A Holistic and Experimentally-Based View on Recycling of Off-Gas Dust within the Integrated Steel Plant

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Abstract: Ore-based ironmaking generates a variety of residues, including slags and fines such as dust and sludges. Recycling of these residues within the integrated steel plant or in other applications is essential from a raw-material efficiency perspective. The main recycling route of off-gas dust is to the blast furnace (BF) via sinter, cold-bonded briquettes and tuyere injection. However, solely relying on the BF for recycling implicates that certain residues cannot be recycled in order to avoid build-up of unwanted elements, such as zinc. By introducing a holistic view on recycling where recycling via other process routes, such as the desulfurization (deS) station and the basic oxygen furnace (BOF), landfilling can be avoided. In the present study, process integration analyses were utilized to determine the most efficient recycling routes for off-gas dust that are currently not recycled within the integrated steel plants of Sweden. The feasibility of recycling was studied in experiments conducted in laboratory, pilot, and full-scale trials in the BF, deS station, and BOF. The process integration analyses suggested that recycling to the BF should be maximized before considering the deS station and BOF. The experiments indicated that the amount of residue that are not recycled could be minimized.

Keywords: recycling; cold-bonded briquettes; blast furnace; desulfurization; basic oxygen furnace; dust; sludge; fines

1. Introduction

The production of steel in integrated steel plants generates a considerable amount of solid residues, such as dust, sludges, slags, and scales. Some of these residues have chemical compositions reflecting the raw materials charged to the process, whereas other residues (mainly slags) have properties suitable for external applications. Recycling of the residues within the process or via utilization in other areas is essential for sustainable steel production from the perspective of raw-material efficiency. However, the recycling has to be economically justified and compatible from a process-technical standpoint.

The residues generated within the integrated steel plant differs between sites, depending on things like gas-cleaning equipment, hot metal treatment (e.g., dephosphorization and/or desulfurization), and rolling operation. In crude steel production, the major residues generated in the treatment of off-gases are BF dust, BF sludge, BOF dust, and BOF sludge.
The off-gas dust generated in the production of crude steel contains useful elements, such as iron, carbon, and calcium, as stated in Table 1. Therefore, recycling of these residues within the integrated steel plant has been thoroughly studied, and industrial use has been developed. In pellet-based BF operation, in-plant residues can be included in cold-bonded briquettes that are top-charged into the BF [1]. If the BF operates on sinter, residues can be included in the sintering mix [2]. Furthermore, BF dust injection in the tuyeres has also been reported as an industrial operation practice [1].

Table 1. Typical composition in wt.% of selected off-gas dusts from the blast furnace (BF) and basic oxygen furnace (BOF) [3].

<table>
<thead>
<tr>
<th>Residue</th>
<th>Fe</th>
<th>C</th>
<th>CaO</th>
<th>SiO$_2$</th>
<th>MgO</th>
<th>Zn</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF dust</td>
<td>15–40</td>
<td>25–40</td>
<td>2–8</td>
<td>4–8</td>
<td>0.3–2</td>
<td>0.1–0.5</td>
<td>0.2–1.3</td>
</tr>
<tr>
<td>BF sludge</td>
<td>7–35</td>
<td>15–47</td>
<td>3.5–18</td>
<td>3–9</td>
<td>3.5–17</td>
<td>1–10</td>
<td>2.4–2.5</td>
</tr>
<tr>
<td>BOF coarse dust</td>
<td>30–85</td>
<td>1.4</td>
<td>8–21</td>
<td>-</td>
<td>-</td>
<td>0.01–0.4</td>
<td>0.02–0.06</td>
</tr>
<tr>
<td>BOF fine dust</td>
<td>54–70</td>
<td>0.7</td>
<td>3–11</td>
<td>-</td>
<td>-</td>
<td>3–11</td>
<td>0.07–0.12</td>
</tr>
<tr>
<td>BOF sludge</td>
<td>48–70</td>
<td>0.7–4.6</td>
<td>3.0–17</td>
<td>-</td>
<td>-</td>
<td>0.2–4.1</td>
<td>0.03–0.35</td>
</tr>
<tr>
<td>BOF primary dedusting</td>
<td>38–85</td>
<td>0.1–6.5</td>
<td>5.7–40</td>
<td>-</td>
<td>-</td>
<td>0.1–1.5</td>
<td>0.02–1.3</td>
</tr>
<tr>
<td>BOF secondary dedusting</td>
<td>32–63</td>
<td>1.0–8</td>
<td>3.7–35</td>
<td>-</td>
<td>-</td>
<td>0.5–13</td>
<td>0.1–1.1</td>
</tr>
</tbody>
</table>

Although thoroughly studied, complete recycling of these residues has not been achieved. The challenges of recycling off-gas dusts to the BF arise when levels of tramp elements, mainly zinc, reach undesired levels. Which levels are considered undesirable differs between sites. However, 150–400 g of zinc per ton of hot metal (HM) are typical values reported as acceptable in operations [4]. In the BF, zinc compounds are reduced to metallic zinc vapor by CO-rich gas in the lower regions of the shaft. The zinc vapor follows the ascending gas and is reoxidized to zinc oxide in the colder parts of the furnace. The zinc reoxidizes and condenses on the walls, the burden material, coke, or fines carried by the gas phase. In the latter case, zinc may exit the BF through the off-gas. The zinc deposited on the burden travels down to the lower region where it is reduced and volatilized again, thus forming cyclical behavior. This means that the BF has a circulating load of zinc. The negative effects of high-circulating loads of zinc in the BF includes increased consumption of reducing agents, reduced carbon-brick-lining life, and scaffold formation, which may ultimately lead to disturbances in the burden descent [4].

