262 Xu et al.

of hydration of the silicate phases. The non-evaporable water is also believed to be an indication of the extent of cement hydration in the system.

The amount of CH and non-evaporable water were markedly reduced for the M-0.8% and M-1.5% specimens at 6 hours. This is consistent with the calorimetric results (Fig. 13a) and the electrical response (Fig. 2a and 3a) indicating retardation at increased PNS dosages during early hydration. After three days, the differences became generally insignificant (for each paste and mortar) with age. The smaller CH contents at 28 days for the mortar specimens could be a result of lime leaching upon immersion curing. It is noted in Table 3 that the hydration process appears to be little affected by the sand inclusions. Winslow and Liu (26) have reported that for mature specimens, the paste in the mortar was more porous than the corresponding plain paste.

CONCLUDING REMARKS

The effect of varying dosages of a PNS superplasticizer on the microstructure of a portland cement paste and on the microstructural and transition zone characteristics of a mortar was investigated, using AC impedance spectroscopy and other techniques. The impedance behavior of both cement paste and mortar systems was altered by the presence of the superplasticizer, implying that the use of superplasticizer has an influence on both the cement/sand interfacial region and the bulk paste component in the mortar. The transition zone was more porous at 4 hours for mortars with high dosage of superplasticizer because of the improved dispersion of cement particles and the set retarding effect. It was also established that the ionic concentration in the pore solution had a significant role in determining the electrical properties of the fresh mortar specimens but a markedly reduced effect when the specimens hardened. A greater electrical resistivity and larger high frequency arc was detected for all the superplasticized mortars after one-day hydration. This was attributed to the modification of the interfacial zone microstructure and density as well as in the pore structure and porosity of the bulk matrix due to presence of the superplasticizer. Results from mercury porosimetry, TGA and conduction calorimetry support this interpretation.

Interestingly, it was found that even a low dosage of PNS superplasticizer (0.1%, 0.3%) can change the impedance response, pore size distribution and porosity of hydrated cement systems. At higher PNS dosages, greater electrical resistance, lower total porosity and modified pore size distribution (relative to the control mortar and low-dosage mortars) were obtained. The dosage levels also appeared to influence the morphology of hydrates.

ACKNOWLEDGEMENTS

This project was financially supported under the NRC-NSERC-Industry program. The contributions of Handy Chemicals and the National Research

Council are appreciated. The assistance of Dr. P. Gu with the AC impedance technique, and Mr. G. Polomark, G. Chan, E. Quinn, B. Myers and J. Margeson with the experimental work conducted at the National Research Council is gratefully acknowledged.

REFERENCES

- 1. Mehta, P.K., Concrete: Structure, Properties, and Materials. Prentice-Hall, 1986, p. 450.
- Interfacial Transition Zone in Concrete, RILEM Report 11, Edited by J.C. Maso, E & FN SPON, 1996, p. 179.
- 3. Mindess, S., "Interfaces in concrete", in Materials Science of Concrete I, Edited by J. Skalny, The American Ceramic Society, 1989, pp. 163-180.
- Frigione, G., Marchese, B. and Sersale, R., "Microcracking Propagation in Flexural Loaded portland and High Slag Cement Concretes", Proceedings of the 8th International Congress on Chemistry of Cement, Rio de Janeiro, 1986, Vol. III, pp. 478-484.
- Odler, I and Zurz, A., "Structure and Bond Strength of Cement Aggregate Interfaces", in Bonding in Cementitious Composites, Edited by S. Mindess and S.P. Shah, Materials Research Society, Proceedings, 1988, Vol. 114, pp. 21-27.
- Xie P., Beaudoin J.J. and Brousseau, R., "Effect of aggregate size on transition zone properties at the portland cement paste interfaces", Cem. Concr. Res., 21, 1991, pp. 999-1005.
- 7. Zimbelmann, R., "A method for strengthening the bond between cement stone and aggregates", Cem. Concr. Res., 17, 1987, pp. 651-660.
- Monteiro, P.J.M. and Mehta, P.K., "Improvement of the Aggregate Cement Paste Transition Zone by Grain-Refinement of Hydration Products", Proceedings of the 8th International Congress on Chemistry of Cement, Rio de Janeiro, 1986, Vol. III, pp. 433-437.
- Su, Z. and Bijen, J.M.J.M., "The Effect of Polymer Dispersions on the Interface between Cement Paste and Aggregates", in Proceedings of the 6th International Congress on Polymers in Concrete. Beijin, China, Edited by Y. Huang, W. Keru and C. Zhiyuan, 1990, pp. 474-481.
- Ramachandran, V.S., Malhotra, V.M., Jolicoeur, C. and Spiratos, N. "Superplasticizers: Properties and Applications in Concrete", Edited by V.M. Malhotra, Canadian Ministry of Public Works, CANMET, Ottawa, 404 p., 1998.
- Jolicoeur, C., Nkinamubanzi, P.C., Simard, M.A. and Piotte, M., "Progress in Understanding the Functional Properties of Superplasticizers in Fresh Concrete", 4th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete", Edited by V.M. Malhotra, Montreal, 1994, pp. 63-88.
- Andersen, P.J. and Roy, D.M., "The influence of superplasticizer molecular weight on its adsorption on, and dispersion of, cement", Cem. Concr. Res., 18, 1988, pp. 980-986.

