

# Development of On-line Manganese Analysis Method for Molten Steel in Converter

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## Abstract:

*As an on-line monitoring method for steelmaking reactions in the converter, a hotspot radiation spectrometric method was developed that analyzes the radiation of a hotspot formed in the bath during oxygen blowing. A hotspot atomic emission model was developed on the basis of the hotspot temperature, the vaporization flux of elements and the excitation energy of atoms, was proposed and tested for verification. An on-line analysis technique based on the principle of the model, was commercialized for the determination of manganese in the metal bath of a 170-ton converter at Sakai Works. The new method can continually measure the manganese content of the melt at 15-s intervals during the oxygen blow. The manganese analyses obtained are extremely high in reliability with a correlation coefficient of 0.942 with the conventional substance sampling method. This on-line analysis method is expected to become applicable also to such other elements as chromium, nickel, copper, and lead.*

## 1. Introduction

As the steelmaking process has advanced in the number of steps involved, speed, and precision in recent years, there has been an increasing demand for the development of on-line analysis methods to monitor and control the metallurgical reactions in the steelmaking converter. In converter operations, the metal and slag chemistry in the bath constantly changes with the progress of decarburization reactions under oxygen blowing. The on-line real-time monitoring of the behavior of elements in the bath is a very effective means of controlling the steelmaking reactions.

With the spread of preliminary hotmetal dephosphorization, converter blowing is now mainly for melt decarburization under a thin slag cover. As a result, the current blowing control manual dictates that manganese ore be added to the bath during the oxygen blow in order to raise the blow-end manganese content. If the manganese content in the bath is directly analyzed or monitored, appropriate judgment can be made in taking necessary operational actions.

Research and development works have been actively conducted to date concerning on-line analysis methods for molten metal in the converter<sup>1-9)</sup>. Those methods proposed, however, are subject to the influences of dust and slag generated from the bath, and of bath surface level fluctuations, and none of them had yet reached the stage of practical application.

As an on-line analysis technique for the composition of molten

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metal in the converter refining process, the authors focused attention on emission from the impinging point of top-blown oxygen onto the melt (hotspot) in the converter, and clarified by laboratory experimentation that spectral analysis of the emission can directly determine the manganese concentration in the metal bath in the converter<sup>10</sup>.

This paper describes the direct analysis technique established on a 170-ton converter for determining the manganese content of molten metal on-line and in real time. Also presented here are the results of study made into the feasibility of applying the hotspot radiation spectrometric method to the analysis of molten metal for elements other than manganese.

## 2. Hotspot Radiation Model and Measuring Principle

The hotspot formed in the bath during top oxygen blowing is known to reach a temperature of over 2,000°C<sup>11,12</sup>. The constituent elements of the metal are believed to be vaporized, atomized, and excited to radiate in such a hot condition. Assuming that the emission intensity of metal atoms depends on the flux and temperature of the vaporized atoms in the thermal medium and the excitation energy of metal atoms, the authors proposed a model for the atomic emission of metal elements at the hotspot.

The atomic emission model is described below taking the manganese determination as an example.

The emission intensity ratio  $I(\text{Mn}/\text{Fe})$  of manganese to iron at the hotspot can be expressed by the following equation, using the vaporization flux, hotspot temperature, and excitation energy:

$$I(\text{Mn}/\text{Fe}) = \frac{I(\text{Mn})}{I(\text{Fe})} = \frac{J_{\text{Mn}}}{J_{\text{Fe}}} \cdot \frac{A_{\text{Mn}} \cdot \exp(-E_{\text{Mn}}/kT)}{A_{\text{Fe}} \cdot \exp(-E_{\text{Fe}}/kT)} \quad \dots\dots(1)$$

where  $I$  = emission intensity of metal atoms;  $J$  = vaporization flux of metal atoms;  $A$  = constant relative to transition probability of element;  $T$  = hotspot temperature;  $E$  = excitation energy of metal atoms; and  $k$  = Boltzmann's constant.

