



(86) Date de dépôt PCT/PCT Filing Date: 2003/05/13  
(87) Date publication PCT/PCT Publication Date: 2003/11/27  
(85) Entrée phase nationale/National Entry: 2005/11/14  
(86) N° demande PCT/PCT Application No.: GB 2003/002051  
(87) N° publication PCT/PCT Publication No.: 2003/097881  
(30) Priorité/Priority: 2002/05/15 (0211154.0) GB

(51) Cl.Int./Int.Cl. *C21C 5/06* (2006.01),  
*C21C 5/36* (2006.01)  
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(54) Titre : SCORIES METALLURGIQUES  
(54) Title: METALLURGICAL SLAG

(57) Abrégé/Abstract:

A method of making a material for use as a steel-making slag comprises mixing sufficient lime and/or magnesia containing materials with combustion ash until the so-formed composition has a basicity ratio appropriate for use in steel making.



## (12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
27 November 2003 (27.11.2003)

PCT

(10) International Publication Number  
**WO 03/097881 A1**

(51) International Patent Classification<sup>7</sup>: C21C 5/06, 5/36

(21) International Application Number: PCT/GB03/02051

(22) International Filing Date: 13 May 2003 (13.05.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
0211154.0 15 May 2002 (15.05.2002) GB

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(81) Designated States (national): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,

CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,  
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,  
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,  
MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD,  
SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US,  
UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),  
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),  
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,  
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,  
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,  
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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**WO 03/097881 A1**

## Metallurgical Slag

5 This invention relates to slag, specifically to that used in the steel-making industry.

A slag is present on the top of the melt in a metallurgical furnace or vessel. The main function of the slag is to combine with unwanted impurities from the melt so that they can be separated from the melt. It also tends to prevent the melt from  
10 picking up gases from the furnace atmosphere.

It is known that the so-called basicity ratio of the slag is important in steel-making. The basicity ratio is defined as the ratio of basic oxides to acidic oxides.

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One measure of the basicity ratio ( $B$ ) is defined thus:

$$B = \frac{\%CaO + \%MgO}{\%SiO_2 + \%Al_2O_3}$$

20 Other, sometimes more useful, measures of the basicity ratio have been proposed (see Turkdogan E.T. *The Fundamentals of Steelmaking*; The Institute of Materials (1996)). Such measures may be expressed thus:

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$$B_{LF} = \frac{\%CaO + 1.4\%MgO}{\%SiO_2 + 0.6\%Al_2O_3}$$

or

$$V = \frac{\%CaO}{\%SiO_2}$$

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Virgin slag compositions are slag compositions which are brought into contact with the melt at the commencement of the steel making process. The values for basicity ratios, as defined above, are typically above 2 for the so-called "virgin" slag compositions.

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Care must be taken when using and referring to the basicity ratio as there are many ways of defining the basicity (see, for example, Sommerville, I.D. and Yindong Yang; *The AusIMM Proceedings*, pp. 71, Vol. 36 No.1; 2001).

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Furnaces used in the steel industry, for example Basic Oxygen Furnaces (BOFs), Electric Arc Furnaces (EAFs) and Ladle Furnaces (LFs) are metal vessels which have a refractory lining to hold the molten metal. The refractory materials are chosen to withstand the extreme temperatures to which they are subjected. It is important for reasons of economy and efficiency that damage to the refractory materials is minimised. Damage to such refractory materials is controlled by, *inter alia*, the basicity and by MgO saturation levels.

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Many industries seek to gain extra benefit out of production processes by reclaiming waste materials. Such reclamation may take the form of recycling unused or partially used materials or the reclamation of say energy in the form of heat by combusting waste materials. One such industry is the paper production industry where the by-product, waste paper pulp or sludge, is often burnt. The product of the so-combusted waste is known as combustion ash.

Combustion ash from the paper production industry is typically a fine powder substantially composed of calcium oxide, silicon dioxide, aluminium oxide, magnesium oxide and iron oxide. Small amounts of other metallic oxides and chlorides are also usually present. Because of the physical composition and state of combustion ash it has heretofore had limited economic use and is typically land-filled. In many parts of Europe, at least, a charge is levied for the disposal and, say, land filling of industrial waste.

