FT-IR Spectroscopic Study on Structure of CaO–SiO2 and CaO–SiO2–CaF2 Slags

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(Received on November 12, 2001; accepted in final form January 10, 2002)

The FT-IR spectra of the CaO–SiO2 and CaO–SiO2–CaF2 slags were measured to understand the structural aspects of (fluoro-) silicate systems. The relative intensity of Si–O rocking band is very strong at SiO2 saturation condition and this band disappears in the composition greater than 44.1 (mol%) CaO in the CaO–SiO2 binary system. The bands for [SiO4]tetrahedra at about 1150–760 cm\(^{-1}\) split up with increasing content of CaO greater than 44.1 mol%. The IR bands in this wavenumber range are divided into four groups, that is about 1090, 990, 920, and 870 cm\(^{-1}\), which have been assigned to NBO/Si=1, 2, 3, and 4, respectively. In the CaO–SiO2–CaF2 (2CaO·SiO2·Satd.) system, the center of gravity of the bands at about 1170–710 cm\(^{-1}\) shifts from about 980 to 850 cm\(^{-1}\) by increasing the ratio \(X_{CaF2}/X_{SiO2}\) from 0.22 to 0.64. The bands for [SiO4]tetrahedra are observed from about 1070 to 730 cm\(^{-1}\) in the CaO–17.6(mol%)SiO2–CaF2 system, while these bands are observed from about 1120 to 720 cm\(^{-1}\) in the CaO–40.0(mol%)SiO2–CaF2 system. The effect of substitution of CaF2 for CaO on the depolymerization of silicate network is observed to significantly depend on the SiO2 content in the slags. The bands for [SiO4]tetrahedra are observed from about 1110 to 720 cm\(^{-1}\) in the CaO–SiO2–14.1(mol%)CaF2 system and the center of gravity of these bands shifts from about 990 to 850 cm\(^{-1}\) with increasing CaO/SiO2 ratio. The fraction of the relatively depolymerized units continuously increases from about 0.5 to 0.8 as the composition of slags changes from 2CaO·SiO2 to CaO saturation condition.

KEY WORDS: FT-IR spectra; Si–O rocking; [SiO4]tetrahedra; NBO/Si; depolymerization; silicate network.

1. Introduction

Since the silicate melts have been basic systems in iron and steelmaking as well as in glassmaking processes and geosciences, various physicochemical properties of silicates have been reported. Especially, the structural aspects of silicate systems have mainly been investigated on the basis of various thermodynamic models,1–7) of some experimental techniques,8–26) and, recently, of some computer simulations,27–30) because the almost properties of slags would be affected by its structure. Although the structure of simple binary and aluminosilicate systems would occur in the composition of MO–SiO2 (MO represents a basic oxide) systems would occur in the composition of MO content greater than 33.3 mol%, i.e., disilicate (MO·2SiO2) composition from an analysis of Raman spectra.21) The structural studies of silicates based on Raman spectra have comprehensively been reviewed by McMillan.19,20) Because the vibration modes of the Si–O bond in silicates are generally IR and Raman active, these considerations could also be employed in the structural study based on infrared spectra.16) Actually, the IR wavenumbers (cm\(^{-1}\)) and Raman shift (cm\(^{-1}\)) corresponding to the Si–O bonds in [SiO4]tetrahedra are measured within the identical ranges.8–21)

Although the structure of MO·SiO2 systems has extensively been studied by metallurgists, glass scientists, and mineralogists, the CaO–SiO2–CaF2 system has not widely been studied yet. Tsunawaki et al. concluded that CaF2 contributed to the breakage of some Si–O bonds, when its content was less than 20 mol% and the CaO/SiO2 ratio was smaller than unity from the Raman spectra of the CaO–SiO2–CaF2 system.18) Similar conclusions were drawn by Iguchi et al.22) On the other hand, Luth suggested that
the substitution of fluorine for oxygen ions in the CaO–SiO2–CaF2 system increased the degree of polymerization (DOP) due to the formation of Ca–F complexes.21) Ueda et al. concluded that F– ions would not affect the wavenumber of silicate IR bands.15)

