

DESULPHURIZATION OF COKE-MIXED IRON ORE PELLETS

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THE AUTHORS have published reports^{1,2} concerning the simultaneous process for making the reduced pellets on the firing stage from the coke-mixed iron ore pellets. From the above experiments almost 90% reduced and strong pellets could be obtained in a short reduction period using the pellets mixed with coke of 20% addition. This method was considered to be effective and economical, but it was liable to form the pellets containing relatively high content of sulphur because of sulphur in the reductant.

With regard to the investigations of desulphurization, almost previous reports have dealt with the process in the course of sintering, while there are very few for the pellets. In U.S.S.R. investigations have been carried out on desulphurization during firing of fluxed iron oxide pellets.^{3,9}

The purpose of this investigation was to obtain an appropriate firing condition, in which sulphur does not remain in the reduced pellets. The pellets were fired at 800-1,200°C in the

nitrogen atmosphere on the basis of our previous good results. The influences due to additive lime, porosity distribution, and reduced layer were investigated and changing composition of the waste gas was also discussed.

2. Experimental Apparatus and Procedures

2-1. Specimens

The composition of the Indian hematite ore used in this experiment is shown in Table 1. As this table shows, this is a hematite ore containing a slightly higher percentage of SiO₂ and Al₂O₃.

The industrial analysis of the used coke is given in Table 2.

TABLE 2
Industrial analysis of the used coke (%)

F. C.	Ash	V. M.	S
87.0	10.5	1.6	0.5

These iron ore and coke were crushed minus 280 mesh size, then the ore was blended with coke in the ratio of 20 per cent. Furthermore, bentonite in the ratio of 2 per cent and optimum moisture of about 10 per cent were added and finally this mixture was made to pellets of 13 mm diameter by hand.

TABLE 1
Chemical analysis of the Indian iron ore (%)

T. Fe	FeO	CaO	SiO ₂	Al ₂ O ₃	P	S
65.36	-	0.12	2.26	2.04	0.032	0.01

2-2. Heating furnaces and heating methods

The furnaces used for firing were an electric mufnal furnace and a horizontal tube silicon carbide-resisting furnace. Firing temperature was up to 1200°C.

Prior to heating, the reaction tube was evacuated to about 10⁻³ mmHg, and then N₂ gas was flowed at rate of 200 ml/min during the experiments. Since there is no oxidation, coke consumption is due to only the oxygen of iron ore. Heating rate was controlled almost constantly at a rate of 10°C/min. After the pellets were held at the firing temperature for a predetermined time, these were cooled to the room temperature rapidly in N₂ flow, and then analysed chemically.

2-3. Measurement of porosity.

To examine the porosity and pore distribution of the pellets, the mercury pressure porosimeter made by CARLO-ERBA Co. was used. The pore radiuses of the pellets can be recorded automatically as a function of exerted pressure by measuring a height of mercury in a capillary, which corresponds to the mercury volume penetrated into the pores of the pellets.

The low pressure piston is actuated by oil pump and the high pressure transmission connecting to mercury is transferred through ethyl alcohol. This device is applicable in the pressure range from 0 to 1000 kg/cm² and radius of the pores up to 75 Å.

2-4. Analysis of sulphur.

The content of sulphur was determined by the method recommended by Analysis Committee of BISRA¹⁰. This method, a combination of combustion and neutralimetry is applicable for sulphur content more than 0.005%. The specimen is heated at high temperature in oxygen flow to change sulphur to SO₂ and then CO₂ is forced to absorb in the aqueous H₂O₂ to change to H₂SO₄, and finally it is titrated with a standard sodium borate solution (N/20).

2-5. Analysis of the waste gases

Analysis of the gases produced in pellet-firing was made by gas-chromatography using SHIMADZU GC-2A. Carrier gas was He and column filler were Molecular Sieve, 5 A, D.O.P. (Dioctyle Phthalate) suitable for sulphur compounds. Sulphur compound was collected in the diatom-earth trap cooled by liquid nitrogen, and then the gas was analysed by gas-chromatography after its temperature increases to the room temperature.

3. Experimental Results and Discussion

3-1. Desulphurization under the vacuum condition

The sulphur content in the coke-mixed pellet is considered to be derived mainly from the coke as shown in the analysis of the specimen. Although the form of sulphur in the common coke is not clear, in the report of Horikawa¹¹, he mentions that more than 50 per cent of sulphur is involved in the carbon as a solid solution, about 20 per cent free sulphur, about 20 per cent sulphide respectively and sulphate is minute. Moreover, Kelley¹² and other investigators^{13,14} found that free sulphur vaporizes easily above its boiling point, 650°C.

