High Thermal Electrical Property of Manganese Ore in Production of High Carbon Ferromanganese

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ABSTRACT

Nippon Denko Tokushima Plant produces high-carbon ferromanganese by electric-furnace smelting using various brands of manganese ore. However, in accord with producing districts of ore used, operating results greatly vary. This is assumed to be attributed to properties of manganese ore, and particularly, high-temperature electric characteristics are assumed to be responsible.

In order to maintain stable operation in electric furnaces, the electrode tip position must be properly maintained. Because the electrode tip position is defined by the electric resistance of in-furnace burden material, it is extremely important to confirm in advance the high-temperature electric characteristics of material ore, specifically, specific electric conductivity. Presently, in our company, as a means for evaluating the manganese ore quality, investigation of mineral composition and measurement of specific electric conductivity are adopted in addition to the composition analysis. Of these, for the specific electric conductivity, we have developed an apparatus for measuring the specific electric conductivity even at high temperature (up to 1600°C) by ourselves and carried out measurements on various kinds of material ore. As a result, it has been identified that the specific electric conductivity greatly varies in accord with producing regions, and the difference is caused by the structure of mineral composition. In addition, an indepth examination of the measurement results of specific electric conductivity to electric furnace operation results have identified the standard of material ores for maintaining stable operation.

1. INTRODUCTION

In recent years, with respect to iron ores used for blast furnaces, it has been identified that properties of raw materials in the high-temperature region are concerned in the productivity and fuel ratio, and studies on softening and melting properties of blast-furnace burden materials are actively carried out using the under load test. On the other hand, similar research has scarcely been done on material ores related to ferroalloys.

In the production of ferroalloys using submerged type electric furnaces, the material ore cost and electric power expenses account for the majority of the production cost. Consequently, in Japan with little resources and high electric power unit price, it becomes essential to carry out the operation for maintaining the metal Mn recovery to a high level while the power consumption is kept to a minimal level.

In our company, high-carbon ferromanganese (Mn74.5%, C6.8%, Si0.1%) is produced with two closed type electric furnaces, but since the operation results greatly vary in accord with the producing region and chemical composition of material ore, a means for assessing material ore was required. The electric furnace operation greatly depends on electric characteristics in the reduction process, which is the property of material ore, permeability of generated gas, viscosity of molten slag, etc. Above all, the electric characteristics of material ore in the reduction process is extremely important.

Therefore, with attention placed on the high-temperature specific conductivity of material ore which exerts great influences on the electric furnace operation, the apparatus unique to our company was developed, and the specific conductivity measuring technique using the apparatus and the assessment method have been established. In addition, the results were comprehensively compared and examined with the operating results of actual furnaces and the assessment criteria of material ore required for stabilizing the operation has been identified.

2. EXPERIMENTAL

2-1 Samples and Test Method

The samples used for measurement of specific conductivity are four kinds of raw ore. Table 1 shows the chemical composition of raw ore. Using the powder X-ray diffraction, the Mn form was investigated, and the investigation results indicated that ores A and B primarily comprise Mn_2O_3 and Mn_3O_4, while ores C and D primarily have forms of MnO_2 and

$MnO_2 \cdot 2H_2O$.

Table 1. Chemical composition of samples (mass.%)

Sample	Mn	SiO_2	Fe	Al_2O_3	CaO
A	49.2	4.0	10.7	0.3	6.5
B	40.5	5.1	17.7	0.4	5.9
C	38.9	2.5	15.3	5.6	0.3
D	48.2	6.4	3.5	3.6	0.1

Fig. 1 shows the specific conductivity measuring apparatus, while Table 2 shows measuring conditions.

