

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification⁶ : C22B 7/02, 1/14, 1/244</p>	<p>A1</p>	<p>(11) International Publication Number: WO 96/09416 (43) International Publication Date: 28 March 1996 (28.03.96)</p>
<p>(21) International Application Number: PCT/GB95/02223 (22) International Filing Date: 19 September 1995 (19.09.95) (30) Priority Data: 9418849.7 19 September 1994 (19.09.94) GB (71)(72) Applicant and Inventor: REES, Geraint [GB/GB]; 54 Rehoboth Road, Five Roads, Llanelli, Dyfed SA15 5DJ (GB). (74) Agent: AUSTIN, Hedley, William; Urquhart-Dykes & Lord, Alexandra House, Alexandra Road, Swansea, West Glamorgan SA1 5ED (GB).</p>	<p>(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).</p> <p>Published <i>With international search report.</i></p>	
<p>(54) Title: BONDED MEDIUM</p> <p>(57) Abstract</p> <p>Thermally shock stable bonded solid materials are formed by mixing a solid mineral or inorganic material in an aqueous medium with a lignosulfonate, treating the aqueous medium with a metal ion-based complexing agent (such as lime), with application of heat sufficient to maintain the lignosulfonate in fluid form, so as to produce an intimate mix of saturated slaked lime with lignosulfonate and the mineral or inorganic material, and thoroughly mixing the resulting substantially dry material with dry urea (or a derivative thereof) so as to cause the mix to agglomerate, preferably followed by shaping the agglomerates by briquetting or the like.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgystan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Larvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

Bonded Medium

The present invention is concerned with bonded media.

Certain inorganic materials are sometimes present in a form in which they are difficult to handle and use. For example, basic oxygen steelmaking sludge (which is a waste product from the basic oxygen steelmaking process), contains up to 30% moisture and solids, including ferrous sulfide, iron oxide and various foundry additives, as well as other metals such as zinc.

Basic oxygen steelmaking sludge is generally considered to be a waste product, for which disposal is very expensive and difficult, partly because of its zinc content. We have now devised a way of using such basic oxygen steelmaking sludge, and other mineral and inorganic materials.

According to the present invention therefore, there is provided a method of forming thermally shock stable bonded solid materials, which comprises mixing a solid mineral or inorganic material in an aqueous medium with a lignosulfonate, treating the aqueous medium with a polyvalent or polydentate cationic complexing agent for lignosulfonate, with application of heat sufficient to maintain said lignosulfonate in fluid form, so as to produce an intimate mix of said complexing agent with said lignosulfonate and said mineral or inorganic material, and thoroughly mixing the resulting substantially dry material with a substantially dry further reagent comprising urea or a urea derivative, so as to cause the mix to agglomerate.

The resulting agglomerates can be shaped into, for example, briquettes (formed between shaped dies or the like) or pellets, or similar bodies formed by extrusion, pan agglomeration or the like.

The lignosulfonate may be used in method according to the invention in the form of a solution (such as an aqueous solution). Alternatively, when the mineral or organic material is itself aqueous, the lignosulfonate may be used in powder form. The lignosulfonate may include any suitable cation(s); examples of suitable cations are ammonium, calcium, magnesium, sodium or potassium. Of these, calcium is most preferred.

-2-

The cationic complexing agent may comprise a transition metal or an alkaline earth metal; the metal is preferably of the fourth period of the Periodic Table of the elements, such as calcium, iron or the like. Of these, calcium is preferred, preferably in the form of the oxide (preferably as lime, which has the advantage of reacting with any free water in the mix).

When lime is used, it is preferably added to the aqueous medium in such an amount as to produce a saturated slaked mix, having a pH typically in excess of 10.

The further reagent is preferably added in powdered form and mixed with the saturated slaked mix by contra-rotating blade mixing or by tumbling, until the mix becomes plastic; this mixing may be carried out at a temperature ranging from ambient to up to about 80°C. The further reagent is preferably urea or a urea derivative (such as an alkyl urea).

When the mineral or inorganic material treated by the method according to the invention is basic oxygen steelmaking sludge, then the resulting shaped agglomerates can undergo direct reduction to a ferrous metal source, for addition to molten steel or iron in a steelmaking process. The direct reduction with carbon as reducing agent, which is typically carried out at about 900-1000°C, is advantageously without disintegration of the agglomerates because of their highly advantageous thermal shock resistance. Any zinc, furthermore, may be volatilised off from the shaped agglomerates during the direct reduction phase.

It is a particular advantage of the present invention, when applied to the process of forming agglomerates from basic oxygen steelmaking sludge or other inorganic or mineral materials, that highly thermal shock-resistant agglomerates can be formed. Such agglomerates are substantially dry and can be added to high temperature direct reduction processes or the like without any deleterious water evolution (which could otherwise have potentially devastating, explosive consequences). It is believed that this thermal shock resistance is beneficially associated with the formation of sulfonyl and sulfur bridges between the polymeric (lignin-based) backbones. Calcium sulfate formed in the slaking step is also believed to beneficially contribute to such thermal shock resistance. The sulfur present in the resulting agglomerates is stoichiometrically bonded in such a form that disadvantageous evolution of oxides of sulfur, or other noxious sulfur compounds, is substantially precluded.