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It is an object of the present invention to provide a cheap source of virgin slag, whilst providing an economic sink for combustion ash, thereby reducing land-fill and producing a further income stream. It is a further object of the invention to provide a so-called "artificial" slag made at least partially from waste materials. It is a yet further and more specific object of the invention to provide an artificial slag from waste materials which causes no, little or not excessive damage to the refractory materials used in steel-making processes.

Accordingly, a first aspect of the invention provides a method of making a material for use as a steel-making slag, the method comprising mixing sufficient lime

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and/or magnesia containing materials with combustion ash until the so-formed composition has a basicity ratio appropriate for use in steel making.

A further aspect of the invention provides a material for use as a slag in the steel-making industry, comprising a mixture of combustion ash and lime and/or magnesia containing materials and having a basicity ratio appropriate to the steel to be made and/or steel making process to be utilised.

Preferably, the ratio of add-mixed lime to combustion ash is from 1:2 to 2:1, calculated as parts by mass, but may be more or less depending on the composition of the combustion ash. The ratio of add-mixed magnesia to combustion ash is preferably no more than 1:4, more preferably no more than 1:5.

The basicity ratio (V) of the product may be advantageously adjusted to a range of from 2.0 to 9.0, depending upon the metallurgical requirements of the process in which the slag is intended to be used, by the addition of appropriate amounts of lime and/or magnesia containing materials.

The added or add-mixed lime and magnesia are preferably in either or both powder or granular form, most preferably each with a nominal diameter of less than 10mm. The lime and magnesia may be separate components and/or may be in the form of dolomitic lime which may have a lime to magnesia ratio of about 3:1 and/or other materials rich in lime and/or magnesia.

It will be appreciated by those of skill in the art that the term 'lime', as used herein, typically refers to burnt lime (CaO). However, in special and rare situations, CaCO<sub>3</sub> may be used in addition, or as an alternative to, CaO.

5 A yet further aspect of the invention provides a method of generating artificial slag, the method comprising treating combustion ash to provide a material with a basicity ratio appropriate for use in steel making.

10 Preferably, the combustion ash is treated by adding substances thereto, for example lime and/or magnesia, or removing components thereof, for example silica and/or alumina.

A still further aspect of the invention provides the use of combustion ash as at least a part component of artificial slag for use in steel making.

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In order that the invention may be more fully understood it will now be described with reference to the accompanying Examples.

20 Table 1, below, provides details of a typical composition of combustion ash. The range shown is typical of combustion ashes although some may vary outside of the ranges shown. All combustion ashes are considered to be suitable for use in the current invention.

As can be seen, Table 1 shows that the specific example of typical combustion ash has basicity ratio values which are too low to use it as a virgin slag.

5 **Table 1. Typical Composition of Combustion Ash**

Component	Range (w/w%)	Composition (w/w%)
SiO <sub>2</sub>	22 – 34	27
Al <sub>2</sub> O <sub>3</sub>	15 – 22	19
Fe <sub>2</sub> O <sub>3</sub>	7 – 1.3	1
CaO	37 – 47	42
MgO	4 - 6	5
B (calculated)		1.0
B <sub>LF</sub> (calculated)		1.3
V (calculated)		1.6

### **Example 1**

10 To 100 parts by mass of the above-specified combustion ash were added and mixed 50 parts by mass of lime. The components were mixed to provide a substantially homogeneous mixture. The resultant mixture had basicity ratios, B of 2.1 B<sub>LF</sub> of 2.6 and V of 3.4. The mixture was found to be suitable as an artificial virgin slag material in the steel making industry.

**Example 2**

To 100 parts by mass of the above-specified combustion ash were added and mixed 200 parts by mass of lime and 20 parts by mass of magnesia. The components were mixed to provide a substantially homogeneous mixture. The resultant mixture had basicity ratios B of 5.8,  $B_{LF}$  of 7.1 and a basicity ratio V of 8.4 by calculation. The mixture was found to be suitable as an artificial virgin slag material in the steel making industry.

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**Example 3**

To 100 parts by mass of the above-specified combustion ash were added and mixed 40 parts by mass of lime and 40 parts by mass of dolomitic lime (25% by mass magnesia, 75% by mass lime). The components were mixed to provide a substantially homogeneous mixture. The resultant mixture had basicity ratios B of 2.8,  $B_{LF}$  of 3.4 and a basicity ratio V of 4.1. The mixture was found to be suitable as an artificial virgin slag material in the steel making industry.

