must be developed.

Customers will continue to require improved properties and quicker and more reliable delivery of steel at a good value relative to competitive materials. Development of a technology allowing coal and ore to be directly transformed into base iron solid/liquid products will enhance the flexibility and reliability of steel industry in order to maintain its competitive position. For industrialized areas such as the US, Japan and Europe a coal based and low capital cost process must be developed 1 and 4.

IRON MAKING ALTERNATIVE TECHNOLOGIES

It is well known that the quality of the main raw materials for EAF plants - scrap - has deteriorated during recent years. Scrap becomes more and more polluted by metallic tramp elements and organic compounds; this requires improved cleaning and sorting of scrap, by physical and chemical treatments. If the scrap quality is insufficient for achieving the required steel properties, virgin iron has to be added to the metallic charge. This addition can be hot metal, cold pig iron or direct reduced iron in order to improve the quality of products because they are tramp elements free 1, 4. Another reason for developing iron making alternative technologies is the possibility of wastes recycling as raw materials. Waste recycling processes will reduce the environmental impact of waste disposal. Minimizing plant waste/by-products (by in-works recycling) and valorizing them (by the use of slag in agriculture or civil engineering) are other important objectives including the ecological one.

In recent years, many alternative iron making processes have been proposed and developed to replace the conventional iron making process - the blast furnace process. Blast furnaces have played a major part in pig iron production because of their high heat and gas utilization efficiency, mass production. In present blast furnace processes have some unavoidable problems, environmental pollution by the coke plants, lower production flexibility and high degree of raw materials preparations.
The alternative iron making process may be required to satisfy the criteria such as the use of different coals, simplified material preparation, metal with little impurities, independent process steps, closed energy system, efficient pollution control and no waste generation. They also may have a higher productivity per unit volume than a blast furnace and the capital cost seems to be significantly lower than the conventional process 1, 2 and 4.

Until now, the Corex process was the most fully developed, which uses lump ore, pellets or sinter, as well as lumpy coal as raw materials, producing 300,000 tons of pig iron annually without any problems. In this process, coal is charged into the melter-gasifier reactor and is combusted to CO and H2 to produce the heat to melt the iron pellets. Then the off-gas is used to reduce iron ore to more than 90% metallization in the shaft-type prereduce. The other smelting reduction processes presently under development throughout the world use ore fines and coal fines as feedstock in order to avoid as well the coking operation and the agglomeration of iron ores. They generally consist of two superposed reactors: a prereduction vessel and a smelting vessel. None of these processes (Hismelt, Dios, CCF and Circofer) has out passed the pilot and demonstration stage in spite of the considerable amount of research funds already invested. In view of the risks and costs inherent to developments it is questionable when they will reach industrial maturity 1, 4.

The direct reduction processes which today are in commercial use - Midrex, Hyl, Fior - produce about 20-25 million tones DRI (direct reduced iron) per annum, which is a rather small amount compared to the roughly 200-220 million tones of steel per annum produced by the EAF in the world.

**Ferrous Wastes - Raw Materials for Alternative Iron Making**

An efficient way to decrease the cost of raw materials and to meet the environmental requirements is to use alternative technologies for iron and steel making. For the alternative technologies the costs of raw materials and preparation is not so high especially if they are by-products from own or related industries. The environment protection is double, directly because the waste will be recycled in-works and not land filled and indirectly because the natural resources will be preserved.

In the world ferrous metallurgy around 75-80% of wastes are recycled. Unfortunately in the same time in Romania only 40-45 % of them are recycled. There are a lot of problems concerning collection, transportation, storage and recycling of all kinds of wastes from metallurgical and chemical industries. Subsequent problems with maintenance and extension of landfills are expected 1, 3 and 4.

In ferrous metallurgy an important part of the wastes are from blast furnaces (flue dust and sludge), sinter plants (dust and fines) and from EAF's and LD converters (dust and slurry). These kinds of wastes are very fine dusts from electrical dust collectors, wet gas cleaner secondary dedusting system.

Another category of by-products are cinder, mill scales, oily sludge, grinding swarf. All this iron sources and moreover cheapest iron ore which is not suitable for blast furnace can be used for alternative iron making processes. Pyrite ashes are chemical by-products form sulphuric acid fabrication which could have great importance for ferrous metallurgy because of their high content in iron.

