INTRODUCTION

The domestic metal processing and metallurgical industries have seen quite considerable restructuring processes and transformations within the recent few years, those resulting mainly from the IPPC (Integrated Pollution Prevention and Control) Directive implementation. The IPPC Directive imposes the necessity of procuring what is referred to as an integrated permit for operation in the European Union upon the installations whose environmental impact is particularly strenuous. The purpose of an integrated approach towards environmental protection is such application of BATs (Best Available Techniques) that enables the negative environmental impact of those installations to be minimised. Application of such solutions has caused the quantities of waste materials retained in deposits of industrial facilities to increase. One of the characteristic properties of those materials is a considerable content of components that may be utilised under numerous technologies, being comparable to the content of the same components in natural resources.

The possibilities of using wastes as raw materials while applying different technologies decrease the quantities being stored. Waste materials, prior to their utilisation, require specific preparation. This paper provides a presentation of various methods enabling appropriate preparation of waste materials in the form of oily deposits (sludges) containing iron oxides for recycling.

METALLURGICAL WASTES

Deposits (sludges) produced while iron and steel are manufactured and processed can be divided into the following groups [1,2]:

- pure iron-bearing deposits of the iron content exceeding 60 wt% including deposits from scraper troughs of sintering plants, deposits (sludge) from wet flue gas treatment at converter plants, deposits from cleaning of cooling installations for metallurgical machinery,
- contaminated iron-bearing deposits containing 15 - 40 wt% of iron – the most common contaminants are alkalis, zinc, oil; they also include deposits (sludge) from blast furnace gas treatment, deposits from neutralisation of chemicals used in certain steel manufacturing technologies,
- oily scale of the iron content exceeding 60 wt% mainly formed in continuous steel casting and rolling installations; their oiling degree may exceed 10% on the water content of 25 – 30%,
- deposits formed while working of metal components, e.g. grinding residues containing 10 - 15% of coolant.

Depending on the chemical composition of deposits as well as their contamination and water content, the options of their utilisation as a secondary raw material and recycling preparation technologies may vary.

PREPARING DEPOSITS FOR RECYCLING

Preparing deposits for recycling, regardless of their chemical and phase compositions as well as the subsequent application, may be brought down to the following basic technological operations [2]:

- drying, i.e. moisture reduction in deposits through mechanical or thermal processing,
- mixing which enables homogenisation and correction of chemical composition and moisture content,
- optional operations of contamination reducing, e.g. deoiling,
- granulation or briquetting to reduce the volume and provide the wastes being processed with ad-
vantageous features enabling their transport, storage or recycling.

The choice of methods for preparing deposits for recycling also depends on the type of machinery to be used to utilise the waste material. Regardless of the subsequent recycling manner, the preliminary operations of deposit preparation must be aimed at reduction of the water content and homogenisation of the mixture [2] composed of deposits only or containing both deposits and other waste materials such as dusts. One of the most economically sound ways to remove water from deposits is mixing them with dry waste materials like dusts and ashes. Hence the drying and mixing operations are often conducted alternately. The operations performed to remove the excess of water from deposits are thickening, filtering and drying.

Sludge thickening (thickening of dust particles unevenly scattered in water) is usually conducted in settling tanks where gravitational sedimentation and bottom deposition of solid particles take place. The most common thickening plant is the Dorr settling tank enabling the thickening degree of 50 - 75% to be obtained [3].

The water which accumulates on the settling tank’s surface contains no more than 0.1-0.2 g/dm³ of contaminants and may be used to supply the given facility with process water. The slurry obtained as a result of sedimentation may also contain ca. 25 - 50% of water. Complete separation of deposit lumps can be obtained on the basis of sintering, filtering and drying.

Lumping operations. Industrial lumping methods include sintering of fine-grained materials, pelletising of powdered materials and briquetting. Briquetting can be applied to materials of inhomogeneous grain composition. Sintering is a thermal process as a result of which an agglomerate of specific resistance is obtained through partial melting of the surface of the grains being sintered. This agglomeration method is particularly useful in iron ore enrichment. Lumping is a method of forming lumps from fine and powdered materials of the grain size not exceeding 0.1 mm. It is recommended that intense mixers should be used for this operation, since granulation in an intense mixer occurs across the entire volume of the material being processed, it does not require as complex control as in a plate or drum mixer and it provides the surface of granules with advantageous features influencing their rheological properties as well as prevents the typical granulate defects such as empty centre from occurring [4, 5, 7]. In the process of fine-grained and powdered material lumping through briquetting, in the first stage, the materials are subject to pressing under a specific pressure followed by the second stage of the briquette hardening. In the technology of material briquetting, besides the strength factors, another important parameter is the ability to absorb water which is referred to as moisture absorption [8]. It is particularly crucial when the product subject to briquetting is assumed to be stored or transported under diverse weather conditions.

UTILISATION OF OILY DEPOSITS CONTAINING IRON

Oily deposits are currently utilised in small quantities, exactly like the EAF dusts [9,10], in production of Portland cement clinker or as a colouring additive in concrete production. Wider application of those waste materials is difficult because of their oiling. The oil content precludes their direct utilisation in sintering plants equipped with electrostatic precipitators due to the hazard of self-ignition and heat fires.

Methods applied for deoiling of deposits containing iron extend the options of utilisation of the iron-bearing metallurgical wastes deposited in dump sites by recycling them into the steel manufacturing process or using them in non-metallurgical industries.