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The so-formed virgin artificial slag may be placed on top of or into the melt by means of a conveyor or the like, thereby drawing off the impurities from the melt. Alternatively, and due to the small particle size of the combustion ash, the so-formed virgin artificial slag may be entrained in, say, a gas stream and injected, pumped or otherwise forced into the melt below its' surface, so that it will remove impurities as it percolates or passes upwards.

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The so-formed virgin artificial slag is useful in EAFs, BOFs and LFs or any vessel containing liquid steel and further can aid elemental phosphorus and sulphur removal from the steel (as  $P_2O_5$  and CaS respectively) in, say, EAFs. Further, due to the presence of MgO in the artificial slag, the tendency for MgO to dissolve from the refractory materials used in the liners of such furnaces is reduced, thereby minimising damage to those refractory materials.

Whilst the above-identified Examples have indicated that the combustion ash and other substances are mixed prior to addition to the melt, it is also within the scope of this invention to add the combustion ash and lime and/or magnesia separately to the melt. Thus, lime, say, may be added to the melt and combustion ash added as a distinct component, the sum of the two parts forming a slag with a basicity ratio appropriate for use in steel making. One component may be forced into the melt below its surface and the other placed on top of the melt, both may be placed on top of the melt, or both may be forced into the melt below its surface.

It will be understood by the skilled man that the sum of lime and/or magnesia additions will be specific to a particular steel making application and even to a particular steel making plant, due to, *inter alia*, the production of oxides during the steel making process which also go to form part of the slag. Thus, the initial basicity ratio will be adjusted and selected to accommodate the impurities produced in the furnace, the quality of steel required and the type of refractory material used to line the furnace.

## Claims

1. A method of making a material for use as a steel-making slag, the method comprising mixing sufficient lime and/or magnesia containing materials with combustion ash until the so-formed composition has a basicity ratio appropriate for use in steel making.
2. A method according to Claim 1, wherein the ratio of add-mixed lime containing material to combustion ash is in a range of from 1:2 to 2:1, calculated as parts by mass.
3. A method according to Claim 1 or 2, wherein the ratio of add-mixed magnesia containing material to combustion ash is no more than 1:4, calculated as parts by mass.
4. A method according to any of Claims 1, 2 or 3, wherein the ratio of add-mixed magnesia containing material to combustion ash is no more than 1:5, calculated as parts by mass.
5. A method according to any preceding Claim, comprising mixing sufficient lime and/or magnesia containing materials such that the basicity ratio (V) of the so-formed material is in a range of from 2.0 to 9.0.

6. A method according to any preceding Claim, comprising mixing lime and/or magnesia containing materials wherein either or both are in powder or granular form.
- 5 7. A method according to any preceding Claim, comprising mixing lime and/or magnesia containing materials with combustion ash, wherein either or both has a nominal diameter (particle size) of less than 10mm.
8. A method according to any preceding Claim, comprising mixing lime and  
10 magnesia containing materials as separate components with the combustion ash.
9. A method according to any preceding Claim, comprising mixing dolomitic lime with the combustion ash.
- 15 10. A method according to any preceding Claim, comprising mixing lime and/or magnesia containing materials with the combustion ash to form a mixture which is suitable for use as a artificial slag.
11. A method according to any of Claims 1 to 9, comprising adding the lime and/or  
20 magnesia containing materials and the combustion ash to a vessel containing liquid steel.
12. A material for use as a slag in the steel-making industry, comprising a mixture of combustion ash and lime and/or magnesia containing materials and having a

basicity ratio appropriate to the steel to be made and/or steel making process to be utilised.

13. A material according to Claim 12, wherein the ratio of added lime containing  
5 material to combustion ash is from 1:2 to 2:1, calculated as parts by mass.

14. A material according to Claim 12 or 13, wherein the ratio of added magnesia  
containing material to combustion ash is no more than 1:4, calculated as parts by  
mass.

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15. A material according to any of Claims 12, 13 or 14, wherein the basicity ratio (V) is  
in a range from 2.0 and 9.0.

16. A method of generating artificial slag, the method comprising treating combustion  
15 ash to provide a material with a basicity ratio appropriate for use in steel making.

17. A method according to Claim 16, comprising treating the combustion ash by  
adding substances thereto, for example lime and/or magnesia, or removing  
components thereof, for example silica and/or alumina.

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18. The use of combustion ash as at least a partial component of artificial slag for use  
in steel making.