Optimization of Integrated Steel Plant Recycling: Fine-Grain Remains and By-Products Synergy

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1. Introduction

The growing production of hot metal - in due relation to the demand - forms the basis of the world’s increasing demand for steel [1].

The metallurgical industry has a very important role in the Serbian economy; a further development and market competitiveness have no alternative but to follow the principles of cleaner production. Therefore, a need for a new well-structured production model, which should achieve a substantial prevention of waste generation and resources use optimization, seems to be more urgent now than ever before [2]. The iron and steel production in Serbia is solely related to the US Steel Serbia in Smederevo steelworks.

Recycling of “fine-grained remains”, arising from iron and steel making processes, by means of returning to the same process is more common than separate processing. However, this is not necessarily justified, since separate recycling might be a better choice, both economically...
and ecologically [3]. Moreover, separate processing represents an advanced research subject, but still without industrial application [4].

For the past 22 years, the steel industry in the USA has been trying to process EAF dust, a typical example of fine grain remains from the steel industry, in an environmentally friendly way, but generally without success [5].

Additionally, by-products synergy should be taken into consideration, with emphasis on local supply opportunities [6, 7].

Secondary raw materials possess a significant amount of iron, fluxes and combustible components and hence their complete recycling, resulting in an increased utilisation level, significantly contributes to the reduction of the total production costs. The secondary raw materials of highest value are those formed in the processes of iron desulphurisation at the steel plant and slab facility, and they are, according to their granulometric composition, suitable for technology of direct utilisation in blast furnace. The metallurgical – economic value of these raw materials ranges from 69 to 115 US $/per t of iron. The agglomeration sludge has the lowest value and it amounts to 17.93 US$/t of sludge. This is certainly a result of the low content of iron (37.09%), high content of Al₂O₃ (4.64%) and particularly high humidity content (25%) [8, 9].

According to the World Steel Association, the steel industry’s by-products recovery rate has increased significantly over the past 20 years [10]. There are specialised companies in the world, involved in operating preparation procedures for ferrous secondary raw materials, their re-entering the agglomeration, blast furnace and steel plant processes. This particularly pertains to frozen metal (berne) and blast furnace slag processing, which enables obtaining iron materials, as well as materials for refractory, construction and road industry. These companies have facilities that can process several million tons of ferrous raw materials per year.

Furthermore, the available scientific literature reports of attempts to produce iron oxide from waste materials such as slag, iron ore and mill scale by solvent extraction and combustion method [11].

A further contribution to generation minimization and improved recycling and valorisation of wastes and by-products from iron and steel plants is expected during the course of IPPC Directive implementation, scheduled to be completed in Serbia by 2015 [12].

Another serious environmental issue is the emission of PCDD/PCDF, which can occur in ore sintering processes, pig iron production in blast furnace, steel production in converters and re-melting steel scrap process [13]. In order to eliminate unintentionally produced POPs from the metallurgical industry, the Central and Eastern European Regional forum on BAT/BEP was founded in November 2009.

2. Recycling, valorisation and disposal practice in the Smederevo Steel Plant

In the course of sintering process, iron and steel production and production of final cold and hot rolled sheets, different forms of waste and by-product materials, (according to their qualitative and quantitative characteristics), are obtained in the Smederevo Steel Plant.

The problem of valorisation of sludge and other remains is reflected in the instability of their chemical, that is, granulometric composition, which entails the need for optimization of the technology of their re-entering the primary process, for each specific case.

Chemical compositions and quantities of wastes and by-product materials generated in the primary production are presented in the Table 1.

In the Agglomeration Plant, a dewatered sludge from the de-dusting system is returned to sintering process, in the form of so-called „cake“, in the amount of 10.97t/h or 53kg/t of solid material. The filter cake contains 37-40% of Fe and it is included into the process without controlled dosing and mixing, which has an adverse impact on the quality of the final sinter product. In the ESP process, fine dust, 95% below 0.2 mm, with the average Fe content of 40-45%, is separated in the amount of 1.77t/h, and returned to the sintering process unprepared.

Wastes, by-products and remains formed in the blast furnace plant are partly recycled, and partly valorised in other fields of industry, or disposed. Materials which are fully returned into the process, as an addition to a sinter mixture, are sinter, pellets and ore undersize, as well as ESP and blast furnace dust. The blast furnace sludge which is formed in the process of off-gas treatment is sent to settling basins. The useful components contained in the sludge are iron (30-35%) and carbon (25-35%).

A certain quantity of this material is returned to the sintering process by transferring gravitational decanted sludge into the ore bedding (about 1000 t per pyramid), but this experiment is abandoned due to the increased content of harmful components (Zn, Pb, P), and the sludge is, in a fully inappropriate manner, disposed in ground pits near the plant, a practice which poses a serious ecological problem, as it pollutes nearby water flows.

