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Silicate Structure and Redox Reaction of Manganese Ion[†]

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Abstract

Redox reaction of manganese ion in soda-silicate was investigated with optical absorption method and the relation between silicate structure and state of manganese ion was discussed. In order to interpret the behaviour of manganese ion in reducing condition, a new equation of redox reaction of manganese was proposed. It was suggested that, with increasing P_{O_2}, free oxygen ion in soda-silicate is inclined to be consumed in the form of octahedrally coordinated Mn^{3+} whereas, with decreasing P_{O_2}, in the form of octahedrally coordinated Mn^{2+}. Further, it was also indicated that the application of manganese ion to the indicator of basicity of slag was difficult unless the coordination change is clarified quantitatively.

1. Introduction

Up to present time, structure of slag has been studied with various methods because the roles of slag are very significant in iron- and steel-making. The significance of slag in welding is being reconsidered from structural standpoint. In general, complex silicates are mainly used as slag. Therefore, in order to clarify the essential properties of slag, simple silicates were investigated in many cases in iron- and steel-making. Thus, the clarification of silicate structure is essentially and approximately identified as that of slag structure.

In 1954, the concept of three kinds of oxygens in silicate was introduced by Fincham and Richardson[1] on account of the explanation of desulpherization reaction. Subsequently, Toop and Samis[2] theoretically determined the distribution of free oxygen in several binary silicates from thermodynamical data. In 1970, Kapoor and Frohberg[3] decided the better expressions than those by Toop and Samis. On the other hand, Masson and Whiteway[4],[5],[6] approached to silicate structure by use of polymer theory. Their results were expressed in the form of polyionic distributions instead of free oxygen. Further, Yokokawa and Niwa[7],[8] calculated the activities of component oxides in a few binary and ternary silicate using quasi-lattice theory. Recently, Kapoor and Frohberg developed a model based on statistical thermodynamics of athermal mixture to determine the distributions of complex silicate anions and thermodynamical properties of silicate.[9]

As is generally, the main roles of slag are to remove non-metallic inclusions, to prevent molten metal from reacting to atomsphere and to control the contents of alloying elements. Nowadays, it is doubtless fact that these roles are closely related to the structure of slag. As described above, such relations were approached from following points of view;
(1) the determination of activity of component
(2) the activity (practically, content) of free oxygen, $a_{O^2-}(N_{O^2-})$.
These approaches seem to produce essentially similar results but latter approach has many advantages in order to clarify desulpherization and the distributions of alloy elements. As descussed in the previous paper[10], a_{O^2-} is not perfectly identified as basicity of slag but the physical quantity characterizing slag. Until today, two different approaches have been tried in order to clarify the state of oxygen ion in slag. One is direct approach in which the state of oxygen, especially free oxygen, is clarified. Many succeeds were theoretically obtained whereas few experimental succeeds were reported except the studies with molar refractivity[10] and ESCA[11]. The other is indirect approach in which state of cations affected by oxygen are studied. In most cases of indirect approach, the

valency change of transition metal ion is used. In particular, the behaviour of iron ion in slag has been studied by Mössbauer spectroscopy. However, it is difficult to separate the absorption spectra correctly, and, in most cases, the separation is performed by the aid of computer calculation. On the other hand, it is well known that most of first row transition metal ions have the optical absorption bands in visible region. Some of them, especially manganese and copper, show simple absorption bands in visible region.

From many investigations by magnetic and other methods, it is well established that manganese ion is present in glass as divalent or trivalent. The optical absorptions due to these manganese ions were successfully explained by the application of ligand field theory.[12] From ligand field theory, it can also indicated that there is no ligand field stabilization for divalent manganese ion, Mn^{2+}, in cubic symmetrical field, so that both tetrahedral and octahedral occupations are equally probable if other factors are the same in both cases. In addition, the electronic transitions in Mn^{2+} are all spin-forbidden by Laport's selection rule and this means that the intensities of the absorptions are very weak. On the other hand, the trivalent manganese ion, Mn^{3+}, in an octahedral ligand field gives a single absorption band corresponding to the $^5T_{2g}-{}^5E_g$ transition. Besides, Jahn-Teller distortion is expected when the electronic configuration of Mn^{3+} can be high spin state. On the contrary, Mn^{3+} in a tetrahedral field does not show any optical absorption in visible region but, in most cases, in near infrared region becase cubic crystal splitting energy in tetrahedrally coordinated Mn^{3+} corresponds to 4/9 times of that in octahedrally coordinated Mn^{3+}.