The main output of zinc from the BF is via the top-gas [5], i.e., the BF dust and sludge. If the dust is recycled internally to the BF, the sludge cannot be recycled, as this would reintroduce the main output of zinc from the BF back to the BF. Furthermore, as there are no external industrial-scale operations utilizing BF sludge, this fraction would be landfilled within the integrated steel plant. This has been recognized and the removal of zinc from BF sludge and recycling of the low-zinc fraction via the sinter [6] or cold-bonded pellets [7] to the BF has been implemented in full-scale operations. However, on-site recycling of the high-zinc fraction generated in the dezincing process has not been reported.

Recycling of the off-gas dust from the BOF to the BF has been successfully achieved using both cold-bonded briquettes [1] and sinter [8]. Again, one of the limiting factors in recycling the dust generated in the BOF process is the zinc content. In the case of BOF dust, the main input of zinc is via the cooling scrap charged to the converter. The zinc content in BOF dust has been addressed by hydrometallurgical approaches [9–12] and by employing a coke breeze-less sintering operation [13]. Also, as zinc evaporation mainly occurs early in the converting process, the possibility of in-process separation of zinc has been suggested [14]. In-process separation of zinc has also been addressed by optimizing the design of the gas-cleaning equipment [15,16]. Another way to enable recycling of a major portion of the BOF dust back to the BF is by avoiding the use of scrap qualities containing zinc by minimizing the zinc input to the BOF [1].

The challenge of zinc mainly applies when considering recycling of off-gas dust to the BF. Thus, if other recycling routes are considered, the raw-material efficiency within the integrated steel plant can be improved. The BOF has been acknowledged as an alternative route for recycling off-gas
dust [8,17–20]. In one publication, recycling to the BOF by replacing the sinter coolant was recognized to be limited in tonnage [17]. However, full-scale trials have shown that off-gas dust can successfully be recycled via cold-bonded agglomerates to the BOF in amounts of 23 [18] and 40 kg/tHM [19]. Furthermore, cold-bonded briquettes were shown to be suitable for the recycling of all BOF sludge back to the BOF [20]. In addition, hot briquetting has been employed to recycle the BOF dust back to the BOF in industrial practice [8]. Nonetheless, adopting the BOF recycling route still requires considerations of zinc, especially when BOF dust is recycled to the BF. If the BOF dust is recycled in a closed-loop system to the BOF, zinc can be concentrated in the BOF dust [14]. When the zinc content reaches a certain level, zinc producers can utilize the dust [14].

Based on the above, means for on-site recycling of off-gas dust from the integrated steel plants have already been far-developed. However, there are still residues difficult to recycle, and a holistic view of recycling within the process chain is required in order to find solutions to this issue. The present paper sets out to develop such a holistic approach. Utilizing process-integration analyses, considering the effects on raw materials and energy consumption for steel production, and different recycling scenarios were studied. Based on the results of these analyses, experiments were conducted to analyze recycling approaches that maximize the raw material and energy efficiency while addressing the challenges of zinc. The approach included recycling of cold-bonded agglomerates to the BF, deS station, and BOF.

2. Materials and Methods

2.1. Process Integration Analyses

The reference case used in the process integration analyses was the present scenario of in-plant recycling at the two integrated steel plants in Sweden. The change in energy consumption for a fixed crude steel production was considered in different recycling scenarios. These scenarios are presented as the five cases shown in Figure 1. In the figure, the leftmost column presents the annual generation of non-recycled off-gas dust generated at the BF, deS station, and BOF. The process integration analyses were performed using the Excel spreadsheet-based model, TOTMOD. This model is based on the spreadsheet model Masmod, presented by Hooey et al. [21]. The BF, deS station, BOF, and upgraded method of BF sludge were included in the calculations. In addition, the calorific value of the BF gas and the consumption of gas in the hot stoves were considered. Furthermore, an estimation of the change in energy consumption corresponding to the reduced or increased charging rate of coke and pellets were included.

![Figure 1. Annual generation of residues not recycled as of 2012, as well as recycling considered in cases 1 through 5. All weights are given in dry weights.](image-url)
Case 1 through 5 in Figure 1 includes recycling of the BF sludge to the BF. Therefore, the BF sludge has to be dezinced prior to recycling to avoid the accumulation of zinc in the BF. The BFs in Sweden operate on pellets, and use cyclones recovering approximately 80% of the off-gas dust as dry BF dust in the primary gas-cleaning equipment. Research on dezincing of sludges collected under those conditions when only the finest particles are collected in wet gas cleaning were missing. Therefore, experiments aiming at upgrading the BF sludge by generating a low-zinc and high-zinc fraction were performed.

