SEPARATION OF METAL VALUES IN ZINC LEACHING RESIDUES

Inventors: Maurits Van Camp, Mortsel (BE); Charles Geenen, Overpelt (BE); Jonathan Aerts, Wommelgem (BE)

Correspondence Address: HUTCHISON LAW GROUP PLLC PO BOX 31686 RALEIGH, NC 27612

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Abstract

The invention relates to the separation of metals in Fe-bearing zinc leaching residues, in particular neutral and weak acid leach residues.

The process comprises the steps of:
preparing agglomerates containing, besides the Zn leaching residue, at least 5 wt % of carbon and 2 to 10 wt. % of S;
fuming said agglomerates in a static bed at a temperature above 1250°C, thereby producing a reduced Fe-bearing phase and Zn-bearing fumes; and
extracting said Zn-bearing fumes.

The high S content of the feed allows for a relatively high operating temperature without production of molten phases. This guarantees fast reduction and fuming kinetics, and permits the use of a compact technology such as a static bed furnace.
SEPARATION OF METAL VALUES IN ZINC LEACHING RESIDUES

[0001] This invention relates to the separation of metals in Fe-bearing zinc leaching residues, in particular neutral and weak acid leach residues.

[0002] Blende, which is an impure ZnS ore, is, in the main starting material for the production of Zn. The typical industrial practice encompasses an oxidative roasting step, producing ZnO together with sulphates or oxides of the impurities. In subsequent steps, the ZnO is roasted in a blende is brought into solution by leaching in neutral conditions or in weak acid conditions, thereby producing Zn-depleted residues, respectively referred to as neutral leach residue and as weak acid leach residue in this description. These residues typically contain from 2 to 10 wt. % S, up to 30 wt % Zn, 35 wt % Fe, 7 wt % Pb and 7 wt % SiO₂.

[0003] However, during roasting, part of the Zn reacts with Fe, a typical impurity present in blende, and forms relatively insoluble zinc ferrite. The leach residues therefore contain, besides lead sulphate, calcium sulphate and other impurities, a sizeable fraction of Zn in the form of ferrite. According to present practice, the recovery of the Zn from ferrite requires a specific hydro-metallurgical residue treatment using high acid concentrations of 50 to 200 g/l H₂SO₄. A disadvantage of this acidic treatment is that besides Zn, almost all the Fe and also other impurities such as As, Cu, Cd, Ni, Co, Ti, Sb are dissolved. As even low concentrations of these elements interfere with the subsequent electrowinning of Zn, they must be removed from the zinc sulphate solution. While Cu, Cd, Co, Ni and Ti are precipitated by addition of Zn powder, Fe is typically discarded as hematite, jarosite or goethite through hydrolysis. Due to the danger of washout of heavy metals, these Fe-bearing residues have to be disposed off in a well-controlled landfill. Land-filling of such residues has however come under heavy environmental pressure, rendering the sustainability of the process questionable. Another drawback of the above treatment is the loss of metals such as In, Ge, Ag and Zn in the Fe-bearing residue.

[0004] An alternative treatment of the ferrite-bearing residues is applied in some plants, using Waelz kilns, which produce a slag and a Zn and Pb containing fume. Such a process is described in ‘Steelworks residues and the Waelz kiln treatment of electric arc furnace dust’, G. Strohmeyer and J. Bonestell, Iron and Steel Engineer vol. 73, N° 4, pp. 87-90. In the Waelz kiln, zinc enters in the form of ferrites and sulphate, and is vaporized after being reduced by CO generated by burning coke. In the reaction zone of the kiln, where iron is reduced to metal, the problem of overheating occurs frequently. In such cases, the charge in the kiln melts and accretions are formed, mainly due to the formation of the eutectic 2FeO·SiO₂—FeO, which has a melting point of approximately 1180° C. The dissolution of FeO further lowers the melting point and through combination with zinc sulphide, reduced from zinc sulphate in the earlier stages, solid crusts are formed. The furnace rotation is further hampered by the formation of large balls consisting of carbonized iron, which are formed as a molten metallic phase at approx. 1150° C. This again leads to a decreased reduction of ZnO and iron oxide, which are formed in the earlier stages of the furnace from reduced zinc ferrites overheating accelerates the wear of the brick lining of the kiln. In order to limit the risks of overheating, the CaO/SiO₂ ratio in the feed has to be monitored closely by setting it to a value of 0.8 to 1.8.

