

1

3,194,673

HYDRAULIC CEMENT AND PROCESS FOR MAKING SAME

Andor Schedel, Budapest, Hungary, assignor to Licencia Talalmanyokat Ertekesito Vallalat, Budapest, Hungary
No Drawing. Filed Aug. 29, 1961, Ser. No. 135,408
3 Claims. (Cl. 106—100)

This invention relates to a process for agglomerating iron ores as well as for preparing hydraulic binding material usable in structural engineering. Moreover, this invention relates to a process for agglomerating iron powders by the aid of this binding material.

It is generally known that lumpy ores having the high iron content necessary for ferrous-metal metallurgy are being depleted; therefore the ferrous-metal industry is compelled to use powdery ores and to enrich such ores having a relatively low iron content.

These iron-ore powders cannot be fed directly into blast-furnaces because part of the powdery mass would be carried away by the blast air and because they would pack together and cause channeling in the blast furnaces. Open-hearth furnaces cannot be fed with refining ore powders either, because these powders would be carried away by the stack gases, and part of these powders would penetrate into the heat-resistant lining of the furnace, thereby rendering the lining fusible.

The agglomerating processes known and used hitherto can be divided into two groups.

(a) During thermal agglomeration the ore powders are mixed with coke powder and burned until the particles are sintered, or pellets, bricks and/or briquettes are pressed formed from the ore powder and then these bodies are baked.

(b) During cold agglomeration, the ore powder is agglomerated with the aid of pressure, with or without a binding material.

Shrinking agglomeration (Dwight-Lloyd, Greenewalt etc. processes) is economical for blast-furnace ores only where the necessary coke powder is available as in inexpensive waste material and is not economical for agglomerating the refining ores necessary for steel production because it reduces part of the Fe_2O_3 content of the ore to FeO so that the employment of the refining ore in a larger quantity becomes necessary. The apparent density of ore sintered in this way is usually lower than that of the open-hearth slag; consequently it floats on the surface of the slag and is less readily refinable.

The most important obstacle to the general use of the cold agglomerating process is the lack of a suitable binding material. For briquetting iron ores, an inexpensive, quick setting and rapidly solidifying binding material having an adequately high strength is necessary. The binder must contain no contaminants harmful from the iron-metallurgy point of view, or must contain any such contaminant only in small amounts. The Portland cements or Portland slag cements can be used for this purpose only to a very limited degree because, on the one hand they have a high silicic-acid content, and on the other hand, they set and, solidify slowly 4-6 hours), so that the briquettes do not have sufficient strength to stand up to the stresses of treatment and the transport even after several hours.

The present process is based on the discovery that from most of the iron ores to be smelted a hydraulic binding material satisfying the above requirements can be produced if an aluminum compound and a calcium com-

2

pound (e.g. bauxite and limestone) are added in a quantity depending on the composition of the impurity.

A hydraulic binding material suitable for agglomerating iron ores and usable for construction is produced according to the invention by calcinating a mixture of compounds containing lime and/or aluminum with a crude, enriched or calcinated ore containing iron, in a manner known in the manufacture of cement, to cement clinkers, then producing from it a mixed comminuted product with addition to limestone to limestone or some other material for adjusting the setting time.

According to the invention the individual additive agents can be used in such ratio that, in the finished cement clinker, the quantity of the aluminum oxide and iron oxide is higher than twice the silicic-acid content, and the amount of the aluminum oxide is, at the maximum, one-and-a-half times greater than that of the iron oxide.

The agglomeration of the by-products, droppings, alloying elements and other iron-containing additives used in the production of iron and steel can be accomplished with the aid of the hydraulic binding material described above.

According to the invention, carbon (coke, coal etc.) can be added to the agglomerated ore.

It is advantageous to add the bauxite and the limestone in a quantity varying within the limits calculated on a stoichiometrical basis. The mixture thus obtained may be ground to a fineness on the order of that employed in the cement industry and then can be sintered in a rotary furnace. The hydraulic binding material is obtained after adding limestone in a quantity ranging from 1 to 5% by weight or adding some other material capable of regulating the setting time.

It is advantageous to establish the quantity of the iron ore, aluminum and calcium compounds (bauxite and limestone) so that the composition of the baked clinker remains within the following values:

	Percent
SiO_2 -----	4-12
Al_2O_3 -----	8-21
Fe_2O_3 -----	13-33
CaO -----	40-50

This composition is characterized by the fact that the silicate ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) of the binding material is smaller than 0.5 and its aluminate ratio ($\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$) is smaller than 1.5. The process according to the invention can be carried out, accordingly, by employing the individual additive agents in such a quantitative ratio that, in the finished cement clinker, the total quantity of aluminum oxide and iron oxide exceeds twice the quantity of silicic acid, and the quantity of aluminum oxide does not exceed 1.5 times the quantity of iron oxide.

