

Effect of HPMC on the properties of cement

N K Singh^{a*}, P C Mishra^a, V K Singh^b & K K Narang^c

^aDepartment of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi 221 005, India

^bDepartment of Ceramic Engineering, Institute of Technology, Banaras Hindu University, Varanasi 221 005, India

^cDepartment of Applied Chemistry, Institute of Technology, Banaras Hindu University, Varanasi 221 005, India

Received 28 February 2001; revised 23 December 2001; accepted 10 January 2002

The HPMC (hydroxypropyl methyl cellulose) has been taken as an additive, which retard the setting of cement. The cement-HPMC mixes were prepared having improved compressive strength, tensile strength and fracture toughness in comparison to ordinary Portland cement at late curing ages. The heat of hydration of different cement-HPMC mixes show that the lower contents of HPMC interact with hydrated cement at early curing while higher content at late. The cement-HPMC mix has been found to have better corrosion resistance than OPC in H₂SO₄, HCl and sea-water. Spectroscopic studies suggested that HPMC bind with free lime. X-ray diffractogram of 91days hydrated cement-HPMC mix displays some new peaks as well as few peaks appeared with low intensities showing interaction of HPMC with hydrated cementitious phases.

Several papers related to polymer modified cement in the field of macro-defect-free (M.D.F) systems have been published¹⁻³. Water soluble cellulose based polymers such as hydroxymethyl cellulose (HMC)⁴, hydroxyethyl cellulose (HEC)⁵, hydroxypropylmethyl cellulose (HPMC)⁶ and carboxymethyl cellulose (CMC) have been reported as a high performance materials for plastering and for use in the underwater concrete works. Cellulose components with modifiers such as antifoaming agents and glasses have improved bending strength and other properties⁷. HPMC with viscosity modifying admixture can show frost durability and high flowability because of having cohesive property and can be used in a variety of land based application.

In the process of modification with hydroxy cellulose derivatives, a small amount of polymer is added as powder or aqueous solution to the cement. The surface activity of water-soluble polymers prevent the "dry out" phenomenon⁸ with increasing the viscosity of paste in the modified cement mortar. The sealing effect is also improved due to the formation of very thin, water impervious film⁹, embedded between hydrated cement particles.

There has been no comprehensive work on the single water soluble polymer modified system exploring the various properties viz. setting time, heat of hydration, compressive strength, tensile strength, fracture toughness, water absorption, corrosion, spectroscopic

(IR, XRD) and optical studies. In view of the above facts, a detailed study of the hydroxypropyl methyl cellulose (HPMC) as an additive to cement was carried out so as to optimize the conditions for obtaining materials with improved properties as compared to ordinary Portland cement and mortars.

Experimental Procedure

Ordinary Portland Cement (43 grade) was taken from the local market and local sand from the Sone river. Reagent grade hydroxypropyl methyl cellulose (99 % purity), zinc oxide, nitric acid, sulphuric acid, hydrofluoric acid and hydrochloric acid were used in the present experiments. Sea-water was taken from the Arabian sea for corrosion studies.

Standard vicat apparatus was used for the determination of setting time. Additives were dissolved in the required volume of water for preparing the cement paste. The setting time experiment was performed at 27±2°C. Heat of hydration at 3, 7, 28 and 91 days cured samples were determined by calorimetric method using Beckmann thermometer and a constant speed stirrer arranged in a thermos flask. The compressive strength was determined on cube samples with 50 cm² cross-section area using 1:3 cement-sand mix. 11.5% water was taken for preparing the mortar in which additives were dissolved. The mortar was filled in six moulds for each test. These were kept in 90% relative humidity (*r/h*). After 24 h, samples were demoulded and again placed in 90% *r/h* for 7, 28 and 91 days for

*For correspondence

Table 1—Setting time, heat of hydration, compressive strength and tensile strength of cement in the presence of HPMC

