1. Introduction

In recent years world’s production of refined zinc was about 12.5 million tonnes per year, about 30% of which was metal produced from recycled materials [1, 2]. The iron and steel industries produce large quantities of waste with significant zinc content. The highest Zn content is observed in the dust from electric arc furnaces (EAF: 22 - 33%), and a much lower content can be observed in dust and sludges from basic oxygen furnaces (BOF: 0.5 - 8%) [3, 4]. Sludges from BOF are usually stored for a long time under conditions allowing the atmospheric effects. Performed tests [5] indicate the possibilities of leaching the significant amounts of zinc and their penetration into the soil and groundwater. The recovery of zinc from such a material is consistent with the policy of sustainable development and helps to reduce the environmental load of stored waste. After removal of zinc, waste becomes an excellent iron-bearing material that can be used as a feed component for the production of iron and steel.

The recovery of zinc from recycled materials can be generally divided into two types of methods - pyro and hydrometallurgical. The first one includes the Waelz process, Imperial Smelting Process and a number of others (Ausmelt, Enviroplas, Rapid). The group of hydrometallurgical methods includes acid leaching with either H₂SO₄ or HCl, ammonia leaching, alkaline leaching and methods using the ion exchanging processes. An important advantage of alkaline leaching is that only zinc and lead pass into the solution. Reactions between the iron or its compounds and NaOH occur in a limited range. Unlike acid leaching, there is no need to remove the iron compounds from leached solution. Alkaline leaching requires highly concentrated leaching solution, elevated temperatures and can be done effectively at high ratios of the liquid/solid phases. Although NaOH is the basic reagent in this method, it can be found in the literature, that there is also the possibility of using KOH, LiOH or Ba(OH)₂ solutions [6]. Standard procedure after the zinc transfer into solution is electrolysis and deposition of Zn at the cathode [7]. The recovery of zinc in this method may be as high as 95% [8]. The aim of the research was to decrease the content of the zinc in the sludge to the level where it is suitable as an iron-bearing material for iron production (~1% Zn). Leaching at elevated temperatures (368 K, 60 min) has led to a decrease in the zinc content in the sludge of about 66%. The research revealed that long hour leaching (298 K, 100 hours) carried out at ambient temperatures caused a reduction in zinc content by 60% to the value of 1.15-1.2% Zn.

Keywords: sludge, dust, alkaline leaching, Zn recovery, recycling

2. Materials and methods

2.1. Analysis of the raw material

A sample of a sludge (BOF) obtained from purification of gases from steelmaking plants has been tested in this study. The contents of the most significant components were: Fe – 58.9%, Zn – 2.82%, CaO – 6.14%, SiO₂ – 1.9%, Na₂O – 1.62%. The sludge was subjected to the analysis of the elemental, phase and grain size composition, and analysis of the thermodynamic conditions of the leaching process. The main aim of research was to decrease the content of the zinc in the sludge to the level where it is suitable as iron-bearing material for iron production (~1% Zn).
to many other similar materials which processing methods are discussed in the literature [9]. It was decided to perform a sieve analysis of the studied material, followed by an elemental composition analysis of selected material fractions. Size fraction analysis results are given in Table 1. It can be seen that analysed sludge is a material in which over 60% of its weight is in the 0.4-0.1 mm grain range. Of nine size fraction, three were selected for further detailed analyses:

<table>
<thead>
<tr>
<th>grain range, [mm]</th>
<th>[%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>+0.63</td>
<td>14.88</td>
</tr>
<tr>
<td>0.63-0.4</td>
<td>13.65</td>
</tr>
<tr>
<td>0.4-0.25</td>
<td>13.85</td>
</tr>
<tr>
<td>0.25-0.16</td>
<td>8.56</td>
</tr>
<tr>
<td>0.16-0.125</td>
<td>27.08</td>
</tr>
<tr>
<td>0.125-0.1</td>
<td>10.74</td>
</tr>
<tr>
<td>0.1-0.09</td>
<td>4.04</td>
</tr>
<tr>
<td>0.09-0.071</td>
<td>3.46</td>
</tr>
<tr>
<td>0.071-0</td>
<td>3.74</td>
</tr>
</tbody>
</table>

These fractions were analysed with a scanning electron microscope and an X-ray microprobe. These studies aimed at a qualitative analysis of the elemental composition of the studied sludge and at preparing elements distribution analyses in a selected area. Three selected sludge fractions were analysed. Figure 3 shows images of a coarse sludge fraction (a), a medium grain fraction (b) and a fine fraction (c), magnified 200 times. EDSs were performed for these fields, showing presence of specific elements in studied grain fractions. An exemplary EDS for the coarse sludge fraction is shown in Figure 4.