The binding material thus prepared is mixed with the ore to be agglomerated in a quantity depending on the particle size of the ore and is moistened to produce a state corresponding to that of damp soil; then it is pressed into briquettes. The resulting ore concrete can be transported after two hours, and can be fed after 24 hours into a blast furnace or an open-hearth furnace. The fine ore powders can be agglomerated also by pelleting, whereby the mixture of moistened ore powder and the binding material is formed into balls in a rotary drum, or by rolling the pulverulent mixture on a tray.

Thus the process of ore agglomeration is, in effect, the production of ore concrete. The expenses of invest-

3

ment and production are considerably lower than in case of the pyrometallurgical agglomerating processes. A great advantage of the briquetting or pelleting lies in the fact that other components, including even a smaller or larger part of the necessary furnace coke, can be added to the ore to be agglomerated in the form of a cheap coke powder, hence the production of the so-called "furnace-mixture" is, in the majority of cases, concluded with the agglomeration step.

The process according to the invention renders possible the production of a cheap binding material, because, on the one hand, the binding material is produced from the iron ore which anyway would be fed into the furnace, and, on the other hand, the quantity of the limestone to be supplied additionally to the furnace can be

4

In Table 2 the quantities of the individual components necessary for the production of the binding material are given.

In Table 3 the composition of the baked clinker is given, without the limestone that may be added for regulating the setting time.

Table 4 lists the calculated mineral compositions, while in Table 5, the silicate ratios ($\text{SiO}_2/\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) and aluminate ratios ($\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$) are shown. The designation C_4AF represents tetracalcium aluminoferrite ($\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$); C_2F , CS and C_2S are calcium ferrite, calcium silicate and dicalcium silicate, respectively.

In Tables 2 to 5, in the first column the denominations of the iron ores are identical with those given in Table 1.

Table 1

[Percent by weight]

Denomination	Fe_2O_3	SiO_2	Al_2O_3	CaO	CO_2	H_2O	Balance (impurities)
1. Magnetite from Kiruna	80.00	3.50	2.24	9.20	-----	1.07	3.99
2. Hematite from Krivoi-Rog (Soviet Union)	74.30	16.00	2.87	0.28	-----	4.00	2.55
3. Iron ore from Chattanooga District (U.S.A.)	48.00	7.28	3.14	21.40	16.50	2.14	1.64
4. Hematite from Alabama (U.S.A.)	48.00	10.84	2.88	19.73	15.00	2.00	1.55
5. Siderite from Steyr Erzberg (Austria)	47.20	5.50	1.57	8.99	32.60	-----	4.01
6. Iron ore from Salzgitter Haverlachwiese (Germany)	49.30	24.80	9.20	4.90	4.20	7.10	9.50
7. Basic minette from Anderney (France)	44.00	8.20	4.25	17.20	15.70	7.50	3.15
8. Raw iron ore from Oxford (Great Britain)	34.30	10.20	7.60	12.20	10.00	15.60	10.10
Bauxite having a good alumina/silica ratio	18.50	3.50	56.00	0.30	0.10	16.50	5.00
Bauxite having a poor alumina/silica ratio	20.00	10.00	50.00	0.30	0.10	10.00	9.60
Limestone	0.17	0.14	0.11	54.94	43.35	-----	1.29

reduced by the amount of limestone added to the binder; thus the expenses connected with the use of limestone for the binder can be recovered.

A further advantage of the process is that bauxites having an alumina/silica ratio ($\text{Al}_2\text{O}_3/\text{SiO}_2$) smaller than 5 and not usable in the Bayer process for the production of aluminum can be employed for cement production; this raw material is available in very large, unmarketable quantities in the waste heaps of bauxite mines. Additionally, in the furnace any iron content of the bauxite is utilized while the aluminum-oxide content of the bauxite improves the blast-furnace cinder. The feeding of good-quality bauxite is reasonable only in case of ores having a high content of free silicic acid.

If the powdery ore can be easily screened, that part of the powder which has a particle size smaller than 1 mm. is utilized to reduce the expense of grinding. Thanks to the high iron-oxide content of the raw material, the sintering can be carried-out at temperatures not exceeding 1300° C. The result of the low sintering temperature is that the output of the rotary furnace (or, alternatively, a shaft or cupola furnace) increases as compared to the yield of a cement furnace, for sintering Portland-cement clinker at a temperature of about 1750° C. so that the heat-energy requirement of the baking is lower.

Besides its suitability in the metallurgy of ferrous metals, the process according to the invention can be employed also in other fields, such as in structural engineering, mining or deep drilling.

Most iron-ore types are suitable for the production of this binding material but it can be produced at the lowest cost from basic iron ores containing calcium and only a small quantity of iron.

In the following tables data concerning the composition of eight known iron ores as well as of the binding material produced from these ores are summarized.

In Table 1 the compositions of eight different iron ores, of a good bauxite having an alumina/silica ratio greater than 5 and a poor bauxite having an alumina/silica ratio ($\text{Al}_2\text{O}_3/\text{SiO}_2$) lower than 5, as well as of a limestone of better quality, are given.