For brevity, the structural aspects of the CaO–SiO2 binary system could be understood on the basis of a decrease in the relative abundance of three dimensional silicate units and an increase in SiO4-tetrahedra with high number of NBO/Si by increasing the content of CaO. However, the effect of CaF2 on the modification of silicate network has ambiguously been reported by some researchers as mentioned above. Hence, the possibility and validity of the Luth’s conclusions with regard to the effect of F– ions on an increase in the DOP of silicates should be reexamined through wide composition ranges.

Therefore, in the present study, the FT-IR spectra of the CaO–SiO2 binary system were simply interpreted on the basis of SiO4-tetrahedral units with various NBO/Si. Furthermore, the role of F– ions in the depolymerization of silicate network was discussed in the viewpoint of NBO/Si of the CaO–SiO2–CaF2 (XCaF2=0.1–0.4) slags from an analysis of FT-IR spectra.

2. Experimental

2.1. Specimen Preparation

Reagent-grade SiO2, CaF2 and CaO calcined from reagent-grade CaCO3 were mixed and melted in a graphite crucible under CO atmosphere during 64 800 sec at 1 823 and 1 773 K for the CaO–SiO2 binary and CaO–SiO2–CaF2 ternary slags, respectively, then water quenched. The experimental samples were confirmed as a glassy type by X-ray diffraction analysis. The quenched samples were crushed to the size less than 100 μm. The contents of each component were determined by conventional titration methods and listed in Table 1.

2.2. Infrared Spectra Measurements

The structure of the investigated slags was analyzed by FT-IR spectroscopy (Nicolet, Avatar 360). FT-IR transmitting spectra were recorded in the 4000–400 cm−1 range using a spectrometer, equipped with a KBr (deuterated triglycerine sulfate with potassium bromide windows) detector. A spectral resolution of 2 cm−1 was chosen. Each sample of 2.0 mg was mixed with 200 mg of KBr in an agate mortar, and then pressed into pellets of 13 mm diameter. The spectrum for each sample represents an average of 20 scans, which were normalized to the spectrum of the blank KBr pellet. The FT-IR spectra have been analyzed by computer software.

3. Results and Discussion

3.1. Infrared Spectra of CaO–SiO2 Binary System

The IR-transmittance of the CaO–SiO2 binary slags is shown in Fig. 1 as a function of wavenumber at different CaO contents. The several kinds of band groups are observed at about 1150–760, 780, 720, 560, 480, and 420 cm−1; these groups correspond to the stretching vibration of SiO4-tetrahedra with various NBO/Si, SiO4-3 ring, SiO4-6 dimer, bending and rocking modes of Si–O bonds, and to the vibration of Ca–O complexes, respectively.5–21,31,32) Changes of the IR bands with CaO content are very similar to the results available in the research literature.12,16–21)

The broad rocking band at about 480 cm−1 stems from rocking of bridging oxygen in a fully polymerized, three-dimensional network.17,33) The relative intensity of this band is very strong at SiO2 saturation condition and it disappears