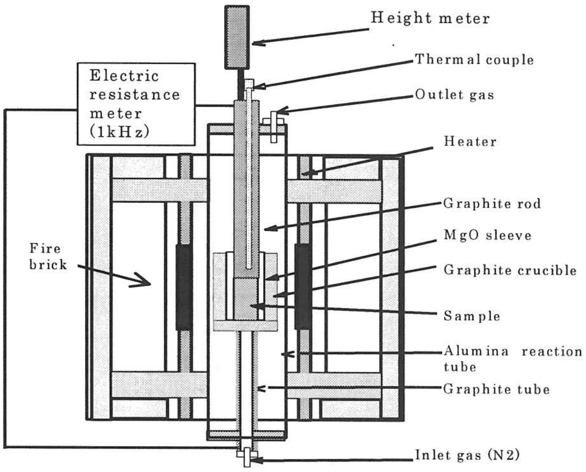

Fig. 1. Schematic drawing of testing system.

Measurement conditions using the present method are approximated to the actual furnace conditions as much as possible, but with respect to the coke mixing ratio, if it is around 20 mass%, which is same as in actual furnaces, since the bulk specific gravity of coke is too small, the charge ratio of material ore, subject of assessment, decreases, and the difference of electric conductivity originating from material ore between ores became inaccurate. Consequently, the coke mixing ratio in the present measurement was set to 10 mass.%.

Table 2. Experimental condition of the specific conductivity measurement.

Items	Experimental Condition	Electric Furnace [2]
Crucible Dia.	Constant	10.52 m
Sample Dia	3 ~ 5 mm	10 ~ 100 mm
Bed Height	Constant	~ 2 m
Sample Weight	~ 50 g ~	~ 300 t ~
Mixing Ratio of Coke	10%(3 ~ 5 mm)	~ 20 % ~
Gas Composition	N_2 : 100% [1]	CO:60%,CO_2:35%, H_2:5%
Gas Flow Rate	-	0.01 ~ 0.02 m/sec
Load	20 k Pa	[3]
Frequency	1 kHz	-
Max .Temperature	1,600 ℃	-
Heating Rate ~ 800℃ ~ 1,500℃	 10℃/min 3℃/min	0.6 ~ 1.5 ℃/min (average)

1) Nitrogen gas is used for protecting electrodes.
2) Data of the electric furnace actually in operation is used.
3) Trial calculation is impossible.

2-2 Calculation of Specific Conductivity and Assessment Method

The specific conductivity referred to here is the apparent specific conductivity calculated by the following procedure. Specifically, with a predetermined load applied to material ore to be assessed, electric resistance (R) and thickness of sample layer (h) are continuously measured while heating, and changes of the apparent specific conductivity (κ) is found from Eq. (1). Similarly, the specific conductivity of carbon-based reducing agent is measured. The behaviors of specific conductivity of these two are compared and material ore is assessed. The electric resistance with sample in the blank condition (electric resistance of the apparatus itself) is negligibly small compared to that of material ore or coke.

$$\kappa = h/(S \cdot R) \;\ldots\ldots (1)$$

κ : apparent specific conductivity ($\Omega^{-1}cm^{-1}$)
h : sample layer thickness (cm)
S : electrode area (constant)
R : electric resistance of sample layer (Ω)

3. RESULTS AND DISCUSSION

3-1 High-temperature Electric Characteristics of Raw Ore

a) Specific conductivity in low-temperature region (up to 1100°C)

Fig. 2 shows apparent specific conductivity curves of ores A, B, C, D, HCFeMn slag, and coke at 1100°C or lower, respectively. In the temperature region where ore is not melted, each brand exhibit its own characteristics. In general, it is said that the lower the Mn oxidation number, the lower is the specific conductivity, and the same results were obtained in the present measurement. At room temperature to 700°C, the apparent specific conductivity of ores A, B with less Mn higher oxides is lower than that of ores C, D containing larger amount of Mn higher oxides, and indicates linear ascending trends with respect to temperature rise. On the other hand, ores C, D increase the apparent specific conductivity suddenly from the vicinity of 500°C and show the maximum value at about 600°C. It is assumed that the phase transformation from MnO_2 to Mn_2O_3 participates in this phenomenon. The change corresponding to phase transformation from Mn_2O_3 to Mn_3O_4 was unable to be definitely identified on the apparent specific conductivity curves.