The vaporization flux of iron atoms is given by

$$J_{\text{Fe}} = K_{\text{Fe}}^p(T) \cdot C_{\text{Fe}}^s \quad \dots\dots(2)$$

where  $K_{\text{Fe}}^p$  = vaporization rate coefficient when vaporization is a rate-determining step; and  $C_{\text{Fe}}^s$  = iron concentration at the metal bath surface (approximately unity).

The vaporization flux of manganese,  $J_{\text{Mn}}$ , is given by

$$J_{\text{Mn}} = K'_{\text{Mn}}(T) \cdot [\text{Mn}] \quad \dots\dots(3)$$

The vaporization rate of manganese atoms is governed by the diffusion of manganese atoms in the molten metal bath and the process of their vaporization from the bath surface<sup>12</sup>.  $K'_{\text{Mn}}(T)$  is defined as a mass transfer coefficient when both diffusion and vaporization are assumed to be rate-determining steps.  $[\text{Mn}]$  is the manganese concentration in the bath.

Substitution of Eqs. (2) and (3) into Eq. (1) yields Eq. (4).

$$\begin{aligned} I(\text{Mn}/\text{Fe}) &= \frac{K'_{\text{Mn}}(T) \cdot [\text{Mn}]}{K_{\text{Fe}}^p(T)} \cdot \frac{A_{\text{Mn}} \cdot \exp(-E_{\text{Mn}}/kT)}{A_{\text{Fe}} \cdot \exp(-E_{\text{Fe}}/kT)} \\ &= A \cdot \frac{K'_{\text{Mn}}(T)}{K_{\text{Fe}}^p(T)} \cdot [\text{Mn}] \cdot \exp(\Delta E/kT) \quad \dots\dots(4) \end{aligned}$$

It is also necessary to take into account the effects of self-absorption<sup>13,14</sup> by those atoms that are present near the hotspot

but are not thermally excited and remain in the ground state. Equation (4) should be thus arranged as follows:

$$I(\text{Mn}/\text{Fe}) = A \cdot \frac{(K'_{\text{Mn}}(T))^n}{(K_{\text{Fe}}^p(T))^m} \cdot [\text{Mn}]^n \cdot \exp(\Delta E/kT) \quad \dots\dots(5)$$

where  $m$  and  $n$  are constants indicating the degree of self-absorption for iron and manganese ( $m, n \leq 1$ ), respectively, and  $A$  is a proportionality constant. These constants are uniquely determined for specific measuring systems.

Over the range where the hotspot temperature changes,  $\exp(\Delta E/kT)$  can be assumed to be constant. If

$$K'(T) = A \cdot \frac{(K'_{\text{Mn}}(T))^n}{(K_{\text{Fe}}^p(T))^m} \quad \dots\dots(6)$$

Eq. (5) can be reduced to:

$$I(\text{Mn}/\text{Fe}) = K'(T) \cdot [\text{Mn}]^n \quad \dots\dots(7)$$

$$\log(I(\text{Mn}/\text{Fe})) = \log(K'(T)) + n \cdot \log([\text{Mn}]) \quad \dots\dots(8)$$

In this way, the iron/manganese emission intensity ratio can be separated into the term  $K'(T)$  that is dependent on the hotspot temperature and the term  $[\text{Mn}]^n$  that is proportional to the manganese concentration. In other words, if the coefficient  $K'(T)$  related to the hotspot temperature and the self-absorption coefficient  $n$  of manganese are obtained beforehand, the manganese content can be directly determined from the measurement of emission intensity ratio and hotspot temperature.

## 3. Experimental Apparatus and Methods

### 3.1 Laboratory experiment

To study the relationship of hotspot atomic emission with the vapor pressure of each element<sup>10</sup>, hotspot radiation was measured for three classified element groups, namely, nickel and chromium with approximately the same vapor pressure as that of iron; copper and lead with higher vapor pressures; and molybdenum and vanadium with lower vapor pressures.

