

CHARACTERISTICS OF FIRE PROTECTIVE COATING USING TERNARY SOLUBLE SILICATE

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ABSTRACT

The fire protective coating can reduce certain damages in case of fire, also conserve energy by thermal insulation and prevent corrosion and erosion in normal daily life by means of blocking thermal transfer, that were generally made of organic, inorganic and metallic materials as adiabatic coating. In case of inorganic material such as soluble silicate, it produces less toxic substances which are exposed to fire, and have a plenty of raw material. Also inorganic thermal insulator is good in heat resistance.

To develop such an excellent inorganic thermal insulator, the study of fire protective coating using the alkali silicate is necessary. The principle of intumescence for alkali silicate is from rapid evolution of water in the coating material, the quantity of water in it is of course influenced on the degree of intumescence. The phenomenon of intumescence in ternary silicate is increased as the radius of ion is bigger, and this is caused by evolution of so many kinds of water. The individual degree of intumescence is ordered like this ; $K^+ > Na^+ > Li^+$.

The best protection effect is similarly found to intumescence of ternary silicate. The result of X-ray diffraction analysis indicates that $KHSi_2O_5$ is an important ingredient in K-silicate.

INTRODUCTION

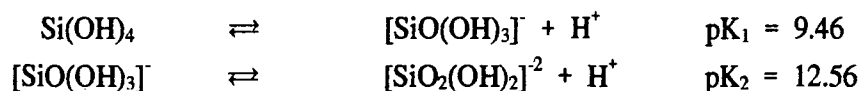
Steel is mostly used as a framework of large buildings and containing facilities for dangerous substances. Provided that steel framework is exposed to fire without any protection in case of accident, the tensile and compressive strength of the material will be rapidly decreased. This accelerates the rate of fire spreading and results a great disaster as well as the collapse of the building itself. The fire protective coating should be good in fire proofing characteristics and does not produce any harmful substance. It is a significant work to develop such a fire protective coating [1-3].

In case of inorganic material such as soluble silicate, it produces less toxic substances when exposed to fire and a plenty of raw material can be supplied. Inorganic thermal insulator is good in heat resistance and therefore is effective in fire proofing. and amount of coating to unit area should also be reduced at least. It is desirable that the construction of the coating should be simple and capable of blocking temperature is high. This soluble silicate, when applied, has the property of fire proofing characteristics by expansion of various internal water content when exposed to fire [4,5]. Concerning the fire protection of the silicate, D.E. Veinot has conducted several studies on expansion and intumescence [6,7]. They gave us useful information on advantages of using soluble silicate-based coating to organic-based. They also stressed that the physical structure of silicate solution which is necessary to understand the chemical composition and the state of coating in dry condition.

In this work, therefore, to investigate the properties of protective coating, studied the effect of molar ratio for lithium, sodium and potassium silicates to enhance the degree of heat resistance. Therefore, thermal characteristics, solubility, crystal structure, intumescence and protection time of various mixture which are influenced to the physical and chemical properties of the protective coatings were investigated.

THEORETICAL DISCUSSION

Soluble silicate is consisted of various forms of silica component in a solution and this is shown in Fig. 1 which represents the boundary of solubility curve [8]. Mononuclear $\text{Si}(\text{OH})_4$ in a low concentration region is in equilibrium, at 25°C , with $[\text{SiO}(\text{OH})_3]^-$, $[\text{SiO}_2(\text{OH})_2]^{2-}$ which have dissociation constants as below. If strongly alkalized, it has a few $[\text{SiO}(\text{OH})_3]^-$ ions.



In a high concentration region the equilibrium of the solution is extremely complicated due to the mononuclear $\text{Si}(\text{OH})_4$ and the ionic species of $\text{Si}(\text{OH})_4$ that form siloxane(-Si-O-Si-) groups. According to Iler [9], silicic acid, $\text{Si}(\text{OH})_4$ tends to be polymerized in the form of a polymer that has mostly siloxane bondings and the least non-condensed -SiOH. As the polymerization proceeds in this way, condensation induces ring structure by addition of monomers and other types of ring structure to form larger three-dimensional spherical structure. These ring structures is changed to their most condensed state by the -Si(OH) and SiO^- groups in the border. The diameter of these polymers are in the range of 1-2 nm.