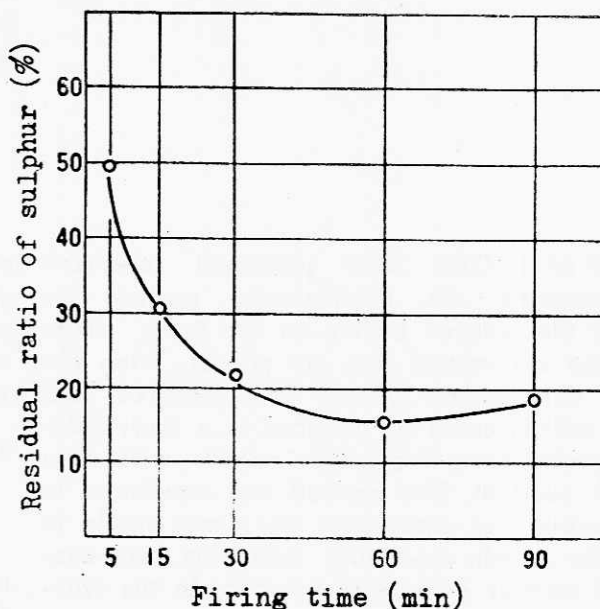


Fig. 1 Desulphurization curve of the coke-mixed pellets treated under vacuum sintering at 900°C

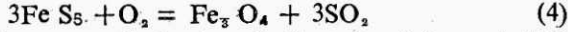
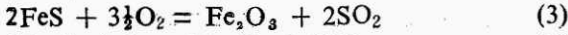
Fig. 1 shows the result obtained in the vacuum condition of 10⁻³ mmHg at 900°C. In this figure, residual ratio of sulphur was calculated as follows,

$$\text{residual ratio of sulphur} = \frac{\text{S\% in the fired pellet} \times \text{weight of the fired pellet}}{\text{S\% in the green pellet} \times \text{weight of the green pellet}}$$

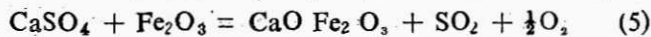
As this figure indicates, more than 80 per cent of sulphur in the green pellets are removed. It is recognized that desulphurization proceeds remarkably in vacuum, and it can be assumed that the sulphur in coke is removed as the gas species such as an elementary or a compound form.

3-2. The effect of addition of CaO and Ca(OH)₂ on the desulphurization.

The mechanism of desulphurization of self-fluxed cinder or self-fluxed pellets is considered as follows.



Moreover, it is found that in firing at 750–1000°C, CaO resulted from decomposition of CaSO₃ becomes CaCO₃ due to reaction with SO₂ and finally it reacts with iron ore as follows,



Therefore, it is considered that calcium ferrite is formed and sulphur is removed as SO₂ in the self-fluxed sinter or self-fluxed pellets containing additive life, while the desulphurization mechanism of sulphur in the coke such as the present work is not clear.

The coke-mixed pellets were fired in the high-alumina crucible under the enveloping condition with CaO or Ca(OH)₂. As shown in Fig. 2 and Fig. 3, the pellets fired at about 900°C led to a good result for desulphurization. In case of addition of Ca(OH)₂ a rather better result was obtained in comparison with that of CaO. This result may be caused by the fact that the evaporating H₂O produced by the thermal decomposition of Ca(OH)₂ brings the outward

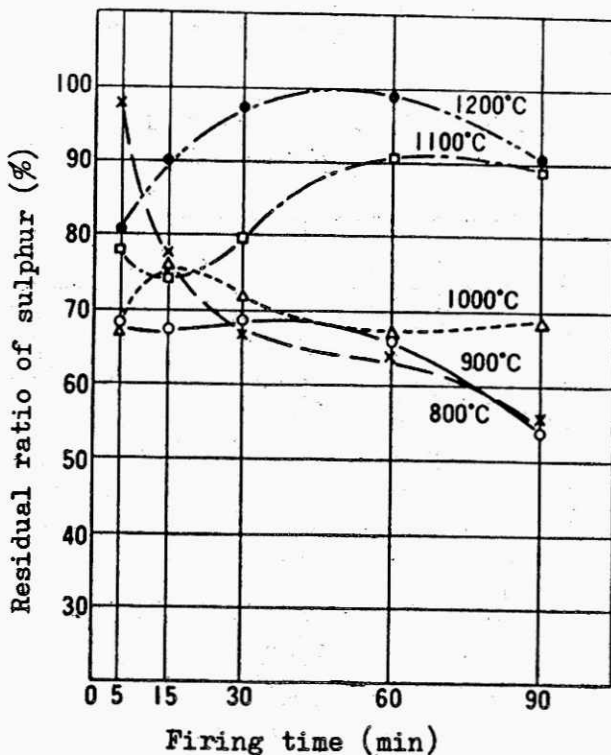


Fig. 2 Desulphurization curve of the coke-mixed pellets covered with CaO

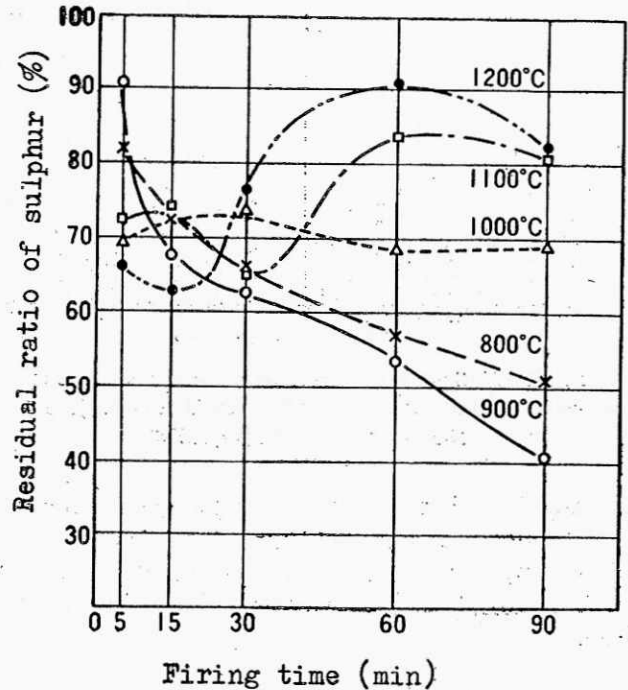
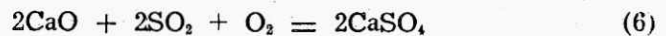