#### 3.1.1 Experimental apparatus

The experimental system used here consists of a 50-kg-capacity air high-frequency induction furnace, a water-cooled lance for blowing oxygen and observing the hotspot, an optical fiber cable, a two-color thermometer, and a spectrometer, as schematically illustrated in Fig. 1. The spectrometer uses a monochromator with a focal distance of 50 cm and has a resolution of 0.8 nm/mm in terms of reciprocal linear dispersion. The spectrometer is provided with a wavelength modulator to measure a spectrum over the range of  $\pm 1$  nm from the center wavelength.

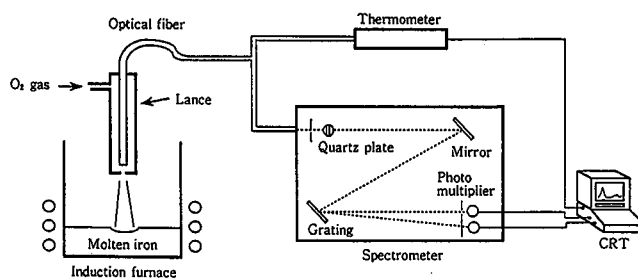


Fig. 1 Photometric system in experimental furnace

3.1.2 Experimental method

About 20 kg of electrolytic iron was melted in a graphite crucible in the high-frequency induction furnace, and held at a constant temperature of 1,450°C during the experiment. To facilitate the hotspot formation, graphite was added and the initial carbon concentration was brought to a saturation level. Nickel, chromium, lead, copper, molybdenum, and vanadium to be examined were dissolved respectively in the molten metal to the desired concentrations.

The lance was positioned with its nozzle at 50 mm above the metal bath surface, and oxygen was blown through it at a rate of 20 liters per minute against the bath surface to form the hotspot. The radiation of the hotspot was observed through the nozzle hole of the lance and transmitted by an optical fiber cable to the spectrometer and the two-color thermometer. The emission spectra of the elements were measured by the spectrometer, and the hotspot temperature by the two-color thermometer. The data were stored in the personal computer and analyzed.

3.2 On-line manganese analysis in converter

A converter experiment was carried out in order to establish an on-line analytical technique for manganese.

3.2.1 Apparatus

Radiation spectra of the hotspot in a 170-ton converter were measured. The on-line analytical system used for the direct analysis of manganese is as schematically illustrated in Fig. 2. The system consists of a hotspot observation optical fiber cable, a photometric system, a two-color thermometer, a control system, and a data analysis system.

The optical fiber cable is installed in the inner pipe of the oxygen top blowing lance and is protected by a stainless steel guide pipe. The hotspot is observed through the main pipe. Radiation of the hotspot is transmitted through the optical fiber cable to the photometric system and the two-color thermometer, and is semi-continuously measured from the hotspot ignition to the end of the oxygen blow. The photometric system is located close to the converter in order to minimize attenuation through the optical fiber cable and to measure the emission spectra with a good signal/background (S/B) ratio. The photometric system control and data analysis computer are installed in an instrument room and are remotely operated. The spectrometer used in the laboratory experiment was also used in the photometric system in the converter experiment.

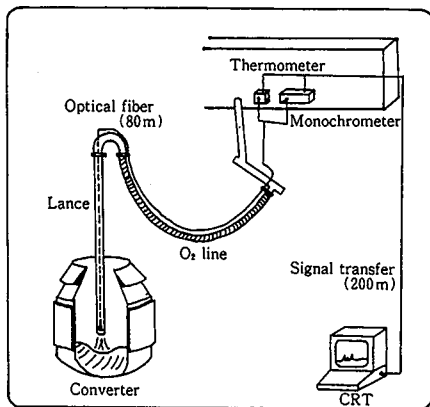


Fig. 2 On-line analysis system in converter

3.2.2 Measurement and analysis methods

Emission spectra of elements at the hotspot were measured using main resonance lines that efficiently radiate even in a low-temperature heat transfer medium. Two wavelengths,  $\lambda_{Mn} = 403.4 \text{ nm}$  and  $\lambda_{Fe} = 386.0 \text{ nm}$ , were selected as actual measurement wavelengths, and the emission intensity and hotspot temperature were simultaneously measured.