Polymerization is a reversible process in views of siloxane production. The increase of OH concentration accelerates ionization, condensation, hydrolysis and depolymerization, also the increase of it makes that the monomer $\text{Si}(\text{OH})_4$ reaches to equilibrium that contains polymers. The size and concentration of the polymers depend on the concentration of silica and the molar ratio of silica

for the metallic oxide. Through the increase of molar ratio, higher polymerization, that is, larger size and particles can be formed [9].

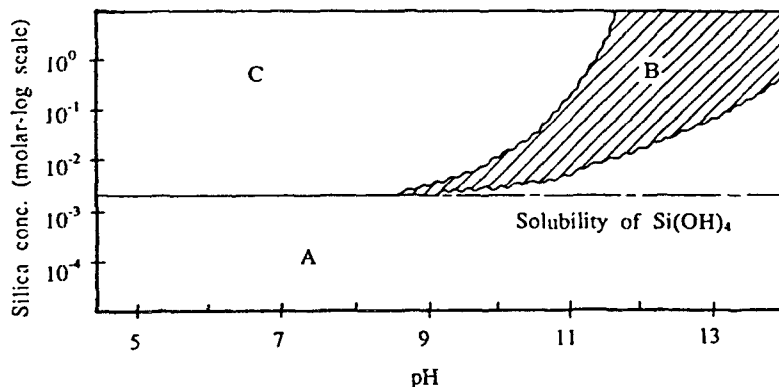


Fig. 1. Summary of silicate in solution

- A) Mononuclear species
- B) Polysilicate ions in solution
- C) Solution unstable with respect to amorphous silica.

EXPERIMENT

Experimental Apparatus

A test device was designed to investigate the protection time and the degree of intumescence of alkali silicate. The structure is shown in Fig. 2. The outside of this device was made of steel tube with inner diameter of 160mm. A cylindrical ceramic tube was inserted into the inner surface of the device. The ceramic tube is 390mm high and the inner diameter of it is 90mm. Thermal insulator was filled between the two tubes to block any heat loss that can be caused from the cylindrical furnace inside, and to make the heat flow constant. The cylindrical part of the furnace was fixed above a steel plate welded at the height of 210mm from the bottom where the bunsen burner will be placed.

The experiment of intumescence and protection time were followed on the time-temperature curve of ASTM E 119 [10]. The bunsen burner is properly placed inside of the cylindrical furnace to prevent unstable air flow that affect the flame. The aluminum plate(150mm×150mm×1.5mm) coated with silicate sample is placed at upper part of the device and fixed with a cylindrical ceramic tube which is about 50mm high. A heat diffuser is fixed at the lower part of sample.

The surface of the plate coated with the alkali silicate is facing high-temperature part of the device and the other surface is facing upward where is not coated. Two sensors of the thermocouple lead wire, installed to measure the temperature of both sides of the device, are placed, respectively, at a distance of 10mm from the plate. Protection time was checked from the moment that coated surface of the aluminum plate is exposed to the flame until unexposed surface of the plate is reached at 300°C.

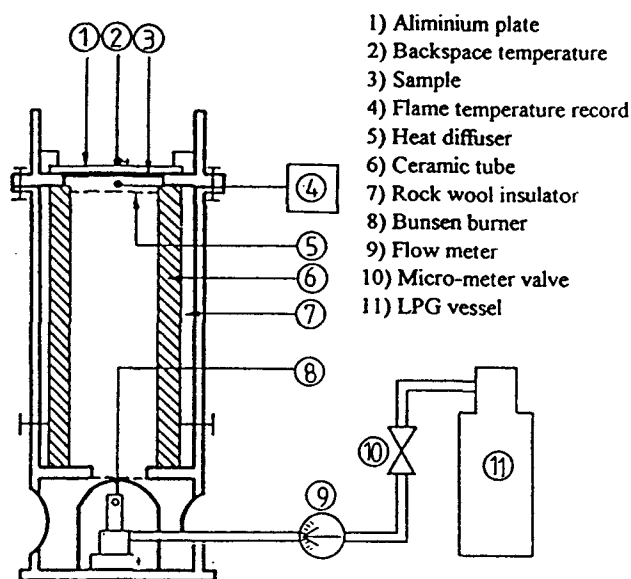


Fig. 2. Schematic diagram of fire testing apparatus for intumescence and protection experiment.