Two environment friendly solutions for deoiling of iron-bearing deposits have been described below.
The first one, being a system for utilisation of oily metallurgical wastes, has been depicted in Figure 1 [11]. It consists of a reactor (1) equipped with a feeding screw (2) and nozzles (3) installed along the entire length of the feeder. The nozzles are used to pulverise the deoiling and/or degreasing solution delivered to them via tubes (4) from a mixer (5). In the lower section of the reactor (1), there is a feeding mechanism (6) for the oily deposits containing iron, whereas in the upper section, one will find the outlet of the deoiled waste, usually having the form of scale. Oily deposits are deoiled by spraying with a 3-15% solution of organic acid or detergent in the reactor at the temperature of 330-350 K for 20-45 minutes depending on the waste material size grade and oiling degree. The reactor is connected with an overflow-type effluent settling tank (8) and a treatment plant (7) owing to which the system does not exert a negative environmental impact. There is also a possibility that the deoiling and/or degreasing agent should be recycled to the process. The deoiled scale may be subject to granulation in a plate or briquetting prior to its further utilisation.

Figure 1 System for utilisation of oily metallurgical wastes [11]

The second solution is an installation for metallurgical waste deoiling provided by Eko-Fortuna Sp. z o.o. (Figure 2) [12] which consists of the following units:
- deposit batching point,
- heating chamber with a pallet conveyor,
- cooler for pure deoiled metallurgical wastes,
- pure metallurgical waste storage point,
- condensing point for fumes from the heating chamber (steam and oil vapour condenser, separator).

The oily metallurgical waste is subject to preliminary drying in a storage reservoir after which it is delivered to the batching tank with a water jacket where further heating takes place. Heated batch (metallurgical waste) is supplied with a belt conveyor to the heating chamber equipped with a pallet conveyor where the metallurgical waste is deoiled. The waste material deoiling occurs under the impact of the temperature inside the heating chamber which comes to ca. 670 K, followed by evaporation of the remaining moisture and degrading of petroleum derivatives. The deoiling products are: hydrocarbon vapours, steam and deoiled metallurgical waste (scale). The deoiled scale is delivered to the cooling chamber, whereas the degrading process vapours to the condenser. After the deoiling process, the deoiled metallurgical waste becomes an iron-bearing raw material containing iron oxides. There is, however, a certain problem on the way, since the deoiled scale is very broken-up. The deoiled scale may be subsequently subjected to granulation or briquetting. The installation delivered by Eko-Fortuna Sp. z o.o. exerts no negative impact on the natural environment. It is used to deoil both iron-bearing discards from rolling as well as deposited waste. The chemical composition of such deposits received from a single facility has been provided in Table 1 – they represent averaged deposits from two bore-holes of the depth up to 5 m. The moisture content

Table 1 Chemical composition of the deposits obtained / wt%    

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Bore-hole I</th>
<th>Bore-hole II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>86,1</td>
<td>81,6</td>
</tr>
<tr>
<td>FeO</td>
<td>4,62</td>
<td>2,61</td>
</tr>
<tr>
<td>CaO</td>
<td>3,26</td>
<td>4,76</td>
</tr>
<tr>
<td>SiO₂</td>
<td>2,01</td>
<td>2,34</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0,20</td>
<td>0,43</td>
</tr>
<tr>
<td>MgO</td>
<td>0,79</td>
<td>1,52</td>
</tr>
<tr>
<td>MnO</td>
<td>0,78</td>
<td>0,82</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0,03</td>
<td>0,03</td>
</tr>
<tr>
<td>K₂O</td>
<td>0,08</td>
<td>0,10</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0,06</td>
<td>0,05</td>
</tr>
<tr>
<td>P</td>
<td>0,04</td>
<td>0,04</td>
</tr>
<tr>
<td>S</td>
<td>0,10</td>
<td>0,11</td>
</tr>
<tr>
<td>Zn</td>
<td>2,02</td>
<td>1,52</td>
</tr>
<tr>
<td>Pb</td>
<td>0,36</td>
<td>0,37</td>
</tr>
<tr>
<td>C</td>
<td>1,09</td>
<td>2,01</td>
</tr>
</tbody>
</table>
of the deposits came to 28 - 36 % whereas their proper density was 4.56 - 4.86 g/cm³.

The deoiled iron-bearing deposits obtained from the aforementioned installation contain from 58.7 % to 63.8 % of Fe. After the deoiling, they can be used for manufacturing of blast furnace sinter as the iron ore replacement. The iron content in the deoiled deposits is only slightly lower than in imported iron ores which, for instance for Canadian red iron ore, comes to 67 % Fe.

CONCLUSIONS

Protection of natural resources should become the superior goal of mankind. One of the ways to achieve this goal is recycling of the wastes produced and deposited. Developing further methods and technologies enabling utilisation of materials currently being classified as wastes is, therefore, highly reasonable. Installations used to prepare wastes for recycling, including oily deposits containing iron oxides, must not exert negative impact on the natural environment, and this is the case for the installations described in this paper.

The products of deoiling of iron-bearing deposits using the installation provided by Eko-Fortuna are water steam, hydrocarbon vapours and scale having the iron content of ca. 60 %. The scale obtained, assumed to be used in the sintering process, may well replace the ore, and not only does it reduce the current production costs but also contributes to preservation of natural resources. The steam after condensation is used to heat the deposits introduced to the installation, and after its complete cooling it may be utilised as process water, whereas the condensed hydrocarbon vapours are a high-quality fuel.

REFERENCES

[12] Instalacja odolejania odpadów hutniczych firmy Eko-Fortuna sp. z o.o., patent application no P 395190 (10. 06. 2011)

Note: P. Nowak is responsible for English language.