Thus, the possibility of manganese ion as indicator of basicity is considerably expected. Besides, clarification of state of manganese ion in slag is very important because manganese oxide is very often contained in slag. In this study, therefore, relationship between state of manganese ion and structure of slag, especially soda-silicate, was investigated with optical absorption method. Further, these results were discussed by use of theoretial results in previous papers.

2. Experimental Procedures

Specimen slags were prepared from reagent grade Na_2CO_3, $MnCO_3$ and SiO_2. These materials were accurately weighed and mixed in a agate mortar and pestle. After all specimens were melted and equilibrated in a platinum crucible at 1600 °C under various oxygen partial pressures, they were taken out in the

top of the furnace and cooled. In order to estimate whether the equilibrium was attained or not, a few specimens which were prepared at 1600 °C for 48 hr were compared with the corresponding specimens prepared at 1600 °C for 2 hr. It was shown from the comparison that they gave all the same signals, respectively. Therefore, almost all specimen slags were prepared by melting for 2 hr. Subsequently, in order to make parallel planes, they were polished using ethyl-alcohol as coolant. In every optical absorption measurements, blank glasses with the same composition and similar thickness but without any coloring ion were used for the references. Optical absorption spectra were measured in the range of 340 nm to 1500 nm. The apparatus used was a spectrometer of 323 type (Hitachi Co., Ltd.). Specific extinction coefficient was calculated with following equation;

$$E=\frac{1}{C}\log\left(\frac{I^\circ}{I}\right)\frac{1}{T}$$

where E : specific extinction
  C : gram atom of coloring ion per liter of glass
  I° : intensity of the incident light
  I : intensity of the transmitted light
  T : thickness of the glass specimen (cm).

3. Results and Discussion

The assignments of the absorption bands of manganese ion in aqueous solution[13],[14] and several single crystals[15],[16],[17] were well established and, therefore, it is important to examine these spectra beforehand in order to compare the absorption spectra in glasses with those in solution or single crystal. The spectra of divalent manganese ion in a few solutions or single crystal are shown in **Fig. 1**. Divalent manganese ion exhibits several absorption bands. How-
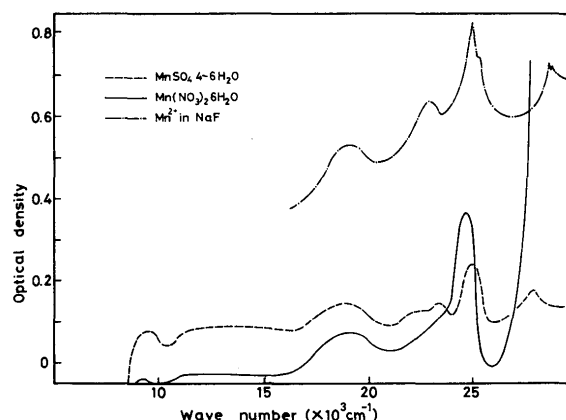

Fig. 1 Optical absorption spectra of Mn^{2+} ion in a few aqueous solutions and a single crystal.