In Romania these kinds of wastes were land filled and the environment was damaged in that area (Valea Călugărească, Turnu Măgurele and Năvodari). The pyrite ashes are very light and in dust presentation (average diameter is 50µm). Land filling with this waste has lead to severe environmental impact on air, soil and surface and underground water in extended areas than landfills. It is creating a much polluted environment in plant proximity and affects also their own equipments and control devices, moreover agricultural areas are unproductive.

All types of low cost carbon bearing materials such as medium and low volatile coals, coke fines, coke breeze, graphite, pet coke, ground electrodes and toner can be used as reductants.

Taking into account the above mentioned reasons and the existence of such kind of wastes suitable for recycling Romania has to initiate projects in the alternative iron making area. This will be a good step for both steel industry and the environment.

Moreover, it will enhance the level of integration in the European Union.

**Experiments**

Direct reduction processes are widely known alternatives for the blast furnace route to iron manufacture. In direct reduction rotary kilns, the solid reductant serves the purpose of both fuels and reducing agent.

In order to make estimation about using pyrite ashes and blast furnace dust like raw materials for a direct reduction process some preliminary experiments have been conducted.
For direct reduction experimental heats a lab scale rotary furnace with 2kW electrical resistance was used (figure 1). Internal space has a cylindrical shape with 200mm diameter and 350mm length. The raw materials chemical compositions used for the experimental heats are presented in table 1. The reduction and combustion agent was fine coal (87.5% carbon, 1% sulphur, 11% ash, 1.5% volatile) with dimension between 0 - 5mm.

Table 1. Chemical composition of raw materials (%)

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Fe</th>
<th>Mn</th>
<th>SiO₂</th>
<th>CaO</th>
<th>MgO</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>K</th>
<th>As</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blast furnace dust</td>
<td>41.2</td>
<td>1.03</td>
<td>9.28</td>
<td>9.76</td>
<td>1.8</td>
<td>0.01</td>
<td>0.2</td>
<td>0.86</td>
<td>0.14</td>
<td>-</td>
<td>0.05</td>
</tr>
<tr>
<td>Pyrite ash Valea Călugărească 1</td>
<td>51.4</td>
<td>-</td>
<td>6.8</td>
<td>-</td>
<td>-</td>
<td>0.46</td>
<td>0.53</td>
<td>1.13</td>
<td>-</td>
<td>0.01</td>
<td>-</td>
</tr>
<tr>
<td>Pyrite ash Valea Călugărească 2</td>
<td>53.5</td>
<td>-</td>
<td>7.0</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>0.5</td>
<td>1.1</td>
<td>-</td>
<td>0.6</td>
<td>-</td>
</tr>
<tr>
<td>Pyrite ash Turnu Măgurele</td>
<td>51</td>
<td>-</td>
<td>6</td>
<td>-</td>
<td>-</td>
<td>0.35</td>
<td>0.25</td>
<td>0.4</td>
<td>-</td>
<td>0.25</td>
<td>-</td>
</tr>
<tr>
<td>Pyrite ash Năvodari</td>
<td>53</td>
<td>-</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>0.3</td>
<td>1.1</td>
<td>-</td>
<td>0.4</td>
<td>-</td>
</tr>
</tbody>
</table>

The raw materials (dusts and coal fines) were introduced in the rotary furnace together with a dispersion agent. This agent consists in 10-12 mm diameter wear resistant ceramic balls. Around 1.5 kg ceramic balls were introduced. The role of the dispersion agent was to mix the charge increasing the reaction area, initiating the direct reduction process and preventing floating of coal on the raw materials. The types of charge and experimental conditions are depicted in table 2. The temperature was measured with a Pt/Pt-10%Rh thermocouple coupled with a digitally display device. In order to melt the obtained iron base powder a Tammann furnace was used. The samples of iron base powder from each charge were melted at 1700°C in 10-15 minutes, in reductive atmosphere in graphite or alumina crucibles.