HPMC wt. %	Setting time (min)		Heat of hydration (J/g)				Compressive strength (MPa)			Tensile strength (MPa)		
	Initial	Final	3	7	28	91	7	28	91	7	28	91
			days	days	days	days	days	days	days	days	days	days
0.00	130	230	259.57	326.41	364.11	439.35	31.93	43.73	58.50	2.98	3.92	5.36
0.25	165	320	283.48	332.43	368.80	440.36	32.34	43.63	57.63	3.24	4.35	5.39
0.50	185	390	310.65	340.37	373.10	441.40	30.40	44.40	58.44	3.01	4.55	6.33
1.00	215	430	294.94	354.49	382.17	443.95	29.13	48.38	59.59	2.73	4.70	6.48
2.00	350	555	277.67	336.19	398.52	450.31	26.44	48.45	63.47	2.50	4.42	6.73
4.00	520	695	245.49	319.89	383.89	455.74	23.92	42.67	64.42	2.22	4.05	6.70

curing at $27 \pm 2^\circ\text{C}$. The tensile strength was determined using standard briquette samples cured under similar conditions of temperature and humidity. Fracture toughness was tested by universal testing machine (Shimadzu AGS-5KND) under three point bending system using 20 mm span length and cross-head speed of 0.5 mm/min. Six samples for each set were prepared. In the preparation of each sample, 9.5 g of dry cement and 0.3% water with and without additive were mixed in aggregate mortar for one minute. The mixture was poured in a mould ($10 \times 10 \times 50$ mm) and 15 MPa load was applied for one minute. After demoulding, 1.1 mm depth notch was made in the middle of sample length and the samples were placed in 90% r/h at $27 \pm 2^\circ\text{C}$. Corrosion studies have been carried out on the cube samples with 25 cm^2 cross section area using 1:3 cement-sand ratio. Mortar was prepared adopting the mixing condition of compressive strength samples, applying 15-tonne load by hydraulic press. After demoulding, samples were placed in the same condition for 180 days.

The FT-IR spectra of 91 days hydrated cement and polymer modified cement were taken in KBr medium in the region of $4000\text{--}400 \text{ cm}^{-1}$. X-ray diffraction patterns of the neat hydrated cement and polymer modified cement were recorded on a X-ray diffractometer using Cu K α radiation with Ni filter. Intensity and d-values were compared with the values given in JCPDS file.

Results and Discussion

The values of setting times, heat of hydration, compressive and tensile strengths of cement-HPMC mix as a function of the amount of HPMC (0.1, 0.5,

1.0, 2.0 and 4.0 %) as an additive of cement were determined and these are given in Table 1.

Setting time

The initial and final setting times of cement were found to be 130 and 230 min, respectively. The initial and final setting times for lower addition (0.1%) of HPMC were observed as 145 and 250 min and for higher (4%) as 250 and 695 min, respectively, showing that HPMC acts as a retarder. Generally, organic polymers act as retarder and have distinct behaviour towards the setting of cement¹⁰. The setting time may be varied according to the physical and chemical properties of organic polymers like solubility, viscosity, chain length, polarity and functional group(s) etc. HPMC is a derivative of cellulose (a long chain polymer which is a member of carbohydrate group). Hansen^{11,12} pointed out that organic set retarding agent containing HC-OH group in their molecules, retard the rate of absorption of H_3O^+ ions on cement universal surface and slow down the setting reactions¹³. The set retardation may primarily be due to the retardation of hydration of $3\text{CaO} \cdot \text{SiO}_2$ through adsorption of the organic admixture on the calcium hydroxide. Steinour¹⁴ considered that the organic agents are adsorbed by hydrogen bonding through their hydroxyl group. The hydroxyl group being polar and hygroscopic in nature, thus, diminishes the amount of water available for the hydration of silicate¹⁵. It seems that the retardation process in the presence of HPMC due to the chemical interaction between $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{SiO}_2$ and polar functional groups of organic polymers to yield amorphous materials which are scattered between the crystalline mass of cement