ever, all of them have only less extinction coefficients than 0.1. Further, Weyl showed that Mn^{2+} in soda-lime-silica glass had only one absorption band at 425 nm[18]. Subsequently, the absorption spectra of trivalent manganese ion in several solutions are shown in **Fig. 2.** As shown in the figure, Mn^{3+} ion exhibits a single absorption band near 500 nm. As is generally, it can be considered that the asymmetric band near 500 nm attributes to trivalent manganese ion whereas the very weak band near 420 nm originates in divalent manganese ion. Further, the optical absorption of Mn^{2+} is practically negligible because the extinction
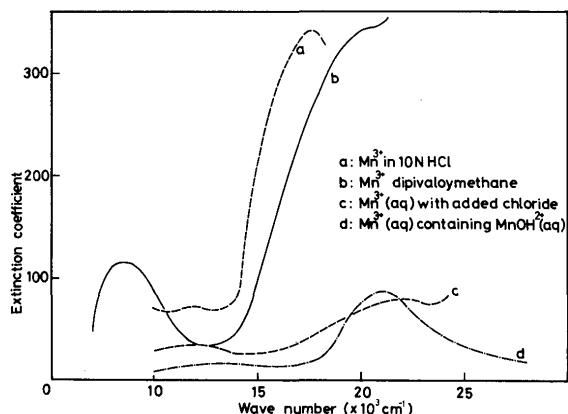

Fig. 2 Optical absorption spectra of Mn^{3+} ion in several solutions.

coefficient of the band caused by Mn^{3+} is 100–1000 times larger than those by Mn^{2+}. The absorption spectra of manganese ion in soda silicate glasses produced in air are shown in **Fig. 3.** The results in the same glasses with a constant composition produced under various oxygen partial pressures are also shown in **Figs. 4, 5 and 6.** As shown in these figures, the ratio $(Mn^{3+})/(Mn^{2+})$ increased (a) with increasing the content of sodium oxide and (b) with increasing the oxygen partial pressure of the atmosphere.

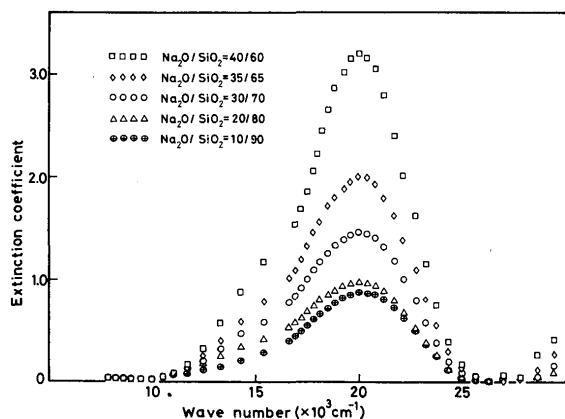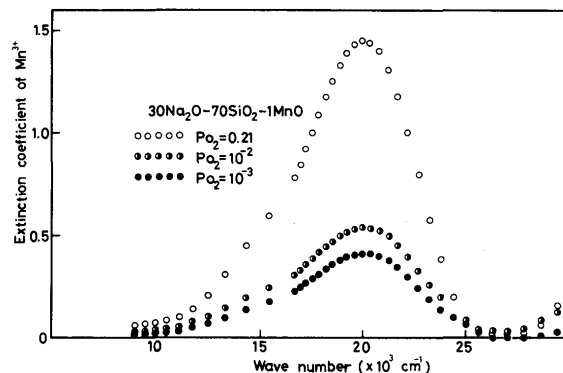**Fig. 3** Optical absorption spectra of manganese ion in soda silicate glasses produced in air.

Fig. 4 Optical absorption spectra of manganese ion in soda silicate glasses produced in the reducing conditions.
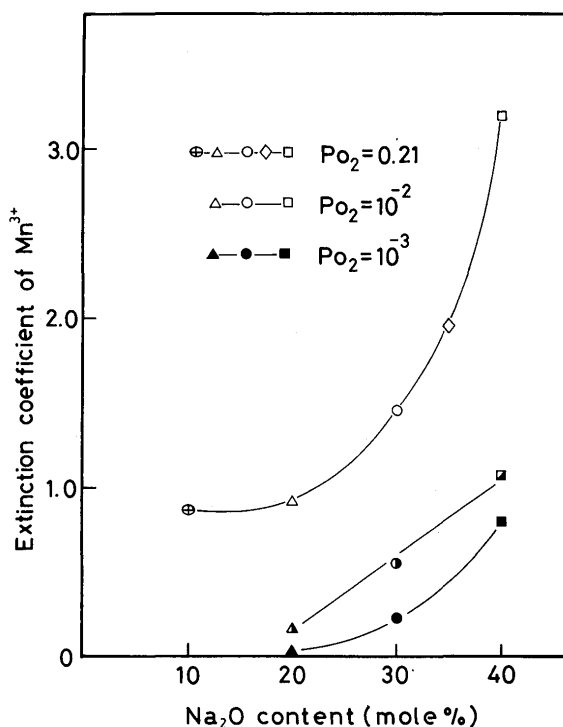