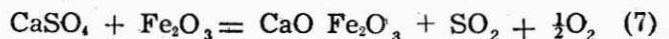
Fig. 3 Desulphurization curve of the coke-mixed pellets covered with Ca(OH)₂

paths for gaseous flow, thus it derives a effective desulphurization. Fig. 4 shows clearly that calcium ferrite is formed above 1100°C on the surface of the fired pellets, whereas there is no identification of CaS because of the minute sulphur content of specimen.

Moreover, in Fig. 2 & 3 in the residual ratio of sulphur increased again more than 1000°C. This result may be explained followingly. The sulphur in the pellets with additive CaO or CaO dissociated from Ca(OH)₂ within a few minutes on heating.

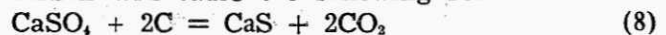


CaSO₄ thus formed is unstable at high temperature, then it combines with ferric oxide in the pellets.



This reaction could be confirmed by the X-Ray diffraction in Fig. 4, and it evolves SO₂. Since this reaction is endothermic, this process proceeds in accordance with rising temperature. On the other hand, the reducing reaction of the pellets will progress remarkably at higher temperature, thus the reduced iron, which is active, easily combines with SO₂ to increase sulphur content in the pellets again.

In the decomposition of CaSO₄, presence of carbon will cause the following reaction.



and as CaS is stable at high temperature, sulphur content in the pellet will be increased. For this

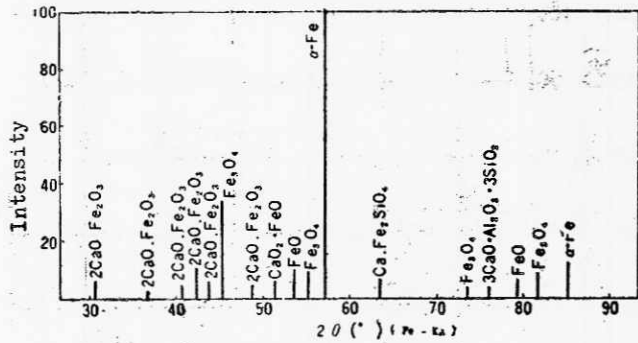


Fig. 4 X-Ray diffraction of the surface of the coke-mixed pellets covered with $\text{Ca}(\text{OH})_2$ in the experiment at $1,100^\circ\text{C}$

reason, CaO that is present outside of the pellets will take place desulphurization did not occur at high temperature. Therefore, it can be considered that desulphurization is caused by the reduced iron.

As the results of this experiment, the desulphurization effect due to the addition of CaO was not so effective in comparison with that of firing in vacuum, specially at higher temperatures.

3-3. Relationship between porosity and desulphurization.

To explain the larger desulphurization ratio at 900°C in the case of CaO addition, porosities of the pellets maintained at the desired temperatures and periods were measured by a mercury pressure porosimeter. The result of the porosity measurement is shown in Fig. 5. When the results of Fig. 5 are compared with those of Fig. 3, it is recognized that there is a correlation or difference between the porosity and desulphurization at above 1000°C and below 1000°C respectively. The better desulphurization in case of firing at 900°C shown in Fig. 5 may be explained by its larger porosity.

Fig. 6 indicates the relationship between the porosity and the degree of desulphurization. From this figure, it is clear that desulphurization is small up to 40 per cent porosity, but above 40 per cent, desulphurization increases markedly.

Fig. 7 is a pore distribution curve of the green pellets mixed with coke and it shows comparatively rough pores. Fig. 8 is a pore-distribution curve of the pellets at 900°C , and it shows a uniform distribution of large and small pores. Fig. 9 is a pore distribution curve of the fired pellets at 1200°C , and it shows abundant fine pores resulted from advanced sintering.

From these results, it is found that the firing, in which uniform pore distribution is obtained, is preferable because of a smooth gas exhaustion out of the pellets.

3-4. The effect of metallic iron and magnetite produced during reduction on desulphurization.

The effects on desulphurization due to magnetite and metallic iron produced during reduction from the coke-mixed hematite pellets were examined.

Fig. 10 shows the desulphurization of the coke-mixed hematite pellets containing an addition of 10% electrolytic iron powder under the condition of 45 minutes holding in N_2 stream.

