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(54) **Direct reduction process using shaft furnace.**

(57) A direct reduction process using a vertical furnace is disclosed in which iron ore (including lump ore and pellets) charged in the furnace is previously treated with a cement coating applied to the surface of the ore. The cement may be Portland cement and is used in a quantity within a predetermined range.

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DIRECT REDUCTION PROCESS USING SHAFT FURNACE

The present invention relates to a method for use with a direct reduction process to reduce or prevent the occurrence of clustering of material, such as iron ore, in the furnace, thereby to improve efficiency and stability of the operation.

The direct reduction process is suited to small scale production and is very flexible so that coal, natural gas, or the like can be used as the reduction agent, and therefore, the process is being increasingly adopted.

The systems now predomindating in the direct reduction process are the Midrex system and the HyL system which use as a reduction furnace a vertical furnace, typically a shaft furnace. As charge material for the shaft furnace, iron ore in massive form (lump ore) or pellets (powder ore compressed in ball form) is used, but it is known that these materials, when treated in a high temperature reduction atmosphere within the shaft furnace, often present a phenomenon called clustering and the efficiency of the operation is thereby greatly impaired. Clustering is a phenomenon in which masses of lump ore or pellets fuse and adhere to each other and become large size masses due to the high temperature reduction atmosphere within the shaft furnace. Once such a phenomenon develops, discharging of the reduced iron from the bottom of the furnace becomes difficult, as a bridging phenomenon, called "hanging", of the charged ore and other material hereinafter referred to as "charge") occurs within the shaft furnace, whereby the steady descent of the charge is impaired and the operating efficiency is greatly decreased. For this reason, during ordinary operation of the shaft furnace, the maximum reduction temperature is kept relatively low to prevent the occurrence of clustering, and therefore, one cannot increase the reduction rate to the full extent and improve productivity to a satisfactory degree.

For example, the maximum reduction temperature is determined by the temperature of the reduction gas blown into the shaft furnace, and the temperature of the reduction gas delivered from an ordinary reduction gas generating apparatus is generally rather higher than the above mentioned maximum reduction temperature. Therefore, the reduction gas must be cooled down to the mentioned maximum reduction temperature before reaching the furnace and this causes a loss of thermal energy. The problem is especially serious because there is currently being studied a melt reduction process for producing reduction gas at an extremely high temperature and the loss of heat energy incurred by lowering the temperature of this reduction gas to the mentioned maximum reduction temperature would be even greater.

As an example, a typical maximum reduction temperature of a shaft furnace currently in operation is approximately 830°C in the case of the Midrex system and most furnaces of other systems are operated below that temperature. On the other hand, the operating temperature of a reformer apparatus for manufacturing the reduction gas is approximately 1100°C and this apparatus produces reducing gas at a temperature of approximately 970°C. Therefore, the gas when blown into a shaft furnace must be cooled down to 850 - 900°C, and thus, heat loss corresponding to the temperature difference of 100°C is incurred.

In the case of the melt reduction process, since the reduction gas is manufactured at a temperature above the melting point of metallic iron, the temperature of the gas generated in this system sometimes becomes as high as approximately 1500°C, and in the case where a shaft furnace is employed as its preliminary reduction furnace, the reduction gas must be cooled from approximately 1500°C to around 850 - 900°C and the heat loss thus caused is very great.

Further, it has theoretically been established that the reduction reaction rate of the ore material is increased 1.3 times by a rise of 100°C in the operating temperature. If such a raised temperature is utilized to the full for improving productivity, an increase of 30% in productivity will be achieved.

In the present state operations are being conducted with the reduction temperature unavoidably kept rather low, because, if the reduction temperature is raised, clustering occurs as previously described and thereby the stability and efficiency of the operation is greatly impaired.

Such being the case, studies have been advanced in some quarters to raise the reduction reaction temperature while preventing the formation of clusters. According to the method disclosed in Japanese Patent Publication No 59-10411 (1984), for example, water solution containing $Ca(OH)_2$ or $Mg(OH)_2$ is attached to material iron ore and then the material is heat treated so that a film composed of CaO or MgO is formed on the material according to the following reaction thereby to prevent the clustering

$Ca(OH)_2$ - $CaO + H_2O$

$Mg(OH)_2$ - $MgO + H_2O$.