The emission spectra of the elements are superimposed on the continuous background emission resulting from radiation from the metal bath. In the subsequent analysis, net peak heights from which the background emission was subtracted were taken as the emission intensities  $I_{Mn}$  and  $I_{Fe}$ , and the ratio of these emission intensities was adopted as  $I(Mn/Fe)$ . The correlation between the net emission intensity ratio  $I(Mn/Fe)$  and the manganese analysis of sub-lance samples taken at the same timing as the radiation intensity measurements was obtained and studied relative to Eq. (8).

The optical fiber cable of the on-line analysis system is installed in a conventional top oxygen blowing lance and is operated remotely and automatically. The radiation of the hotspot can be continuously measured without any adverse effects on the converter operation.

4. Experimental Results

4.1 Results of laboratory experiment

(1) Atomic emission of Ni, Cr, Pb, and Cu at hotspot

The atomic emission of the elements Ni, Cr, Pb, and Cu at the hotspot was measured. In Fig. 3, an atomic emission spectrum of nickel near the wavelength of 346 nm is shown as an example. The spectrum was measured at a nickel concentration of about 3% in the bath. The emission intensity is similar to that of the matrix Fe. The atomic emission lines of nickel were also confirmed at 352.5 nm, 351.5 nm, and 346.2 nm.

Chromium revealed atomic emission lines at 357.6 and 359.4 nm, and had an emission intensity similar to that of nickel. The atomic emission line of 405.8 nm was identified for lead and was measurable down to a lead concentration of about 0.01%. Atomic emission lines of 324.75 and 328.0 nm were confirmed for copper and were observable down to a copper concentration of about 0.01%.

(2) Study of Mo and V emissions at hotspot

Molybdenum and vanadium were selected as typical elements of lower vapor pressure. The atomic emission lines of 379.8 and 386.4 nm for molybdenum and 437.9 and 411.2 nm for vanadium were selected as those that are low in excitation energy. The atomic emission of molybdenum and vanadium was sought while

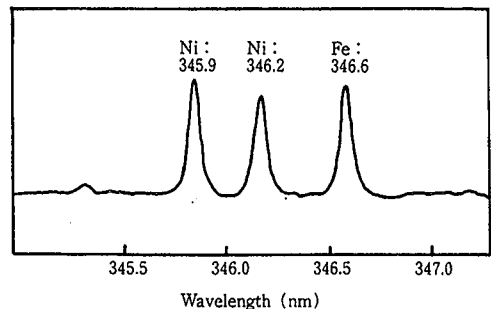


Fig. 3 Hotspot atomic emission spectrum

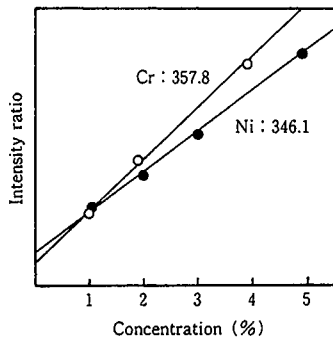


Fig. 4 Correlation between emission intensity and concentration in metal bath

sequentially changing the concentrations of the two elements in the bath to a several-percent level, but no atomic emission was identified at the hotspot.

(3) Relationship between emission intensity and element concentration

The elements whose atomic emissions at the hotspot were identified were then studied as to the relationship between emission intensity and concentration. As an example, the experimental results of nickel and chromium are given in Fig. 4. The spectral area intensity was adopted as the emission intensity, and the correlation of the emission intensity with the element concentration was studied by use of the intensity ratio relative to iron. In the experiment, no strict hotspot temperature compensation was made, and the effect of hotspot temperature was offset by using the data obtained at the same hotspot temperature. As shown in Fig. 4, an extremely good linear relation holds between the emission intensity and the concentration of the elements chromium and nickel in the bath.