| No. | CaO (mol%) | SiO2 (mol%) | CaF2 (mol%) |
|-----|------------|-------------|-------------|
| 1-1 | 35.5       | 64.5        | 0.0         |
| 1-2 | 38.9       | 61.1        | 0.0         |
| 1-3 | 44.1       | 55.9        | 0.0         |
| 1-4 | 48.0       | 52.0        | 0.0         |
| 1-5 | 58.3       | 41.7        | 0.0         |
| 2-1 | 29.9       | 70.1        |             |
| 2-2 | 44.9       | 37.6        |             |
| 2-3 | 46.1       | 35.5        |             |
| 2-4 | 57.5       | 25.9        |             |
| 2-5 | 68.5       | 17.8        |             |
| 2-6 | 65.1       | 13.0        |             |
| 2-7 | 51.9       | 18.7        |             |
| 2-8 | 44.0       | 28.8        |             |
| 2-9 | 34.5       | 26.3        |             |
| 2-10| 27.7       | 31.8        |             |
| 2-11| 35.5       | 30.6        |             |
| 2-12| 40.8       | 24.1        |             |
| 2-13| 53.0       | 15.5        |             |
| 2-14| 52.1       | 8.7         |             |
| 2-15| 38.7       | 20.4        |             |
| 2-16| 36.4       | 22.8        |             |
| 2-17| 37.2       | 23.2        |             |
| 2-18| 34.4       | 25.5        |             |
| 2-19| 32.6       | 23.4        |             |
| 2-20| 23.2       | 31.1        |             |
in the composition greater than 44.1 mol% CaO. Further addition of CaO results in the transition of Si–O rocking to Si–O bending mode and the formation of Ca–O complexes. In addition, the weak IR band for [Si\textsubscript{2}O\textsubscript{7}]\textsuperscript{6}\textsuperscript{3+}-dimer is observed at SiO\textsubscript{2} saturated composition and disappears at 38.9 mol% CaO. The relative intensity of the IR band for [Si\textsubscript{2}O\textsubscript{7}]\textsuperscript{6}\textsuperscript{3+}-dimer increases with increasing CaO content from 44.1 to 58.3 mol%.

The bands for [Si\textsubscript{2}O\textsubscript{7}]\textsuperscript{6}\textsuperscript{3+}-tetrahedra at about 1150–820 cm\textsuperscript{-1} at SiO\textsubscript{2} saturation condition extend to about 1150–760 cm\textsuperscript{-1} at dicalcium silicate saturation and continuously split up with increasing content of CaO greater than 44.1 mol%. The IR bands in this wavenumber range are divided into four groups, that is about 1090, 990, 920, and 870 cm\textsuperscript{-1}, which have generally been assigned to [Si\textsubscript{3}O\textsubscript{10}]\textsuperscript{8}\textsuperscript{2+}-(ring), [Si\textsubscript{3}O\textsubscript{10}]\textsuperscript{8}\textsuperscript{2+}-(chain), [Si\textsubscript{3}O\textsubscript{10}]\textsuperscript{8}\textsuperscript{2+}-(dimer), and [Si\textsubscript{3}O\textsubscript{9}]\textsuperscript{6}\textsuperscript{2+}-(monomer, tetrahedra)\textsuperscript{25}

Hence, the spontaneous depolymerization reaction such as Eqs. (1) and (2) results in the formation of [Si\textsubscript{3}O\textsubscript{9}]\textsuperscript{6}\textsuperscript{2+}-tetrahedra (NBO/Si = 3) and [Si\textsubscript{2}O\textsubscript{4}]\textsuperscript{4+}-tetrahedra (NBO/Si = 4) units. This is in good correspondence with the results shown in Fig. 1, where the bands for the NBO/Si = 3 (920 and 720 cm\textsuperscript{-1}) and 4 (870 cm\textsuperscript{-1}) units are observed in the composition greater than 44.1 mol% CaO at the expense of NBO/Si = 2 (780 cm\textsuperscript{-1}) band.

The fractions of [Si\textsubscript{2}O\textsubscript{4}]\textsuperscript{4+}-tetrahedra with NBO/Si = 4, 3, 2, and 1 can be estimated from the relative intensity of each band from 1150 to 760 cm\textsuperscript{-1} consists of four Gaussian bands at 870, 920, 990, and 1090 cm\textsuperscript{-1}, respectively.