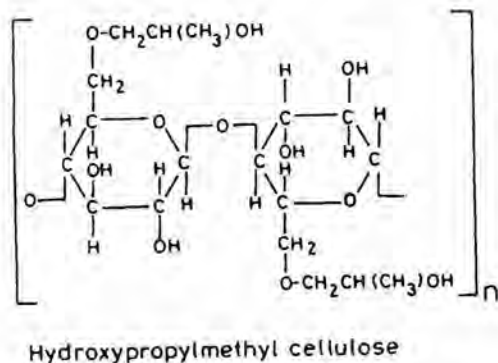


Fig. 1—Chemical structure of the additive used in the present investigation

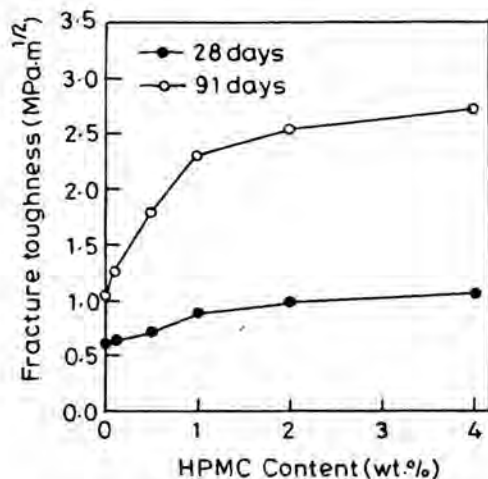


Fig. 2—Variation of fracture toughness of cement with different quantities of HPMC

paste. They might be quite insoluble and not removable from the stiffened mass.

Heat of hydration

The heat of hydration of hydrated cement obtained at 3, 7, 28 and 91 days of curing period were 259.57, 326.41, 364.11 and 439.35 J/g, respectively. For cement HPMC mixes, the heat of hydration increases with increasing additive content up to a certain extent and then decreases. The optimum concentration of HPMC for maximum heat of hydration differs for different curing periods.

It has been reported¹⁶ that carbohydrate and some other water-soluble polysaccharides when mixed with cement give higher heat of hydration at early ages. It seems that during early hydration period the unhydrated cementitious phases actively participated in hydration, so the tendency to react with small amount

of additive is stronger which slows down with late stages.

Compressive and tensile strengths

The compressive strength of cement at 7, 28 and 91 days were observed as 31.3, 43.7 and 53.5 MPa and tensile strength, 2.9, 3.9 and 5.3 MPa, respectively. In cement-HPMC mixes, 0.25% additive content at 7 days has given maximum compressive strength 32.2 MPa; 1% at 28 days, 48.3 MPa and 4% at 91 days 64.4 MPa. The maximum tensile strength for 0.25% addition at 7 days was 3.2 MPa; 1% at 28 days, 4.7 MPa and 4% at 91 days, 6.4 MPa.

It was reported that organic set retarders^{17,18} increase the strength of cement at late curing ages. The effect of strength depends on the nature and amount of additive and water cement ratio. There is no strict correlation between setting and strength development in cement mortar containing set retarders. The setting delays are the consequence of the ageing of the cement hydration process and also retard the generation of heat of hydration¹⁹.

Fracture toughness

The values of compressive and tensile strength show that there is a contribution of optimum percentage of HPMC in late age of curing. So, only 28 and 91 days cured samples were preferred for fracture toughness test. Fig. 2 shows the variation of fracture toughness with different quantities of HPMC. The fracture toughness of cement at 28 and 91 days were observed as 0.62 and 1.03 MPa.m^{1/2}, respectively. It seems that the longer curing period results from alternative forces developed between the polymer and cementitious material caused by hydrodynamic forces²⁰. Hydrodynamic forces are of repulsive nature, which appear when the cementitious particles try to move against viscosity of polymer solution during setting. These forces slowly change into an electrostatic attractive force as the curing period increases. Some workers have suggested^{21,22} that the electrostatic forces are operative in dry atmosphere when the crack faces become charged during fracturing process. It is also possible that same polymer molecule act as bridging force²³ between more than one cementitious particles at the same time, thereby forming a link which holds the particles with hydrogen/chemical bonding which may resist²⁴ crack propagation.