In the temperature region of 1100°C or lower, Mn ore is electrically an insulator or semiconductor according to Fig. 2, and as compared to the specific conductivity of coke, reducing agent, its specific conductivity is negligibly low. That is, in this temperature region, the electric resistance of electric-furnace charge material is controlled by the electric resistance of coke.

b) Specific conductivity in high-temperature region (1100-1550°C)

Fig. 3 shows the apparent specific conductivity curves of ores A, B, C, D, HCFeMn slag, and coke at 1100 through 1550°C. The specific conductivity greatly varies in accord with brands and exceeds the apparent specific conductivity of coke in the vicinity of about 1300°C, though it depends on brands. This is because the contact area with the electrode increases as ore softens and melts and ore becomes an ionic conductor as a result of phase change from "solid" to "liquid".

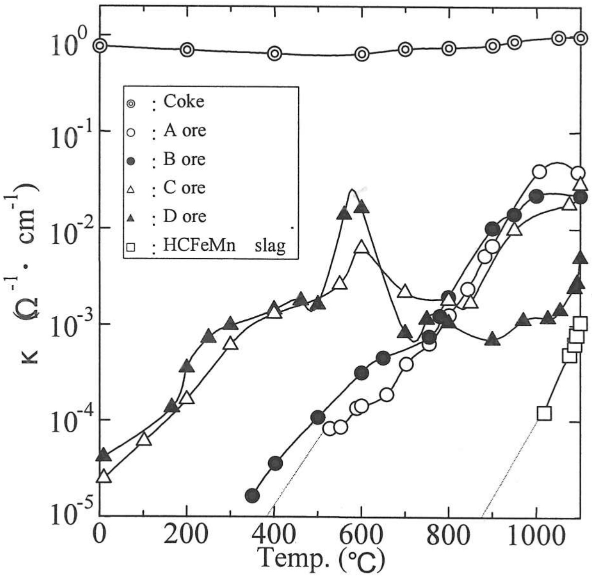

Fig.2. The relationship of temperature(~ 1100°C) vs appearent specific conductivity.

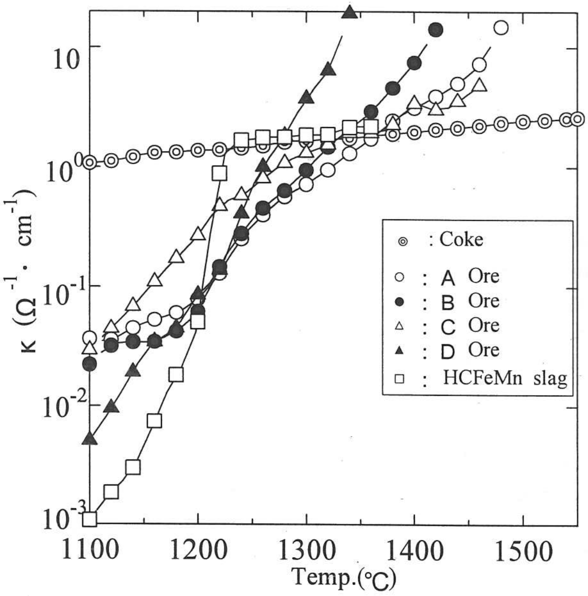

Fig.3. The relationship of temperature(1100 ~ 1550°C) vs appeearent specific conductivity.

In actual furnaces, as the specific conductivity of material ore increases in the reducing temperature region, the secondary current increases. Because the maximum secondary current is determined by transformer specifications and the secondary current must be lowered in order to prevent tripping caused by overcurrent. In such event, there a method for raising the electrode tip position and a method for lowering the tap voltage. In the former method, the reaction zone ascends, the heat exchange between generated gas and material layer is degraded, and the power consumption and Mn recovery are degraded. On the other hand, in the latter method, since the electric load lowers, the reaction zone becomes narrow, electric furnace operation becomes unstable, the productivity is lowered, and power consumption is degraded. Consequently, the ore with lower apparent specific conductivity in the reducing temperature region is assumed to be suited for electric furnaces, and judging from the results of Fig. 3, the order of raw ores that would contribute to stabilization of electric furnace operation is shown as follows:

