A method of processing a ferroalloy waste slag in a reactor which includes the steps of treating the slag with a metallic reductant and a conditioning flux to release a metal oxide and reduce it to metallic form, to use as a commercially acceptable silicon-containing alloy and to form a waste slag which is detoxified by means of granulation and separating the detoxified slag from silicon-containing alloy particles.
MANGANESE WASTE SLAG TREATMENT

BACKGROUND OF THE INVENTION

[0001] This invention relates to the treatment of a ferroalloy waste slag. In particular the invention provides a method of processing and detoxifying a ferrochrome or a manganese ferroalloy waste slag.

[0002] South African ferroalloy ores, such as manganese ferroalloy (including ferromanganese and silicomanganese) and ferrochrome respectively, typically have a relatively low Mn/Fe or Cr/Fe ratio. Producers of ferromanganese thus operate according to the so-called "discard slag" smelting practice. This means that the slag has a manganese level that is too low for the slag to be used economically in the production of a saleable product such as silicon-manganese and the slag is therefore discarded as waste. A similar situation occurs in the production of ferrochromium and silicomanganese. In each case, the level of manganese or chrome in the so-called respective waste slag is nonetheless appreciable, i.e. typically between 15 and 35% MnO and between 10 and 20% Cr₂O₃ for the two types of manganese ferroalloy slags and ferrochrome slag, respectively.

[0003] Also, there are legitimate concerns about the leaching of manganese or chrome and other toxic elements from the respective slags into ground water. For this reason manganese and chrome slags have traditionally been classified as hazardous industrial wastes and, in terms of existing legislation, may only be disposed of in a designated hazardous waste site at the prevailing cost.
[0004] A possible alternative to disposing of the discard slag as waste would be to subject the low grade ores for example ferromanganese ores to an initial iron-removal smelting step leaving most of the manganese in the slag. The manganese-rich slag could then be cooled, crushed and used as feedstock in ferromanganese or silico-manganese production. This technique is however not economical even though the first smelting step produces a potentially usable iron-rich product. This is because the ore must be smelted twice.

[0005] In an article entitled "Further processing and granulation of slags with entrained metal and high metal compound content, with specific reference to present manganese slag dumps as well as additions due to daily production" by Norval et al (hereinafter "Norval"), a process is disclosed wherein manganese waste slag is conditioned in a furnace using basic oxygen furnace (BOF) slag as a source of CaO to increase the basicity. The manganese is reduced to around 6% MnO using a carbonaceous reductant in the form of coal. The slag is granulated to make it suitable as a cement extender. It is mentioned that a FeMn product was obtained, but a mass balance indicates that the alloy would be off-grade with less than 50% Mn, whereas both the BOF slag and coal would introduce phosphorus such that this impurity would exceed 0.5% in the alloy. Additionally, electric smelting of manganese oxide in slag or ore with a carbonaceous reductant usually results in considerable fuming of manganese and sometimes silicon to produce a toxic manganese dust or slurry, resulting in another waste stream that needs to be processed separately.

[0006] US 3329497 and US4363657 teach the use of waste slag to produce a high silicon containing ferroalloy with low impurities such as carbon, phosphorus etc. A throw-away slag containing low levels of manganese oxide is produced. A saleable product and a toxic throw-away slag are thus produced in each instance.
An object of the invention is to provide a commercially viable method of processing manganese ferroalloy waste slag or ferrochrome waste slag to produce a saleable alloy product and to detoxify the remaining slag.

SUMMARY OF THE INVENTION

The invention provides a method of processing a ferroalloy waste slag in a reactor which includes the steps of:

a) treating the slag, in a molten form, with at least one of a metallic reductant and a conditioning flux to release a metal oxide, contained in the ferroalloy waste slag, and produce;

a reduced metallic form of the metal oxide as a commercially acceptable silicon-containing alloy; and

a remaining waste slag,

b) tapping the silicon-containing alloy from the reactor;

c) quenching the remaining waste slag by means of granulation to form a granular detoxified slag, in a glass phase, that is suitable for use in making a cement extender; and

d) separating the detoxified slag from any entrained silicon-containing alloy particles by means of gravity separation.

The ferroalloy waste slag may be manganese ferroalloy or ferrochrome and the respective metal oxide may be manganese oxide or chrome oxide.

The manganese ferroalloy refers to, at least, ferromanganese waste slag or silicomanganese waste slag.
The manganese ferroalloy waste slag may be treated to release the manganese oxide, from the slag, and form, a silicomanganese product and a manganese-poor waste slag.

A similar silicomanganese product may be produced from the treatment of silicomanganese waste slag, but the quantity of this commercial product would be lower than in the case of ferromanganese waste slag treatment, since the starting waste slag in this case contains less MnO (about 15%) compared to the ferromanganese waste slag, which contains typically 25 to 35% MnO.