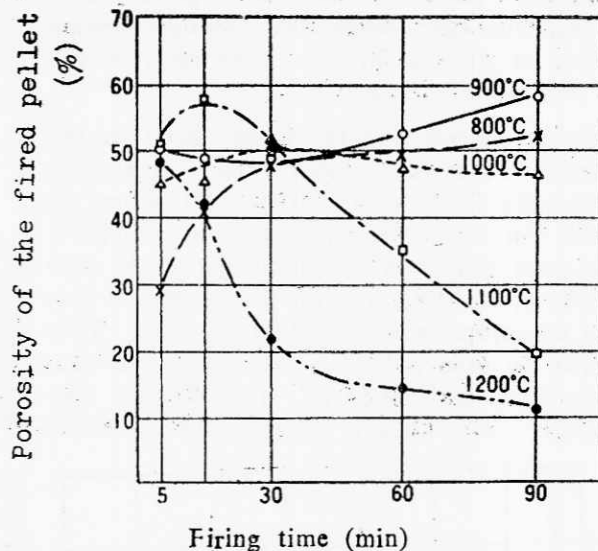


Fig. 5 Porosity of the coke-mixed pellets covered with $\text{Ca}(\text{OH})_2$

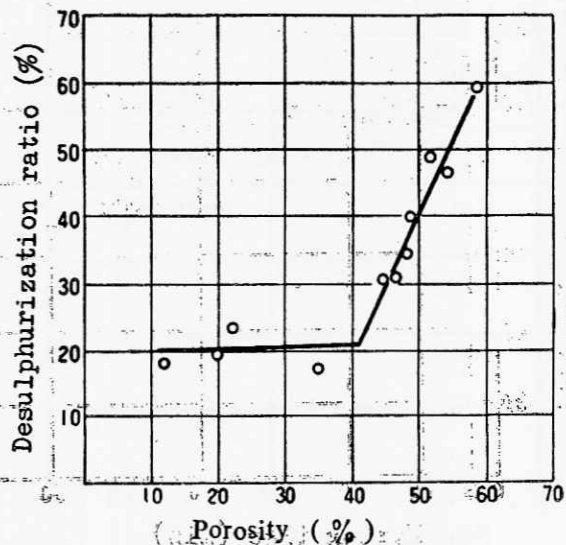


Fig. 6 Relation between porosity and desulphurization ratio of the coke-mixed pellets

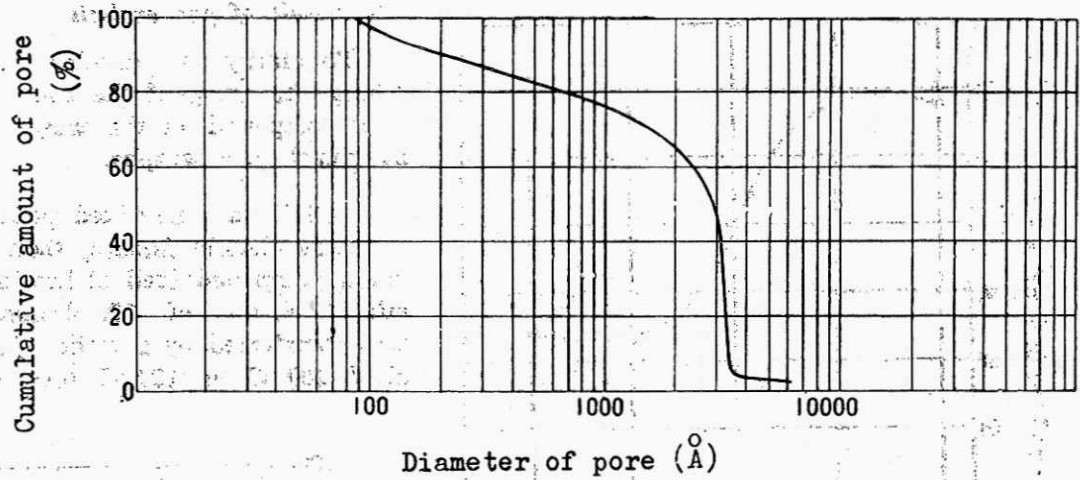


Fig. 7 Porosity distribution curve of the green coke-mixed pellets.