Ore A > Ore B > Ore C> Ore D> HCFeMn slag

Conversely, when the specific conductivity of raw ore in the reducing temperature region is excessively low, it is feared that power more than required is consumed for melting ore, but there was no ore that falls under this category, judging from the measurement results of the present method and operation results of actual furnaces.

c) Behavior of coke and raw ore in the high-temperature region

As discussed in the preceding section, the specific conductivity obtained in the present measurement is not an absolute value. Consequently, in the present method, in order to relatively compare electric resistance between brands, first of all, the apparent conductivity of coke was set as a standard, and the temperature at which the apparent specific conductivity of material ore to be evaluated exceeded that of coke was designated as the evaluated value. This is explained as follows.

Because the electricity flows preferentially in the section with less resistance as its basic characteristics, the factors that control the electric resistance of electric furnaces are the half-molten or molten ore and reducing agent (coke bed). What is important from the viewpoint of operating electric furnaces is which would become dominant, and the boundary is the temperature where the specific conductivity of ore and coke bed becomes same. Since a large volume of residual coke is observed in the furnace at the time of blowing down of material, it is apparent that coke bed exists in the electric furnace during regular operation.

Table 3 shows the evaluated specific conductivity of ores A through D and HCFeMn slag, respectively. Comparison of these evaluated values with the chemical composition of Table 1 indicates that the evaluated specific conductivity of the ore that contains a larger volume of basic components (CaO, MgO) and a less volume of acidic components (SiO_2) is higher, but the difference of evaluated specific conductivities is unable to be thoroughly explained with the chemical composition alone. It is assumed that the difference of mineral composition would contribute in the difference.

Table 3. The evaluated specific conductivity of the ore.

	A Ore	B Ore	C Ore	D Ore	Slag
Conductivity	1355℃	1322℃	1305℃	1270℃	1224℃

(The conductivity is the temperature exceeding the apparent specific conductivity of coke.)

In addition, as a result the comparison of the evaluated specific conductivity of material ore with the operation results, the specific conductivity and mixing ratio standard of required material ores were established, which will be discussed in the subsequent section.

3-2 Mineral Composition and High-temperature Electric Characteristics of Manganese Ore

Ores A, C, and D of Table 1 were investigated for the mineral composition (existing form of gangue) using an optical microscope and EPMA analysis. Table 4 shows the investigation results.

Softening and melting of ore in the reduction process is rapidly accelerated by the formation of the melt. It is assumed that the ore whose melt is generated at lower temperature or the ore that generates a greater volume of melt exhibits a marked increase of the specific conductivity.

The melt in the reduction process is generated as a result of reactions between MnO and gangue. Because, for ore A, the CaO component uniformly exists in gangue, generation of the melt at low temperature is suppressed.

Ore C has gangue that primarily consists of clay mineral SiO_2-Al_2O_3, and forms the melt at temperatures as low as 1140°C. However, since the concentration of chemical component SiO_2 is as low a 2.5%, it is assumed that the generation of the melt is comparatively small. Al_2O_3 that exists in Mn oxide would exert small influence on the specific conductivity because the temperature of initial melt of MnO-Al_2O_3 system is 1520°C, which is comparatively high.

Table 4. Mineral characteristics of Mn ore and its specific conductivity.