The ferrochrome waste slag may be treated to release the chromium oxide, from the slag, and form, a ferrochromium silicide and a chromium-poor waste slag

One objective is to process a ferroalloy waste slag (manganese ferroalloy or ferrochrome) to produce a remaining slag (manganese-poor or chromium-poor) with a composition similar to that of slag produced by an iron blast furnace. The ferroalloy waste slag may be a cold slag from a dump or it may be in molten form e.g. produced from a submerged arc furnace and tapped into a refractory-lined ladle.

The metallic reductant may be selected from aluminium granules, aluminium powder, pulverised FeSi and fine Si metal.

The conditioning flux may be selected from bauxite, alumina, quicklime (calcined lime) or limestone. The conditioning flux is used to raise the alumina content and the basicity ratio of the reduced waste slag.
[0017] The aluminium reductant may react with the metal oxide to give a slag composition which is similar to that achieved if bauxite is added as a flux.

[0018] The pulverised FeSi and Si metal (with or without aluminium) may react to some extent with the metal oxide to produce a commercially acceptable silicon-containing alloy.

[0019] The remaining waste slag may be water granulated to ensure the formation of at least 95% glass as per requirement for slag to be used for cement making. The granulation may be carried out to control a particle size of the granular detoxified slag. The particle size may be between 4.5mm and 5.5mm.

[0020] The particles may be separated from the reduced metallic particles and entrained silicon-containing alloy particles by means of spiral separation.

BRIEF DESCRIPTION OF THE DRAWING

[0021] The invention is further described by way of example with reference to the accompanying drawing which illustrates in flow-chart form a method of the invention as applied to a cold slag and to a molten slag.

DESCRIPTION OF PREFERRED EMBODIMENT

[0022] The accompanying flow-chart depicts a process for treating a ferroalloy waste slag.

[0023] In one application a waste slag 10 e.g. from a dump site is crushed (step 12). if necessary, and is screened to produce granules 14 of less than 5mm in size. The small
particles can then react rapidly with a metallic reductant 16 in an electric conditioning furnace 18.

[0024] The metallic reductant 16 is selected from aluminium granules or powder and pulverised FeSi or fine metallurgical grade silicon metal. A flux 20 selected from bauxite and calcined lime is added, as required, to condition the slag 22 produced in the furnace to conform to the chemical specification of a conventional steel blast furnace slag.

[0025] The furnace 18 produces a commercially acceptable silicon-containing alloy 24 which is tapped intermittently from the furnace.

[0026] During the metallothermic reduction no gas phase is produced. Some vapours may be generated as a result of the vaporisation of volatile species. Off-gas dust from the furnace may be emitted. A small bagplant may be used to capture vapours from the furnace off-gas and fugitive emissions during tapping operations.

[0027] The hot slag 22 from the furnace is delivered to a water slag granulator 26 and quenched slag 28 from the granulator 26 is directed to a separator 30.

[0028] The slag 28 has more than 95% glass phase present - this meets the requirement for slag which is to be used in cement making. Any metallic inclusions 32 in the slag product 28 are removed in the separator 30 which, for example, makes use of spiral separation techniques. The metallic inclusions 32 are returned to the furnace 18.

[0029] The granulated slag product 34 emerging from the separator 30 is available for use in cement making processes 36.
The principles of the invention are also usable for the processing of a hot slag 40 which is produced by a conventional submerged arc furnace 42 used for the processing of ferroalloy 44. The hot slag 40 is fed to a ladle furnace 48 and, as before, a metallic reductant 50 similar to the reductant 16 and a conditioning flux or fluxes 52 similar to the flux or fluxes 20, are added to the ladle or the ladle furnace. Hot slag 54 from the ladle or ladle furnace is fed to the granulator 26 and processed in the manner which has been described to produce a conditioned slag 34 which is suitable for use in a cement making process 36.

The ladle 46 and a ladle 60 can be used in a "cock-tailing" mode, indicated by a double-headed arrow 62 in the drawing, or stirring or shaking mechanisms can be employed, to promote reactions to proceed to equilibrium.

From the ladle 46 a commercial silicon-containing alloy product 64 is tapped from the refractory lined ladle after decanting of the slag.

In the processing of hot slag i.e. in the second form of the invention, the exothermic nature of the metallothermic reduction reactions may require the addition of coolants such as recycled metal or solid dump waste slag to the ladle or ladle furnace.