When analysing EDSs performed for individual sludge grain fractions it can be concluded that they are characterised by a similar elemental composition. Peak heights corresponding to zinc content in the analysed material are in all cases very similar, so this can be a basis for a conclusion that this metal is present in each analysed fraction at a similar level. The images of the fine and the medium grain fractions indicate presence of small amounts of lead and sulphur that were not recorded in a coarse fraction. The coarse fraction, on the other hand, contains manganese which is not observed in two remaining fractions of the analysed material. The detailed digital data on content of individual elements obtained from EDS analysis is provided in Table 2.

<table>
<thead>
<tr>
<th>element</th>
<th>coarse sludge</th>
<th>medium grain</th>
<th>fine fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>32.09</td>
<td>31.98</td>
<td>33.29</td>
</tr>
<tr>
<td>Mg</td>
<td>0.96</td>
<td>0.70</td>
<td>0.97</td>
</tr>
</tbody>
</table>
2.2. Thermodynamic conditions of the leaching process

The performed analysis indicates presence of ZnO and iron in its metallic form, and of FeO, Fe₂O₃, and Fe₃O₄. Therefore, it was decided to perform a thermodynamic analysis to determine possible course of selected chemical reactions during alkaline leaching of the studied sludge. For zinc, a number of chemical reactions were analysed, with ZnO being a substrate, and products including one of the following ions: \( \text{ZnO}^{+}, \text{ZnO}^{2-}, \text{Zn(OH)}^{2-}, \text{or Zn(OH)}^{3-} \). For selected reactions, a change in Gibbs free energy at 298 K was calculated.

\[
\begin{align*}
\Delta G_{298}^{0} &= 14.89 \text{ kJ} \quad (1) \\
\Delta G_{298}^{0} &= 7.94 \text{ kJ} \quad (2) \\
\Delta G_{298}^{0} &= -61.39 \text{ kJ} \quad (3) \\
\Delta G_{298}^{0} &= -68.43 \text{ kJ} \quad (4) \\
\Delta G_{298}^{0} &= -19.31 \text{ kJ} \quad (5) \\
\Delta G_{298}^{0} &= -49.60 \text{ kJ} \quad (6) \\
\Delta G_{298}^{0} &= -56.64 \text{ kJ} \quad (7) \\
\Delta G_{298}^{0} &= -7.05 \text{ kJ} \quad (8)
\end{align*}
\]

Calculations of \( \Delta G_{298}^{0} \) for the above-mentioned chemical reactions were performed with the HSC Chemistry (ver. 6.12) application and the literature data [10, 11]. The obtained results indicate that reactions (1–4) are crucial for alkaline leaching, essential for the whole process to occur. In these reactions ZnO present as a substrate migrates to the solution. For leaching at relatively low hydroxide levels, it is possible for the reaction (5) to occur, being a condition for subsequent reactions (6–8). The environment in reactions (3–5) contains \( \text{H}^{+} \) ions. They can therefore occur only when these ions are present in the leaching solution, and the process kinetics will be proportional to hydrogen cation levels in the solution.

It can be assumed that the source of these ions in the analysed process will be the water dissociation process. Water is a very weak electrolyte that undergoes autoionisation.

The concentration dissociation constant is described by the following formula:

\[
K_{\text{H}_2\text{O}} = \frac{[\text{H}^{+}][\text{OH}^{-}]}{[\text{H}_2\text{O}]} \quad (9)
\]

where \([\text{H}_2\text{O}]\) means the molar concentration of undissociated water. The molar concentration of pure water \([\text{H}_2\text{O}]\) is relatively high (about 55.6 mol/dm³), and depends on the temperature only to a small extent. The ionic product of water \(K_{w} = K_{\text{H}_2\text{O}}[\text{H}_2\text{O}]\) is also a constant value for a specific temperature. The \(K_{w}\) values for temperatures ranging from 273 to 373 K are listed in Table 3 [12].