2.2. Upgrading of BF Sludge

In order to upgrade the BF sludge, physical separation methods and a hydrometallurgical approach were tested on a sludge sample, with a \(d_{90}\) of 25.0 \(\mu\)m, provided by SSAB Merox. Hydrocycloning and tornado-processing were employed as the physical separation methods. The hydrocycloning of BF sludge has been presented in a previous publication [22]. The tornado process is a high-velocity dry cyclone utilizing pre-heated air, as described by Tikka et al. [23,24]. The hydrometallurgical process employed was leaching in sulfuric acid at different pH levels at 80 °C, as described previously [22]. After generating two fractions of the BF sludge, recycling of the low-zinc fraction to the BF was studied.

2.3. Recycling to the BF

2.3.1. Experiments in Laboratory Scale and Pilot-Plant Scale

Recycling of the low-zinc fraction of upgraded BF sludge to the BF via cold-bonded briquettes was studied in laboratory-scale and pilot-plant scale experiments. The iron, carbon, and zinc content of the low-zinc fraction was 38.1%, 27.1%, and 0.24%, respectively. The different recipes for the briquettes are presented in Table 2. The reference recipe represented a briquette composition used in industrial practice at SSAB in Luleå. Upgraded BF sludge from the tornado process was used in the B1 and B2 recipes.

Table 2. Recipes of the briquettes used in the laboratory scale and pilot-plant scale BF experiments.

<table>
<thead>
<tr>
<th>Recipe</th>
<th>Upgraded BF Sludge</th>
<th>deS Scrap</th>
<th>BOF Coarse Sludge</th>
<th>BOF Fine Sludge</th>
<th>Briquette Fines</th>
<th>BF Dust</th>
<th>Cement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref.</td>
<td>0.0</td>
<td>36.0</td>
<td>18.0</td>
<td>12.0</td>
<td>12.0</td>
<td>10.0</td>
<td>12.0</td>
</tr>
<tr>
<td>B1</td>
<td>10.0</td>
<td>31.4</td>
<td>15.7</td>
<td>10.5</td>
<td>10.5</td>
<td>10.0</td>
<td>12.0</td>
</tr>
<tr>
<td>B2</td>
<td>20.0</td>
<td>26.8</td>
<td>13.4</td>
<td>8.9</td>
<td>8.9</td>
<td>10.0</td>
<td>12.0</td>
</tr>
</tbody>
</table>

After briquetting, the tumbling index (TI) was determined after 24 h and 28 days of curing in ambient room conditions. The measurements were made in accordance with a modified version of ISO 3271, the modification being the final sieving performed using a 6.0 mm instead of a 6.3 mm sieve.

The reduction of the different briquettes in BF shaft conditions were studied using a laboratory-scale BF shaft simulation experiment. The equipment has been described previously by Robinson [25]. Two programs were run, one representing the descent of the briquette along the wall of the BF and one of the descent in the center. The two programs are depicted in Figure 2. A total gas flow of 50 Nl/min was used in the experiments. The mechanical pressure applied on the sample did not affect the total pressure of the gas phase, as shown in Figure 2.
2.3.2. Full-Scale Trials in the BF

The results of the laboratory-scale and pilot-plant scale experiments were verified in full-scale trials in BF No. 3 at SSAB Luleå. The upgrading of BF sludge, presented in Section 2.2, was done in laboratory-scale experiments. Therefore, non-upgraded BF sludge was utilized in the full-scale trials. Two briquette recipes were studied: one reference briquette (RB), and one briquette containing BF sludge (BSB). In the latter recipe, part of the deS scrap was substituted with BF sludge, Table 3. The briquettes were produced in industrial scale according to the standard method employed at SSAB Luleå. The strength of the briquettes was evaluated after one day and after three weeks using the same TI method as previously described.

After approximately three weeks of curing, the BSBs were charged over three days to BF No. 3 in SSAB Luleå, using a charging rate that averaged at 97.3 kg/tHM. A reference period with three days of stable operation was selected, during which the RBs were charged at an average rate of 99.6 kg/tHM. The evaluation of the full-scale trials was conducted by studying changes in generated sludge and dust amounts and their compositions. Also, the effect on the BF process was analyzed using operational data, direct reduction rate, and mass and energy-balance calculations, deducing things such as the carbon consumed by the process.
Table 3. Recipes of the BF sludge briquette (BSB) and reference briquette (RB) used in the full-scale BF trials (wt.%).

<table>
<thead>
<tr>
<th>Recipe</th>
<th>Steel Scrap</th>
<th>deS Scrap</th>
<th>BOF Coarse Sludge</th>
<th>BOF Fine Sludge</th>
<th>Briquette Fines</th>
<th>Mill Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSB</td>
<td>10.0</td>
<td>22.5</td>
<td>6.6</td>
<td>6.6</td>
<td>20.6</td>
<td>2.0</td>
</tr>
<tr>
<td>RB</td>
<td>10.0</td>
<td>26.3</td>
<td>6.6</td>
<td>6.6</td>
<td>20.6</td>
<td>2.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Recipe</th>
<th>Cont.</th>
<th>BF Dust (Stored)</th>
<th>BF Dust (Fresh)</th>
<th>BF Sludge</th>
<th>Filter Dust</th>
<th>Cement</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSB</td>
<td>4.0</td>
<td>7.6</td>
<td>3.8</td>
<td>1.9</td>
<td>11.6</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>RB</td>
<td>4.0</td>
<td>7.6</td>
<td>0.0</td>
<td>1.9</td>
<td>11.6</td>
<td>2.9</td>
<td></td>
</tr>
</tbody>
</table>

2.4. Recycling of Off-Gas Dust to the Steel Shop

2.4.1. Experiments in Laboratory Scale

As only the low-zinc fraction of upgraded BF sludge can be recycled to the BF, the high-zinc fraction has to be recycled in the steel shop. The iron, carbon, and zinc content of this fraction was 29.6%, 19.5%, and 2.18%, respectively. The high-zinc fraction of the tornado-treated BF sludge was incorporated in cold-bonded briquettes and pellets using the recipe presented in Table 4. The mixture was designed to form a self-reducing agglomerate. Screening of the pellets was performed to achieve a narrow fraction between 9.5 and 10 mm.