Corrosion behaviour

Only 91 days cured samples were used for corrosion studies. The corrosion test was carried out by weight loss method in different corrosive media, like H_2SO_4 (0.1 and 1N), HCl (0.1 and 1N) and sea-water. Fig. 3 shows the variation of corrosion resistance of samples in different corrosive media. The percent weight loss of cement samples after 4 days in 0.1 and 1N H_2SO_4 were observed as 1.15 and 6.25%, respectively. The weight loss in 0.1 and 1N HCl were 4.95 and 8.61%, respectively. After 91 days immersion in sea-water, corrosion was observed to be 3.48%.

The sulphuric acid forms gypsum with calcium hydroxide and ettringite with calcium aluminate²⁵. Chandra²⁶ has described the attack of HCl as a reaction occurring in layers forming distinct zone and found that HCl dissolution of calcium hydroxide was three times more than that of H_2SO_4 . The influence of sea-water was studied by Conjeaud²⁷ and Regourd²⁸. They reported that the sea-water corrosion is the net effect of several salts like NaCl and $MgCl_2$ present in sea-water. The attack of chloride from NaCl and $MgCl_2$ was observed on the aluminates of cement phases which form monochloroaluminate ($3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$). They also transform hydrated calcite fibers into a more porous reticular network. The development of porosity in cement is probably due to leaching out of above monochloroaluminate.

For cement-HPMC mixes, 4% HPMC content has given minimum corrosion in 0.1N H_2SO_4 while, 2% addition was found better in 1N H_2SO_4 . In 0.1N HCl, 4% HPMC addition has given excellent resistance

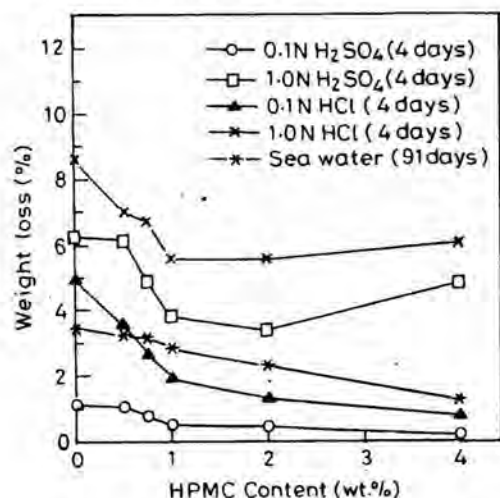


Fig. 3—Weight loss due to corrosion for 91 days cured cement mortars with different quantities of HPMC

against corrosion and in 1N HCl, 2% addition has also given excellent resistance against sea-water. The minimum percent weight loss of cement-HPMC mixes in 0.1N H_2SO_4 , 1N H_2SO_4 , 0.1 N HCl, 1N HCl and sea water were observed as 0.23, 3.38, 0.78, 5.55 and 1.23%, respectively.

The polymer-modified cements are reported²⁹ to be corrosion resistance with corrosive media. It seems that in polymer modified cements, the pores are filled with polymer or reactant product(s) which reduce the porosity and capillary systems and resist corrosion to some extent.

Spectroscopic studies

FT-IR and XRD techniques have been used to characterize the cement-HPMC mix (4% HPMC mix). IR spectra of the 91 days hydrated cement (with and without additive) are shown in Fig. 4.

IR spectra—The IR spectra of the 91 days hydrated cement sample shows bands at 3645, 3445, 1613, 1413, 1417, 968, 875 and 503 cm^{-1} . Several workers have reported the spectra of the hydrated products of cement phases³⁰⁻³². Studies on hydrated products of cement phases revealed that the bands observed in the range of 700 to 1200 cm^{-1} are lost when C_3S is hydrated³³. The band observed at 968 cm^{-1} is due to the higher shifting of anhydrous phase³⁴ and/or ν_3 (SiO) absorption band of C_2SH_2 and C-S-H (B) type phases present in the cement³⁵. The absorption band due to $\nu(OH)$ of $Ca(OH)_2$ is present at 3645 cm^{-1} . The bands at 1635 and 3445 cm^{-1} are due to the presence of calcium sulphate in the form of ettringite (mono and tri sulphate) in cement. The band at 1417 cm^{-1} shows the presence of carbon dioxide.