In order to minimize environmental pollution, the Steel Plant is planning to invest into the new dewatering and disposal system.

At the present production rate, 20,000t of blast furnace sludge is formed annually at the Steel Plant Smederevo.
Apart from sludge recycling, valorisation of this material as a fertiliser, alternative fuel, etc. has been studied. Numerous research, which produced positive results, has been conducted in that direction in co-operation with fertilizer producers (Prahovo and Zorka, Subotica, Vinča), but they did not achieve significant results.

Most part of the blast furnace slag, generated in the amount of over 1 mil t/year, is 80% granulated. Due to its well-known hydraulic properties, it presents a valuable raw material for cement industry, where it is added to cement clinker. The rest of the blast furnace slag is mainly deposited, although, from the aspect of chemical composition and mineralogical constitution, it presents the material which is identical to granulated slag, but with more pronounced hydraulic properties and thus it could be also used in cement industry.

The possibilities of higher level of valorisation of this type of slag are exceptionally broad, particularly in the construction industry (production of favourable aggregate for production of light and gas concrete,

### Table 1. Chemical compositions and quantities of wastes and by-products from primary productions

<table>
<thead>
<tr>
<th>Material / Materijal</th>
<th>Fe_{tot}</th>
<th>MnO</th>
<th>SiO_{2}</th>
<th>Al_{2}O_{3}</th>
<th>CaO</th>
<th>MgO</th>
<th>S</th>
<th>P</th>
<th>C</th>
<th>H_{2}O</th>
<th>kg/t of product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agglomeruation sludge / Aglomeracioni mulj</td>
<td>37.1</td>
<td>0.03</td>
<td>17.8</td>
<td>4.64</td>
<td>23.2</td>
<td>1.20</td>
<td>0.03</td>
<td>0.01</td>
<td>25</td>
<td></td>
<td>31.00 kg/t sinter</td>
</tr>
<tr>
<td>Blast furnace dust / Visokopećna prašina</td>
<td>32.2</td>
<td>1.50</td>
<td>8.08</td>
<td>2.71</td>
<td>6.40</td>
<td>1.50</td>
<td>0.80</td>
<td>5</td>
<td>29.1</td>
<td>5</td>
<td>13.00 kg/t iron</td>
</tr>
<tr>
<td>Blast furnace sludge / Visokopećni mulj</td>
<td>41.2</td>
<td>1.05</td>
<td>8.53</td>
<td>0.41</td>
<td>6.25</td>
<td>1.33</td>
<td>0.93</td>
<td>0.05</td>
<td>21.5</td>
<td>25</td>
<td>10.00 kg/t iron</td>
</tr>
<tr>
<td>Converter sludge / Konvertorski mulj</td>
<td>59.6</td>
<td>0.05</td>
<td>3.70</td>
<td>1.00</td>
<td>6.60</td>
<td>0.18</td>
<td>0.54</td>
<td></td>
<td>25</td>
<td></td>
<td>24.13 kg/t steel</td>
</tr>
<tr>
<td>Fines from desulphurisation / Prašina sa desulforacije čelika</td>
<td>33.8</td>
<td>1.05</td>
<td>17.1</td>
<td>4.10</td>
<td>24.7</td>
<td>6.23</td>
<td>0.40</td>
<td>0.05</td>
<td>5</td>
<td></td>
<td>7.09 kg/t steel</td>
</tr>
<tr>
<td>Fines under converter / Prašina iz konvertorske čeličane</td>
<td>41.3</td>
<td>3.81</td>
<td>9.84</td>
<td>0.94</td>
<td>21.5</td>
<td>8.17</td>
<td>0.09</td>
<td>0.65</td>
<td>5</td>
<td></td>
<td>4.61 kg/t steel</td>
</tr>
<tr>
<td>Mixer slag I / Mikiserska troska</td>
<td>39.5</td>
<td>0.06</td>
<td>7.03</td>
<td>0.56</td>
<td>36.0</td>
<td>5.68</td>
<td>1.82</td>
<td>0.06</td>
<td>5</td>
<td></td>
<td>9.55 kg/t steel</td>
</tr>
<tr>
<td>Scale from Continuous Casting / Čelični otpad ispod RKL</td>
<td>64.7</td>
<td>1.38</td>
<td>4.45</td>
<td>2.75</td>
<td>4.78</td>
<td>0.52</td>
<td>0.05</td>
<td>0.34</td>
<td>10</td>
<td></td>
<td>8.29 kg/t steel</td>
</tr>
<tr>
<td>Scale from Hot Rolling Mill Plant / Čelični otpad u odelj. sl. i TV</td>
<td>73.09</td>
<td>0.55</td>
<td>0.94</td>
<td>0.52</td>
<td>0.89</td>
<td>0.25</td>
<td>0.03</td>
<td>0.01</td>
<td>10</td>
<td></td>
<td>4.95 kg/t hot rolled prod.</td>
</tr>
<tr>
<td>Cold rolling mill granules / Granule H. valjaonice</td>
<td>69.3</td>
<td>0.25</td>
<td>0.32</td>
<td>0.08</td>
<td>0.07</td>
<td>0.05</td>
<td></td>
<td></td>
<td>5</td>
<td></td>
<td>5.32 kg/t hot rolled prod.</td>
</tr>
<tr>
<td>Ferrous secondary raw materials from desulphurisation / ŽSS sa desulforacije čelika</td>
<td>73.6</td>
<td>1.61</td>
<td>5.50</td>
<td>1.09</td>
<td>7.03</td>
<td>1.24</td>
<td>0.13</td>
<td>0.04</td>
<td>0</td>
<td></td>
<td>7.08 kg/t steel</td>
</tr>
<tr>
<td>Mixer slag II / Mikiserska troska</td>
<td>64.1</td>
<td>7.45</td>
<td>0.33</td>
<td>21.4</td>
<td>3.02</td>
<td>0.90</td>
<td>0.07</td>
<td></td>
<td>0</td>
<td></td>
<td>9.55 kg/t steel</td>
</tr>
<tr>
<td>Ferrous secondary raw materials under converter / ŽSS iz konvertorske čeličane</td>
<td>52.3</td>
<td>4.63</td>
<td>6.99</td>
<td>0.71</td>
<td>16.8</td>
<td>4.55</td>
<td>0.08</td>
<td>0.59</td>
<td>0</td>
<td></td>
<td>4.61 kg/t steel</td>
</tr>
<tr>
<td>Scale from Slab Facility / Čelični otpad iz odelj. slabova</td>
<td>73.1</td>
<td>0.55</td>
<td>0.94</td>
<td>0.52</td>
<td>0.89</td>
<td>0.25</td>
<td>0.03</td>
<td>0.34</td>
<td>5</td>
<td></td>
<td>8.29 kg/t steel</td>
</tr>
<tr>
<td>Frozen metal (berne) (+10 - 100mm) / Berne (+10 - 100mm)</td>
<td>86.9</td>
<td>0.32</td>
<td>4.46</td>
<td>1.05</td>
<td>5.25</td>
<td>0.76</td>
<td>0.06</td>
<td>0.02</td>
<td>0</td>
<td></td>
<td>19.9 kg/t iron</td>
</tr>
</tbody>
</table>
asphalt, slag-blocks, mineral wool, different road construction fillers, etc.), glass and ceramic industry, as a substitute for silica glass and slag sitalls, which has been experimentally confirmed by the research conducted at the Metallurgical Institute Smederevo and other Serbian research institutions.