<table>
<thead>
<tr>
<th>(T, [K])</th>
<th>(K_{w}, [(mol/dm^3)^2])</th>
</tr>
</thead>
<tbody>
<tr>
<td>273</td>
<td>0.114·10^-14</td>
</tr>
<tr>
<td>298</td>
<td>1.008·10^-14</td>
</tr>
<tr>
<td>303</td>
<td>1.471·10^-14</td>
</tr>
<tr>
<td>313</td>
<td>2.916·10^-14</td>
</tr>
<tr>
<td>323</td>
<td>5.476·10^-14</td>
</tr>
<tr>
<td>348</td>
<td>20.420·10^-14</td>
</tr>
<tr>
<td>373</td>
<td>51.300·10^-14</td>
</tr>
</tbody>
</table>

The presented data shows clearly that the increase in the temperature is accompanied by the increase in the ionic product of water, particularly at 348–373 K, when this product is from 20 to 50 times higher than the one at 298 K. This means that at increased temperatures the \( \text{H}^{+} \) ion levels increases from above 4 to 7 times versus the one at 298 K, and therefore, the conditions are much better for the reaction to occur (3–5).

Figure 5 shows a diagram illustrating areas of thermodynamic phase stability in the Zn-H₂O configuration [13]. It can be clearly seen that in solutions of \( \text{pH} \) exceeding 9 \( \text{Zn(OH)}^{2-} \) ions can appear, while when \( \text{pH} \) exceeds 11, the solution can contain \( \text{Zn(OH)}^{3-} \) ions. For \( \text{pH} \) ranging from 7 to 10, that is, for slightly alkaline solutions, a small amount of \( \text{Zn(OH)}^{2+} \) can be present, so the reaction (5) can occur.

![Fig. 5. Solubility of ZnO as a function of pH, at 298 K [13]](image-url)

In the literature, \( \text{ZnO}^{2-} \) present in the Zn-H₂O configuration is often identified with the \( \text{Zn(OH)}^{2+} \) ion, and...
a difference in stoichiometry results from two H₂O molecules absorbed by the ZnO₂⁻ ion. Figure 6 shows the area of the ZnO₂⁻ ion presence at 298 K for the zine level of 0.01 mol/dm³. The mentioned ion appears at pH exceeding 13.65.

Fig. 6. E – pH diagram in Zn-H₂O system at 298 K

At higher temperatures, it is possible for higher zine levels to appear in the solution in the form of this anion. Calculations of E-pH diagrams performed for 298, 343 and 368 K for different concentrations of zine ions allowed to achieve the pH value at which the above-mentioned ion starts to appear. Fig. 7 presents a relationship between logarithm for the zine concentration in the solution and pH of the solution.

Fig. 7. Logarithm of the concentration of zinc in solution as a function of pH limit value at 298, 343 and 368 K

At high hydroxide levels in the leaching solutions and increased temperatures, zinc can be present in the solution as the ZnO₂⁻ ion at levels reaching even several mol/dm³ of the solution.

For alkaline leaching of materials containing iron oxide in the second and third oxidation state, there is a low possibility for its migration into the solution and its presence there in its ion form. Solubility diagrams for various iron ion forms (bi and trivalent) shown in Fig. 8 [13] indicate this element can be present at the level of ca. 10⁻⁴ mol/dm³ at pH close to 14.

In the specific conditions, the FeO⁻ ion appears in the Fe-H₂O configuration, which in the literature is treated similarly to the Fe(OH)₂⁻ anion, and the difference results from two water molecules added to FeO⁻. However, the area of the FeO⁻ anion presence is relatively limited and depends on the solution pH, the Fe ion level and the temperature. Fig. 9 shows the E-pH diagram calculated for 298 K and the iron level of 10⁻⁴ mol/dm³. In currentless conditions, FeO⁻ ions are present only above pH of 13.8.