In cement-HPMC mix the spectral bands of cementitious phases were observed at 3654, 3418, 1635, 1419, 973, 875 and 502 cm^{-1} . The $\delta(OH)$ of HPMC at 1649 cm^{-1} has been found absent in the 91 days hydrated cement-HPMC mix. The absorption band due to calcium sulphate appears with a negative shift of 28 cm^{-1} , indicating interaction of CH_2OH group of HPMC with $C_3A \cdot 3CaSO_4 \cdot 32H_2O$ of cement. The ν_4 band of $[SiO_4]^{4-}$ at 530 cm^{-1} (in cement without additive) is also present in the cement-HPMC mix system with a negative shift of 10 cm^{-1} showing interaction of HPMC with C-S-H phases.

X-ray diffraction—Important phases detected in the cement were $Ca_2SiO_3(OH)_2$ at $d = 7.98, 5.61, 4.92, 3.33, 2.62, 2.18, 1.48 \text{ \AA}$; $Ca_2Al_3Fe_3Si_3O_{13}H$ at d

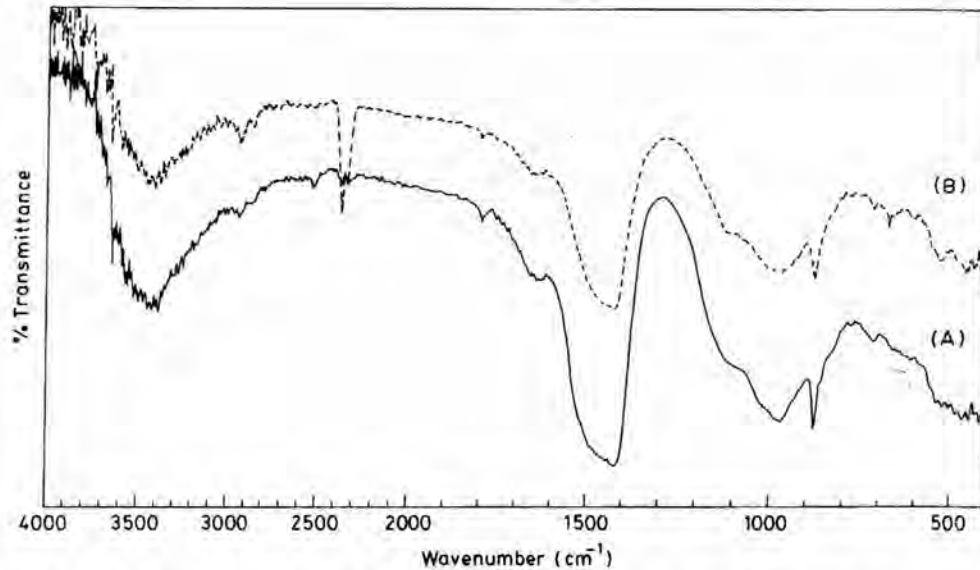


Fig. 4—IR spectra of 91 days hydrated samples of (A) Cement and (B) Cement-HPMC mix

$= 3.02$; $\text{Ca}_3\text{Fe}_2\text{O}_{12}\text{H}_2$ at $d = 3.33, 3.09, 3.02$ and 2.77 \AA and free lime at $d = 2.62, 2.18, 2.10, 1.92, 1.79, 1.68$ and 1.53 \AA . The hydrated phases of $\text{Ca}_2\text{SiO}_5\text{H}_2$ and $\text{Ca}(\text{OH})_2$ appeared in 7 days hydrated cement which decreases with increasing curing periods. The ettringite (trisulphate) ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$) appeared in 7 days hydrated cement sample, which marginally increased in 91 days samples, while ettringite (monosulphate) ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot 13\text{H}_2\text{O}$) appeared only in 91 days hydrated sample. The peak at $d = 2.62 \text{ \AA}$ remains practically constant. It seems that $\text{Ca}(\text{OH})_2$ and $\text{Ca}_2\text{SiO}_3(\text{OH})_2$ are formed but with increased curing period there is a strong possibility of the formation of $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$.