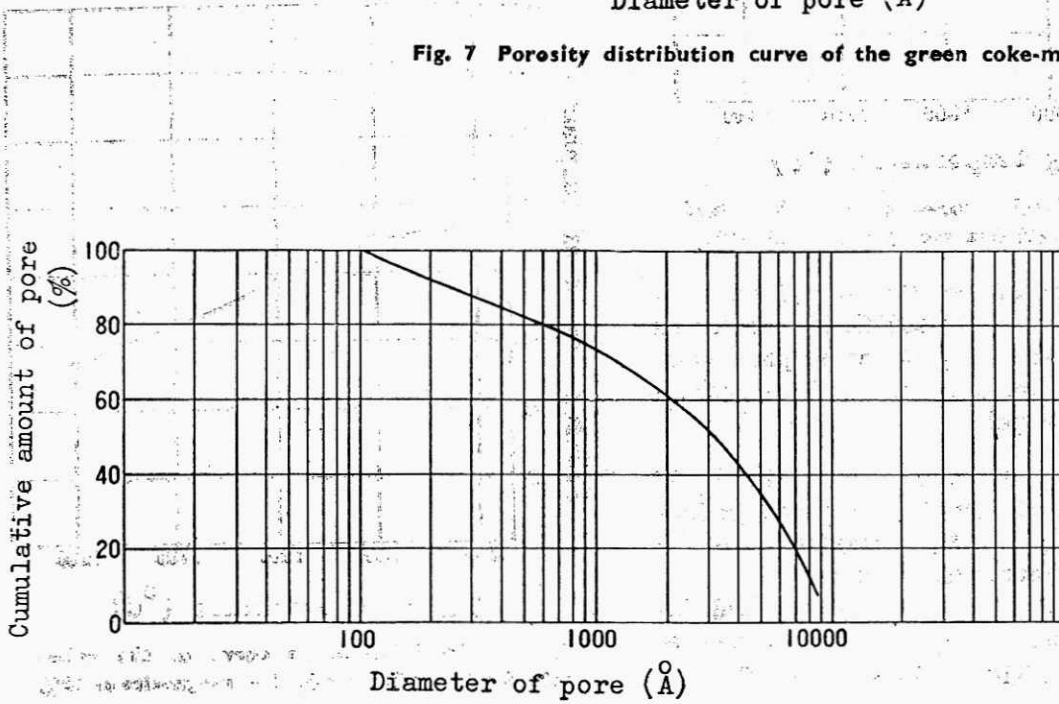


Fig. 8 Porosity distribution curve of the coke-mixed pellets fired at 900°C.

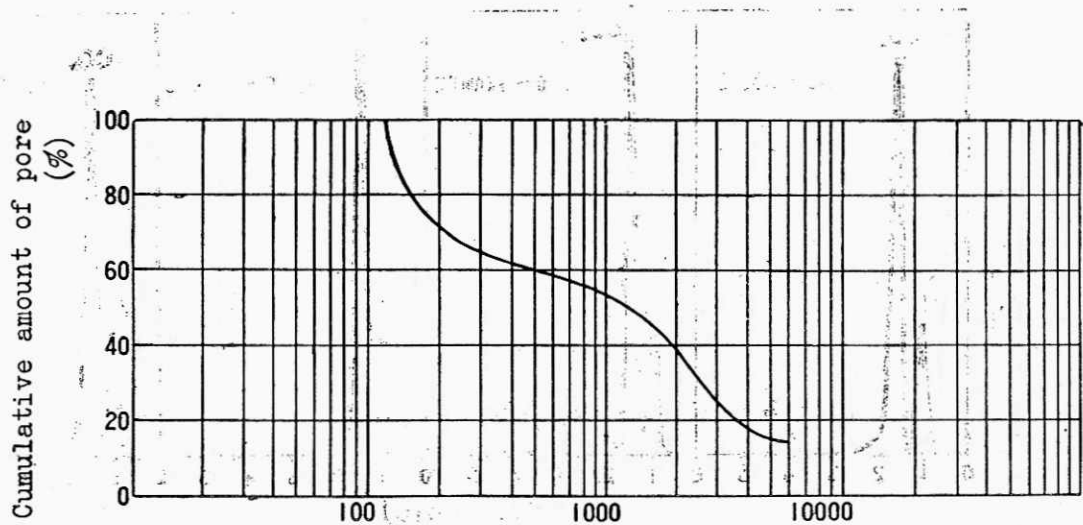


Fig. 9 Porosity distribution curve of the coke-mixed pellets fired at 1200°C.

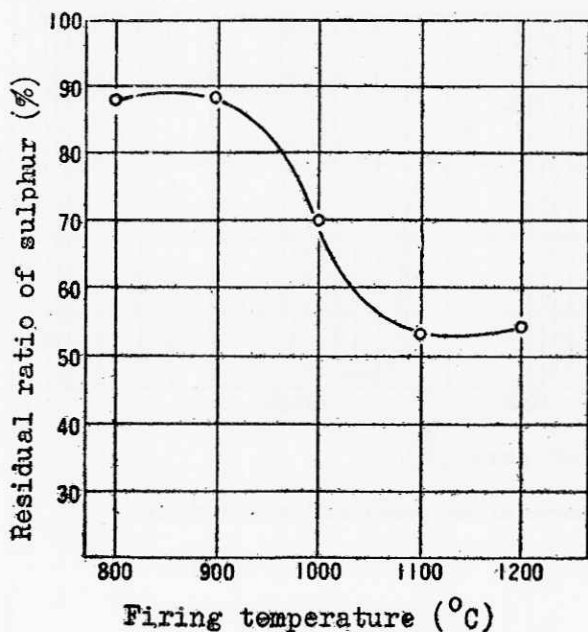


Fig. 10 Desulphurization curve of the coke-mixed pellets with an additive metallic iron of 10%.

In case of presence of metallic iron, desulphurization does not occur until 900°C. It is assumed that the vapourized sulphur or sulphur compound reacts with metallic iron and as such it may remain in the pellets.

Fig. 11 shows the result obtained in the 10 per cent magnetite addition to the mixed pellets. In this case, desulphurization increases with increase in firing temperature. It is suggested that an addition of magnetite to the coke-mixed hematite pellets cause prevention of sintering as well as holding a proper pore distribution.