The majority of steel scrap produced in the converter plant is returned into the primary processes. The slag from desulphurisation and under converter, as well as the mixer slag, which, (apart from iron), contain MgO, and are very suitable to be used as a substitute for flux components, after a prior preparation.

About 160 kg of converter slag per ton of iron, or 320,000t per year, is currently generated at the present steel plant production rate, with basicity (CaO/SiO\textsubscript{2} ratio) ranging from 2.5 to 3.5 and mineral composition appropriate for its valorisation in agglomeration and blast furnace processes as a flux component. A significant presence of secondary minerals (crystalline CaO, periclase, Ca ferrites) reduces the thermic demand for formation or disassociation in the heat balance, which results in fuel saving and better process efficiency. Manganese is bound to wustite (FeO), making the solid solution FeOMnO, which is very desirable in metallurgical processes. Unfortunately, its utilisation is limited by the necessity for prior preparation, which involves size reduction, classifying and magnetic separation, so that it is deposited or used for road construction instead. Furthermore, the utilisation of prepared slag, mixed with blast furnace slag, has been proved beneficial in the construction industry, as a material for the construction of lower parts of roads, as well as in the fertilizers industry for neutralization of acidic soils. Additionally, it is used as an additive for rinsing blast furnace fore-hearth, a substitute for sprinkling roads in winter conditions and as a sandblasting material, because of its abrasive properties.

The converter sludge is formed by converter off-gases treatment and it subsides in radial settlers in the amount of 42,000t/year. Due to its hematite composition, and more than 60% of Fe and 25-35% moisture content, its complete recycling, in the form of an additive to a sinter mixture, has been envisaged. This material, given its favourable granulometric composition and pure hematite content, presents a finished synthetic pigment for the application in the construction industry. Industrial trials for tile, concrete block and ceramics pigmenting, despite the existing demand from the construction industry sector, have not been realised.

Figures 1 to 4 schematically present waste and by-product material formation in different plants of the integral steel plant in Smederevo.