Tests have been conducted to confirm the production of a commercial silicon-containing product and to determine that the milled granulated slag emerging from the separator 30 is suitable for use in the production of cement.
[0035] Table 1 presents results which confirm that the process applied to a ferromanganese waste slag generates a commercially acceptable silico-manganese product and a conditioned manganese poor slag suitable for use in cement making.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Chemistry of slag</th>
<th>Chemistry of metal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% MnO B3 Σ % glass</td>
<td>% Mn % Si</td>
</tr>
<tr>
<td>Feed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeMn waste slag</td>
<td>31.5 1.1 62.0</td>
<td>N/A - -</td>
</tr>
<tr>
<td>Products</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Modified slag</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Test 1 (Batches B2 to B5)</td>
<td>11.4 1.0 76.6 98</td>
<td>- -</td>
</tr>
<tr>
<td>2. Silico-manganese</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Test 1 (Batches B2 to B5)</td>
<td>- - - -</td>
<td>66 16.1</td>
</tr>
<tr>
<td>Specifications</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. GGBFS</td>
<td>N/A ≥ 1.0 ≥ &gt; 95</td>
<td>66.7</td>
</tr>
<tr>
<td>2. SiMn (Grade B)</td>
<td>- - - -</td>
<td>65 16.0 68 18.5</td>
</tr>
</tbody>
</table>
\[ \Sigma = \% \text{MgO} + \% \text{CaO} + \% \text{SiO}_2 \]

\[ \text{Basicity} = \frac{\% \text{MgO} + \% \text{CaO}}{\% \text{SiO}_2} \]

[0036] Two slag samples identified as T1B5 and T2B3 (chemical composition given in Table 2) were milled fine and their leaching stability compared with WHO (World Health Organisation) standards as well as a blended cement (CEM V-A (S-V) 32.5N). Table 3 presents the results of synthetic precipitation leaching procedure tests to confirm that the milled granulated slag has the required stability.

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical composition, mass per cent</th>
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<tbody>
<tr>
<td></td>
<td>MnO</td>
</tr>
<tr>
<td>T1B5</td>
<td>12.4</td>
</tr>
<tr>
<td>T2B3</td>
<td>7.8</td>
</tr>
<tr>
<td>CEM V-A (S-V) 32.5N</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ca</th>
<th>Mg</th>
<th>Ag</th>
<th>Al</th>
<th>As</th>
<th>Be</th>
<th>Cd</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
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<tbody>
<tr>
<td>T1B5</td>
<td>27</td>
<td>4</td>
<td>&lt;0.0</td>
<td>&lt;0.0</td>
<td>&lt;0.0</td>
<td>&lt;0.0</td>
<td>&lt;0.0</td>
<td>&lt;0.0</td>
<td>&lt;0.0</td>
<td>&lt;0.0</td>
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<tr>
<td>T2B3</td>
<td>71</td>
<td>7</td>
<td>&lt;0.0</td>
<td>&lt;0.0</td>
<td>&lt;0.0</td>
<td>&lt;0.0</td>
<td>&lt;0.0</td>
<td>&lt;0.0</td>
<td>&lt;0.0</td>
<td>&lt;0.0</td>
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<td>2</td>
<td>2</td>
<td>2</td>
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</tr>
</tbody>
</table>
[0037] The reduction of the manganese waste slag using finely sized aluminium or silicon-rich alloys or metallic silicon waste as described produces a commercially acceptable silico-manganese product and a saleable non-hazardous granulated slag suitable for use in cement making. Fluxes such as bauxite and lime can be used in the reaction to condition hazardous waste slag to have a composition so that when granulated and milled it conforms to specifications for commercial ground granulated blast furnace slag (GGBFS).
Example 2

Table 4 presents results that confirm that the process applied to a chromium waste slag generates a commercially acceptable ferrochromium silicide product and a conditioned slag suitable for use in cement making.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Chemistry of the slag</th>
<th>Chemistry of alloy</th>
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<tbody>
<tr>
<td></td>
<td>% Cr₂O₃</td>
<td>Basicity</td>
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<tr>
<td>Feed</td>
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<td></td>
</tr>
<tr>
<td>FeCr waste slag</td>
<td>10 to 20</td>
<td>1.1</td>
</tr>
<tr>
<td>Products</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Modified slag</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Ferrochromium silicide</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GGBFS</td>
<td>N/A</td>
<td>≥ 1.0</td>
</tr>
<tr>
<td>Ferrochromium silicide (Grade A)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Oxide sum = % MgO + % CaO + % SiO₂

[0039] The steps carried out in Example 2 for chromium waste slag are essentially the same as those carried out on the manganese waste slag.
Waste slag which otherwise needs to be disposed of in a hazardous industrial waste landfill site is formed into the two mentioned products. All streams of dust and metallic inclusions are recovered and recycled to ensure that no secondary waste results.

The process of the invention can be applied to waste slag e.g. from a dump, or to hot molten slag coming from an existing manganese ferroalloy or ferrochromium furnace. In the latter case the exothermic reaction of the processing technology means that very little, if any, additional energy, whether fossil or electric, is required for slag conditioning.