[0005] Although numerous Zn fuming processes have been described, recent literature concentrates on the treatment of Zn-containing Fe secondary residues, such as EAF dusts. In this respect, the Waelz kiln is well suited, but its productivity is nevertheless hindered by its sensitivity to overheating.

[0006] In WO2005-005674 a process for the separation and recovery of non-ferrous metals from zinc-bearing residues was disclosed. The process comprises the steps of subjecting the residue to a direct reduction step, extracting Zn- and Pb-bearing fumes, and subjecting the resulting metallic Fe-bearing phase to an oxidising smelting step. The direct reduction is performed in a multiple hearth furnace operating at 1100° C, in the reduction zone. One disadvantage of the use of such a reduction furnace is that the reduction kinetics are limited by the temperature. Temperatures above 1100° C can however not be reached in a multiple hearth furnace.

[0007] JP2004-107748 describes a process for the treatment of zinc leaching residues in a rotary hearth furnace, at a reduction temperature up to 1250° C. The burner air ratio is set within a limited range.

[0008] In U.S. Pat. No. 5,906,671 Zn plant leach residues are treated in a rotary kiln at temperatures up to 1150° C, after being agglomerated together with alkali earth and alkali metal complexes of alumina and silice oxides and a reducing agent.

[0009] In U.S. Pat. No. 5,667,553 neutral leach residue by-products of zinc electrowinning are heat treated in a reduction furnace, in the same way as EAF dust.

[0010] The aim of the present invention is to provide a process for the separation of the metals contained in Fe-bearing zinc leaching residues, which does not have the disadvantages described above. This process comprises the steps of:

- [0011] preparing agglomerates containing, besides the Zn leaching residue, at least 5 wt % of carbon and 2 to 10 wt % of S;

- [0012] fuming said agglomerates in a static bed at a temperature above 1250° C, thereby producing a reduced Fe-bearing phase and Zn-bearing fumes; and

- [0013] extracting said Zn-bearing fumes.

[0014] The Zn leaching residue should preferably be dried to a moisture content of less than 12 wt % H₂O, or even to less than 5 wt % H₂O, before preparing the agglomerates.

[0015] A carbon content in the agglomerates of at least 15 wt % is preferred, as is a CaO equivalent of at least 10 wt %, or even at least 15 wt %.

[0016] The strength of the pellets, expressed as their Mass Pellet Strength, should preferably be at least 5 kg, or even 10 kg. This way dust carry over is avoided and the fusion of the charge is better prevented at the high process temperatures.

[0017] The fuming should advantageously be performed at a temperature of at least 1300° C, in a carbon monoxide containing atmosphere.

[0018] The process is ideally suited for processing neutral or weak acid Zn leach residues.

[0019] The invented process can be performed in a in a rotary hearth furnace; it can optionally be followed by a process whereby the reduced Fe-bearing phase is melted and oxidised.

[0020] It may thus be necessary to add a S-bearing component to the residue, so as to bring its total S content into the
required range. Gypsum would be a typical additive in this case. Using a S-rich carbon source could also be envisaged in this case.

As evidenced by the Examples below, the high S content of the feed allows for a relatively high operating temperature without producing molten phases. There is thus no danger for the formation of accretions at the discharge port of the furnace. High temperatures guarantee fast reduction and fuming kinetics, which permit the use of a compact technology such as a static bed furnace. This type of furnace furthermore preserves the integrity of the agglomerates, avoiding to a large extent the production of dust and limiting the ensuing pollution of the fumes.

EXAMPLE 1

The following example illustrates the separation of different non-ferrous metals contained in a roasted and subsequently leached blend.

Approximately 400 g briquettes was placed on the bottom of the clean graphite crucible, in such a way that the crucible surface is covered with a single layer of material. The crucible was then placed in the induction furnace, and a monitoring thermocouple was mounted between the briquettes without touching the crucible bottom. The crucible was covered by a refractory plate. The fumed metals were post combusted above the crucible and captured in a filter under the form of flue dust. The reactor and the material were heated at to 1300°C, as measured with a Pt/PtRh10 thermocouple mounted between the briquettes. Up to 600°C, heating was performed under a protective N₂ gas atmosphere at a gas flow rate of 200 l/h. From 600°C to 1300°C, CO was injected into the crucible at a flow rate of 200 l/h.