However as will be made clear in the later description of the preferred embodiment, no satisfactory cluster preventing effect can be obtained through this method.

The present invention under the above described circumstances reduces or eliminates the difficulties encountered in the conventional reduction process.

It is accordingly a primary object of the described embodiment to provide a direct reduction process wherein the occurrence of clustering of the ore in the reduced iron manufacturing process through the use of a vertical shaft will be effectively reduced or prevented and improvement of stability in the operation will thereby be achieved and also the reduction temperature can be raised and thereby the reduction efficiency will be improved and the heat loss will be decreased.

The direct reduction process according to the present invention consists in the application of cement to the surface of iron ore material (including lump ore and pellets) before the same is charged in a direct reduction vertical furnace.

As previously described, the reduction temperature used in the direct reduction process in a vertical furnace is determined by the temperature at which clustering occurs. The clustering temperature, when iron ore is used as the material, depends on such factors as grade of iron and composition of gangue, and, when pellets are used, depends on the basic components thereof, ie, calcium compounds and magnesium compounds (CaO,

$Ca(OH)_2$, $CaCO_3$, $CaCO_3.MgCO_3$), etc. The composition of lump ore cannot be changed artificially; it has properties and composition peculiar to its place of origin, and the clustering temperature is determined accordingly. In the case of pellets, the clustering temperature is changed by the kinds and quantities of the additives and also by the firing temperatures and other factors. But, as the iron ore material for the direct reduction (the method in which iron after being reduced is melted in an electric furnace), high grade iron ore is originally selected for economies of operating cost of the electric furnace. Therefore, there is little room for adjusting the clustering temperature by changing the kinds and quantities of the additives and other factors. In this connection, it has already been established that the clustering temperature can be raised for pellets by adding some limed minerals thereto so that the ratio CaO/SiO_2 in the ore, ie, the basicity, may be increased. But this method lowers the grade of iron. On the other hand, it is said that the required grade of iron as raw material for direct reduction process is "67% at the lowest". With such a restriction, if limed mineral is to be added, there is naturally a limit in the quantity to be added and therefore occurrence of the clustering cannot be effectively prevented.

The present invention shows that, if the surface of the iron ore material is covered with a certain amount of cement, the occurrence of clustering can be prevented very effectively and thus the reduction temperature can be raised considerably.

The reason why the above effect is obtained can be considered like this. It is considered that the fusion between pieces of the iron ore that occurs at a late stage of the reduction of the iron ore is due to diffusion among particles of iron metal or entanglement of whisker-like projections or due to fusion welding by low melting point slag which is produced at that time. Covering the surface of the iron ore with cement prevents direct contact between the pieces of iron ore, whereby the diffusion and sintering which is regarded as the cause of formation of the clusters at the contacting surfaces is prevented. Hence clustering is prevented.

The preferred quantity of cement for effectively preventing clustering is within the range of 0.05 to 1.0% by weight of the iron ore material. If it is less than 0.05% by weight, the clustering preventing effect is not well exhibited, and if it is more than 1.0%, the cement coating tends to suppress the reduction reaction itself. But if the cement deposit quantity is set within the range of 0.05 to 1.0% by weight, the clustering can be effectively prevented without supressing the reduction reaction, and as a result, the reduction temperature can be raised and the reduction effect can thereby be greatly improved.

There is no specific restriction as to the kinds of cement to be used. All kinds of cement, such as Portland cement, hydraulic cement, and natural cement, can be used. From the point of view of adhesive strength to the iron ore, however, normal Portland cement, high early strength Portland cement, and high strength Portland cement are preferred which have higher hydraulic property, contain large amount of the compound ($3CaO.SiO_2$) show a high degree of hydration reaction, and in addition are readily available at low cost. Also there is no restriction as to the method of applying the cement to the surface of the material ore. As the commonest examples, the methods as indicated in Figs 1 and 2 (each being a schematic process chart) may be mentioned.

That is, Fig 1 shows a method in which iron ore material O is dropped from above to a bucket conveyer 2 dipped into a tank 1 of an aqueous solution of cement so that the cement solution C is applied to the surface of the ore, the iron ore material O is then conveyed upward from the cement solution tank 1 and in succession is sent through a hopper 3 to a drum type drier 4 to be dried and burned therein (4a in the drawing denotes a screen, fine particles of the iron ore material passing through the screen 4a are sent back as recovered ore for reuse).