Method of Experiment

Alkali silicates used in this experiment are lithium, sodium and potassium silicate. Silica sol was used as the basic material to prepare these alkali silicates. $\text{LiOH}\cdot\text{H}_2\text{O}$, NaOH and KOH were added to silica sol to make the solutions which is demanded molar concentrations. The silica sol used is SNOWTEX-N of Nissan Chemical Co., the properties of it are shown in Table 1 and mixing ratios of ternary are in Table 2.

Table 1. Characteristics of SNOWTEX-N^a.

Item	Specification
SiO_2	20-21%
Na_2O	0.04% or less
pH	9.0-10.0
Particle size	10-20 μm
Viscosity (at 25°C)	8 c.p. or less
Specific gravity (at 20°C)	1.12-1.14
Appearance	Transparent milky white sol
Freezing point	0°C
Stability	Semi permanent

^a Nissan Chemical Industry Co. Product.

Infrared spectroscopic analysis was conducted at the range from 1600 to 500 cm^{-1} (6.25-20 μm) wave number using FT-IR(Jasco Co. 5300 type) in order to get information about the structure and characteristics of the alkali silicate.

To examine the amount and the kinds of water in the samples, the alkali silicate solutions prepared according to mixing ratios were dried for a week at room temperature, and it was inserted and sealed in a vinyl container until the test. The thermal analysis of these dried samples were conducted by DSC-TG(Shmazu 50) under nitrogen atmosphere at 40cc/min. The temperature range of the test was from room temperature to 600°C and, during the analysis, the samples were heated at the rate of 10°C/min.

Table 2. Preparation of ternary silicate solutions.

Standard Classification	Mixed Ratio (SiO ₂ /M ₂ O=3.30)		
	Li-silicate	Na-silicate	K-silicate
Component	5	47.5	47.5
	10	45	45
	15	42.5	42.5
	25	37.5	37.5
	33.3	33.3	33.3
	40	30	30
	50	25	25
	47.5	5	47.5
	45	10	45
	42.5	15	42.5
	37.5	25	37.5
	33.3	33.3	33.3
	30	40	30
	25	50	25
	47.5	47.5	5
	45	45	10
	42.5	42.5	15
	37.5	37.5	25
33.3	33.3	33.3	
30	30	40	
25	25	50	

RESULT AND CONSIDERATION

Intumescence Test

Intumescence test result on ternary alkali silicate is shown in Fig. 3, and the sample used for this experiment was manufactured by the preparation of ternary solution in Table 2. Fig. 3 showed the fact that Na-/K-silicate compositions added by Li-silicate makes decreasing the degree of intumescence. From the intumescence phenomena of ternary compositions, the degree of intumescence is increasing as the radius of cation and concentration of Na- and K-silicate. Bonding

intensity is known as Li- > Na- >K- silicate [11], but the intumescence effectiveness of mixture has a little difference. Eventhough intumescence of K-silicate is expected to be the highest, actually Na-K silicate had a better synergistic effect. Also the other reason is that the driving forces of intumescence are caused by the free water and the evolution of vapor which is ionic bond in the silicate. The individual order is like this ; $K^+ > Na^+ > Li^+$.

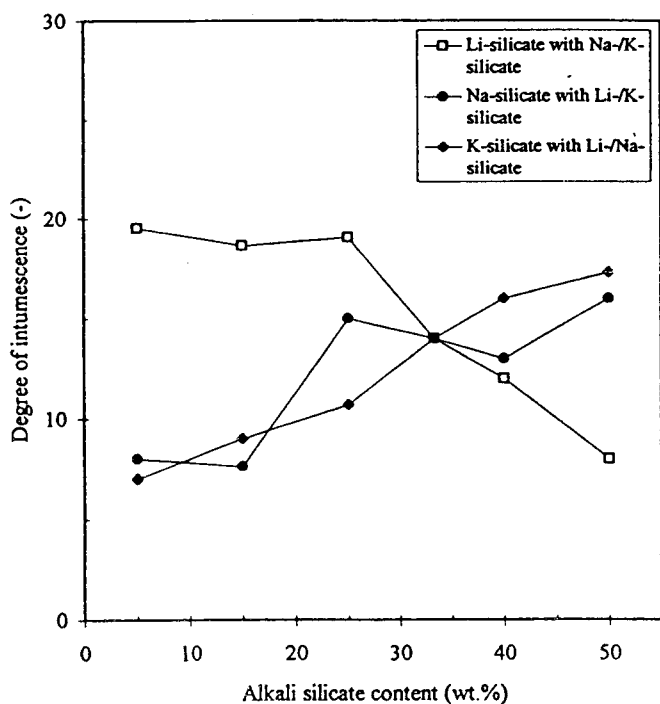


Fig. 3. Degree of intumescence plotted against ternary soluble silicate.