The effect of HPMC on hydrated phases of the cement was observed by relative intensities of peaks. XRD results show some important information about cement-HPMC mix after 91 days moist curing. X-ray diffraction of the above mix displays some new peaks as compared to 91 days hydrated cement, which shows the possibility of the formation of new product(s) (Fig. 5). Some cementitious phases disappeared and a few appeared with low intensities, which shows interaction of polymer with cementitious phases. A few cementitious phases appearing at 7 days hydrated cement were also present in 91 days hydrated cement-HPMC mix, thereby showing the retardation effect of HPMC on the particular phases. A few new peaks at $d = 4.57, 4.01, 3.86, 3.45, 3.24, 1.65$ and 1.60 \AA show the possibility of the formation of new product(s). The

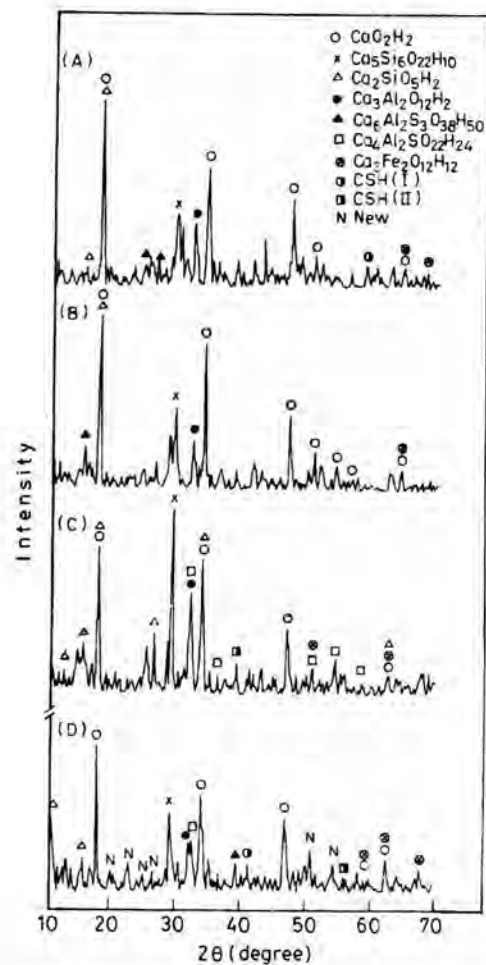


Fig. 5—X-ray diffraction patterns of hydrated cement: (A) 7 days, (B) 28 days, (C) 91 days and (D) Cement-HPMC mix (91 days)

peaks at $d = 3.49, 3.33, 1.79$ and 1.68 \AA assigned to $\text{CaSi}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$, $\text{Ca}_5\text{Si}_2\text{O}_8(\text{OH})_2$, respectively, appeared with negligible intensities as compared to their intensities in 91 days hydrated neat cement showing the interaction of HPMC with calcite phases of the cement. The intensities of some peaks at $d=5.15$ and 2.27 \AA assigned to $\text{Ca}_3\text{Fe}_2\text{O}_{12}\text{H}_2$ and $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_{12}$, respectively, marginally decreased. The peaks at $d=2.62, 1.92$ and 1.76 \AA have increased intensities as compared to their intensities in the hydrated cement and are assigned to $\text{Ca}_2\text{SiO}_3(\text{OH})_2$, $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$; and $\text{Ca}_3\text{Fe}_2\text{O}_{12}\text{H}_2$, respectively, marginally decreased. The peak at 4.92 \AA due to the free lime appeared with low intensity, showing interaction of HPMC with free lime.

Conclusion

Cement—HPMC (1%) mix has been found to have improved strength and fracture toughness as compared to OPC. The material has shown better corrosion resistance in HCl, H_2SO_4 and sea-water. The IR and X-ray studies revealed interaction of HPMC with lime as well as various hydrated cementitious phases, which is expected to yield more durable material.