Figure 1. Schematic presentation of waste and by-product materials formation, recycling, valorisation or disposal in agglomeration and blast furnace processes

Slika 1. Shematski prikaz nastanka sekundarnih sirovina, njihova reciklaža, valorizacija ili deponiranje iz aglomeracijskog i visokopećnog procesa
Figure 2. Schematic presentation of waste and by-product materials formation, recycling, valorisation or disposal in converter plant

Slika 2. Shematski prikaz nastanka sekundarnih sirovina, njihova reciklaža, valorizacija ili deponiranje iz konvertorske čeličane

Figure 3. Schematic presentation of waste and by-product materials formation, recycling, valorisation or disposal in hot and cold roll mill

Slika 3. Shematski prikaz nastanka sekundarnih sirovina, njihova reciklaža, valorizacija ili deponiranje iz pogona toplog i hladnog valjanja
According to their importance, quantity and quality, iron oxides have the particular prominence in processing plants, that is, the scale from hot rolling mill, which is formed in the process of slag and waste heating in the course of rolling, as well as hematite granules formed by regeneration of hydrochloric acid from the pickling process in the cold roll mill plant. About 25,000t of scale and 10,000t of granule is formed annually and they are returned into the primary process as a substitute for the iron ore. This practice presents the lowest form of their valorisation, since, due to specificity of their characteristics (iron oxides: wustite, magnetite and hematite composition cannot be found in nature, and they are obtained by special, expensive procedures), these oxides present strategic materials for various purposes. Their industrial utilisation includes production of important components for: paint industry, ferrite for the electronic industry, friction materials, iron powder for sinter metallurgy, exothermic mixtures, powders for nickel-cadmium batteries, of enamel paintings for ceramics and kitchenware, gas concrete, silicate-lime tiles, and others.

An example of innovative synergy is application of mill scale in aluminothermic welding mixtures, recently patented [14] and already industrially applied.

3. Economic effects

It has been established that, at the present production rate of 2,000,000t of steel, (by means of material balance of agglomeration and blast furnace processes and by returning defined quantities of secondary raw materials into the iron production process), the following raw materials can be substituted: limestone + dolomitised limestone 72,000t; coke fines 5,500t; fine agglomerate ore + large size ore for BF (60% Fe and 5% humidity) 202,548t.

The structure of iron loss in non-recycled raw materials, which, at the present production rate, amounts to 126,102 t is presented in the Table 2.

The structure of the iron losses in non-recycled secondary raw materials (production of 2,000,000 t/year of processed slabs) is presented in Figure 4.

The economic value of secondary ferrous raw materials, provided they are fully recycled and established on the basis of the prices from the year 2009, amounts to 6,830,000 US$/year.

<table>
<thead>
<tr>
<th>Secondary raw material / Sekundarna sirovina</th>
<th>(t)</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel scrap / Čelični lom</td>
<td>9,400</td>
<td>7.45</td>
</tr>
<tr>
<td>Blast furnace sludge / Visokopećni mulj</td>
<td>5,338</td>
<td>4.23</td>
</tr>
<tr>
<td>Converter sludge / Konvertorski mulj</td>
<td>13,856</td>
<td>10.99</td>
</tr>
<tr>
<td>Steel plant scale / Čeličanska kovarina</td>
<td>9,722</td>
<td>7.71</td>
</tr>
<tr>
<td>Secondary raw materials under converter / Sekundarne sirovine ispod konvertora</td>
<td>18,438</td>
<td>14.62</td>
</tr>
<tr>
<td>Mixer slag / Mikserska troska</td>
<td>41,226</td>
<td>32.69</td>
</tr>
<tr>
<td>Slag from desulphurisation / Troska sa odsumporavanja</td>
<td>28,122</td>
<td>22.30</td>
</tr>
<tr>
<td>Total non-recycled / Ukupno nerciklirano</td>
<td>126,102</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 4. The structure of iron losses through non-recycled materials

Slika 4. Struktura gubitaka željeza u nercikliranim sekundarnim sirovinama
4. Conclusion

Irrespective of the fact that the basic concept of secondary raw materials valorisation concerns their re-entering the primary processes, the importance of their utilisation in modern technologies should not be disregarded, as it can enable realisation of the highest degree of their valorisation, with a significant value accumulation. However, economic regulations, operating philosophies and disposal options differ from country to country, which means that local conditions should be considered primarily and that the exact comparison is not possible.

The basic principle of modern iron and steel production is the efficient running of the primary processes, which involves formation of minimum possible quantities of wastes, by-products and remains, as well as establishing efficient procedures for the highest level of their valorisation.

The primary economic effect of secondary raw materials recycling is reduction of production costs, based on the substitution of primary raw materials (steel scrap, coke, welding flux and iron ore). The secondary economic effect is reflected in numerous innovative technological processes in other industrial fields and their synergy.

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REFERENCES