	A ore	C ore	D ore
Electric characteristics	best	good	worse
Mn form	Mn_2O_3, Mn_3O_4	MnO_2, $Mn(OH)_4$	MnO_2, $Mn(OH)_4$
Combined water	Small amount	Large amount	Large amount
Gangue form	Gangue form is available in following three kinds. 1) 【Ca-Mn-Si oxide】 2) 【Ca-Fe-Si oxide】 3) $CaCO_3$ · Structure is uniform as compared to ores C, D. · **Quartz does not exist.**	· Primarily comprising clay mineral ($Al_2O_3 \cdot SiO_2$). · Al_2O_3 exists dispersed in Mn oxide. · Quartz component slightly exists. · A large amount of clayey gangue exists adhering to ore surface.	· SiO_2 exists as single quartz or clay mineral ($Al_2O_3 \cdot SiO_2$). · Quartz is concentrated to a specific ore. · No quartz exists in high-purity ore section. Gangue exists extremely minimal.
Relation with electric characteristics. The ore that generates a greater amount of melt with a low melting point provides higher specific conductivity.	· The melting point of the melt is high because of the existence of CaO. · Because CaO has difficulty reacting with MnO, expansion of the melt is prevented in the reduction process.	· Clayey gangue generates low-melting point melt. · The temperature of initial melt of MnO- Al_2O_3 is higher than MnO- SiO_2. · Because the SiO_2 content is low, the generation of low-melting point melt is smaller than that of ore D.	Because SiO_2 exist concentratedly in the specific ore as quartz, it reacts with MnO to generate the low-melting point melt. The generation of the low-melting point melt is proportional to the SiO_2 concentration.
Production of low-melting point melt	Extremely small.	Small.	Large.
Relation with electric furnace operation	↓ The specific conductivity of material ore in the reduction temperature zone achieves the optimum range.	↓ The specific conductivity of material ore in the reduction temperature zone achieves the optimum range.	↓ The specific conductivity of material ore in the reduction temperature zone increases. (The electrode head end position ascends, load is unable to be applied.)

In Ore D, SiO_2, the gangue component, exists in the form of quartz or clay mineral. Quartz reacts with MnO and generates the melt at 1251°C. The initial melt temperature is higher than the clay mineral but since the chemical component SiO_2 concentration is 6.4%, which is higher than that of ore C, the melt generation is large. In addition, because Ore D comprises a plurality of ore species and quartz exists concentratedly in a specific ore specie, the melt locally generated surrounds the unmelted ore and possibly increases the specific conductivity suddenly. This structural difference is reflected to the behaviors of apparent specific conductivity curves of Fig. 3.

It is unable to definitely state the mineral composition of ore B because the detailed investigation has not yet been carried out, but is assumed to be similar to that of ore A. The difference of ore A and ore B in the evaluated specific conductivity is assumed to be related to the existing amount of Fe component. That is, because the Fe oxide is metallized at lower temperature than Mn oxide, it works to lower the electric resistance. Consequently, it is assumed that the evaluated value of specific conductivity of ore B containing a large amount of Fe is slightly lower than that of ore A.