Samples were taken after 30 minutes after reaching 1300°C. These samples were quenched in liquid N₂, stopping all reactions and freezing the mineralogy. The composition of feed and products is given in Table 1. The elemental distribution across products is shown in Table 2.

### TABLE 1

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass (g)</th>
<th>Pb</th>
<th>Cu</th>
<th>As</th>
<th>Zn</th>
<th>Fe</th>
<th>In</th>
<th>CaO</th>
<th>SiO₂</th>
<th>S</th>
<th>C</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>WAL Residue</td>
<td>1000</td>
<td>5.1</td>
<td>1.74</td>
<td>0.1</td>
<td>28</td>
<td>15</td>
<td>0.02</td>
<td>1.61</td>
<td>5.46</td>
<td>5.9</td>
<td>0.05</td>
<td>0.01</td>
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<td>PET-Cokes</td>
<td>250</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Gypsum</td>
<td>190</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Briquettes</td>
<td>1440</td>
<td>3.5</td>
<td>1.50</td>
<td>0.2</td>
<td>19</td>
<td>10.9</td>
<td>0.02</td>
<td>6.7</td>
<td>3.75</td>
<td>6.8</td>
<td>14.6</td>
<td>0.02</td>
</tr>
<tr>
<td>Reduced residue</td>
<td>365</td>
<td>1.0</td>
<td>4.05</td>
<td>0.47</td>
<td>2.3</td>
<td>30</td>
<td>&lt;0.01</td>
<td>18.0</td>
<td>10.5</td>
<td>14.6</td>
<td>7</td>
<td>0.02</td>
</tr>
<tr>
<td>Flue dust</td>
<td>270</td>
<td>11</td>
<td>0.03</td>
<td>0.07</td>
<td>66</td>
<td>0.15</td>
<td>0.07</td>
<td>&lt;0.01</td>
<td>0.19</td>
<td>0.1</td>
<td>0.043</td>
<td>&lt;0.03</td>
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</tbody>
</table>

### TABLE 2

<table>
<thead>
<tr>
<th>Products</th>
<th>Pb</th>
<th>Cu</th>
<th>As</th>
<th>Zn</th>
<th>Fe</th>
<th>In</th>
<th>CaO</th>
<th>SiO₂</th>
<th>S</th>
<th>C</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduced residue</td>
<td>10.9</td>
<td>99.5</td>
<td>90.1</td>
<td>4.5</td>
<td>99.6</td>
<td>&lt;13</td>
<td>&gt;99.2</td>
<td>98.7</td>
<td>95.2</td>
<td>99.5</td>
<td>&gt;71</td>
</tr>
<tr>
<td>Flue dust</td>
<td>89.1</td>
<td>0.05</td>
<td>9.9</td>
<td>95.5</td>
<td>0.4</td>
<td>&gt;87</td>
<td>&lt;0.8</td>
<td>1.3</td>
<td>4.8</td>
<td>0.5</td>
<td>&lt;29</td>
</tr>
</tbody>
</table>

About 1000 g of Weak Acid Leaching (WAL) residue which mainly consists of zinc ferrite (ZnO. Fe₂O₃), lead sulphate (PbSO₄), calcium sulphate (CaSO₄), zinc sulphate (ZnSO₄) and impurities like CaO, SiO₂, MgO, Al₂O₃, Cu₂O, SnO, was dried to a moisture content below 5 wt% H₂O, and mixed with 15 wt% of CaO or the equivalent gypsum and 25 wt% of PET cokes, having a purity of >85% C. This mixture was compacted in briquettes by pressing it between 2 hydraulic rolls at a pressure of 20 kN/cm² resulting in hard, shiny briquettes, having a Mass Pellet Strength of 20 kg.

The fuming step was carried out in an induction furnace to simulate the process occurring in a rotating hearth furnace. An Indutherm MU-3000 furnace with a maximum power of 15 kW and a frequency of 2000 Hz was used. The internal furnace diameter was 180 mm, and the graphite crucible carrying the briquettes had an internal diameter of 140 mm.