References

- Birchall J D, Howard A J & Kendall K, *Nature*, 289(5769) (1981) 388.
- Moriyoshi A, Fukai I & Takeuchi M A, *Nature*, 344 (6263) (1990) 203.
- Darbik M & Slade R C T, *Br Ceram Trans*, 94 (1995) 224.
- Shinozaki M & Shinozaki M (Talenaka Kouten Co., Japan) *Jpn Kokai Tokkyo J.P.* 08,133,810 [96, 133810] (CI CO4 B 28/02) 28 May 1996, Appl.94/272,405,7 Nov 1994, 7.
- Faure J C, & Joel B (SOGEA) 2709, 122 (CI.Co4 B 24/38) 24 Feb App (1995) 93/10, 156, 20 Aug 1993, 11.
- Khayat Kamal H (USA) *ACI Mater J*, 92 (6) (1995) 625.
- Teliseva Galina, Arsanica A, Dizbite T, Rituma S, Laeis E & Latvia L, 10, 768 (CI CO4B 16/a) 20 Oct Appl (1995) 940, 27 Dec 1994, 9 (RUSS).
- Chandra S & Ohama Y, *Polymers in Concrete* (CRC Press Inc, 2000 Corporate Blvd, NW, Boca Raton, Florida), 33431.
- Ohama Y, *Concrete Admixtures Handbook*, edited by V S Ramachandran (Noyes Publications, Park Ridge, NJ), 1984, 341.
- Taylor H P, *Proc 7th Conference on the Silicate Industry*, 1963 (Publishing House of the Hungarian Academy of Sciences, Budapest), 1965, 199.
- Hansen W C, *Proc 3rd Int Symp Chem Cem*.
- Hansen W C, *Amer Soc Test Mat*, Special Technical Publication No 266, 3 (1960).
- Skalny J & Tadros M E, *J Amer Ceram Soc*, 60 (3-4) (1977) 174.
- Steinour H H, *Amer Soc Test Mat*, Special Technical Publication No. 266, 25 (1960).
- Ben-Dor L, Heitner W C & Diab H, *Cem Conc Res*, 15 (4) (1985) 681.
- Pailier A M, *Application of admixture in concrete* (E & F N Spon, RELIM Report 10, Chapman & Hall, 2-6 Boundary Row, London SE1 8HN).
- Gmankoblaï I G, Kruglitskir N N & Boiki G P (Russ Ed) (1972) 38(6) (CA 7319) 78 (1973) 577.
- Herrero & Nunez E, *Cemento Hormigon*, 46 (499) (1975) 1051.
- Simeonv I, *Baustoffin deestrie* (1976) 27.
- Van de Van G M, *Colloidal Hydrodynamics* (Academic Press, New York), 1989.
- Obreimoff J W, *Proc R Soc London A*, 127 (1930) 290.
- Dickinson J T, Donaldson E F & Park M K, *J Mater Sci*, 16 (1981) 2887.
- Clarke D R & Faber K T, *J Phys Chem, Solids*, 48 (1987) 1115.
- Evans A G & Marshall D B, *Acta Mater*, 37 (1989) 2567.
- Attigobe E K & Rajkalla S H, *ACI Mater J*, 85 (6) (1988) 481.
- Chandra S, *Cem Conc Res*, 18 (1988) 193.
- Conjeaud M L, *ED ACI Spec Publ*, 65 (1980) 39.
- Regourd M & Malhotra V M, *Ed ACI Spec Publ*, SP, 63 (1980).
- Ohama Y, Masaki & Shiroishida K, *Gijustu Nempo*, 32 (1978) 308.
- Lehman H & Dutz H, *5th Symp Chem Cem*, 1 Tokyo (1968) 513.
- Midgley H G, *5th Symp Chem Cem*, 1 Tokyo (1968) 479.
- Ghosh S N & Chatterjee A K, *J Mater Sci*, 9 (1974) 1457.
- Hunt C M, *5th Symp Chem Cem* 1 Tokyo (1968) 297.
- Bensted J, *Cem Conc Res*, 8,73,9,97 (1979).
- Bensted J, *8th Int Cong Chem Brazil*, 3, 3 (1968) 331.