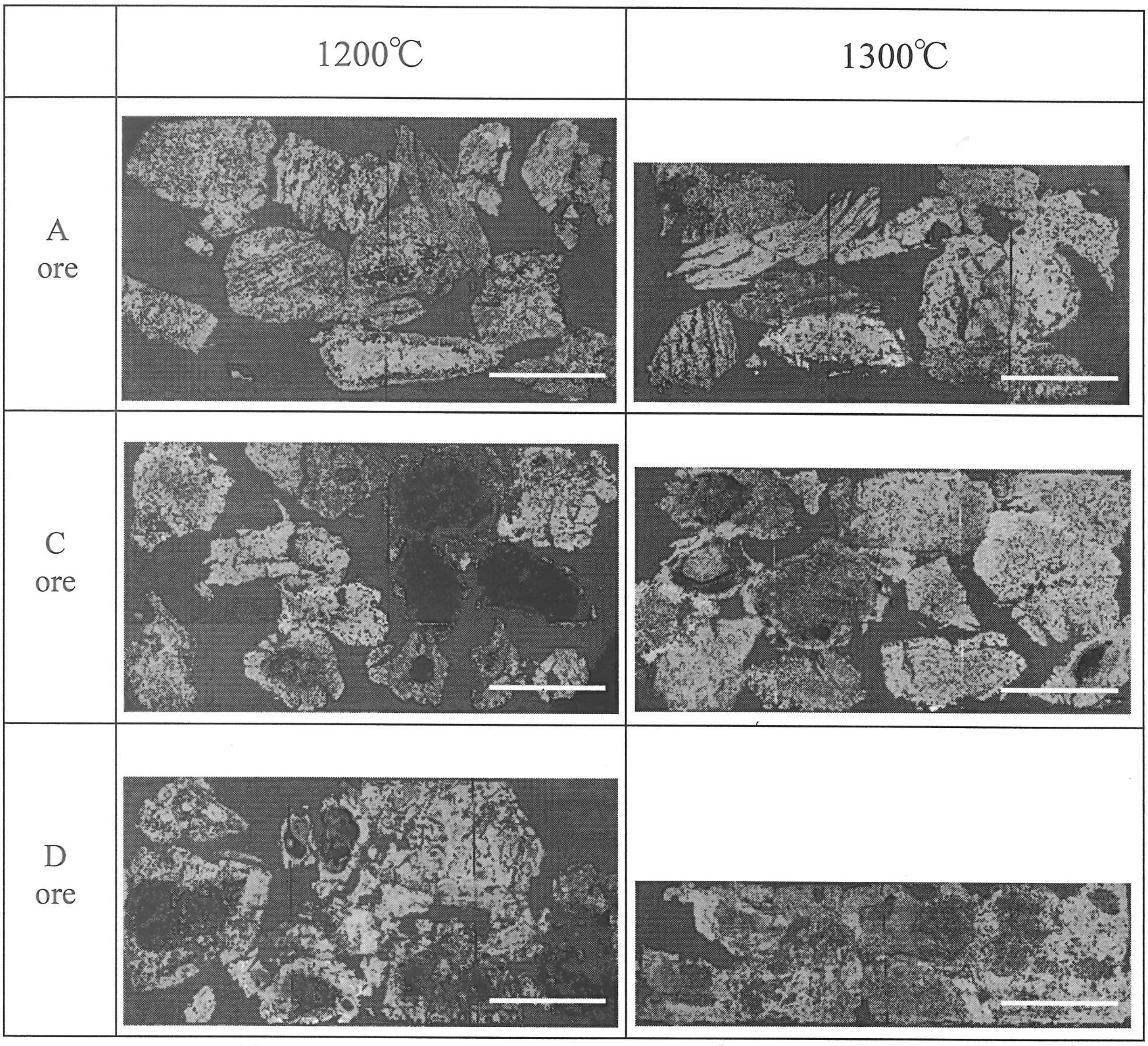

Fig. 4. The melting behavior for A, C and D ore in 1200 and 1300℃ (atmosphere : CO 60%, N2 40%, load : 0.1MPa)

In order to confirm the above discussion, ores A, C, and D were heated to 1300°C with 0.1 MPa load applied in the reducing atmosphere (CO60%, N2.40%) and softening and melting condition of ores were confirmed. Fig. 4 shows the cross-sectional structures of ores at 1200°C and 1300°C, respectively.

At 1200°C, ores A, C have already begun melting, and fusion between ore particles is able to be identified, but expansion of the melt has not yet taken place. On the other hand, in ore D which comprises a plurality of ore species, melting takes place in part of ore species, and the fissure assumed to be the mark from which the combined water might have escaped is filled with the melt. It is assumed that this ore specie possibly has a large volume of quartz that exists as gangue.

Then, at 1300°C, melting takes place in all ores. In particular, in ore D, the melt is rapidly formed to such an extent that the ore profile becomes obscure. This is because the generated melt of MnO-SiO_2 enters forcibly fissures caused by combined water and further promotes softening and melting. As against this, in ores A and C, gangue exists dispersively and expansion of the melt is suppressed.

The melt is generated at 1300°C in order of D > C > A. This difference also appears in the specific conductivity curve of Fig. 3.

Based on the above results, it could be stated that the ore contains a smaller amount of gangue, clay mineral or quartz, or the ore in which the gangue is uniformly dispersed would provide lower specific conductivity at temperature higher than 1300°C.