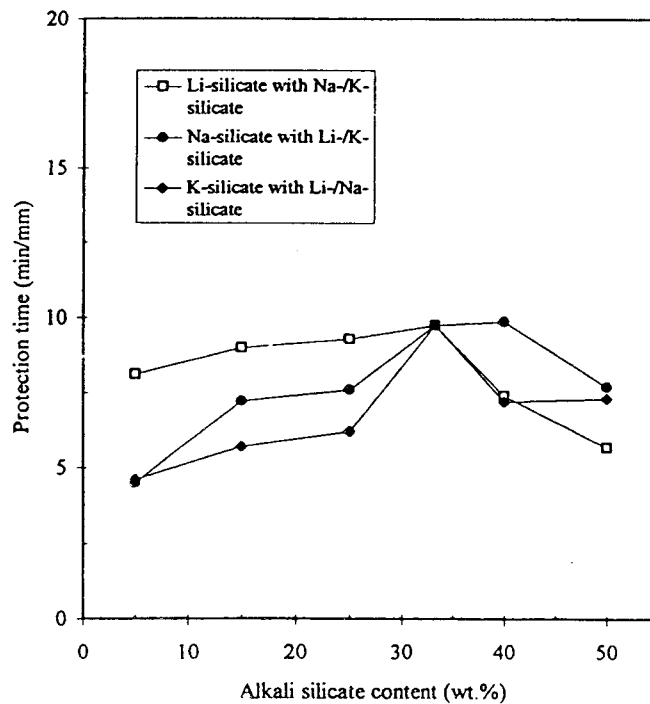


Fig. 4. Protection time against ternary soluble silicate.

Protection Time Test

Protection time increases as the quantity of sodium silicate is added partly which is compared with potassium silicate. Its reason is not clear, but can be guessed as the mutual synergistic effect according to the mixture. Fig. 4 shows the protection test over ternary silicate was done by the method shown in Table 2 and Fig. 2. Protection time over the three types of mixtures are shown in Fig. 4. When the content of potassium and sodium showed better characteristics of intumescence are higher, the protection times are longer than other, and potassium is better than sodium when the same amount of its are mixed. This means that protection times are corresponded upon the intumescence. When the compositions of ternary mixtures are similar, the best protection effect is obtained. This can be also guessed by the synergistic effect by the mutual alkali metals.

Infrared Spectroscopic Analysis

Figure 5 shows the result of infrared spectroscopic analysis to check the effect of various molar

ratios. The five of potassium silicate samples(2.75, 3.00, 3.30, 3.50 and 4.60 molar ratio) were heated for two minutes on the electric furnace which kept 500°C, then the analysis were done by penetrating the infrared ray to the constant direction in the range of 1600-500 cm^{-1} wave number.

As Fig. 5 and 6 indicate that all the samples got the strongest and largest band in the range of 1100-1000 cm^{-1} . This bond is caused by the stretching vibration of Si-O-Si [12]. The width of this band shows the irregular structure of soluble silicate. And it is connected with 967 cm^{-1} band which belongs to the vibration of SiO $^-$. As the degree of polymerization increases in silicate structure, the numbers of SiO $^-$ group decreases, the molar ratio of SiO $_2$ /K $_2$ O increases and the width of band is smaller.

The spectra of 2.75, 3.00 and 3.30 molar ratios show the peaks at around 620 cm^{-1} wave number and these are caused by the bending of SiO $^-$ [12]. This peak got weaker as the molar ratio of SiO $_2$ /K $_2$ O increased, and moved to lower wave number. And this movement is observed in 4.60 molar ratio, and the shift is observed when the peak is out of the range below 600 cm^{-1} . In the spectrum 800 cm^{-1} , there was no difference of O-S-O band over five types of sample.

The spectra in 1440 cm^{-1} over the 2.75, 3.00, 3.30 and 3.50 molar ratio were quite different from the spectra which were measured from the alkali silicate glass [13]. This shows a sharp band as the silicate ion (SiO $_4^{2-}$) which exists in the sodium ortho-silicate (Na $_4$ SiO $_4$) [14].