-3-

The present invention will now be further illustrated, by way of example only, in the following Examples.

Example 1

100 grams of basic oxygen steelmaking sludge, which contained 30% by weight of water, was partially dried, to a solids content of about 12% by weight.

10 grams of calcium lignosulfonate was added as a dry powder, with stirring. Lime (calcium oxide) was then added incrementally, so as to be slaked by the water present in the mix, resulting in a dry powder (the amount of lime being about 5 grams).

3 grams of powdered urea were then added and the mix was tumbled together at a temperature of about 60°C, so as to produce an agglomerated mass. The resulting mass (which had a pH in excess of 10) was formed into briquettes between shaped dies.

The resulting briquettes were highly stable to thermal shock, and could be added in the form of briquettes to a direct reduction process, as referred to above without disintegration.

Example 2

200 grams of ferrous sulfide was supplied to a Bekin double-blade contra-rotating mixer; 20 grams of an aqueous solution of calcium lignosulfonate containing 50% by weight of water, was added to obtain a fairly wet mix.

10 grams of lime (calcium oxide) was then added incrementally, so as to be slaked by the water present in the mix, and the plastic mix was thereby converted to a free-flowing powder.

5 grams of powdered urea were then added and the mix was blended, so as to result in a volume increase in the mixer, and an increase in the power input to the mixer (from 65 to 95 watts), the resulting mix being plastic. The resulting mass (which had a pH of about 12) was formed into briquettes in a single floating ring die.

The resulting briquettes were highly stable to thermal shock, and could be added directly to molten ferrous sulfide, without disintegration. (In a test, thirty of the briquettes were thrown into molten ferrous sulfide; none broke and the briquettes floated and gradually melted in the ferrous sulfide.)

Claims:

1. A method of forming thermally shock stable bonded solid materials, which comprises mixing a solid mineral or inorganic material in an aqueous medium with a lignosulfonate, treating the aqueous medium with a polyvalent or polydentate cationic complexing agent for lignosulfonate, with application of heat sufficient to maintain said lignosulfonate in fluid form, so as to produce an intimate mix of said complexing agent with said lignosulfonate and said mineral or inorganic material, and thoroughly mixing the resulting substantially dry material with a substantially dry further reagent comprising urea or a urea derivative, so as to cause the mix to agglomerate.
2. A method according to claim 1, wherein the lignosulfonate is in the form of an aqueous solution.
3. A method according to claim 1 or 2, wherein the complexing reagent lignosulfonate is in the form of a calcium salt.
4. A method according to any of claims 1 to 3, wherein the complexing agent comprises a transition metal or an alkaline earth metal
5. A method according to claim 3, wherein the metal is of the fourth period of the Periodic Table of the elements.
6. A method according to any of claims 1 to 5, wherein the complexing agent comprises a calcium compound.
7. A method according to claim 6, wherein the calcium compound is the oxide.

-5-

8. A method according to any of claims 1 to 7, wherein the further reagent comprises urea
9. A method according to claim 8, wherein the urea is added in powdered form and mixed with the saturated slaked mix by tumbling or by means of contra-rotating blades, until the mix becomes plastic.
10. A method according to claim 9, wherein the mixing is carried out at a temperature in the range from ambient to about 80°C.
11. A method according to any of claims 1 to 10, which further comprises shaping the agglomerates into briquettes, pellets or extruded bodies.
12. A method according to any of claims 1 to 11, wherein the mineral or inorganic material comprises basic oxygen steelmaking sludge.
13. A method according to claim 12 as appendant to claim 11, wherein the shaped agglomerates are added to molten steel or iron in a steelmaking process.
14. A method according to any of claims 1 to 11, wherein the mineral or inorganic material comprises ferrous sulfide.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 95/02223

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C22B7/02 C22B1/14 C22B1/244

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,3 895 088 (GOKSEL MEHMET ADNAN) 15 July 1975 see claims; examples ---	1
A	DE,A,41 01 584 (SAAR KOKEREI GMBH) 23 July 1992 see claims ---	1
A	US,A,5 328 497 (HAZLETT SCOTT) 12 July 1994 ---	
A	US,A,4 704 230 (BLACKMORE KENNETH A E) 3 November 1987 ---	
A	US,A,4 743 289 (MICKUS J C ET AL) 10 May 1988 -----	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- * 'A' document defining the general state of the art which is not considered to be of particular relevance
- * 'E' earlier document but published on or after the international filing date
- * 'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- * 'O' document referring to an oral disclosure, use, exhibition or other means
- * 'P' document published prior to the international filing date but later than the priority date claimed

- * '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
- * 'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- * '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 such documents, such combination being obvious to a person skilled in the art.
- * '&' document member of the same patent family

Date of the actual completion of the international search

5 January 1996

Date of mailing of the international search report

12.01.96

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

Wittblad, U

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 95/02223

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3895088	15-07-75	NONE	
DE-A-4101584	23-07-92	NONE	
US-A-5328497	12-07-94	NONE	
US-A-4704230	03-11-87	US-A- 4786438	22-11-88
US-A-4743289	10-05-88	NONE	