Table 4. Recipe of the briquettes and pellets used in the laboratory-scale smelting reduction experiments (wt.%).

<table>
<thead>
<tr>
<th>High-Zinc Fraction of BF Sludge</th>
<th>deS Scrap</th>
<th>Secondary Dust</th>
<th>Cement</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>50</td>
<td>15</td>
<td>10</td>
</tr>
</tbody>
</table>

The briquettes and pellets were subjected to lab-scale smelting reduction experiments to study the melt-in behavior in conditions similar to charging the agglomerates in a ladle with hot metal. The experiments using the briquettes were performed in an induction furnace with 80 kg of hot metal. A smaller induction furnace with 10 kg of hot metal was used in the experiments for testing the pellets. In both cases, the hot metal was taken from SSAB Luleå and the temperature of the melt during the experiments was 1350 °C. The principle of the tests was the same in both setups: an agglomerate was added to the surface of the melt and removed after predetermined times and quenched in nitrogen gas. XRF analysis, titration, and LECO analysis were employed to analyze the chemical composition of the agglomerates. Furthermore, XRD was used to determine the mineralogical composition. The mass loss of the agglomerates was also recorded.

2.4.2. Full-Scale Trials in the deS Station and BOF

After the laboratory-scale experiments were performed, full-scale trials in the deS station and BOF were executed. Again, the upgrading of the BF sludge was made in laboratory scale, meaning that the high-zinc fraction of BF sludge could not be included in the cold-bonded briquettes used in the full-scale experiments. Instead, fine and coarse BOF sludge were used, shown in Table 5. The upgraded BF sludge was assumed to have sufficiently similar characteristics to the BOF sludges to partly replace these residues in future recipes. The steel scrap fines shown in Table 5 comes from the BOF process; it consists of material from the treatment of skulls and material from slopping during the blowing. In order to balance the water content of the mixture prior to briquetting, dry-cast house dust from the BF and water were added.
Table 5. Recipe used for the briquettes used in the full-scale trials in the steel shop (wt.%).

<table>
<thead>
<tr>
<th>Steel Scrap Fines</th>
<th>BOF Coarse Sludge</th>
<th>BOF Fine Sludge</th>
<th>Mill Scale from Cont. Casting</th>
<th>Cast House Dust</th>
<th>Water</th>
<th>Cement</th>
</tr>
</thead>
<tbody>
<tr>
<td>44</td>
<td>22</td>
<td>18</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>10</td>
</tr>
</tbody>
</table>

Prior to charging the briquettes to the deS station and BOF, the briquettes were dried to 1.2 wt.% moisture to avoid incidents of smaller explosions. In the deS station, the briquettes were added in ten different trials in amounts ranging from 100 to 300 kg per heat. The additions were made to a ladle holding small amounts of hot metal in the bottom. After adding the briquettes, hot metal from the torpedo car was tapped into the ladle. The melt-in was studied visually and the effect of the addition on the final steel quality was evaluated. The charging of the dried briquettes to the BOF was made together with the steel scrap. Nine trials with an amount of 600 to 1250 kg of briquettes per heat were performed.

The results of the process integration analyses and feasibility for recycling methods based on experimental procedures were used in developing a holistic approach towards the recycling of the off-gas dust.

3. Results and Discussion

3.1. Process Integration Analyses

The category labeled non-recycled in Figure 1 illustrates the annual generation of the residues considered in the analyses. The remaining categories in the figure illustrates the increased raw-material efficiency corresponding to each calculation case. The first two cases consider recycling of BOF fine sludge and upgraded BF sludge to the BF. In addition to these residues, the second case considers increased recycling of BF dust back to the BF as well. Based on the second case, the third and fourth case considers the additional recycling of the high-zinc fraction of upgraded BF sludge to the deS and BOF, respectively. The fifth case considers a different scenario where the majority of the residues are recycled to the BOF. In this case, the BF sludge is not upgraded—instead, part of the sludge is recycled to the deS station while the rest is recycled to the BF.

Case three through five have the highest recycling rates. The fine-grained residue not recycled in these cases is the secondary dust. All materials cannot be recycled from a technical point of view due to the accumulation of tramp elements in the process. The secondary dust is a feasible stream to recycle outside the integrated steel plant, as the tonnage of this residue is, by far, the lowest of these fine-grained residues.

Figure 3a illustrates the change in energy consumption in the process system corresponding to the different calculation cases. By summarizing the effect of each individual process, the net change in energy consumption was calculated for each case, shown in Figure 3b. The net change consistently decreases from case one to case four. The energy savings stem from the decreased specific consumption of coke and iron ore pellets connected to the recycling of the iron and carbon in the residues. The most efficient decrease in the net energy consumption was calculated for case four, where a total decrease of 126 GWh/year was estimated.