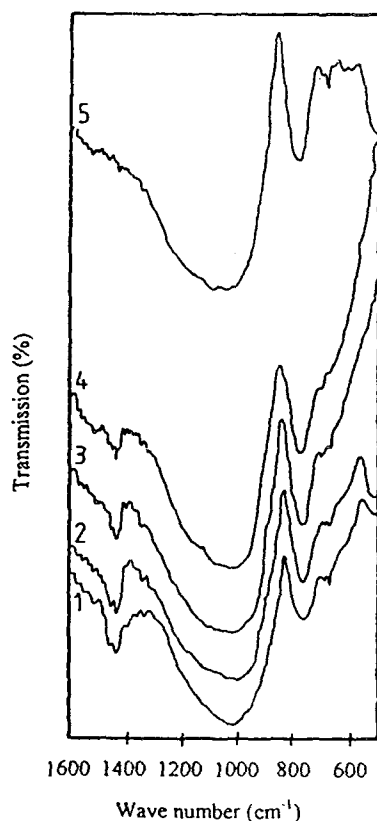


Fig. 5. IR spectroscopy for various molar ratio on potassium silicate at 500 C for 2min

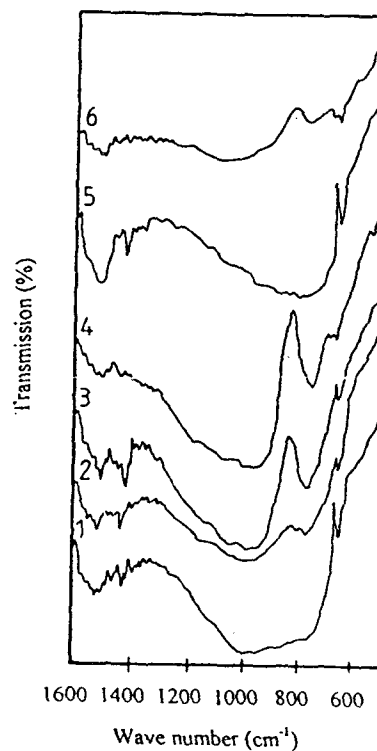
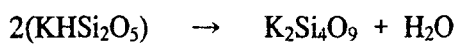


Fig. 6. IR spectroscopy for 3.30 molar ratio potassium silicate intumescenced at various temp. for 5 min

In order to observe the variation caused by the heating temperature, the experimented result at 300°C, 400°C, 500°C, 600°C, 800°C and 980°C were described in Fig. 6. Especially the result in Fig. 6 is based on potassium silicate of 3.30 molar ratio. Within the range of spectra 1600-500 cm^{-1} , a significant change is appeared. The melting point of KHSi_2O_5 is 515°C [15] and above this temperature the shrinkage of the intumesced structure occurs. The change in the spectra may correspond to vitreous state in the samples [12]. This is consistent with the observed in the 800 cm^{-1} band which is strongest for crystalline silicates and weakest for vitreous silica [13].

Thermal Analysis

The results of TGA and DSC in ternary silicates are described in Fig. 7 and 8. Rapid evolution of vapour in the range of 100-200°C comes to a result which is caused by the initial intumescence of sample. Second weight loss appears in the range of around 400-490°C. This corresponds to the endothermic peak of the range 400-490°C. Weight loss caused by the evolution of structural water of KHSi_2O_5 was around 460°C that appeared mostly in K-silicate. This seemed to the bonding force of K^+ ion is relatively lower than those of Li^+ ion and Na^+ ion. The KHSi_2O_5 is a significant ingredient in silicate, and the structural water is expected to be emitted like this ;



The release of structural water and the dehydration of polysilicate silanol groups are the same mechanism, the dehydration of $-\text{Si}(\text{OH})_2$ group. when the ternary alkali silicate are mixed, the trend of water evaporation increases remarkably in Fig. 7, because the bonding forces of free water or bonded water become weak. Especially in the mixture of same components, it seems like that there are much more structural waters [16] released from high temperature and dehydration which are caused by the structure change that H_2O are dehydrated one from every two OH radical of silanol group. This is the absolute cause which improves the phenomenon the of intumescence.