Fig. 8. Solubility of FeO and Fe₂O₃ as a function of pH, at 298 K [13]

The iron levels in the solution were calculated for limiting pH values at 298, 343 and 368 K, facilitating appearance of the FeO⁻ ions. Results are present in Fig. 10.

Fig. 9. E – pH diagram in Fe-H₂O system at 298 K

Fig. 10. Logarithm of the concentration of Fe in solution as a function of pH limit value at 298, 343 and 368 K
The obtained results indicate that during alkaline leaching of material containing iron, the possibility for large iron quantities being transferred into the solution is very low. As calculated E-pH diagrams apply to equilibrium conditions, it can be assumed that even with relatively high hydroxide levels in the leaching solution (pH approaching 14) and raised temperatures the expected iron levels in the solutions will be below $10^{-2}$ mol/dm$^3$.

2.3. Methodology

Samples of the sludge with a mass of 20 grams were leached in a borosilicate glass beaker with a solution of NaOH or KOH of a predetermined concentration in an amount corresponding to the adopted mass ratio of the liquid phase to the solid phase. The vessel was placed on a hot plate providing a stable temperature of the process. The temperature was measured by a thermometer placed in the solution. Leach solution was stirred with a mechanical stirrer rotating in all of the tests at a constant speed of 300 rpm. After a predetermined amount of time, the solution after leaching was filtered, the resulting solid residue was washed on a filter with distilled water, dried, and then analyzed for zinc content. In all tests atomic absorption spectrometer (AAS) was used for determining the concentration of zinc in the samples.

Two series of tests were performed: at 343 K, 368 K and under pressure, using autoclave at 403 K, whose purpose was to determine the optimal parameters for leaching, and long-term trials conducted at a temperature of 298 K, which were to answer the question about the possibility of removing zinc in a low-temperature process. In the first step, the leaching time was varied at a fixed concentration of hydroxides, liquid/solid mass ratio and the temperature. The optimum leaching time was determined on the basis of satisfactory decrease in the content of zinc in the sample. In an analogous manner other leaching parameters were varied, to obtain finally the whole data set at which the process occurs with maximum efficiency. In the second series of tests, sludge was leached at 298 K for a period of 10 to 100 hours at hydroxides concentration and liquid/solid mass ratio determined in the first series of tests.

3. Results and discussion

3.1. Tests at elevated temperature

The aim of the study was to verify the applicability of KOH and NaOH solutions to leach Zn from iron-bearing materials with a low zinc content, and to determine the effectiveness of these reagents. Based on the analysis of reports found in the literature [13-15] the initial parameters of the leaching solution and process conditions were defined. Samples of the material were leached with solutions of hydroxides with a concentration of 5 mol/dm$^3$ at 343 K, and the mass ratio of the liquid phase to the solid phase equal to the 5. Experiments were run for 60, 120 and 180 minutes respectively, samples of the sludge after an appropriate time were analyzed for the content of Zn. The results are shown in Figure 11.

![Graph showing Zn content in the original material and in solid residue after leaching (5 mol/dm$^3$, l/s = 5, 343 K)](image)

Analysis of the results indicates that the optimum leaching time is around 60 minutes. Longer duration of the process does not result in a noticeable decrease of the zinc content in the material after leaching. However, it was planned to determine the possibility to reduce the content of Zn in the material to about 1% (acceptable value for the use of sludge as the charge component to iron and steel industry) consequently it was decided to carry out further studies at higher temperatures (368 and 403 K) for a fixed time of 60 minutes. The results of these tests were compared with the result of leaching at 343 K (Figure 12). A significant effect of temperature on the leaching process is noticeable in the case of temperature equal to 368 K. The increase in temperature from 343 K to 368 K results in a decrease of the zinc content in the sample by about 10%. At highest temperature the phenomenon of decline in the efficiency of the leaching process was observed. According to literature data, when the temperature exceeds 393 K zinc dissolved under these conditions reacts with iron compounds present in the slurry, and therefore precipitation of zinc ferrite in the solid form takes place [13].