Unlike cases one to four, case five mainly considers the recycling of the residues to the steel shop. The calculations suggest that recycling the residues in this manner would generate an increased net energy consumption of 26 GWh/year. This can be explained by the fact that the addition of agglomerates to the BOF will decrease the scrap capacity due to the excess heat required for melting and reduction. To maintain the fixed crude steel production used in the calculations, the hot metal production needs to be increased. This results in a higher energy consumption at the BF, as compared to the reference case.
The calculations suggest that the residues not recycled as of 2012 should primarily be recycled to the BF prior to considering the steel shop. Case four considers recycling of the remaining BF dust to the BF. Furthermore, BOF fine sludge and the low-zinc fraction of upgraded BF sludge are also considered for the BF. The BOF is considered for the recycling of the high-zinc fraction of the BF sludge.

3.2. Upgrading of Blast Furnace Sludge

In order to achieve recycling for the most promising cases shown in Figures 1 and 3, the BF sludge has to be upgraded, creating a low-zinc and high-zinc fraction. Table 6 presents the results from the upgrading methods applied to the BF sludge of the present study. Considering the performance of the different methods, the leaching in sulfuric acid at pH 1 and 80 °C was most promising in terms of removing zinc. However, leaching in sulfuric acid at pH 3 and 80 °C resulted in a higher recovery of iron and solids in the low-zinc fraction. The leaching time at pH 1 and 3 was 30 min and 6 h, respectively. Nonetheless, the sampling during the leaching process indicated that the zinc was successfully leached within 15 min at pH 1 and 1 h at pH 3. After the leaching process, the zinc in the solution can be precipitated by adding alkali carbonates forming zinc carbonate. Thermal decomposition of the zinc carbonate can be applied to form zinc oxide, which may be used by zinc producers to produce metallic zinc [22].

<table>
<thead>
<tr>
<th>Method</th>
<th>% of Total Zinc in High-Zinc Fraction</th>
<th>% of Total Iron in Low-Zinc Fraction</th>
<th>% of Total Carbon in Low-Zinc Fraction</th>
<th>% of Total Solids in Low-Zinc Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leaching, pH 1</td>
<td>95</td>
<td>91</td>
<td>100</td>
<td>86</td>
</tr>
<tr>
<td>Leaching, pH 3</td>
<td>80</td>
<td>96</td>
<td>100</td>
<td>93</td>
</tr>
<tr>
<td>Hydrocyclone</td>
<td>74</td>
<td>66</td>
<td>37</td>
<td>59</td>
</tr>
<tr>
<td>Tornado</td>
<td>81</td>
<td>37</td>
<td>39</td>
<td>31</td>
</tr>
</tbody>
</table>

The results of the leaching experiments suggest that 80% of the zinc in the BF sludge was distributed in weak-acid soluble phases, such as zincite (ZnO) and smithsonite (ZnCO₃). The remaining 20% of the zinc was distributed as franklinite (ZnFe₂O₄).

Using physical separation methods, the results were promising with regard to the removal of zinc. Both the hydrocycloning and the tornado treatment of the sludge proved to be less efficient as compared to the leaching, with regard to recovering the iron, carbon, and solids in the low-zinc fraction. Using ultrasonic sieving, the sludge was separated into narrow size-fractions and analyzed.
for zinc, iron, and carbon. The finest fraction, less than 5 microns in size, carried the majority of the zinc; namely, 73.6% of the total zinc content in the sludge. In addition, this size fraction carried 49.2%, 47.2% and 43.6% of the solids, iron and carbon, respectively. Therefore, the efficiency of these methods were limited by the distribution of zinc, iron, and carbon in the different size fractions.

The results of the upgrading experiments presented in Table 6 illustrates that BF sludge generated by a BF operating on 100% pellets as ferrous burden and utilizing a cyclone as the primary gas cleaning equipment can be upgraded, creating a fraction containing the majority of the zinc.

Although superior in performance, leaching has not been reported in full-scale operation. However, a mobile pilot plant utilizing hydrochloric acid as a leaching agent has been developed and tested [27]. Nonetheless, continuation of the present study was made based on the tornado-treated sludge. The choice was made based on three principal reasons: (i) the zinc removal was satisfactory; (ii) during the upgrading, the material was simultaneously dried to below 1 wt.% moisture; and mainly, (iii) this process was the only one handling enough BF sludge required for the subsequent experiments.

3.3. Recycling to the Blast Furnace

3.3.1. Experiments in Laboratory Scale and Pilot-Plant Scale

The cold strength of the cold-bonded agglomerates is essential when determining whether the agglomerates can sustain the conditions inside the BF. Inadequate cold strength leads to breakage during material handling and charging, which results in increased dust formation from the BF. Furthermore, low cold-strength may cause the agglomerates to disintegrate and impair the gas permeability in the furnace. The tumbling indices of the reference B1 and B2 briquettes were determined as 78%, 84%, and 81%, respectively. Thus, including up to 20 wt.% of the low-zinc fraction of the tornado-treated BF sludge to the cold-bonded briquette recipe, shown in Table 2, resulted in briquettes with sufficient tumbling strength to be top-charged into the BF.