Fig. 5 Dependency of extinction coefficient of spectrum due to Mn^{3+}, $E_{Mn^{3+}}$, upon Na_2O content.
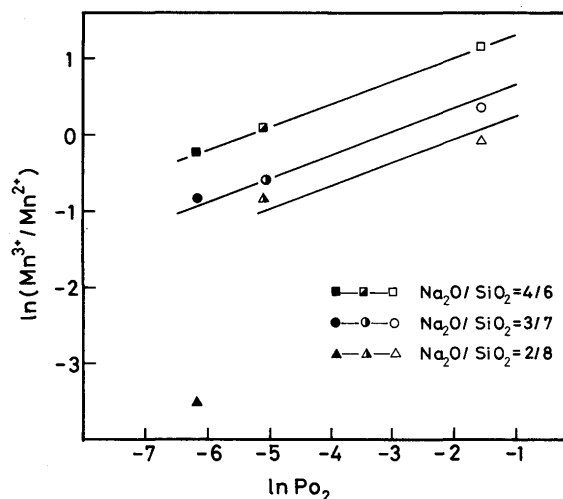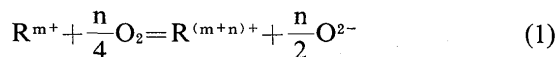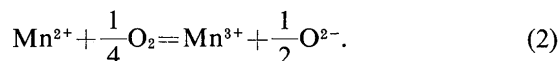

Fig. 6 The relation between P_{O_2} and the ratio $(Mn^{3+})/(Mn^{2+})$.

According to Johnston[19] and Douglas[20], the general form for the redox reaction in glass was expressed as follows;

$$R^{m+}+\frac{n}{4}O_2=R^{(m+n)+}+\frac{n}{2}O^{2-} \tag{1}$$

and redox reaction for manganic-manganous equilibrium in glass is written as follows;

$$Mn^{2+}+\frac{1}{4}O_2=Mn^{3+}+\frac{1}{2}O^{2-}. \tag{2}$$

From equation (2), the equilibrium constant, K_2, is given by

$$K_2=\frac{(Mn^{3+})\,(O^{2-})^{1/2}}{(Mn^{2+})\,(P_{O_2})^{1/4}} \tag{3}$$

Further, this equation can be rewritten as follows;

$$\ln\frac{Mn^{3+}}{Mn^{2+}}=A-\frac{1}{4}\ln P_{O_2} \tag{4}$$

where A is a constant depending K_2 and (O^{2-}). If K_2 and (O^{2-}) are constant in the equation (3), the ratio $(Mn^{3+})/(Mn^{2+})$ increases with increasing oxygen partial pressure. Besides, the slope given by equation (4) is 1/4. Therefore, the experimental result (b) could be successfully explained from equation (4).

On the contrary, the experimental result (a) can not be explained from equation (4) because the ratio (Mn^{3+}/Mn^{2+}) decreases as the content of sodium oxide increases. Thus, the experimental result (a) could not be explainable from the consideration described above. In oraer to interpret such disagreement, Herring suggested that equation (3) may be expressed in terms of activity coefficient, r, and concentration, C, as follows;[21]
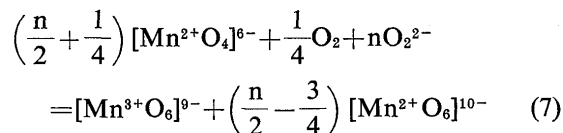
$$K=\frac{r_{Mn^{3+}}\,C_{Mn^{3+}}(O^{2-})}{r_{Mn^{2+}}\,C_{Mn^{2+}}(P_{O_2})^{1/4}}. \tag{5}$$