**Figure 3** exhibits the fractions of [Si\textsubscript{2}O\textsubscript{4}]\textsuperscript{4+}-tetrahedra with each number of NBO/Si as a function of slag composition in the CaO–SiO\textsubscript{2} binary system. In the present work, each NBO/Si unit is grouped into NBO/Si = 1 + 2 and 3 + 4 as a relatively polymerized and depolymerized structural units, respectively, to minimize an analytical error could be occurred during the estimation of the relative area of each IR band. Also it is assumed that the structural changes could dominantly be affected by the fractions of major polyanionic group between NBO/Si = 1 (3) and 2 (4).

The fraction of NBO/Si = 1 + 2 units is about 0.65 at SiO\textsubscript{2} saturated boundary and decreases with increasing CaO content, followed by nearly constant value of about 0.25. The fraction of NBO/Si = 3 + 4 units exhibits an opposite tendency to that of NBO/Si = 1 + 2 units at less than about 45 mol% CaO. Therefore, it is suggested that the structure of silicate melts would not significantly be affected by slag composition at X\textsubscript{CaO} = 0.45, mainly because the silicate structure would be constituted by the dominantly depolymerized units as about 75% NBO/Si = 3 + 4 units. Actually, the viscosity of the CaO–SiO\textsubscript{2} binary system, which could strongly be dependent on slag structure, sharply decreases with increasing CaO content up to about 45 mol%, followed by very slight decrease.\textsuperscript{26}

Recently, Park and Rhee proposed that the dissociation of CaO into Ca\textsuperscript{2+} and O\textsuperscript{2-} ions in the CaO–SiO\textsubscript{2} binary slag would not necessarily be complete and thus the dissociation ratio of CaO would be a function of slag composition from the fractions of bridging and non-bridging oxygen estimated by using X-ray photoelectron spectroscopy (XPS).\textsuperscript{26} It is of interest, in their results, that the dissociation ratio of CaO abruptly increases from 0.74 to 0.92 with increasing CaO content greater than 44.8 mol% (Fig. 3). Based on these results, they suggested that the silicate melts could be divided into two regions on either side of 44.8 mol% CaO. Therefore, by combining this with the present results (Figs. 1 and 3), it is proposed that an abrupt increase in fraction of [Si\textsubscript{2}O\textsubscript{4}]\textsuperscript{4+}-tetrahedra with NBO/Si = 3 + 4...
at about $X_{\text{CaO}}=0.45$ could be associated with nearly complete, that is, close to about 92 to 97%, dissociation of CaO in the silicate melts.

### 3.2. Structural Aspects of CaO–SiO$_2$–CaF$_2$ Ternary System

In fluorine-containing slags, the F$^-$ ions as well as O$^{2-}$ ions play an important role in the depolymerization of network structure. In Sec. 3.1., the role of O$^{2-}$ ions without F$^-$ ions in the depolymerization reaction of silicate network was discussed. From these backgrounds, the effect of F$^-$ ions on silicate structure will be discussed.

#### 3.2.1. Effect of CaF$_2$ Addition at Dicalcium Silicate (C$_2$S) Saturation Condition

**Figure 4** exhibits the IR-transmittance of the CaO–SiO$_2$–CaF$_2$ (C$_2$S-satd.) system as a function of wavenumber at different CaF$_2$/SiO$_2$ ratios. Because the steelmaking slags are generally saturated by solid C$_2$S phase ($a_{\text{C}_2\text{S}}=1$), the effect of CaF$_2$ on the depolymerization of slag saturated by C$_2$S has been discussed in this section.

The transmitting bands from 1170 to 710 cm$^{-1}$ and at about 520 cm$^{-1}$ are assigned to the stretching vibration of [SiO$_4$]-tetrahedra with various NBO/Si and bending mode of Si–O bonds, respectively.\cite{9,21,35,36} It is confirmed that the IR bands for [SiO$_4$]$_2$-dimer and Ca–O complexes are not observed in fluorosilicates. The bands at about 650 cm$^{-1}$ have been speculated to [SiF$_4$]$^{2-}$-octahedral complexes by some researchers.\cite{21,34} However, the exact assignment to this bands is not reported yet. If it is in the case that the bands at about 650 cm$^{-1}$ correspond to [SiF$_4$]$^{2-}$-octahedral complexes, the relative intensity of this bands probably decreases with increasing F/S ratio due to decrease in the activity of SiO$_2$.