The laboratory-scale BF shaft simulation experiments were used to study the reducibility of the three different briquette types. Figure 4a,b shows the diffractograms of each briquette after the wall and center program, respectively. In all cases, metallic iron was the only iron phase, as hematite, magnetite and wüstite were reduced to a level below the detection limit of the XRD. Furthermore, the briquettes with added upgraded BF sludge were consistently less disintegrated and harder to break. These visual observations are in agreement with the tumble indices. Furthermore, the observations are in line with the results presented by Singh and Björkman [28,29], who reported that cold-bonded briquettes with coarser particles had a greater tendency to disintegrate in the LKAB EBF. The \(d_{50}\) of the reference, and B1 and B2 recipes in the present study were determined to be 255, 185, and 145 \(\mu m\), respectively.

The results of the laboratory-scale BF shaft simulation experiments were considered promising and the briquettes were charged as basket samples to the LKAB EBF.

The mass loss of the three different briquettes with respect to the descent in EBF is presented in Figure 5. The reactions presented in the figure were based on the diffractograms of the briquettes at each location. Briquettes descending from the stockline to 1715 mm below the stockline was associated with the reduction of hematite (\(Fe_2O_3\)) to magnetite (\(Fe_3O_4\)) and magnetite to wüstite (FeO), and it the calcination of calcite (CaCO\(_3\)) had also started. Reaching 2422 mm below the stockline, the calcination was completed and the reduction of wüstite to metallic iron had finished in all briquettes. All briquettes retrieved at and below 4246 mm below the stockline were partly broken. Also, cementite (Fe\(_3\)C) formation was observed in all briquettes at these levels.
3.3.2. Full-Scale Trials

Both the laboratory and pilot-plant scale experiments suggested that adding up to 20 wt.% of upgraded BF sludge to a top-charged cold-bonded briquette is feasible in terms of strength and reduction. Based on these results, a decision to charge briquettes containing 3.8 wt.% of non-upgraded BF sludge, shown in Table 4, to BF No. 3 at SSAB Luleå was made. The non-upgraded BF sludge was used as an approximation of the low-zinc fraction of upgraded BF sludge, as no full-scale upgrading method was available. The more conservative addition of 3.8, as compared to 20 wt.%, was based on the required addition to completely recycle the annual generation of BF sludge.

The effect of the addition of BF sludge on the cold strength of the briquettes used in the full-scale BF was assessed with regard to the feasibility of top-charging the agglomerates. Table 7 presents the results of the tumbler test experiments. Replacing deS scrap by BF sludge decreased the cold strength...
both after one day and after three weeks of curing. The general trend during the curing process is an increase in the TI value after the prolonged curing as observed for the RB and the first batch of the BSB. Although the BSB briquettes had lower TI values, the required cold strength for top-charging into BF No. 3 at SSAB Luleå was met. Thus, the briquettes with BF sludge were considered suitable to charge in the full-scale BF.

Table 7. Tumbling strength (TI values in %) of the reference briquettes (RB) and BF sludge briquettes (BSB).

<table>
<thead>
<tr>
<th>Recipe</th>
<th>1 Day Curing</th>
<th>21 Days Curing</th>
</tr>
</thead>
<tbody>
<tr>
<td>RB</td>
<td>74</td>
<td>81</td>
</tr>
<tr>
<td>BSB (first batch)</td>
<td>61</td>
<td>74</td>
</tr>
<tr>
<td>BSB (second batch)</td>
<td>69</td>
<td>68</td>
</tr>
</tbody>
</table>

No disturbances could be attributed to the BSB during the full-scale trials, suggesting that the lower cold strength, shown in Table 7, did not affect the operation. Considering these results, the recycling of BF sludge to the commercial-scale BF via the cold-bonded briquettes was achieved without any negative effect on the operation linked to the briquettes. Thus, the trials in laboratory, pilot plant, and full scale showed that cold-bonded briquettes can be used to recycle upgraded BF sludge to the BF.

The zinc contents of the RB and BSB were determined to be 0.076 and 0.081%, respectively. Therefore, when adding 100 kg of briquettes per ton of hot metal, the increased zinc load was 5 g/tHM. The zinc load from the primary raw materials charged to BF No.3 varied between 30 and 41 g/tHM. Thus, as the zinc input to the furnace from the primary raw materials was reasonably low, the increased zinc load of 81 g/tHM for the BSB instead of the reference scenario of 76 g/tHM for the RB was considered acceptable.

Based on the rate of addition of the cold-bonded briquettes and the annual production of hot metal from BF No. 3, 11.4 tons of upgraded BF sludge can be recycled via cold-bonded briquettes each year. This covers the annual on-site generation of BF sludge.

3.4. Recycling to the Steel Shop

3.4.1. Laboratory Scale Experiments

In order to completely recycle the BF sludge, the high-zinc fraction has to be recycled to the steel shop. From an energy-efficiency standpoint, recycling to the BOF is preferred over the deS station, shown in Figures 1 and 3. However, recycling to the BOF is accompanied by sulfur pick-up in the crude steel [19]. This sulfur comes from the cement and residues in the briquettes. Therefore, adding the briquettes to the deS station, prior to the deS of the hot metal, is of interest during the production of steel grades with low sulfur content.