In the results of DSC in Fig. 8, there are a remarkable difference of water content which are developed by the structure change of silanol groups and bonded water that are existing in individual metal. The contribution of intumescence happens mostly under 200°C or 300°C and it is proven that the moisture content of Na-silicate is higher than those of Li-silicate and K-silicate.

CONCLUSION

In order to develop excellent fire protective coating by using alkali silicate, the effects of molar ratio of the mixtures of lithium, sodium and potassium silicate in ternary system were studied. For this study, crystalline structures of soluble silicate, thermal characteristics, protection time, XRD and intumescence were investigated. The following conclusions can be drawn from the results obtained.

- 1) The principle of intumescence is that rapid evolution of water vapor from the coating material, and the quantity of water contained in coating material is influenced on the degree

of intumescence.

- 2) Solubility is improved by increasing the molar ratio of $\text{SiO}_2/\text{K}_2\text{O}$. But the solubility of ternary mixtures depend on the mutual action of silicate and the order of solubility is $\text{Na}^+ > \text{K}^+ > \text{Li}^+$.
- 3) The intumescence phenomenon of ternary silicate is increased as the radius of ion is bigger, and this is caused by the evolution of ionically bonded free water in silicate. The individual degree of intumescence is ordered like this ; $\text{K}^+ > \text{Na}^+ > \text{Li}^+$.
- 4) For effective protection of fire, the thickness of coating material is recommended over 3-4mm that the best protection effect is found in similar composition of ternary silicate.

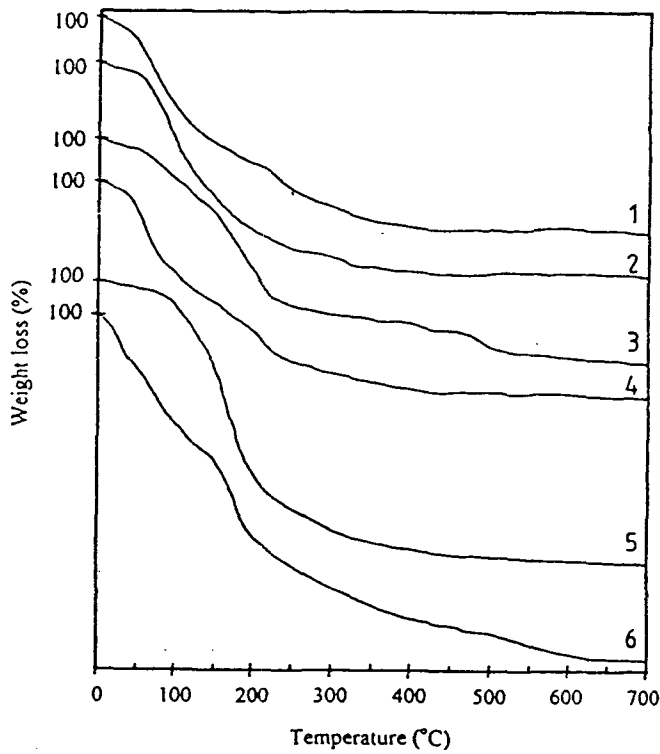


Fig. 7. Comparison of TGA results for various silicate component

- 1) 100% Li-silicate
- 2) 100% Na-silicate
- 3) 100% K-silicate
- 4) 25%Li-/75%K-silicate
- 5) 25%Li-/ 50%Na-/ 25%K-silicate
- 6) 33.3% Li-/Na-/K-silicate