Subsequently, it was decided to investigate the effect of concentration of the leaching solution on the zinc content in the sample after leaching. Thus constant parameters were: time, temperature and the ratio of liquid phase to a solid phase (respectively 60 min., 368 K, 5), and another attempt was carried out at higher concentrations of KOH and NaOH solutions - 7 mol/dm$^3$. The results show a minimal effect of the concentration of the leaching solution on the contents of Zn in the sample at a constant mass ratio (liquid/solid). In the case of KOH solution, Zn content decreased from 1.16 to 1.15%, and there was no change in the content of zinc (1.12%) when NaOH solution was used. With increasing of hydroxide concentration, density of solution increases, and at constant l/s mass ratio the reduction of the volume of the leaching solution is observed. This leads to no growth in the efficiency of the zinc removal from the sludge.
Fig. 12. Zn content in the sample after leaching as a function of the process temperature (60 min., 5 mol/dm³, l/s = 5)

Therefore, it was agreed to carry out the leaching process at unchanged concentration of hydroxides (5 mol/dm³) at mass ratio equal to the 10, and probably optimal process temperature equal to 368 K. The results were compared in Figure 13 with leaching at mass ratio of the 5.

Fig. 13. Zn content in the sample after leaching as a function of the mass ratio (liquid/solid) (60 min., 5 mol/dm³, 368 K)

It can be seen that after leaching a material with desired content of Zn is obtained, slightly in excess of 1% (KOH solution), or already below this level (NaOH solution). Due to the positive results obtained in the experiment with mass ratio equal to the 10, it was decided to perform leaching at three different temperatures (343, 368 and 403 K). Other leaching parameters were assumed at the level of the previous test i.e. 60 minutes, 5 mol/dm³. Results obtained for temperatures selected were compared in Figure 14.

Obtained in presented study results indicate that the optimum value of the leaching time is 60 minutes, and the temperature of the process should be kept at 368 K. A very important factor is the mass ratio - an increase of this parameter causes a noticeable increase in process efficiency. The change in the concentration of hydroxides does not affect apparently on the leaching process in the case of low-zinc material processing.

Tests at ambient temperature

In this part of the study it was decided to determine the possibility of removing zinc from the sludge by alkaline leaching at ambient temperature. The time was a variable parameter in these tests - from 10 to 100 hours. Leaching was carried out with NaOH and KOH solutions. Concentration of hydroxides was 5 mol/dm³, mass ratio (l/s) was 10, and temperature was 298 K. The results of performed experiments are shown in Figure 15.

Obtained results indicate a real possibility of removing zinc from sludge by the alkaline leaching process at ambient temperatures. A necessary condition for a positive effect of this kind of process is to continue leaching for a minimum of 100 hours. Although the effect of leaching is noticeable already after 10 hours of operation (removal of about 50% of the zinc contained in the sludge), it is possible to reach residual content of zinc in the sample near the level of 1% only after about 100 hours of process. As previously stated, as far as the applicability of the sludge as charge component for the production of iron and steel is concerned,
such a concentration is satisfactory. Leaching at ambient temperature does not need such a large energy consumption, as in the case of solutions heated to temperatures close to 368 K, and despite much longer duration of the process, the overall expenses are much lower. As a result, this procedure can be used for the treatment of many wastes that have not been processed so far, because it has not been economic due to the high costs of leaching at elevated temperatures. An additional advantage of both presented versions of processing method is that solution after leaching almost does not contain iron nor iron compounds. Thus, this method does not lead to loss of iron and residue after leaching can be raw material in the iron and steel metallurgical plants.

4. Conclusions

This study confirms the possibility of using aqueous solutions of KOH and NaOH as leaching media in the processing of iron-bearing material with a low zinc content. Obtained results indicate a number of factors influencing the leaching process. Optimization of these parameters performed in the presented study results in a determination of their numerical values with respect to a leaching time, process temperature, the concentration of hydroxides, and the mass ratio of the leaching solution to the processed material. Performed tests indicate the possibility of obtaining materials with zinc content about 1%, that can be used in iron and steel metallurgical industry. Long term leaching at ambient temperature also allowed to obtain a material with a zinc content at a level close to 1%.

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