The process of the invention can be adjusted to accommodate variations in the composition of the waste slag. The MnO content in the waste slag may vary from 15% to 35% and its basicity ratio \((\text{CaO} + \text{MgO})/\text{SiO}_2\) may range from 0.5 to 1.5. It is noted in this respect that silico-manganese waste slags typically have a lower residual MnO and basicity whereas ferromanganese waste slags have a higher MnO content and basicity. The flexibility offered by the technology of the invention ensures that the product slag can always have between 5% and 15% MnO and between 10% and 15% \(\text{Al}_2\text{O}_3\). Also, the sum of the CaO, MgO and SiO\(_2\), as exemplified in Table 3, is in excess of 70% and conforms to accepted specifications for blast furnace slag.

Similarly, in the case of ferrochromium waste slag, the additional lime ensure that the basicity will meet the required target of \(\geq 1.0\). The use of aluminium as reductant or alumina/bauxite as flux would generally not be required as the starting waste slag normally already contains appreciable amounts of alumina.
CLAIMS

1. A method of processing a ferroalloy waste slag in a reactor which includes the steps of:
   a) treating the slag, in a molten form, with at least one of a metallic reductant and a
      conditioning flux to release a metal oxide, contained in the ferroalloy waste slag, and
      produce:
      a reduced metallic form of the metal oxide as a commercially acceptable silicon-containing alloy; and
      a remaining waste slag,
   b) tapping the silicon-containing alloy from the reactor;
   c) quenching the remaining waste slag by means of granulation to form a granular detoxified slag, in a glass phase, that is suitable for use in making a cement extender; and
   d) separating the detoxified slag from any entrained silicon-containing alloy particles.

2. A method according to claim 1 wherein the ferroalloy waste slag is a manganese ferroalloy waste slag or ferrochrome waste slag.

3. A method according to claim 2 wherein the manganese ferroalloy is ferromanganese or silicomanganese.

4. A method according to claim 2 or 3 wherein the metal oxide is manganese oxide or chromium oxide respectively.
5. A method according to claim 2, 3 or 4 wherein the silicon containing alloy produced by each respective waste slag is silico-manganese and ferrochromium silicide.

6. A method according to any one of claims 2 to 5 wherein the remaining waste slag is a manganese-poor slag, or a chromium-poor slag, respectively.

7. A method according to any one of claims 1 to 6 wherein the reduced waste slag is conditioned such that it has a composition which is similar to that of a slag produced by an iron blast furnace.

8. A method according to any one of claims 1 to 7 wherein the ferroalloy slag is a cold slag from a dump or is in a molten form produced from a submerged arc furnace.

9. A method according to any one of claims 1 to 8 wherein the metallic reductant is selected from aluminium granules, aluminium powder, pulverised FeSi and Si metal.

10. A method according to any one of claims 1 to 9 wherein the conditioning flux is selected from bauxite, alumina, quicklime (calcined lime) or limestone.

11. A method according to any one of claims 1 to 10 wherein the conditioning flux is used to raise the alumina content and the basicity ratio of the reduced waste slag to a desired level.

12. A method according to claim 9 wherein the aluminium reacts with the metal oxides to give a slag composition which is similar to that achieved if bauxite is added as a flux thereby forming a viable product.
13. A method according to any one of claims 1 to 12 wherein the remaining waste slag is water granulated to ensure the formation of at least 95% glass as per requirement for slag suitable for use in cement making.

14. A method according to claim 13 wherein the granulation is carried out to control the particle size of the granular detoxified slag.

15. A method according to claim 14 wherein the particle size of the slag is between 4.5mm and 5.5mm.

16. A method according to any one of claims 1 to 15 wherein the particles are separated from any remaining entrained silicon-containing alloy by means of spiral separation.
INTERNATIONAL SEARCH REPORT

International application No

PCT/ZA2016/050051

A. CLASSIFICATION OF SUBJECT MATTER

INV. C21B3/08 C22B7/04 C04B5/06

ADD.

According to International Patent Classification (IPC) of both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C21B C21C C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tr>
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<td>US 3 301 669 A (RATHMANN HEINRICH W ET AL) 31 January 1967 (1967-01-31) figure 1</td>
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Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
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- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other documents, such combination being obvious to a person skilled in the art
- "Z" document member of the same patent family

Date of the actual completion of the international search

3 May 2017

Date of mailing of the international search report

11/05/2017

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Fax: (+31-70) 340-3016

Authorized officer

Gimeno-Fabra, Luis
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<th>Patent family member(s)</th>
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<td>US 3301669</td>
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<td>US 4053307</td>
<td>11-10-1977</td>
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