Table 2. Experimental conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Charge</th>
<th>Temp., °C</th>
<th>Reaction time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 Kg. blast furnace dust + 0.3 Kg coal fines</td>
<td>900</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>1 Kg pyrite ash Valea Călugărească 1 + 0.3 Kg coal fines</td>
<td>920</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>1 Kg pyrite ash Valea Călugărească 2 + 0.3 Kg coal fines</td>
<td>940</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>1 Kg pyrite ash Turnu Măgurele + 0.3 Kg coal fines</td>
<td>820</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>1 Kg. pyrite ash Năvodari + 0.3 Kg coal fines</td>
<td>880</td>
<td>30</td>
</tr>
</tbody>
</table>

**Results**

The products resulted from direct reduction process were: iron base powder, combustion gas, sterile. The iron base powder was separated from sterile with a permanent magnet. The analysis of combustion gases showed that they contain around 70-75% CO. The resulted iron base powders from each charge were chemically analyzed. For iron base powder the metallization degree was establish with this formula:

\[
M = \frac{Fe_{metal}}{Fe_{total}} \times 100
\]

Fe_{metal} - metallic iron%,
Fe_{total} - total iron%

The results are depicted in table 3. After melting iron base powder in a Tammann furnace, the crucibles were quenched and the slag and the metal phases were separated, weighted and analyzed. The results for the metallic phase are depicted in table 4.

Table 3. Chemical composition of iron base powder

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe_{total}%</th>
<th>Fe_{metal}%</th>
<th>M, %</th>
<th>Cu %</th>
<th>Pb %</th>
<th>Zn %</th>
<th>As %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>56,08</td>
<td>50,55</td>
<td>90,1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>61,8</td>
<td>55,87</td>
<td>90,4</td>
<td>0,37</td>
<td>0,18</td>
<td>2,05</td>
<td>0,09</td>
</tr>
<tr>
<td>3</td>
<td>50,55</td>
<td>56,3</td>
<td>93</td>
<td>0,32</td>
<td>0,72</td>
<td>0,97</td>
<td>0,09</td>
</tr>
<tr>
<td>4</td>
<td>55,97</td>
<td>41,4</td>
<td>74</td>
<td>0,31</td>
<td>0,07</td>
<td>0,86</td>
<td>0,07</td>
</tr>
<tr>
<td>5</td>
<td>63,29</td>
<td>55</td>
<td>86,9</td>
<td>0,34</td>
<td>0,06</td>
<td>2,08</td>
<td>0,05</td>
</tr>
</tbody>
</table>

After the melting of the obtained powder bath it is rich in iron, around 85-95%, and also with carbon that is necessary to eliminating the gases and nonmetallic inclusions. The contents of sulphur and phosphorus are not bigger than an usual pig iron as well as those of mangan and silicium.

**Comments**

The iron base powder resulted from direct reduction can be used in steel making (powder injection in EAF, after briquetting as scrap substitute in LD, induction furnace, EAF), or raw material for ductile cast iron or other cast iron qualities.
The sensible heat of directly reduced iron can be utilized by hot charging in the above mentioned melting facility in order to increase the efficiency of the method.

The forecast of the authors to obtain a metallization degree of 85-90% was reached. But, the scale of the rotary lab furnace had a negative influence on direct reduction processes. For industrial scale we predict a metallization degree of 95% in ½ hour.

The forecast for energy consumption in industrial scale plant is around 2.2 Gcal/tFe under the present values 3.5-3.9 Gcal/tFe in other direct reduction processes. Future work has to take into account the recovery of other wastes (EAF, LD, and mill scale etc) and poor iron ore. Moreover topics concerning for example influence of raw material average diameter on reduction degree, slag basicity after melting, removal of sulphur and phosphorous, avoidance of ash sticking on the refractory walls and dispersion agent (balls) should be analyzed. In order to enhance the level of research and to propose a new alternative efficient direct reduction technique is necessary also to improve the experimental device: charge-discharge technique, gas energy recovery, pollution control and continuity of the process.

Efficient recycling metallurgical and chemical industries wastes and waste management are important topics in the European Union.

Taking into account the quantities of these kinds of wastes Romania should solve the problem by developing projects in the alternative iron making and steel making area. According to preliminary researches carried out this is very possible without big financial efforts.

The advantages of direct reduction processes are: using of waste from chemical and metallurgical industry and unmaking coal, small quantities of electrical energy, easy preparation of raw materials, small plants very flexible for different raw materials, high level of environment protection, minimization of land filling of wastes/by-products, saving natural raw materials utilizations.

Implementing at large scale this kind of technologies offers the steel industry flexibility and a chance to decrease the costs of products in the frame of environmental friendly processes.

**REFERENCES**

1. N Constantin: „Procede neconvenţionale de obtinere a materialelor metalice feroase.” tipărit Editura PRINTECH Bucureşti, 2002