The substitution of fluorine for either bridging (O$^9$) or non-bridging (O$^-$) oxygen will distort the electronic environment of the Si atom because of higher electronegativity of fluorine relative to oxygen. This distortion will weaken the remaining Si–O bonds in [SiO$_4$]-tetrahedra, decreasing the force constants and the frequencies of vibrations involving Si–O bonds.\cite{21,35,36} In Fig. 4, it is shown that the center of gravity of the bands at about 1170–710 cm$^{-1}$ slightly shifts from about 980 to 850 cm$^{-1}$ by increasing the ratio F/S from 0.22 to 0.64. This indicates that the degree of polymerization of silicate melts in equilibrium with C$_2$S (2CaO·SiO$_2$) decreases with an increase of F/S ratio. The modification of silicate network can be discussed more quantitatively by estimating the fractions of [SiO$_4$]-tetrahedra with various NBO/Si as described in Sec. 3.1.

**Figure 5** exhibits the fractions of [SiO$_4$]-tetrahedra with NBO/Si=1+2 and 3+4 as a function of F/S ratio in the CaO–SiO$_2$–CaF$_2$ (C$_2$S-satd.) system. The frequency of the band resulting from a Si–F stretching vibration in [SiO$_4$F]$^{5-}$-tetrahedra in CaF$_2$-containing silicates has been known to be about 945 cm$^{-1}$, that is, overlap with bands resulting from Si–O vibrations in the same region.\cite{1,13} These trends are also observed in the CaO–Al$_2$O$_3$ and CaO–Al$_2$O$_3$–CaF$_2$ systems.\cite{35,36} In addition, it has been
reported that an increasing F/O in [SiO\textsubscript{n}F\textsubscript{4-n}]-tetrahedral complexes decreases the frequency of the resultant band in the Raman and IR spectrum by about 50 cm\textsuperscript{-1} per oxygen replaced by fluorine.\textsuperscript{21,37} Therefore, the band shift observed in Fig. 4 could be understood by an increase in the ratio of fluorine to oxygen in [SiO\textsubscript{n}F\textsubscript{4-n}]-tetrahedral complexes on the basis of depolymerization reaction as given in Eqs. (3) and (4).

3.2.2. Effect of Substitution of CaF\textsubscript{2} for CaO at a Fixed SiO\textsubscript{2} Content

Figure 6 exhibits the IR-transmittance of the (a) CaO–17.6(mol%)SiO\textsubscript{2}–CaF\textsubscript{2} and (b) CaF\textsubscript{2}–40.0(mol%)SiO\textsubscript{2}–CaF\textsubscript{2} systems as a function of wavenumber at different \(X_{\text{CaF}/X_{\text{CaO}}}\) (F/C) ratio. The transmitting bands at about 520 cm\textsuperscript{-1} are assigned to the bending mode of Si–O bonds.\textsuperscript{9–21} The bands for [SiO\textsubscript{4}]-tetrahedra with various NBO/Si are observed from about 1070 to 730 cm\textsuperscript{-1} in the 17.6 (mol%) SiO\textsubscript{2} bearing system (Fig. 6 (a)), while these bands are observed from about 1120 to 720 cm\textsuperscript{-1} in the 40.0 (mol%) SiO\textsubscript{2} system (Fig. 6 (b)). It is noticed that the greater the content of SiO\textsubscript{2} in slags, the higher the upper limit of the bands for [SiO\textsubscript{4}]-tetrahedra. This indicates that the more polymerized structural units constitute the network in the high SiO\textsubscript{2}-containing system. Also, the bands at about 1060 to 1030 cm\textsuperscript{-1} (NBO/Si=1 units) are observed in Fig. 6 (b), while these bands are not observed in Fig. 6 (a).