In Cu and Pb also, a similarly good correlation was established between spectrum intensity and concentration in the concentration region of 0.01% and over, indicating the applicability of this direct analysis method also to these elements.

4.2 Results of converter experiment

(1) Emission spectra of Mn and Fe

Fig. 5 shows the emission spectra of manganese and iron measured at the hotspot in the converter experiment. The manganese spectrum had three peaks at 403.1, 403.3 and 403.5 nm, while the iron spectrum had one peak at 386.0 nm. These peaks confirmed the optical emission of manganese and iron atoms at the hotspot.

(2) Hotspot temperature

Fig. 6 shows the result of hotspot temperature measurement. The metal bath temperature rose from about 1,300°C to about 1,700°C with the lapse of the oxygen blowing time. The hotspot temperature reached a level of over 2,000°C immediately after ignition and ranged between 2,100 and 2,500°C during the oxygen blow, irrespective of the bath temperature.

(3) Relationship between emission intensity ratio and manganese concentration in bath

The self-absorption coefficient  $n$  of manganese in the measuring system of the converter experiment was calculated to be 0.25 from the relationship between the emission intensity ratio  $I(\text{Mn}/\text{Fe})$  and the manganese concentration  $[\text{Mn}]_{\text{substance}}$  as measured at the same hotspot temperature.

$K'(T)$  calculated according to Eq. (8) was found to be related

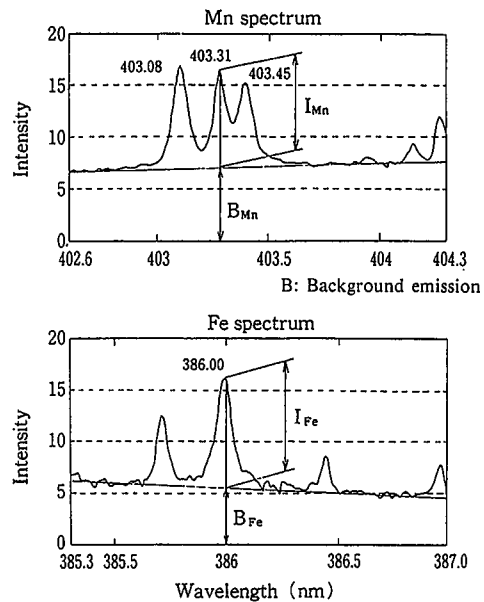


Fig. 5 Atomic emission spectra at hotspot in converter

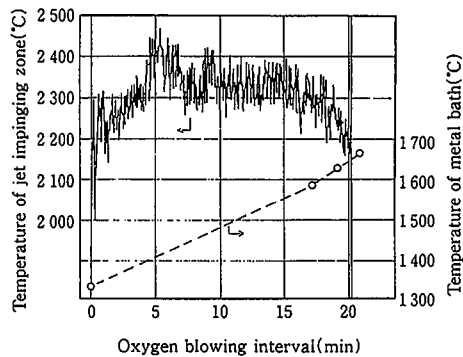


Fig. 6 Hotspot temperature

to the hotspot temperature as given by

$$\log(K'(T)) = -41440/T - 40.555 \times \log(T) + 154.469 \quad \dots\dots(9)$$

Given the fact that  $K'(T)$  in Eq. (9) is a coefficient term correlated to the vaporization rate coefficients of manganese and iron,  $K'_{\text{Mn}}(T)$  and  $K'_{\text{Fe}}(T)$ , the form of its function was arranged so that it became the same as the form of the functions indicating the vaporization rate coefficients.