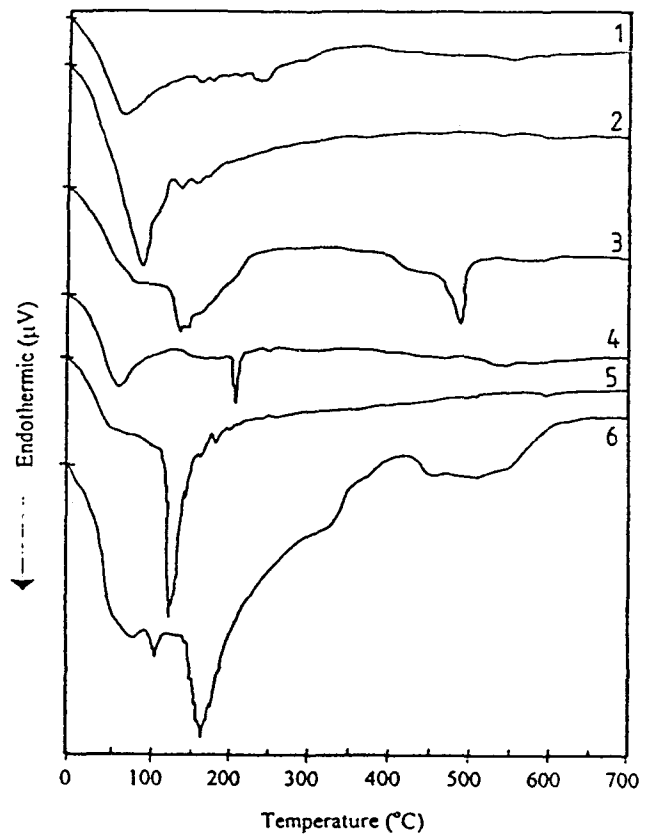


Fig. 8. Comparison of DSC results for various silicate component

- 1) 100% Li-silicate
- 2) 100% Na-silicate
- 3) 100% K-silicate
- 4) 25%Li-/75%K-silicate
- 5) 25%Li-/ 50%Na-/ 25%K-silicate
- 6) 33.3% Li-/Na-/K-silicate

REFERENCES

- 1) Nae-Woo Lee, Jong-Rae Kim and Jeong-Hun Kim, A Development of Fire Protective Coating Based on Soluble Alkali Silicate , J. KIIS., Vol. 8(2), 30-38, 1993

- 2) Nae-Woo Lee and Jeong-Hun Kim, "A Development of Fire Protective Coating Using Ternary (Li/Na/K) Soluble Silicate, J. KIIS., Vol. 10(1), 28-34, 1995
- 3) 日本建築學會・防火委員會構造部材耐火性WG, 鋼構造の耐火設計(2), 日本火災學會, Vol. 40(1), 42-46, 1990
- 4) K.B. Langille, D. Nguyen, J.O. Bernt, D.E. Veinot and M.K. Murthy, Mechanism of Dehydration and Intumescence of Soluble Silicates: Part I Effect of Silica to Metaloxide Molar Ratio, J. Mater. Sci., Vol. 26, 695-703, 1991
- 5) K.B. Langille, D. Nguyen, J.O. Bernt, D.E. Veinot and M.K. Murthy, Mechanism of Dehydration and Intumescence of Soluble Silicates: Part II Effect of the Cation, J. Mater. Sci., Vol. 26, 704-710, 1991
- 6) D.E. Veinot, K.B. Langille, D.T. Nguyen and J.O. Bernt, Fire Protective Coatings Based on the Ternary Na/K/Li-Silicate System, J. Canadian Ceram. Soc., Vol. 59(4), 32-36, 1990
- 7) D.E. Veinot, K.B. Langille, D.T. Nguyen and J.O. Bernt, Soluble Silicate-based Coatings for Fire Protection", J. Fire Tech., 230-240, 1989.
- 8) D. Barby, J.A.R. Griffiths and D. Pawson, edited by R. Thompson, The Modern Inorganic Chemicals Industry, London, Chemical Soc., 320, 1977.
- 9) R. Iler, The Chemistry of Silica, New York, John Wiley, 117, 1977.
- 10) ASTM E 119 (Fire Test of Building Construction and Materials), Philadelphia, 349-375, 1983.
- 11) J. Depasse and A. Watillon, The Stability of Amorphous Colloidal Silica, J. Coll. Interface Sci., Vol. 33(3), 430-438, 1970
- 12) S.A. Brawer and W.B. White, Raman Spectroscopic Investigation of the Structure of Silicate Glasses. I. The Binary Alkali Silicates, J. Chem. Phys., 2421-2432, 1975
- 13) R. Hanna, Infrared Absorption Spectrum of Silicon Dioxide, J. Amer. Ceram. Soc., Vol. 48, 595-599, 1965.
- 14) L.S.D. Glasser, Sodium silicates, Chem. Brit., 33-39, 1982
- 15) R.C. Weast, CRC Handbook of Chemistry and Physics, 68th ed., CRC Press, Florida, 1987
- 16) I. Shapiro and I.M. Kolthoff, Studies on Aging of Precipitates and Coprecipitation XLIII Thermal Aging of Precipitated silica(silicagel), J. Amer. Chem. Soc., Vol. 72, 776, 1950