Besides, he also suggested that the activity coefficient ratio decreases with increasing (O^{2-}). According to Douglas,[21] however, this suggestion can not be accepted because the activity of manganese ion can be replaced by its concentration at low concentration. On the other hand, Homlquist[22] and Budd[21] suggested that these ions exist in the forms of complex ions and the contradiction could be interpreted if their consideration is accepted. According to their proposal, redox reaction of manganese ion are expressed as follows;

$$2Mn^{2+}+\frac{1}{2}O_2+(2x-1)O^{2-}=Mn_2^{3+}O_{2x}^{4x-} \tag{6}$$
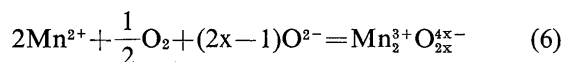
However, any complex ion of divalent manganese was not considered in this suggestion. Thus, clear explanation could not be performed on this behaviour.

By the way, there is no ligand stabilization for divalent manganese ion, so that both tetrahedral and octahedral occupations are equally possible as described above. Therefore, following equation can be suggested;

$$\left(\frac{n}{2}+\frac{1}{4}\right)[Mn^{2+}O_4]^{6-}+\frac{1}{4}O_2+nO_2^{2-}$$

$$=[Mn^{3+}O_6]^{9-}+\left(\frac{n}{2}-\frac{3}{4}\right)[Mn^{2+}O_6]^{10-} \tag{7}$$

Accordingly, it is suggested that divalent manganese ion gradually changes from four coordination to six coordination with decreasing oxygen partial pressure and with increasing the content of free oxygen, (O^{2-}). That is, the increase of free oxygen can be also comsumed by the coordination change of divalent manganese.

Subsequently, the relation between the ratio $(Mn^{3+})/(Mn^{2+})$ and content of free oxygen, $N_{O^{2-}}$, by various approaches are shown in **Figs. 7** and **8**. The content of free oxygen was quated from each result of Kapoor and Frohberg[3] or Masson and Whiteway[6]. The content of free oxygen determined experimentally was quated from the result with molar refractivity[10]. These results clearly showed that the relationship between the ratio $(Mn^{3+})/(Mn^{2+})$ and the content of free oxygen had good linearity at lower partial oxygen
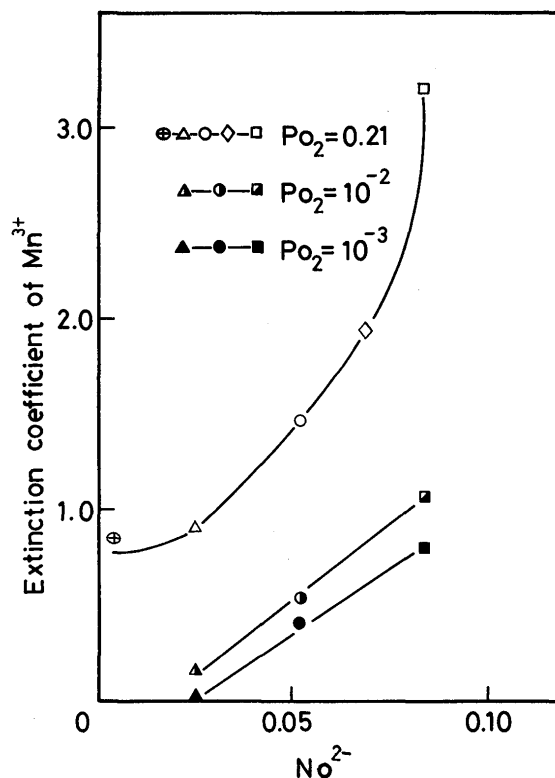