3-5. Result of gas analysis

To clarify the desulphurization mechanism during the firing of the coke-mixed pellets, sulphur compound in the waste gas was analyzed by gas-chromatography.

Initially, a coke-mixed pellet was inserted to the tube electric furnace, then exhausted by vacuum pump and fired at heating speed of 10°C/min in N₂ flow of 220ml/min. The waste gas was transferred by a suction pump in the interval of 200 °C or 100 °C then concentrated in the

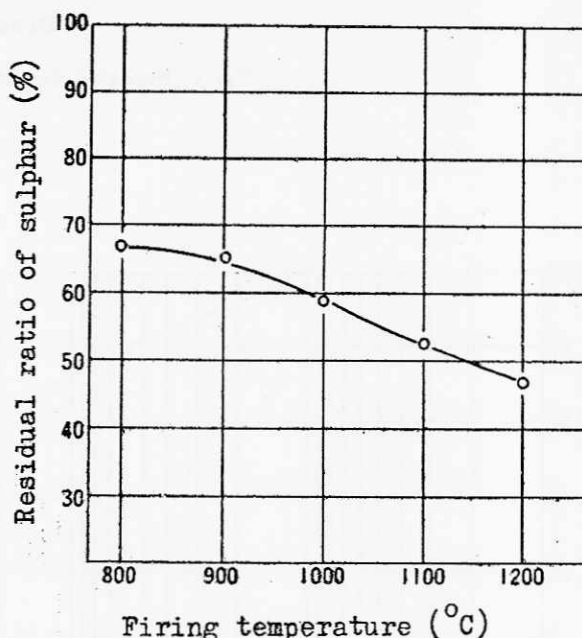


Fig. 11 Desulphurization curve of the coke-mixed pellets with an additive magnetite of 10%

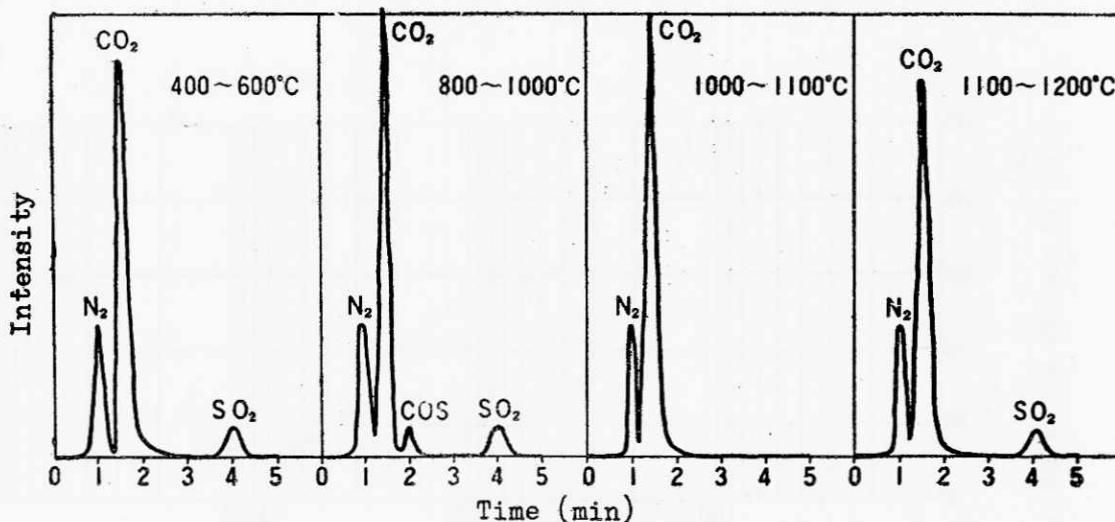


Fig. 12 Gas-chromatography of the waste gas in the case of firing the coke-mixed pellets.

liquid nitrogen trap filled with diatom-earth powder, and analyzed at room temperature.

Column filler was D.O.P., and the result of gas analysis is shown in Fig. 12. As this figure shows, sulphur was identified as SO_2 at 400-600°C, COS and SO_2 at 800-1000 °C respectively, while sulphur compound was not detected at 1000-1100°C, and SO_2 was only caught again at 1100-1200°C.

As mentioned above, the main component of sulphur compounds in the waste gas is SO_2 and it is considered to be formed at rather lower temperature in which metallic iron is not formed, that is only iron oxide is present. At 800-1000°C, reduction of the surface of iron oxide particles leads to increase of CO in the waste gas, and so the firing atmosphere will be reducible or neutral.

Consequently, COS could be found in the waste gas as in the experimental results of Hammer and Fowler.¹⁵

Moreover, the fact that the sulphur compound was not detected at 1000-1100°C may be caused by the increased CO gas, namely reducible atmosphere, and also by the difficulty of removing gas from the pellets due to softing. The fact that SO_2 appeared again at 1100-1200°C may be caused by the almost neutral atmosphere due to lack of reductant or decomposition of sulphur compounds in slag. Although CS_2 is presumed to be formed by the reaction between coke and sulphur, it was not found.