- Yilmaz, V.T. and Glasser, F.P., "Influence of sulphonated melamine formaldehyde superplasticizer on cement hydration and microstructure", Adv. Cem. Res., 2, 1989, pp. 111-119.
- Gu Ping, Xie Ping, Beaudoin, J.J. and Jolicoeur, C., "Investigation of the retarding effect of superplasticizers on cement hydration by impedance spectroscopy and other methods", Cem. Concr. Res., 24, 1994, pp. 433-442.
- 15. Ollivier, J.P., Grandet, J. and Hanna, B., "Action d'un fluidifiant et d'une fumée de silice condensée réactive aux courtes échéances sur la liaison gros granulat-mortier", Proceedings of the 8th International Congress on Chemistry of Cement, Rio de Janeiro, 1986, Vol. IV, pp. 204-209.
- Xu, G., Beaudoin, J.J., Jolicoeur, C. and Pagé, M., "Interfacial transition zone characterization of portland cement mortars containing relatively high dosages of polynaphthalene sulfate superplasticizer", Submitted to Concr. Sci. Eng., 1998.
- Gu Ping, Xie Ping, Beaudoin, J.J. and Brousseau, R., "AC impedance spectroscopy (II): Microstructural characterization of hydrating cement-silica fume systems", Cem. Concr. Res., 23, 1993, pp. 157-168.
- Xie Ping, Beaudoin, J.J. and Brousseau, R., "Flat aggregate-portland cement paste interfaces. I. Electrical conductivity models", Cem. Concr. Res., 21, 1991, pp. 515-522.
- 19. McCarter, W.J., Gearing, S. and Buzzed, N., "Impedance measurements on cement paste", J. Mater. Sci. Lett., 7, 1988, pp. 1056-1057.
- 20. Scuderi, C.A., Mason, T.O. and Jennings, H.M., "Impedance Spectra of hydrating cement pastes", J. Mater. Sci., 26, 1991, pp. 349-353.
- Gu Ping, Xie Ping, Beaudoin, J.J. and Brousseau, R., "AC impedance spectroscopy (I): A new equivalent circuit model for hydrated portland cement paste", Cem. Concr. Res., 22, 1992, pp. 833-840.
- McCarter, W.J., "A parametric study of the impedance characteristics of cement-aggregate systems during early hydration", Cem. Concr. Res., 24, 1994, pp.1097-1110.
- Matsukawa, K. and Diamond, S., "Quantitative study of naphthalene sulfonate effects on cement paste pore solution chemistry", Adv. Cem. Mater., 16, 1991, pp. 41-55.
- 24. Gu Ping, Xie Ping and Beaudoin, J.J., "Microstructural characterization of the transition zone in cement system by means of AC impedance spectroscopy", Cem. Concr. Res., 23, 1993, pp. 581-591.
- 25. Jiang Weimin and Roy. D.M., "Interaction Mechanism of Chemical Admixtures and Other Influences on Microstructure", Proceedings of the 10th International Congress on the Chemistry of Cement, Edited by H. Justnes, Gutenburg, Sweden, 1997, 3iii030.
- Winslow, D. and Liu Ding, "The pore structure of paste in concrete", Cem. Concr. Res., 20, 1990, pp. 227-235.

Mixtures	Portland cement	Silica sand	Superplasticizer	Water
P-0%	1	0	0	0.35
P-0.1%	1	0	0.001	0.35
P-0.3%	1	0	0.003	0.35
P-0.8%	1	0	0.008	0.35
P-1.5%	1	0	0.015	0.35
M-0%	1	0.3	0	0.35
M-0.1%	1	0.3	0.001	0.35
M-0.3%	1	0.3	0.003	0.35
M-0.8%	1	0.3	0.008	0.35
M-1.5%	1	0.3	0.015	0.35

TABLE 1-MIX PROPORTIONS (BY MASS).