The fractions of [SiO\textsubscript{4}]-tetrahedra with NBO/Si=1+2 and 3+4 are shown in Fig. 7 as a function of F/C ratio in the 17.6 (mol%) SiO\textsubscript{2} and 40.0 (mol%) SiO\textsubscript{2} bearing systems. It is of interest that the effect of substitution of CaF\textsubscript{2} for CaO on the depolymerization of silicate network is somewhat different in both of systems.

In the relatively basic region, that is, lower SiO\textsubscript{2} containing system, the fraction of NBO/Si=3+4 units is about 0.8, indicating that the structure of slags would nearly be depolymerized into the simple anionic groups and be independent of CaF\textsubscript{2}/CaO ratio. The fraction of NBO/Si=3+4 units is estimated to be about unity at F/C ≡ 0.84; thus, the slags would qualitatively be composed of discrete anionic groups such as [SiO\textsubscript{4}]\textsuperscript{4-}-tetrahedra (NBO/Si=4) and [Si\textsubscript{3}O\textsubscript{6}2-]-dimer (NBO/Si=3) units.

However, in the relatively acidic region, that is, higher SiO\textsubscript{2} containing system, the fractions of NBO/Si=1+2 and 3+4 units are significantly dependent on the ratio of CaF\textsubscript{2} to CaO. The fraction of NBO/Si=3+4 units increases with increasing F/C ratio up to about 0.5, followed by an abrupt decrease and then a constant value of about 0.5. From the estimated results shown in Fig. 7, the structural role of fluorine and oxygen ions in silicate modification could be discussed.

In the composition less than F/C ≡ 0.5 (i.e., about 20.4 (mol%) CaF\textsubscript{2}), the role of F\textsuperscript{-} ions in the modification reaction of silicate network as given in Eqs. (3) and (4) would be more dominant than that of O\textsuperscript{2-} ions would be. The contribution of both CaF\textsubscript{2} and CaO to the silicate modification would be similar to each other in the composition of F/C ratio from about 0.5 to 0.6; this means that an increase in two moles F\textsuperscript{-} ions would be compensated by one mole O\textsuperscript{2-} ions in this region. Finally, in the composition of F/C ratio greater than about 0.6, the F\textsuperscript{-} ions would behave as a diluent for O\textsuperscript{2-} ions in the depolymerization of silicate polyanions. Tsunawaki et al. reported that the addition of CaF\textsubscript{2}
greater than about 20 mol% was not effective on a decrease in the degree of polymerization, albeit in the highly acidic compositions such as (mol%CaO)/(mol%SiO$_2$)=0.67.\textsuperscript{10} On the other hand, Luth obtained the experimental results that the substitution of CaF$_2$ for CaO in the CaO–SiO$_2$–CaF$_2$ ($X_{\text{SiO}_2}=0.4–0.5$) system caused a decrease in the relative intensity of the band at about 850 cm$^{-1}$ (NBO/Si=4 unit) and an increase in the intensity of the band at about 1 050 cm$^{-1}$ (NBO/Si=1 unit) in the Raman spectra of the quenched glasses.\textsuperscript{21} Thus, he suggested that the substitution of CaF$_2$ for CaO at a fixed SiO$_2$ content would cause an increase in bulk polymerization of the glass and that the mechanism consistent with polymerization accompanying this substitution would be the formation of Ca–F complexes, because the effect of the formation of Si–F bonds on vibrations involving Si–O bonds could not explain the systematic increase in the relative intensity of higher-frequency bands in the 1120 to 720 cm$^{-1}$ region. The formation of such complexes, he explained, would remove Ca$^{2+}$ ions from a network-modifying role. However, their conclusion leaves some room for further discussion, because the F$^-$ ions would directly participate in the network modification as given in Eqs. (3) and (4) rather than Ca$^{2+}$ ions would participate. Therefore, it is proposed, in this study based on thermodynamic view, that the formation of Ca–F complexes at F/C\(\equiv\)0.6 (i.e., \(\geq \)23 (mol%)CaF$_2$) would qualitatively decrease the activity of F$^-$ ions, resulting in a decrease of the driving force of the reaction given in Eq. (3). In addition, because the activity of O$^{2-}$ ions, namely $a$$_{C_{2}O}$ would significantly be low ($a$$_{C_{2}O}$=1.3$\times$10$^{-3}$–6.5$\times$10$^{-4}$ at 1 773 K) in this region, the reactions given in Eqs. (1) and (2) probably forward to the left hand side in some extent.\textsuperscript{38} However, because the Ca–F bond is highly ionic as about 80% based on the Pauling’s electronegativity concept, the intensity of bands in the Raman and IR spectrum from vibrations involving these complexes will be low.\textsuperscript{21,39} Thus, vibrations from fluorine-containing complexes do not contribute detectably to the Raman and IR spectra of these slags and glasses. Consequently, the more quantitative analytical methods would be required than the spectroscopic techniques to investigate the quantitative effect of F$^-$ ions on the structure of silicates at high CaF$_2$ bearing compositions.