Equation (8) can be rewritten as Eq. (10), and when the self-absorption coefficient  $n$  and the relationship of Eq. (9) are substituted into Eq. (10), the manganese concentration can be calculated from the measured emission intensity ratio  $I(\text{Mn}/\text{Fe})$ .

$$[\text{Mn}] = \frac{1}{n} \cdot 10^{(10 \log(I(\text{Mn}/\text{Fe})) - \log(K'(T)))} \quad \dots\dots(10)$$

Fig. 7 shows the relationship between the manganese content  $[\text{Mn}]_{\text{measure}}$  calculated by Eq. (10) from the measured emission intensity ratio  $I(\text{Mn}/\text{Fe})$  and the manganese content  $[\text{Mn}]_{\text{substance}}$  determined by the analysis of substance samples. The calculated values agree well with the measured values with a correlation coefficient of 0.924.

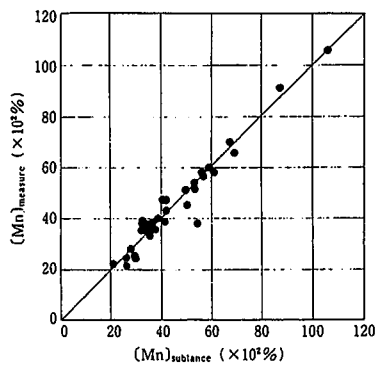


Fig. 7 Correlation between hotspot emission spectrometric method and conventional subplance sampling method

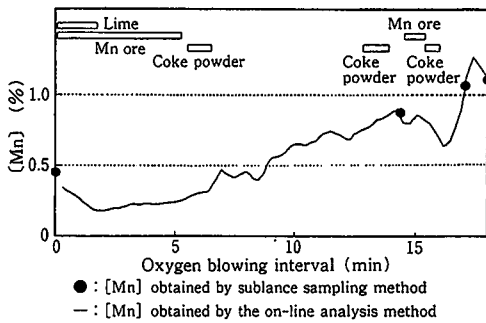


Fig. 8 Measurement of change with time in manganese concentration during oxygen blow

Fig. 8 shows the change in the manganese content [Mn] determined by the on-line analysis method during converter operation. The closed circles indicate the values of manganese content determined by the subplance sampling method. The manganese content values determined by the on-line analysis method are in very close agreement with those determined by the subplance sampling method. In other words, the on-line analysis method can measure in real time the change in the manganese content of the bath during oxygen blowing.

5. Discussion

5.1 Emission of metal elements at hotspot

If metal elements whose concentration is about two orders of magnitude lower than that of iron are to radiate at the hotspot and their emission spectra are to be observed with approximately the same intensity as that of the emission spectrum of iron, the atomic emission efficiency  $A$  expressed by Eq. (1) must be high, or the amount of vaporization at the hotspot must be large.

In Table 1, the relative emission intensity of metal elements at each wavelength is shown as a parameter closely related to the atomic emission efficiency<sup>15)</sup>. Generally, the emission intensity of metal elements does not differ by several orders of magnitude as long as main resonance lines liable to emission are selected.

Fig. 9 shows the temperature dependence of the vapor pressure of metal elements<sup>16)</sup>. The vapor pressures shown are those of single metal elements. It should be noted that they do not necessarily indicate the rate of vaporization from the bath. The vapor pressures of nickel, chromium, copper and lead as well as manganese<sup>10)</sup> studied so far are all higher than the that of iron. Copper and lead, in particular, are higher by more than one order of magnitude than iron in vapor pressure. The element vaporization flux is the greatest factor in the measurement of atomic

Table 1 Relative emission intensity

Element	Wavelength (nm)	Relative intensity (arbitrary unit)
Fe	386.0	4200
Ni	346.1	5000
Cr	357.9	19000
Cu	324.7	50000
Pb	405.7	34000
Mn	403.0	27000
Mo	379.8	29000
	386.4	29000
V	437.9	12000
	411.2	8900