Fig 2 shows a method in which the iron ore is burned in a rotary kiln 5 and sent onto a screen conveyer through a cooler 6 whose outlet temperature is set at about 100°C, and, on the conveyer 7, the iron ore is coated on its surface with cement solution C coming from a cement solution preparing tank 8 through a pump 9 and sprayed thereto by a sprayer 10, and the moisture is removed by evaporation caused by the heat retained in the iron ore (about 100°C). 11 in the drawing denotes a cement solution recovery tank and 12 denotes a drying chamber which is provided when necessary.

BRIEF DESCRIPTION OF THE DRAWINGS

Figs 1 and 2 are explanatory drawings exemplifying methods for applying a cement coating to the iron ore;

Fig 3 is a graph showing the relationships between reduction temperatures and the cluster factor for various iron ore pellets used; and

Fig 4 is a graph showing the relationship between the quantity of cement coating and the cluster factors.

In an example of the method of the invention, iron ore pellets (approximately 500 g) are put in a basket and dipped in an aqueous solution of cement of 20% by weight (hereinafter to be written simply as %) for one - two seconds, are taken out and dried by a drier at 110°C for three hours so as to be dehydrated.

Results of chemical analyses of the pellet before and after the above mentioned treatment are as shown in Table 1.

Table 1
Chemical Analyses (%)

Pellet	T.Fe	FeO	CaO	SiO_2
Before Coating	67.54	1.34	0.04	0.68
After Coating	67.30	0.93	0.21	0.71

As is apparent from Table 1, the total quantity of CaO and SiO_2 in the pellet was increased by 0.2% by the cement coating treatment. An increase of CaO and SiO_2 of such a degree does no substantial harm to the grade of the pellet as an iron source for a direct reduction process.

Then clustering evaluation tests were conducted using the above mentioned two kinds of iron ore pellets in the following manner.

That is, a reduction gas (at 910^{o}C) of the composition as shown in Table 2 was prepared on the assumption that denatured natural gas would be used as the reduction gas, and each sample of the above described pellets of 500 g in weight was charged in to a reaction tube of 75o x 165 l (mm) (wherein the highest layer of the sample reached the height of approximately 50 mm) and subjected to a reduction reaction at a temperature of 910^{o}C for three hours with a load 2 kg/cm^2 applied thereto from above. The pellets were encouraged to fusion weld to each other by the pressure from above. After the reduction ended, the sample was cooled, taken out, and put in a cylinder of 120o x 700 l (mm) and rotated at 30 rpm for five minutes. Then the sample was taken out of the cylinder and the cluster factor (ie the ratio by weight of the clusters formed by fusion welding between two or more pellets to the total weight of the pellets) was determined on the sample. The results are as shown in Table 3.

Table 2

Gas Composition	H_2	CO	CO_2	CH_4
%	55	36	5	4

Table 3

	Shrinkage Factor (%)	Cluster Factor (%)	Rate of Reduction (%)	Rate of Metallization (%)
Untreated	33.75	67.89	97.96	97.60
0.2% Cement Coated	27.11	0	98.88	98.63

As is apparent from Table 3, the shrinkage factor was 29% and improved by 4% as compared with 33% of the untreated sample, and as to the cluster factor, while the untreated sample showed the factor as high as 67.89%, the cement-coated sample showed zero and no clustering was produced. Further, the rate of metallization was improved from 97.6% to 98.6%.

Then, using the cement-coated pelleted obtained in the above described manner, the conditions of the sample after a reduction reaction at raised temperatures to 960°C and 1000°C were investigated and the results as shown in Table 4 were obtained.

Table 4

Cement Deposit (%)	Reducing Temp (°C)	Shrinkage Factor (%)	Cluster Factor (%)	Pressure Loss (%)
0.2	960	31.37	0	8.0
0.2	1000	36.53	0	10.0

As is apparent from Table 4, the sample treated with the cement coating, although the reduction temperature was raised to 960°C, showed a lower shrinkage factor than the untreated sample (33.75%, Table 3), reduced at 910°C, and no clustering was observed. When the reduction temperature was raised to 1000°C, the shrinkage factor was indeed increased but increase in the pressure loss was very small and gas permeability was substantially unaffected and the cluster factor still indicated zero.