The melt-in behavior of the cold-bonded briquettes of Table 4 was studied in laboratory scale. In the full-scale process, the briquettes would be charged to a ladle with small amounts of hot metal. After the charging of the briquettes, the hot metal from the torpedo car would be poured into the ladle. Thereafter, the ladle would be transported to the deS station. The time required for pouring hot metal from the torpedo and transporting the ladle to the deS station was approximately ten minutes. Therefore, ten minutes was chosen as the longest time the briquettes were in contact with the melt in the laboratory-scale experiments. The propagation of the melt-in of the briquettes during these experiments is presented in Figure 6. A majority of the briquette was still to be melted after ten minutes, suggesting that melt-in problems can be expected in the full-scale process.
In order to study the propagation of the reduction in detail, XRD was run on samples within the briquette that were in contact with the melt for 6 min. Five samples from the briquette, distributed perpendicular to the surface of the melt, was analyzed using XRD. The results, provided in-depth in a previous publication [30], showed that as the reduction progressed, the reduced part melted and entered the hot metal. Also, the heat surrounding the rim of the briquette allowed self-reduction of the higher iron oxides.

Four stages need to occur in order for the iron in the cold-bonded briquettes to enter the hot metal: (i) heating, (ii) reduction, (iii) carburization of the iron, and (iv) melting of the carburized iron and slag separation [31]. Based on Figure 6, part of the briquette had gone through all stages. However, the results of the XRD suggested that the middle of the briquette was still undergoing the first stage after 6 min of being in contact with the hot metal.

Considering the indicated slow heat transfer, reduction, and melt-in of the briquettes, the idea of using pellets of the same recipe was to allow these smaller agglomerates to fully reduce and enter the melt. The mineralogy of the pellets being in contact with the melt suggested that the iron oxides were reduced to amounts below the detection limit of the XRD after a time of contact between 4 and 8 min, shown in Figure 7a. Thus, the reduction in the briquettes were limited by a combination of the poor melt-in behavior and limited heat transfer. However, although the pellets were completely reduced and smaller in size as compared to the briquettes, they still had melt-in problems, shown in Figure 7b. These results are in line with the conclusions made by Ding and Warner, who found that the reduction of carbon-chromite composite pellets could be considerably faster than the dissolution when subjected to smelting reduction in high-carbon ferrochromium melts [32]. As the pellets were completely reduced, the poor melt-in suggests that either the carburization of iron or the melting and separation of the slag and carburized iron was the limiting step.

Although the results of the laboratory scale experiments suggested melt-in difficulties, the full-scale trials were considered to be of interest due to the mixing effect during the pouring of hot metal from the torpedo. Also, higher hot metal temperatures than tested in the laboratory-scale experiments are possible, which may facilitate the melting and separation of the slag and carburized iron in the agglomerates. In addition, the internal slag composition of the cold-bonded briquettes used in the full-scale trials was designed to have a lower melting point than that of the laboratory-scale trials.

The upgrading of BF sludge was not made in full-scale. Therefore, the recipe of the briquettes tested in the full-scale trials of the present study did not include any BF sludge. Instead, the briquette recipe included BOF fine and coarse sludge. These two residues can partially be replaced by the high-zinc fraction of the upgraded BF sludge. In such a scenario, the difference in carbon content and oxidation degree of iron between the BF and BOF sludges has to be considered.
Based on Figure 6, part of the briquette had gone through all stages. At the specific plant, 8700 metric tons of briquettes could be added each year. Therefore, the desulfurization station was shown to be a viable recycling route within the steel shop.

3.4.2. Full-Scale Trials

Charging the briquettes to the ladle caused minor dusting. However, the moisture content and strength of the briquettes allowed for safe operation without any incidents. The melt-in of the briquettes prior to the deS started was evaluated visually. Charging up to 150 kg of briquettes enabled melting of all added briquettes. In contrast, only partial melt-in was noticed when charging 300 kg per heat. Nonetheless, after the deS process, no briquettes were observed, indicating a successful melt-in. The final steel quality was not compromised in any of the trials, suggesting that up to 300 kg of briquettes was possible to add into the process. This amounts to about 5400 metric tons of briquettes per year. Therefore, the desulfurization station was shown to be a viable recycling route within the steel shop.

Briquettes of the same recipe were charged in amounts of up to 1250 kg per heat in the BOF. The briquettes were charged with the steel scrap, which had several positive outcomes, such as improved slag formation and improved dephosphorization. However, the addition of the briquettes also resulted in increased sulfur content of 6–17 ppm in the crude steel. Therefore, the recycling of these agglomerates to the BOF is restricted to steel qualities that allow slightly higher sulfur content. At the specific plant, 8700 metric tons of briquettes could be added each year.

In total, 14,100 metric tons of briquettes could be recycled annually. The percentage of the high-zinc fraction of BF sludge required to be included in these briquettes to completely recycle the BF sludge depends on the upgrading method employed, shown in Table 6.

3.5. Holistic View on Recycling of Off-Gas Dust

In order to develop a holistic view regarding on-site recycling of off-gas dust, four key aspects should be considered: (i) maximizing the raw-material efficiency, (ii) maximizing the energy-efficiency, (iii) managing tramp elements in the process, and (iv) maintaining the high steel quality and production. The holistic view on recycling which was developed based on the results of the calculations and experimental work of the present study is illustrated in Figure 8. The flowsheet is an extended version of the on-site recycling within the pellet-based integrated steel plant presented by Wedholm [1].