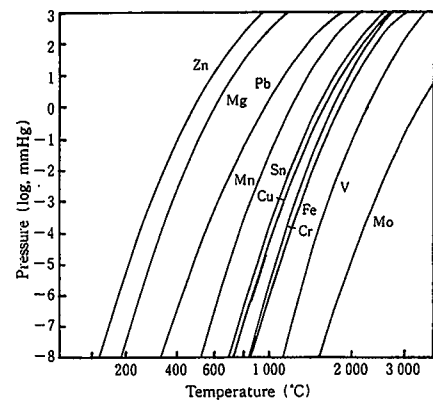


Fig. 9 Vapor pressure curves of elements

emission in the emission spectra from the hotspot. Therefore, such elements as copper and lead that are higher in vapor pressure than iron and are high in emission efficiency are believed to be measurable by the on-line analysis method with high sensitivity.

Molybdenum and vanadium are practically the same in relative emission intensity as the other metal elements, but are lower in vapor pressure at the hotspot temperature than iron by about five and two orders of magnitude, respectively. Molybdenum and vanadium are present in extremely small amounts as atoms at the hotspot and are very weak in emission intensity, as predicted from Eq. (1) in the measurement model. They are thus considered to be unmeasurable by the proposed on-line analysis method.

5.2 Physical significance of  $K'(T)$  in arrangement of data measured in converter experiment

The emission model of the on-line analysis method relates  $K'(T)$  to the temperature-dependence of the vaporization rate of metal elements.

$K_{Fe}^P(T)$  or the vaporization rate coefficient for iron in Eq. (2) is given by the following equation according to Ward et al.<sup>17,18)</sup>:

$$K_{Fe}^P(T) = \frac{\beta P_{Fe}}{\rho} \cdot \frac{M_{Fe}^{1/2}}{2 \pi R T} \text{ (%/s)} \quad \dots\dots(1)$$

where  $M_{Fe}$  is atomic weight of iron; and  $P_{Fe}$  is vapor pressure of iron. A metal data handbook gives the following values for these properties<sup>19)</sup>:

$$P_{Fe} = 10^{(-19710/T - 1.27108(T) + 13.27)} \text{ (mmHg)} \quad \dots\dots(12)$$

$$\rho = 8.34 - 7.76 \times 10^{-4} T \text{ (g/km)} \quad \dots\dots(13)$$

$$\beta = 1333.22, R = 8.314 \times 10^7$$

Ohno et al.<sup>11)</sup> report that the vaporization rate of manganese is governed by diffusion in an iron alloy bath and vaporization from the bath surface when the manganese content is about 1.5% or less. According to their data, the vaporization rate of manganese,  $K'_{Mn}(T)$ , is given by

$$K'_{Mn}(T) = 10^{(-6145/T + 1.7241)} \quad \dots\dots(14)$$

When the self-absorption coefficient  $n$  of 0.25 is substituted into Eq. (6),  $K'(T)$  is given by

$$K'(T) = A' \cdot \frac{(K'_{Mn}(T))^{0.25}}{(K'_{Fe}(T))^m} \quad \dots\dots(15)$$

The substitution of Eqs. (11) to (14) into Eq. (15) yields the relationship between  $K'(T)$ , including the undetermined proportionality constant  $A'$  at a certain value of the self-absorption coefficient  $m$  of iron, and the hotspot temperature  $T$ . The self-absorption coefficient  $m$  of iron can be evaluated by comparing the slope of Eq. (9) with that of Eq. (15).

As shown in Fig. 10, the slope of the experimental results approximately agrees with that of Eq. (15) when  $m = 0.4$ . The finding that the self-absorption coefficient  $m$  of iron is less than 1 means that this result is physically explainable.

The above results show that the data measured in the converter experiment can be explained without contradiction by the hotspot emission model that atoms vaporized near the hotspot radiate and that self-absorbing and nonexcited metal atoms are present in the surrounding region.