The reference photographs 1 - 4 show the external appearances of the pellets after the above described clustering tests, in which the reference photograph 1 shows the untreated pellet processed at the reduction temperature of 910°C and the reference photographs 2 - 4 show the cement-coated pellets processed at the reduction temperatures of 910°C, 960°C, and 1000°C, respectively. Also from these photographs, the excellent clustering preventing effects in the pellets provided with the cement coating treatment can be readily confirmed.

In order to compare the clustering preventing effects of the pellets with CaO attached to the surface thereof as disclosed in previously mentioned Japanese Patent Publication No 59-10411, pellets with added lime stone, and cement-coated pellets according to the present invention, were prepared to investigate the relationship between reduction temperatures and cluster factors of the pellets variously treated as described above and the results are shown in Fig 3.

As is apparent from Fig 3, although the pellets with added lime stone and pellets with CaO attached to the surface thereof showed 0% cluster factor in the case of 910°C of reduction temperature, when the reduction temperature was raised to 1000°C, the cluster factor increased sharply. On the contrary, the cement-coated pellets showed 0% cluster factors even when the reduction temperature was raised to 1000°C, whereby the excellence of the present invention can be confirmed.

Fig 4 shows the results of investigation of relationship between the quantity of cement coating and the cluster factor at the reduction temperature of 1000°C corresponding to the previously mentioned test, from which it is known that clustering can be fully prevented at this reduction temperature by the cement coating of more than 0.05%. However, if the quantity of cement coating exceeds 1.0%, a decrease in the reduction effect and rate of metallization due to lowering of iron content in the iron ore material becomes noticeable. Therefore, the maximum limit of the cement coating quantity is set at 1.0% in the present invention.

The present invention constituted as described above has effects in brief as follows:

(1) By coating with only a small quantity of cement, clustering can be substantially prevented and stability in the operation of a vertical furnace can thereby be improved.

(2) Since the clustering is prevented, the reduction temperature can be raised considerably, to provide an increase in the rate of reduction, a resultant increase in productivity, and further, a reduction in heat loss (ie high-temperature heat quantity) of the reduction gas from a reduction gas generating apparatus.

(3) Since sufficient effect is obtained by very small

quantity of cement coating, the iron content of the iron ore material is not significantly reduced.

CLAIMS

1. A direct reduction process using a vertical furnace, including the step of applying a cement coating to the surface of iron ore before reducing the iron ore.

2. A direct reduction process according to claim 1, wherein said cement is Portland cement.

3. A direct reduction process according to claim 1 or 2, wherein the quantity of said cement surface coating is 0.05 to 1.0% of the weight of the iron ore.

4. A direct reduction process according to any of claims 1 to 3, wherein said iron ore comprises pellets.

5. A direct reduction process according to any of claims 1 to 4, wherein said vertical furnace is a preliminary reduction furnace used in a melt reduction process.

6. A direct reduction process according to any of claims 1 to 5 in which the cement coating is applied by spraying.

7. A direct reduction process according to any of claims 1 to 5 in which the cement coating is applied by passing the on ore through an aqueous cement solution.

8. Iron ore for use in a direct reduction process coated with cement.

9. Iron ore as claimed in claim 8 in which the cement

surface coating comprises 0.05 to 1% of the weight of the iron ore.