Table 2

[Composition of the raw material, percent by weight]

Ore	Bauxite		Limestone
	Good	Bad	
1. 13.20	-----	24.00	57.80
2. 16.90	-----	21.10	62.00
3. 28.70	-----	21.30	50.00
4. 28.50	-----	21.50	50.00
5. 27.40	-----	20.60	52.00
6. 30.00	10.00	-----	60.00
7. 29.30	-----	18.70	52.00
8. 30.00	-----	14.00	50.00

Table 3

[Composition of the binding material, percent by weight]

	SiO_2	Al_2O_3	Fe_2O_3	CaO	Balance (impurities)
1.-----	4.62	18.25	23.00	46.80	2.33
2.-----	7.82	16.80	25.00	48.30	2.08
3.-----	6.75	17.62	26.25	47.60	1.78
4.-----	8.17	17.15	26.30	46.60	1.73
5.-----	6.25	17.18	25.88	47.75	2.94
6.-----	12.05	12.90	20.90	48.83	5.27
7.-----	7.05	16.00	25.10	48.70	3.15
8.-----	8.45	15.28	23.30	46.80	6.17

Table 4

[Mineral composition, percent by weight]

	C_4AF	Ca	C_2F	C_2S	CS	Balance (impurities)
1.-----	87.00	-----	-----	7.40	3.96	1.64
2.-----	76.00	1.33	-----	17.00	3.62	2.05
3.-----	79.60	1.41	-----	12.50	4.65	1.84
4.-----	79.60	0.06	-----	10.35	8.15	1.84
5.-----	81.60	-----	-----	12.68	3.56	2.16
6.-----	61.40	-----	1.14	27.55	4.82	5.09
7.-----	76.20	-----	-----	20.55	-----	3.25
8.-----	70.80	0.71	-----	18.90	3.64	5.95

Table 5

[Mineral composition, percent by weight]

	Silicate ratio	Aluminate ratio
1-----	0.098	0.652
2-----	0.187	0.672
3-----	0.154	0.672
4-----	0.188	0.652
5-----	0.142	0.638
6-----	0.317	0.617
7-----	0.171	0.638
8-----	0.219	0.655

The process according to the invention is illustrated by the following example.

A mixture consisting of 18.4% of iron ore from Krivoj-Rog, 17.6% of bauxite of poor quality and 64% of limestone is baked. In order to increase and render uniform the setting time, 4% of limestone is added and the whole mass is ground to the fineness of cement.

The breaking strength of a concrete composed of the material thus obtained amounted after 24 hours to 145 kg./cm.², after 7 days to 350 kg./cm.², and after 28 days to 469 kg./cm.².

Upon the addition of 5-6% from the thus-prepared binding material to a powdery iron ore screened on a 2-mm.-mesh screen, the properties of the obtained binding material considerably exceed the requirements of the metallurgical industry.

What I claim is:

1. A process for producing a hydraulic cement, comprising the steps of admixing lime, silica, alumina and iron oxide, the weight ratio of the silica content to the sum of the alumina and iron oxide contents being less than about 0.5, the weight ratio of the alumina content to the iron oxide content being less than about 1.5; heating the resulting mixture at a temperature sufficient to convert same into a cement clinker consisting in major part of a tetra-calcium alumino-ferrite; comminuting the clinker thus produced; and admixing with the comminuted

clinker a substance capable of modifying the setting rate of the cement.

2. A process for producing a hydraulic cement, comprising the steps of admixing lime, silica, alumina and iron oxide to produce a mixture, said mixture consisting by weight substantially of 4 to 12% silica, 8 to 21% alumina, 13 to 33% iron oxide, and 40 to 50% lime, the weight ratio of the silica content to the sum of the alumina and iron oxide contents being less than about 0.5, the weight ratio of the alumina content to the iron-oxide content being less than about 1.5; heating the resulting mixture at a temperature sufficient to form a cement clinker therefrom, and comminuting the clinker thus produced.

3. A sintered cement consisting substantially of 4 to 12% silica, 8 to 21% alumina, 13 to 33% iron oxide and 40 to 50% lime, the weight ratio of the silica content to the sum of the alumina and iron-oxide contents being less than about 0.5, the weight ratio of the alumina content to the iron-oxide content being less than about 1.5.

References Cited by the Examiner

UNITED STATES PATENTS

806,161	12/05	Michaelis	106-100
1,586,099	5/26	Martin	106-100
1,594,178	7/26	Kuhl	106-100
1,994,379	3/35	Williams et al.	75-3
2,134,103	10/38	Collord	75-3
2,271,276	1/42	Rolfsen	106-100
2,696,432	12/54	Davis	75-5
2,995,438	8/61	Subervie	75-5

OTHER REFERENCES

The Chemistry of Cement and Concrete, Lea and Desch, Edward Arnold Ltd., London, 2nd Edition, 1956, pages 58, 59, and 278.

TOBIAS E. LEVOW, *Primary Examiner*.

JOSEPH REBOLD, *Examiner*.