4. HIGH-TEMPERATURE CHARACTERISTICS OF MATERIAL ORE AND ELECTRIC FURNACE OPERATION

In order to identify how the above-mentioned electric characteristics would exert effects on the electric furnace operation, electric furnaces were operated at the ore mixture shown in Table 5 and the operation results (average for one month) at each mixture was compared. The operation results were evaluated with the mixture of the ore D with the poorest electric characteristics containing 0% set as the base mixture and the results of base mixture designated as the index 100. The evaluated specific conductivity of ores A, B, C, and D is shown in Table 3. In addition to ores A through D, ores of several brands were used in small quantities, but since the evaluated specific conductivity of these ores all exceeded the evaluated specific conductivity of ore C, they were integrated into one as other. The sintered ores used were all of the same brand.

Mixture (1) is mixed with ore D using 19%. During the operation at this mixture, the furnace operating condition was satisfactory and was nearly same as at the time of operating at the base mixture. The difference in the power consumption was also small and could be explained by an increase in sensible heat associated with an increase of generated slag and an influence of ore water content.

However, in the case of mixture (2), shortly after the mixture was changed from mixture (1), the electrode holder position began to ascend and finally reached the upper limit, giving a rise to the condition in which electric load was unable to be applied sufficiently. It was assumed to be caused by the smaller electric resistance of material at the electrode tip section than that at the time of base mixture or mixture (1) used. Therefore, the countermeasure was taken to lower the coke consumption, forcibly increase the electric resistance of materials. As a result, the electrode holder position descended but reduction shortage resulted and the Mn content of slag increased, greatly lowering the Mn recovery. In addition, mixture (2), a large amount of ore D with high SiO_2 content was used and the furnace was operated at the slag basicity same as that of the base mixture and mixture (1), the slag generation quantity naturally increased. This constituted one of the factors of degrading the Mn recovery and the electric power consumption.

The results of Table 5 indicate that ore D with inferior electric characteristics would not exert serious effects on the furnace condition as far as the mixture ratio does not exceed 20%. However, it is assumed that with a certain mixture ratio as a boundary, the electric resistance of the whole burden of the electric furnace suddenly lowers, the electrode tip position ascends, the Mn recovery and power consumption degrade, and the productivity lowers.

Table 5. Ore Mixture and Operational Results

	Evaluated Conductivity	Base Mixture	Mixture (1)	Mixture (2)
A ore	1355℃	11%	25%	0%
B ore	1322℃	0%	11%	23%
C ore	1305℃	30%	5%	2%
D ore	1270℃	0%	19%	27%
other	> 1305℃	24%	7%	11%
Sinter		35%	33%	37%
H_2O in Ores		5.10%	3.50%	3.50%
Coke(kg/t-metal)		380	375	370
【Results】				
Power (kWh/t-metal)		100	100.1	103.6
Slag(kg/t-metal)		100	112	136
Mn recovery		100	97.6	94.1
Slag Mn%		100	100.8	113.6

Slag CaO/SiO_2	0.85	0.85	0.85

1) Mixture and operation results are averages for one month.
2) The evaluated conductivity is the temperature exceeding the apparent electric conductivity of coke.
3) The results are calculated with the base mixture results set as 100.

5. SUMMARY

In manufacture of high-carbon ferromanganese, it is the first priority economical requirement to maintain the metal Mn recovery to a high level and lower the material and power consumption. At the same time, it is essential to continue stable operation for a long time. To achieve this, it is extremely important to control the electrode tip to an optimum position. In order to properly control the electrode tip position, we set the following two items as the control standard of electric furnace burden ore on the basis of actual furnace operating results and the specific conductivity of ore obtained from the present method.

1) The temperature at which the apparent specific conductivity of material ore exceeds the apparent specific conductivity of coke set as the evaluated value of electric characteristics of the ore, and the ore whose evaluated value is within the range of 1300 to 1500°C is designated as the optimum ore for electric furnace burden.
2) The mixture ratio of the optimum ore for electric furnace burden of Paragraph 1) above is 80% or more of the total ore charged into the electric furnace.

The above control standard is induced only from the specific conductivity of single ore. In the future, other factors exerted on electric furnace operation, for example, effects of combinations of ores, reducibility, moisture content, etc. will be investigated and verified, and more stabilized furnace operation will be aimed at.