3.2.3. Effect of Basicity at a Fixed CaF$_2$ Content

Figure 8 exhibits the IR-transmittance of the CaO–SiO$_2$–14.1 (mol%)CaF$_2$ system as a function of wavenumber at different $X_{\text{CaO}}/X_{\text{SiO}_2}$ (C/S) ratio. The compositions saturated by C$_2$S (2CaO·SiO$_2$), C$_3$S (3CaO·SiO$_2$), and CaO were chosen to investigate the effect of basicity on the structure of silicates containing CaF$_2$. The bands for [SiO$_4$]tetrahedra with various NBO/Si are observed from about 1110 to 720 cm$^{-1}$. It is observed that the center of gravity of these bands slightly shifts from about 990 to 850 cm$^{-1}$ with increasing C/S ratio, indicating that the degree of polymerization decreases by increasing the chemical potential of O$^{2-}$ ions. Also, the weak IR bands at about 1 070 through 1 030 cm$^{-1}$ (NBO/Si=1 units) observed in the C$_3$S saturated composition disappear at C$_3$S saturated composition.

The fractions of [SiO$_4$]tetrahedra with NBO/Si=1+2 and 3+4 are shown in Fig. 9 as a function of C/S ratio in the CaO–SiO$_2$–14.1 (mol%)CaF$_2$ system. The fraction of NBO/Si=1+2 units continuously increases from about 0.5 to 0.8 as the composition of slags changes from C$_2$S to CaO saturation condition.

It is meaningful to compare the results shown in Figs. 3 and 9 to understand the effect of basicity and fluorine ions on the silicate depolymerization. The fraction of [SiO$_4$]tetrahedra with NBO/Si=3+4 is about 0.49, 0.66, and 0.84 at C/S ratio of 1.7, 3.0, and 3.8, respectively, in the CaO–SiO$_2$–14.1 (mol%)CaF$_2$ system. However, the same fraction of [SiO$_4$]tetrahedra with NBO/Si=3+4 is obtained at C/S ratio of 0.68, 0.74, and 0.79, respectively, in the CaO–SiO$_2$ binary system. This means that the amount of O$^{2-}$ ions required for the maintaining the similar level of degree of polymerization in the highly basic slags containing F$^-$ ions would be greater than that in the non-fluoride slags. Thus, it is suggested that the CaF$_2$ added into the highly basic system, that is C/S\(\equiv\)1.5 would behave as a diluent of CaO in the CaO–SiO$_2$–CaF$_2$ system.
the viewpoint of silicate modification reaction, which has generally been accepted.