TABLE 2—POROSITY AND PORE SIZE DISTRIBUTION DATA OF MORTARS WITH VARYING DOSAGES OF PNS SUPERPLASTICIZER.

Mixtures	Overall	porosity	Threshold pore		Pore size distributions (vol. %)				
	(vol. %)		diameter (nm)		> 50 nm		50 – 3.2 nm		
	ld	28d	ld	28d	1d	28d	ld	28d	
M-0%	22.6	15.4	50.0	29.2	37.9	12.5	62.1	87.5	
M-0,1%	22.1	14.6	38.9	25.0	37.5	12.5	62.5	87.5	
M-0.3%	23.9	15.1	50.0	25.0	43.6	10.9	56.4	89.1	
M-0.8%	20.9	13.8	38.9	25.0	22.9	10.6	77.1	89.4	
M-1.5%	19.5	14.3	38.9	25.0	29.6	10.7	70.4	89.3	

TABLE $3-Ca(OH)_2$ and non-evaporable water contents determined by TGA method.

Mixtures	Ca(OH) ₂ (%)					Non-evaporable water (%)						
	6h	ld	3d	7d	14d	28d	6h	ld	3d	7d	14d	28d
P-0%	2.5	9.2	12.7	13.2	13.7	13.1	6.1	11.1	14.9	13.6	14.0	13.9
P-0.1%	2.1	8.7	13.1	13.4	14.0	13.3	6.1	11.0	15.1	14.2	14.9	14.4
P-0.3%	2.0	9.0	13.0	13.2	13.4	14.0	5.5	12.4	14.8	14.7	14.3	15.1
P-0.8%	1.2	8.4	11.7	11.7	12.1	12.6	4.9	10.9	14.7	14.3	13.9	13.7
P-1.5%	1.4	6.7	11.2	11.1	11.4	12.0	4.8	10.7	15.1	14.5	14.3	14.8
M-0%	2.1	10.4	12.4	12.7	14.5	12.2	4.9	12.3	13.3	14.4	14.3	16.0
M-0.1%	2.4	9.9	12.6	13.1	14.9	13.4	4.6	12.3	13.8	14.2	14.4	15.8
M-0.3%	2.2	10.3	13.0	12.9	14.5	12.2	4.8	12.9	13.8	14.3	14.3	15.9
M-0.8%	1.4	9.8	11.8	12.2	14.0	12.1	4.0	12.5	13.7	14.1	15.1	15.9
M-1.5%	1.3	9.7	12.9	12.1	12.6	11.3	4.0	13.1	16,1	14.3	13.5	16.8



Fig. 1-(a) Schematic plot of an AC impedance spectrum in the real-imaginary complex plane for cement pastes; (b) equivalent electrical circuit model.



Fig. 2—AC impedance spectra of cement pastes prepared with and without PNS superplasticizer at various hydration times. W/C = 0.35. (a) 4 hours; (b) 1 day; (c) 28 days; (d) 120 days.



Fig. 3–AC impedance spectra of mortars prepared with and without PNS superplasticizer at various hydration times. S/C = 0.3, W/C = 0.35. (a) 4 hours; (b) 1 day; (c) 28 days; (d) 120 days.



Fig. 4–AC impedance spectra of limewater with different PNS superplasticizer contents.



Fig. 5—Effect of PNS superplasticizer of varying dosages on electrical resistivity of cement pastes. W/C = 0.35.



Fig. 6—Effect of PNS superplasticizer of varying dosages on electrical resistivity of mortars. S/C = 0.3, W/C = 0.35.



Fig. 7—Effect of PNS superplasticizer on high frequency arc (HFA) diameter, R_2 of cement pastes. W/C = 0.35.



Fig. 8—Effect of PNS superplasticizer on high frequency arc (HFA) diameter, R_2 of mortars. S/C = 0.3, W/C = 0.35.





Fig. 9—Sand grain-paste interfacial zone of portland cement mortars at one day—top: 0.8 percent PNS superplasticizer; bottom: without superplasticizer.





Fig. 10—Sand grain-paste interfacial zone of portland cement mortars at 28 days—top: 0.8 percent PNS superplasticizer; bottom: without superplasticizer.