3-6. Thermodynamical consideration of desulphurization of the coke-mixed pellets.

As mentioned above, sulphur in the coke is mainly in the state of solid solution in carbon and the other part consists of free sulphur or sulphide. Sulphur in the solid solution increases its activity with consumption of carbon and finally become free.

On the other hand, carbon reduces iron oxide to become CO and CO_2 in accordance with reduction degree, therefore inside of the firing pellets is filled with CO- CO_2 mixture. The CO/ CO_2 ratio of gas mixture changes with firing temperature and heating speed that influence on reducing reaction.

Concerning to the desulphurization mechanism of the coke-mixed pellets, thermodynamical consideration of oxidizing reaction among sulphur in the coke, pyrite and Na_2S in the CO- CO_2 mixture was discussed. Evolved sulphur in

CO- CO_2 may be oxidized by the following reactions,



$$\Delta F^\circ_9 = 96,960 - 48.92T_{16} \quad (10)$$

The equilibrium constant of equation (10), can be written at 900°C.

$$K_9 = \frac{(\text{PCO})^{4.P2}}{(\text{PCO}_2)^{SO_2}} = 4.3 \times 10^{-8} \quad (11)$$

From equation (11), formation of SO_2 is dependent on PCO/PCO_2 . Fig. 13 shows the relationship between CO, CO_2 gas and firing temperature obtained from gas-chromatography, and in this figure CO is not found up to 900°C. Since PCO/PCO_2 of equation (11) can not be obtained at 900°C, PO_2 was calculated from the following reaction,



$$\Delta F^\circ_{12} = 18,661 - 10.73T_{16} \quad (13)$$

From the above equation, PO_2 can be written as $\text{PO}_2 = 1.6 \times 10^{-7}$. Furthermore, there is a following reaction,



$$\Delta F^\circ_{14} = 67,500 - 20.98T_{16} \quad (15)$$

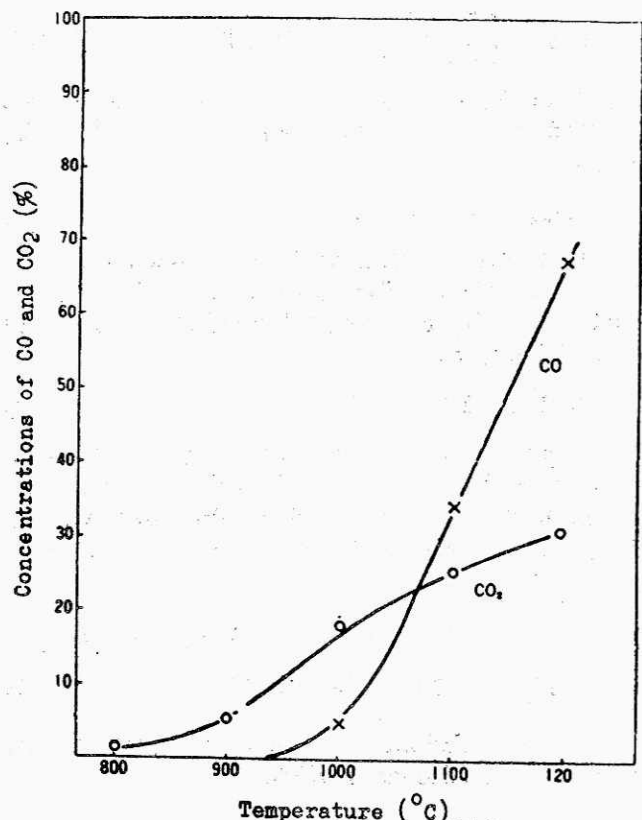


Fig. 13 Result of gas analysis in the case of firing the coke-mixed pellets.

From the above equilibrium constant,

$K_{14} = 1.0 \times 10^{-8}$ at 900°C , and the previous PO_2 value of 1.6×10^{-7} ,

$$\text{PCO}/\text{PCO}_2 = 2.5 \times 10^{-5} \quad (16)$$

When this value is substituted to equation (11), SO_2 partial pressure becomes as follows at 900°C .

$$\text{PSO}_2 = 3.2 \times 10^5 \quad (16)$$

It is recognized that the oxidation of sulphur will take place at 900°C . From Fig. 13, gas composition at 1000°C becomes $\text{CO}/\text{CO}_2 = 1/3.6$. Then, if it is introduced in equation (11) at 1000°C ,

$$\text{PSO}_2 = 2.7 \times 10^{-3} \quad (18)$$

Consequently, oxidation of sulphur will be rather difficult in this condition.