4. Conclusions

The FT-IR spectra of the CaO–SiO$_2$ and CaO–SiO$_2$–CaF$_2$ slags were measured to understand the structural aspects of (fluoro-) silicate systems. The infrared spectra of the CaO–SiO$_2$ binary system were interpreted on the basis of [SiO$_4$]-tetrahedral units with various NBO/Si. Furthermore, the role of F$^-$ ions in the depolymerization of silicate network was discussed. The results of the present study can be summarized as follows:

1. The relative intensity of Si–O rocking band is very strong at SiO$_2$ saturation condition and this band disappears in the composition greater than 44.1 (mol%) CaO in the CaO–SiO$_2$ binary system. Further addition of CaO results in the transition of Si–O rocking to Si–O bending mode and the formation of Ca–O complexes. The weak IR band for [SiO$_4$]$^{4-}$-ring is observed at SiO$_2$ saturated composition and disappears over 38.9 (mol%) CaO. The relative intensity of the IR band for [SiO$_4$]$^{4-}$-dimer increases with increasing CaO content from 44.1 to 58.3 mol%. The bands for [SiO$_4$]-tetrahedra at about 1 150–760 cm$^{-1}$ split up with increasing content of CaO greater than 44.1 mol%. The IR bands in this wavenumber range are divided into four groups, that is about 1 090, 990, 920, and 870 cm$^{-1}$, which have been assigned to NBO/Si$^1$ and decreases with increasing CaO content, followed by nearly constant value of about 0.25.

2. The IR bands for [SiO$_4$]$^{4-}$-dimer and Ca–O complexes are not observed in the CaO–SiO$_2$–CaF$_2$ ternary system. The center of gravity of the bands at about 1 170–710 cm$^{-1}$ slightly shifts from about 980 to 850 cm$^{-1}$ by increasing the ratio $X_{Ca}/X_{SiO_2}$ from 0.22 to 0.64 at C$_2$S saturation condition. Also, the fraction of NBO/Si=3+4 units increases by increasing the ratio CaF$_2$/SiO$_2$.

3. The bands for [SiO$_4$]-tetrahedra with various NBO/Si are observed from about 1 070 to 730 cm$^{-1}$ in the CaO–17.6 (mol%)SiO$_2$–CaF$_2$ system, while these bands are observed from about 1 120 to 720 cm$^{-1}$ in the CaO–40.0 (mol%)SiO$_2$–CaF$_2$ system. The bands at about 1 060 through 1 030 cm$^{-1}$ (NBO/Si=1 units) are only observed in the 40.0 (mol%) SiO$_2$ bearing system.

4. In the lower SiO$_2$ containing system, the fraction of NBO/Si=3+4 units is about 0.8, which is independent of CaF$_2$/CaO ratio. The fraction of these units is estimated to be about unity at $X_{CaF_2}/X_{CaO}$=0.84. However, in the higher SiO$_2$ containing system, the fraction of NBO=3+4 units increases with increasing $X_{CaF_2}/X_{CaO}$ ratio up to about 0.5, followed by an abrupt decrease and then a constant value of about 0.5.

5. The bands for [SiO$_4$]-tetrahedra with various NBO/Si are observed from about 1 110 to 720 cm$^{-1}$ in the CaO–SiO$_2$–14.1 (mol%)CaF$_2$ system and the center of gravity of these bands slightly shifts from about 990 to 850 cm$^{-1}$ with increasing CaO/SiO$_2$ ratio. Also, the weak IR bands at about 1 070 through 1 030 cm$^{-1}$ (NBO/Si=1 units) observed in the 2CaO·SiO$_2$ saturated composition disappear at 3CaO·SiO$_2$ saturated composition. The fraction of NBO/Si=3+4 units continuously increases from about 0.5 to 0.8 as the composition of slags changes from 2CaO·SiO$_2$ to CaO saturation condition.

Acknowledgments

This work was financially supported by POSCO (Grant No.: 2000X060) and one of the authors (JHP) was supported by the Brain Korea 21 Project. Discussions with Prof. J. Newack at the University of Applied Sciences (Germany) are also appreciated.

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