Fig. 7 Dependency of $E_{Mn^{3+}}$ upon the content of free oxygen, $N_{O^{2-}}$, decided from molar refractivity.
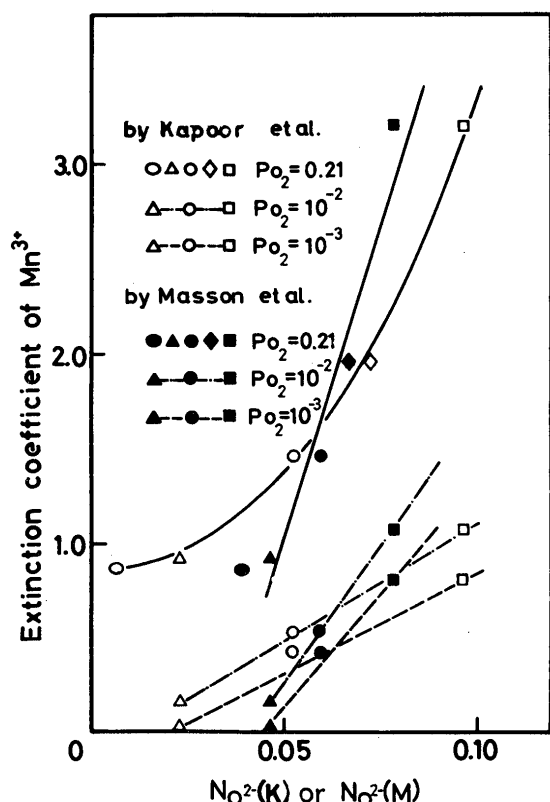
Fig. 8 Dependency of $E_{Mn^{3+}}$ upon $N_{O^{2-}}$ decided from theoretical approaches. ($N_{O^{2-}}$-(K); after Kapoor and Frohberg, $N_{O^{2-}}$-(M); after Masson, Smith and Whiteway)

pressure. From this phenomenon, any definite mechanism can be suggested and this seems to correspond to the determination of n in the equation (7). Further, the fact that the slope was steeper with increasing partial oxygen pressure is also remarkable. This phenomenon can be interpreted as follows;

(1) at higher partial oxygen pressure, free oxygen is inclined to be consumed by occurrence of octahedrally coordinated Mn^{3+},

(2) at lower partial oxygen pressure, free oxygen is inclined to be consumed by occurrence of octahedrally coordinated Mn^{2+}.

Thus, the application of manganese ion to the indicator of basicity of slag seems to be difficult because of following reasons;

(1) the coordination number of Mn^{2+} depends on P_{O_2}

(2) their application is limited to fairly narrow region.

It is also significant to estimate the abscissa and ordinate in Figs. 7 and 8 when state of manganese ion is discussed in detail. The asymmerty of the peak due to octahedrally coordinated Mn^{3+} is not so important if each wave function of 3d electron keeps orthogonality. The influence of divalent manganese is also negligible as described above. However, the dertermination free oxygen content in every approaches were performed

under the various assumptions. For example, the application of Temkin's model is questionable. In molar refractivity method, molar refractivities of some standard materials are unknown and were also decided under a few assumptions. Although there are many unsolved problems on the basicity of slag, the application of manganese ion to indicator of basicity may be possible if the coordination change of divalent manganese ion is clarified.

4. Summary

Redox reaction of manganese ion in soda silicate, especially in reducing condition, was investigated with optical absorption method and the relationship between silicate structure and redox equilibrium or state of manganese ion was discussed using the content of free oxygen which was determined with a few different approaches. In order to clarify the behaviour of manganese ion, especially in reducing condition, a new equation of redox reaction of manganese ion was proposed. In this proposal, the coordination change was taken into consideration with the aid of ligand field theory. Subsequently, it was suggested that with increasing partial oxygen pressure, free oxygen ion in soda silicate slag is inclined to be consumed in the form of octahedrally coordinated Mn^{3+} whereas, with decreasing partial oxygen pressure, in the form of octahedrally coordinated Mn^{2+}. However, it is necessary to certify the existence of octahedrally and tetrahedrally coordinated manganous ion and their ratio with other methods. Further, it was indicated that it was difficult to apply manganese ion to the indicator of the basicity of slag unless the coordination change is clarified quantitatively.

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