**[0024]** The experimental results clearly show that after 30 minutes of roasting, Zn, Pb and In are effectively fumed out of the briquettes, while Fe, Cu, As and F are concentrated in the reduced residue. The good selectivity towards As and F is particularly interesting in view of the subsequent processing of the fumes by hydrometallurgical means.

EXAMPLE 2

This example illustrates the crucial role of S the briquettes, as it avoids the softening and melting of the material during the roasting process without loss in the selectivity.

Two mixtures were prepared using a synthetic, S-free zinc leach residue comprising zinc ferrite with 5 wt% SiO₂, and:

15 wt. % CaO and 25 wt. % finely ground cokes (Mixture 1);
36.7 wt.% of gypsum and 25 wt.% finely ground cokes (Mixture 2).

Both mixtures were compacted to briquettes and fumed according to the procedure of Example 1.
The briquettes corresponding to Mixture 1, containing only about 0.3 wt.% S, appeared to smelt, indicating the formation of low smelting phases like 2FeO·SiO2. However, the briquettes corresponding to Mixture 2, containing about 6.5 wt.% S, did not show any formation of such phases, thanks to the presence of an adequate amount of S.

1-10. (canceled)

11. Process for the separation of metal values in a Fe-bearing Zn leaching residue comprising the steps of:
preparing agglomerates containing a Fe-bearing Zn leaching residue, at least 5 wt.% of carbon and 2 to 10 wt.% of S;
fuming the agglomerates in a static bed at a temperature above 1250°C, wherein a reduced Fe-bearing phase and Zn-bearing fumes are produced; and
extracting the Zn-bearing fumes;
wherein metal values of the Fe-bearing Zn leaching residue are separated.

12. Process according to claim 11, further comprising the step of drying the Fe-bearing Zn leaching residue to a moisture content of less than 12 wt.% H2O, before the step of preparing agglomerates.

13. Process according to claim 11, further comprising the step of drying the Fe-bearing Zn leaching residue to a moisture content of less than 5 wt.% H2O, before the step of preparing agglomerates.

14. Process according to claim 11, wherein the agglomerates comprise at least 15 wt.% of carbon.

15. Process according to claim 11, wherein the agglomerates further comprise a Ca compound, the Ca compound having at least 10 wt.% of CaO equivalent in the agglomerates.

16. Process according to claim 14, wherein the agglomerates further comprise a Ca compound, the Ca compound having at least 10 wt.% of CaO equivalent in the agglomerates.

17. Process according to claim 11, wherein the agglomerates further comprise a Ca compound, the Ca compound having at least 15 wt.% of CaO equivalent in the agglomerates.

18. Process according to claim 14, wherein the agglomerates further comprise a Ca compound, the Ca compound having at least 15 wt.% of CaO equivalent in the agglomerates.

19. Process according to claim 11, wherein the agglomerates are pellets having a Mass Pellet Strength of at least 5 kg.

20. Process according to claim 11, wherein the agglomerates are pellets having a Mass Pellet Strength of at least 10 kg.

21. Process according to claim 11, wherein the fuming step temperature is at least 1300°C.

22. Process according to claim 11, wherein the fuming step is carried out in a carbon monoxide containing atmosphere.

23. Process according to claim 21, wherein the fuming step is carried out in a carbon monoxide containing atmosphere.

24. Process according to claim 11, wherein the Fe-bearing Zn leaching residue is a neutral or weak acid Fe-bearing Zn leach residue.

25. Process according to claim 11, wherein the fuming step is carried out in a rotary hearth furnace.

26. Process according to claim 21, wherein the fuming step is carried out in a rotary hearth furnace.

27. Process according to claim 23, wherein the fuming step is carried out in a rotary hearth furnace.

28. Process according to claim 11, further comprising the step of subjecting the reduced Fe-bearing phase to an oxidising smelting step.

29. Process according to claim 21, further comprising the step of subjecting the reduced Fe-bearing phase to an oxidising smelting step.

30. Process according to claim 23, further comprising the step of subjecting the reduced Fe-bearing phase to an oxidising smelting step.

*b** * * * *