Figure 7. (a) Diffractograms of pellets with 100% peaks of the iron phases denoted; (b) mass loss of the pellets with respect to the time of contact with hot metal at 1350 °C [30].
In the present study, the process integration analyses suggested that the BF should be utilized as the main recycling route in order to maximize energy efficiency. Therefore, the existing recycling route where the BF dust was generated on-site was completely recycled via the top-charging of cold-bonded briquettes, and injection of BF dust in the tuyeres [1] was maintained in the flowsheet. In order to address the third aspect in the list, the tramp elements, a dezincing step of the BF sludge was introduced. The present study showed that the BF sludge could be upgraded and the low-zinc fraction could be recycled to the BF via the cold-bonded briquettes. This layout allows an outlet of zinc to be introduced from the recycling system of the BF, which mitigates the accumulation and excessive circulating loads of zinc in the BF.

The BOF coarse sludge has previously been successfully recycled via the cold-bonded briquettes to the BF [1]. Also, the BOF fine sludge has recently been included in these briquettes [1,33]. The zinc content of the sludges from the BOF is managed by managing the quality of the cooling scrap [1]. Both of these residues were included in the briquettes used in the experimental work of the present study, Tables 2 and 3, further establishing the possibility of this recycling route.

In order to maximize the raw-material efficiency and manage the tramp elements in the process, part of the off-gas dust has to be recycled to the steel shop. In the present study, residues that are recycled to the BF has been included in the recipes of briquettes that were recycled to the deS station and BOF, shown in Table 5. This contradicts the energy-efficiency maximization, as shown in the results of the process integration analyses in Figure 3. However, including these residues in the briquettes is fundamental to achieve a recipe with a particle-size distribution that is suitable for producing cold-bonded briquettes with adequate properties for handling during recycling.

Recycling via the steel shop using cold-bonded briquettes was shown to be feasible in the present study. By avoiding recycling to steel grades of low sulfur content, the recycling route did not affect the final steel quality. The incorporation of the high-zinc fraction of BF sludge in the briquettes, replacing the BOF sludges, would enable the complete recycling of this residue. The laboratory experiments with the briquettes and pellets containing the high-zinc fraction of the upgraded BF sludge showed melt-in problems in hot metal at 1350 °C. If the addition of this fraction of the BF sludge would facilitate
melt-in problems in the deS station, cold-bonded pellets could be used instead of briquettes in order to improve the melt-in. The complete reduction of the pellets, without dissolution in the steel, would still allow them to be recycled as the deS slag is crushed and the magnetic fraction is recycled to the BF via the briquettes.

In the present recycling scenario, the main output of zinc would be the secondary dust. This residue is by far the lowest in tonnage, shown in Figure 1, which poses two benefits: (i) the raw-material efficiency of the on-site recycling is maximized, and (ii) the ability to concentrate tramp elements is easiest. The secondary dust is residue generated in a filter treating the off-gas from the deS station and the off-gas from the BOF prior to the start of blowing. Thus, the zinc being reduced and evaporated from the cold-bonded briquettes charged to the deS station would enter this residue. Furthermore, the zinc in the residues charged together with the cooling scrap to the BOF would at least partly be reduced and evaporated during the charging of desulfurized hot metal to the converter. Thus, an outlet of zinc from the process is created. The efficiency of this outlet depends, to some extent, on the amount of zinc evaporating from the agglomerates prior to the start of blowing. Zinc evaporated after the start of blowing in the BOF would enter the BOF coarse and fine sludge. As these are partly recycled to the BF, the zinc load in the BF would increase. In conclusion, a system analysis is required in order to analyze the effect on the overall zinc load in the integrated steel plant when operating on the proposed recycling scheme presented in Figure 8.

Finally, in order to maximize the recycling, the secondary dust can be recycled outside the process. In that case, the zinc content in the secondary dust has to be concentrated by closed-loop recycling. When the zinc content is sufficiently high, external zinc producers can utilize the residue.

Based on the above, the present paper illustrated the possibility of utilizing process integration analyses to decide the most efficient recycling routes of off-gas dust not being recycled today. Furthermore, the experiments ranging from laboratory scale to pilot-plant scale and full scale showed the feasibility of realizing these efficient recycling routes.

4. Conclusions

In the present paper, process integration analyses and laboratory, pilot plant, and full scale experiments were utilized to develop a holistic view for the recycling of off-gas dust generated in the BF, deS station, and BOF. The holistic approach considered a compromise between energy efficiency and raw-material efficiency for the process system including the BF, BOF, and deS station. Furthermore, the approach accounted for tramp elements, mainly zinc, while maintaining the production of high-quality steel. The study suggested that the off-gas dust could be recycled, minimizing the amount of non-recycled residues. The following findings improved knowledge considering recycling within the integrated steel plant:

- Physical separation or hydrometallurgical approaches were shown to be feasible in upgrading fine-grained BF sludge, although the sludge was low in zinc from the start.
- The low-zinc fraction of BF sludge can be completely recycled to the BF using cold-bonded briquettes.
- Recycling of cold-bonded briquettes to the deS station is feasible but restricted due to melt-in capacity.
- The possible recycling rate to the steel shop is sufficient to completely recycle the high-zinc fraction of upgraded BF sludge, depending on the chosen upgrading method.

A system analysis is required to estimate the increased zinc load in the integrated steel plant when operating the recycling scenario presented in the holistic view.

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References


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