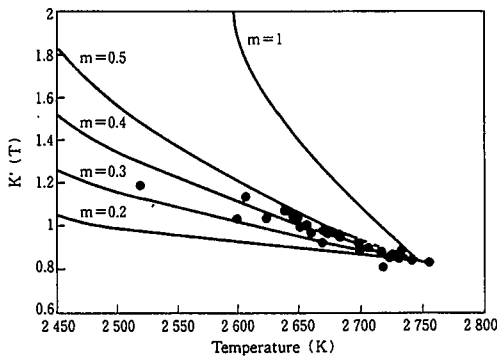


Fig. 10 Effect of self-absorption

## 6. Conclusions

The radiation of atoms at the hotspot formed in the converter during oxygen blowing was studied, and the validity of a proposed hotspot atomic emission model was verified. An on-line analysis method was developed for determining the manganese content of molten steel in the converter by measuring atomic emission spectra from the hotspot. The findings obtained may be summarized as follows:

- (1) Hotspot atomic emission spectra were identified for iron, manganese, nickel, chromium, copper, and lead. A strong correlation was recognized between the emission intensity of each element at the hotspot and the concentration of the element in the bath.
- (2) As expected from the principle of measurement, it was confirmed that no hotspot emission is measurable for such elements as molybdenum and vanadium that is lower in vapor pressure than iron.
- (3) Hotspot emission intensity and hotspot temperature were measured in a 170-ton converter at Sakai Works, and an on-line analysis technique was established for directly determining the manganese concentration in the bath.
- (4) The correlation coefficient of the regression line between the manganese content calculated from the emission intensities of manganese and iron measured by the on-line analysis method and the manganese content determined by the subsample sampling method was 0.942 over the manganese content range of 0.26 to 1.09%.

## References

- 1) Baladin, V.N., Mandel'shtam, S.L.: *Zavod. Lab.* 23, 545 (1957)
- 2) Schaverich, A.B., Shubina, S.B., Danilevokaya, V.V.: *Zavod. Lab.* 31, 169 (1965)
- 3) Bonjic, M., Bourdieu, J.B., Torr, D., Bavber, G.: *Rev. Met.* 67, 237 (1970)
- 4) Ozaki, F., Takahashi, T., Iwai, Y., Gunji, Y., Sudo, E.: *Tetsu-to-Hagané.* 68, 872 (1982)
- 5) Tsunoda, K., Tanimoto, W., Hisada, S., Asakawa, H.: *Tetsu-to-Hagané.* 71, A133 (1985)
- 6) BISRA Annual Report 1966, p. 78; 1967, p. 56; 1968, p. 35
- 7) Ono, A., Chiba, K., Saeki, M., Nibe, Y., Kasai, S.: *Tetsu-to-Hagané.* 71, A129 (1985)
- 8) Golloch, A.: *Proc. of 38th Chemists' Conf.* 1985, p. 31
- 9) Jowitt, R.: *Proc. of 38th Chemists' Conf.* 1985, p. 19
- 10) Chiba, K., Ono, A., Saeki, M., Ohno, T.: *Bunseki Kagaku.* 37, 365 (1988)
- 11) Kawakami, K.: *Tetsu-to-Hagané.* 74, 831 (1988)
- 12) Ohno, T., Ozaki, H., Tsujino, R.: *Tetsu-to-Hagané.* 75, 910 (1988)
- 13) Ikeda, S.: *Journal of the Chemical Society of Japan.* 78, 1232 (1957)
- 14) Kubota, M., Ishida, R.: *Bunko Kenkyu.* 23, 74 (1974)
- 15) *Tables of Spectra-Line Intensities.* NBS Monograph 145, 1975
- 16) Elliott, J.F., Gleiser, M.: *Thermochemistry for Steelmaking.* Vol. 1, Addison-Wesley Publishing Company Inc., p. 269
- 17) Ward, R.G., Aurini, T.D.: *J. Iron Steel Inst.* 204, 920 (1966)
- 18) Ward, R.G.: *J. Iron Steel Inst.* 201, 11 (1963)
- 19) *Japan Institute of Metals: Metal Data Handbook.* Maruzen, 1974, p. 73