FIGURE 1

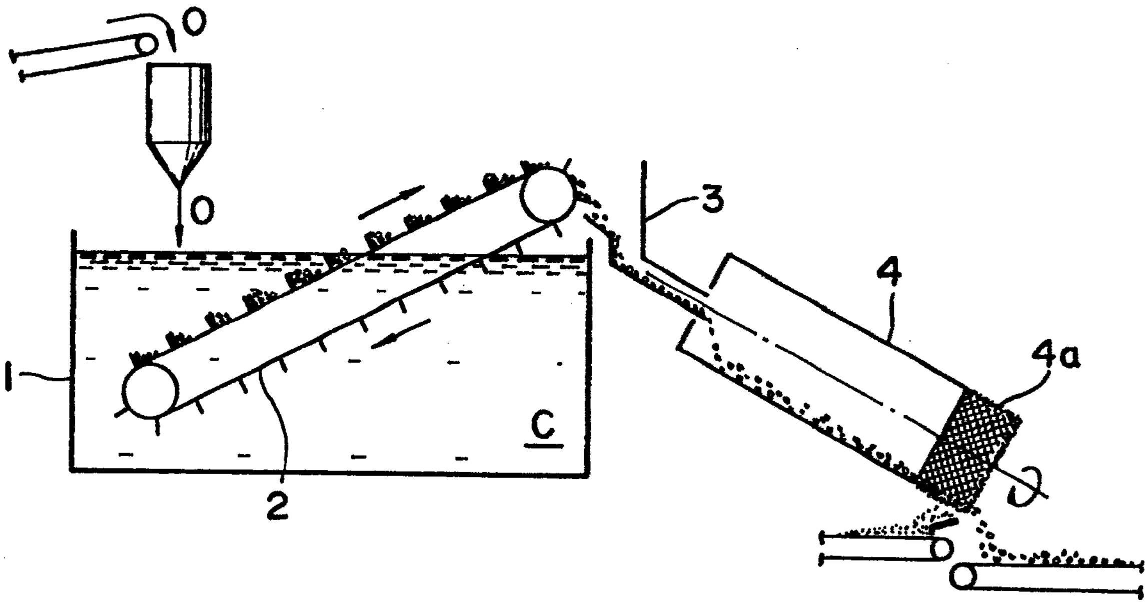


FIGURE 2

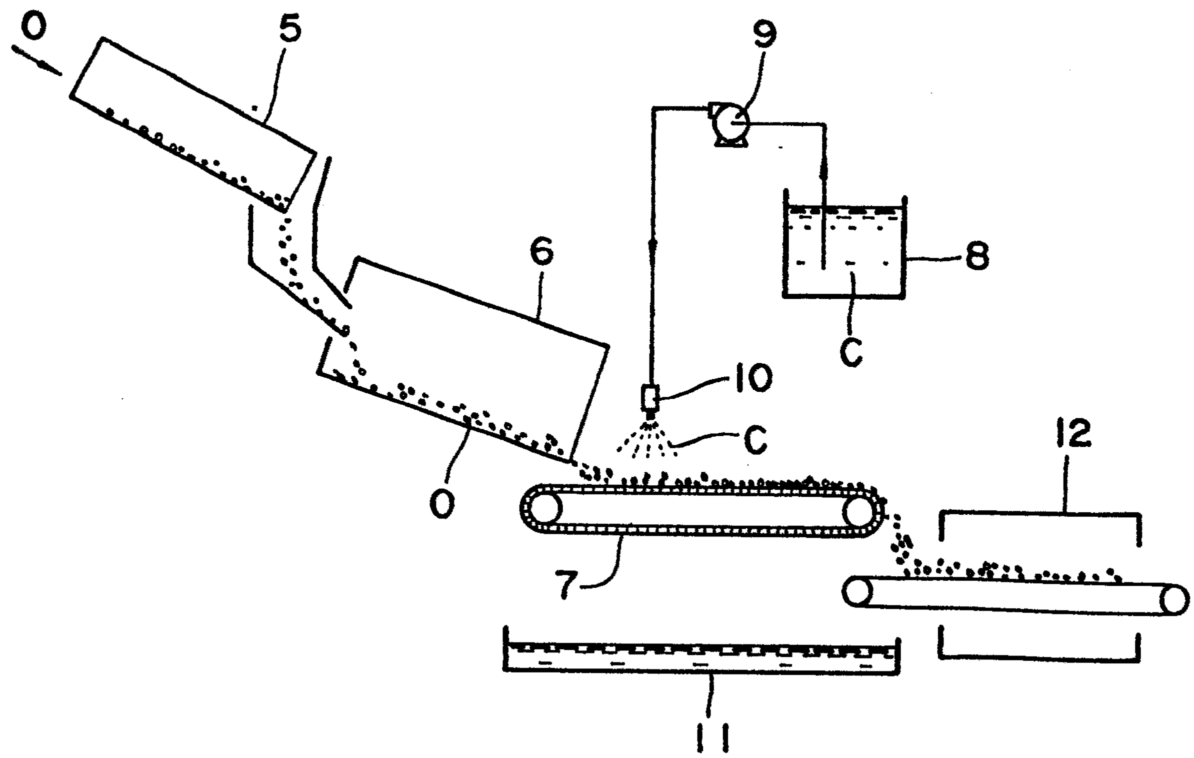


FIGURE 3

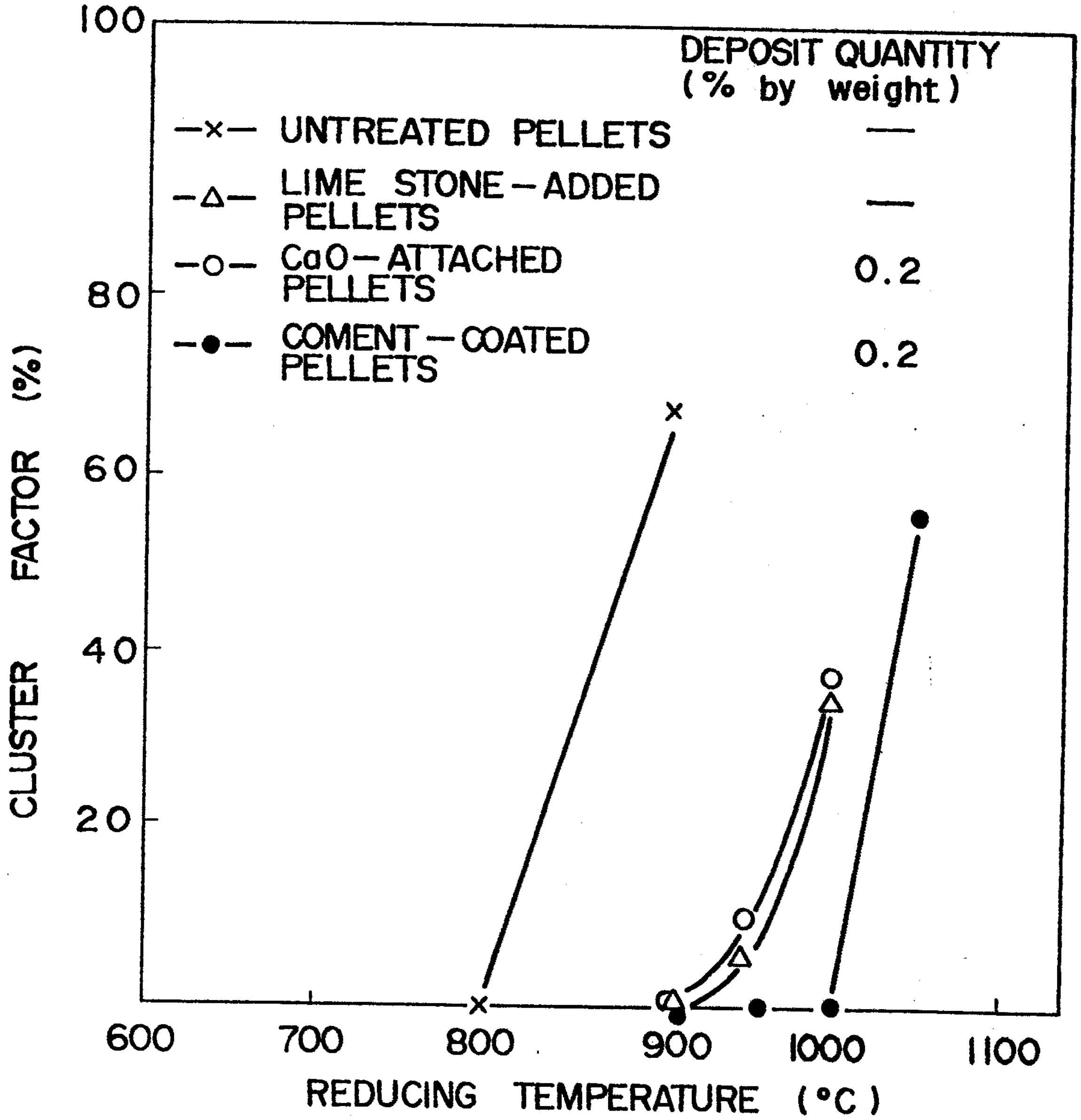
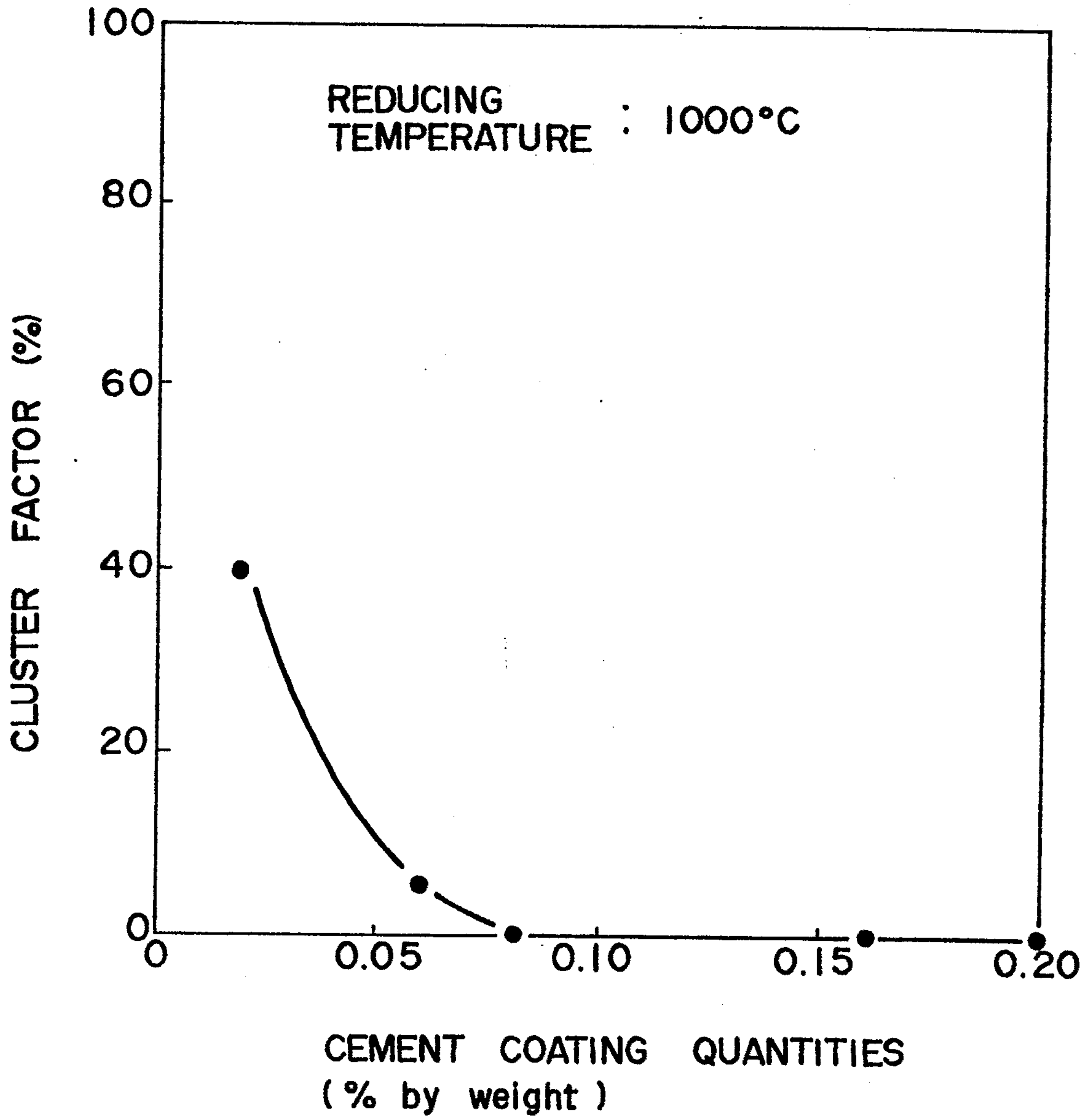

100
80
60
40
20
CLUSTER FACTOR (%)
DEPOSIT QUANTITY
(% by weight)
—×— UNTREATED PELLETS —
—△— LIME STONE—ADDED PELLETS —
—○— CaO—ATTACHED PELLETS 0.2
—●— COMENT—COATED PELLETS 0.2
600
700
800
900
1000
1100
REDUCING TEMPERATURE (°C)

FIGURE 4


REDUCING TEMPERATURE : 1000°C
100
80
60
40
20
0
CLUSTER FACTOR (%)
0
0.05
0.10
0.15
0.20
CEMENT COATING QUANTITIES
(% by weight)

REFERENCE
PHOTOGRAPH 1

REFERENCE
PHOTOGRAPH 2

REFERENCE
PHOTOGRAPH 3

REFERENCE
PHOTOGRAPH 4