On the other hand, pyrite is considered to be a main component of sulphur compounds in the coke. Thus this pyrite reacts in $\text{CO}-\text{CO}_2$ gas mixture as follows,



$$\Delta F^\circ_{19} = 175,830 - 75.64T^{16} \quad (20)$$

According to equation (19), the equilibrium constant is obtained at 900°C followingly,

$$K_{19} = \left(\frac{\text{PCO}^7}{\text{PCO}_2}\right) \text{PSO}_2 = 5.9 \times 10^{17} \quad (21)$$

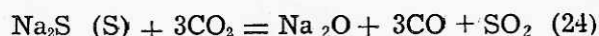
Since $\text{PCO}/\text{PCO}_2 = 2.5 \times 10^{-5}$ at 900°C can be used also in this case, PSO_2 in equation (21) becomes,

$$\text{PSO}_2 = 9.4 \times 10^7 \quad (22)$$

Therefore, sulphur will be oxidized easily in CO_2 atmosphere. Similarly, since CO/CO_2 at 1000°C can be obtained from Fig. 13, PSO_2 at 1000°C becomes,

$$\text{PSO}_2 = 1.4 \times 10^{-5} \quad (23)$$

Therefore, it suggests that oxidation will be difficult in this condition. A fairly large amount of alkali metal is involved in the coke ash, so sulphide of alkali metal is assumed to react in CO/CO_2 mixture as follows;



$$\Delta F^\circ_{24} = 120,990 - 42.35T^{16} \quad (25)$$

The equilibrium constant of equation (24) is written as follows at 900°C ,

$$K_{24} = \left(\frac{\text{PCO}^3}{\text{PCO}_2}\right) \text{PSO}_2 = 5.2 \times 10^{-14} \quad (26)$$

and PSO_2 of this reaction can be calculated at 900°C ,

$$\text{PSO}_2 = 3.1 \quad (27)$$

and at 1000°C .

$$\text{PSO}_2 = 1.5 \times 10^{-10} \quad (28)$$

Thus, Na_2S is easily oxidized at 900°C , but it is scarcely oxidized at 1000°C .

It was found that the free sulphur or solid soluble sulphur in the coke will be oxidized to SO_2 up to firing temperature 900°C . Furthermore, the sulphur consisting pyrite may be oxidized to SO_2 while the sulphide of alkali metal will be difficult to oxidize in comparison with the formers.

At temperature 1000°C , where CO is evolved remarkably, oxidation was scarcely found in each case. Consequently, desulphurization treatment should be performed in the oxidizing atmosphere such as high content of CO_2 .

Furthermore, it is necessary to remove SO_2 smoothly out of the pellets, because delay of gas flow has a trend that SO_2 reacts with the reduced metallic iron to form a soluble form.

4. Conclusion

As to the desulphurization using the coke-mixed ore pellets, the influences of additive lime, porosity and pore distribution of the pellets during firing, and reduced products on the process, and furthermore composition of the waste gas were examined.

1. An effective desulphurization was obtained under the vacuum condition at 900°C .
2. A better desulphurization was obtained in the case of additive Ca(OH)_2 in comparison with that of CaO .
3. Desulphurization occurred efficiently more than 40 per cent of porosity, and the smooth pore distribution caused a better desulphurization.
4. It was found that formation of reduced iron tends to disturb the desulphurization process therefore desulphurization treatment should be performed during the period in which iron oxide remains.
5. The sulphur in the coke-mixed pellets was removed as SO_2 and it should be removed during the firing up to 900°C .

Acknowledgement

The authors would like to express their thanks to Dr. M. Tanaka, Head of Process Metallurgy Division at NRIM for their valuable discussions and encouragements.

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DISCUSSION

Mr. H. Patnaik (National Metallurgical Laboratory, Jamshedpur). As are clear from the graphs presented, it is the physical change in a structure of ore i.e. porosity due to introduction of $\text{Ca}(\text{OH})_2$ as an ingredient of pellets (internal additive) which contributes to desulphurization. What is the role of MgO or dolomite in desul-

phurization which is commonly used in rotary kiln as an external additive?

The effect of gaseous atmosphere (i. e. CO , CO_2 etc.) on desulphurization as shown in the graph is not very clear. Kindly highlight some of these points.

Mr. S. Dharanipalan (Bhilai Steel Plant, Bhilai). I would like to know from the authors: (a) Whether addition of MgO to pellet mix has anything to do with desulphurization? (b) Whether the cooling rate after firing of pellets has any effect on desulphurization and is there any optimum cooling rate for a particular basicity of pellet?

Mr. Minoru Tanaka, National Research Institute for Metals, Japan (On behalf of Author).

1) We did not study the desulphurization of coke mixed iron ore pellets with MgO. It is certain that MgO is added into the high Al_2O_3 slag with a view to increase the fluidity of slag and to eliminate sulphur in metal.

From many previous investigations, however, it seems most reasonable to conclude that the desulphurization ability of MgO is less than CaO. In view of the above consideration, the present investigation was undertaken in order to clarify the desulphurization mechanism of coke mixed with CaO in comparative lower temperature.

2) Fig. 13 shows the change of gas composition during firing the coke mixed iron ore pellets, but the effect of atmosphere on desulphurization is not clear. Fig. A shows our previous results which the coke mixed pellets were fired in various atmosphere (N_2 , Ar, air and CO_2) for 30 minutes at 1200°C .

It may be concluded from this result that the desulphurization of coke mixed pellets is promoted very much by CO_2 or air.

a) Same answer as 1).

b) It has been shown by our investigation that the desulphurization reaction in the coke mixed pellets proceeds preferentially in the first period of reduction which the metallic iron is not formed yet and the pellets are kept in porous state. Therefore, we did not attach importance to the effect of cooling rate after firing on the desulphurization of coke mixed pellets.