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Mechanical Properties and Freezing and Thawing Resistance of Concrete Incorporating Wood Fly Ash

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Synopsis: This paper presents the results of a long-term project at the UWM Center for By-Products Utilization to investigate the effect of wood fly ash on the strength and durability aspects of concrete. Four series of concrete mixtures were proportioned to achieve a 28-day compressive strength of approximately 34.5 MPa. All mixtures contained between nine and 33 percent of fly ash (ratio of wood fly ash and Class C fly was varied (0, 0.3, 0.4, and 0.6). Tests were performed for density, compressive strength, splitting-tensile strength, flexural strength, shrinkage, and freezing and thawing resistance. Based on the results, it was concluded that durable structural-grade concrete could be manufactured using 50% blend of wood and coal fly ash as a replacement of cement.

Keywords: Coal fly ash, compressive strength, concrete, density, drying shrinkage, dynamic modulus, flexural strength, freezing and thawing resistance, splitting-tensile strength, wood fly ash.

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INTRODUCTION

Wood fly ash (WFA) is generated due to combustion of wood for energy production at pulp and paper mills, saw mills, and wood-products manufacturing facilities. Physical and chemical properties of wood fly ash are influenced by species of trees, tree growing regions and conditions, method and manner of combustion including combustion temperature and type and age of the boiler, other supplementary fuel used with wood fuel, and method of WFA collection (1-3). Approximately 70% of the wood fly ash generated in the U.S.A. is landfilled; and approximately 25% is applied on land as a soil supplement (4-12). The remaining 5% has been used for miscellaneous applications (1-4), including construction materials, metal recovery, and pollution control. Landfilling is becoming very restrictive due to shrinking landfill space and more stringent environmental regulations. Due to the presence of some heavy metals, the use of wood fly ash as a soil supplement is also becoming limited, as well as reduced availability of land for application. Due to some of these reasons, attempts have recently been made at the UWM Center for By-Products Utilization to develop high-volume use technologies for WFA, especially for use as construction materials (8,13). Due to the high-carbon content in wood fly ash, use may be limited to low- and medium-strength and/or non-air entrained concrete. Naik (8) has reported that wood fly ash has a substantial potential for use as a pozzolanic mineral admixture and as an activator in cement-based materials. This paper presents the effect of wood fly ash on the strength and freezing and thawing resistance of concrete.

EXPERIMENTAL PROGRAM

Materials utilized for this project consisted of cement, fine aggregate, coarse aggregate, wood fly ash, and coal fly ash. All test materials were characterized for physical and chemical properties in accordance with the appropriate ASTM or other applicable standards. Physical and chemical properties of cement are given in Tables 1 and 2, respectively. Physical properties and gradation of fine and coarse aggregates are given in Tables 3 and 4, respectively. Physical properties and chemical composition of wood fly ash and coal fly ash used are given in Tables 5 and 6, respectively.

Mixture Proportions

Four series of concrete mixtures were made at a ready-mixed plant after extensive testing in a laboratory. One Control Mixture (C-1) was proportioned without wood fly ash, and the remaining three Mixtures C-2 (22% fly ash), C-3 (29% fly ash), and C-4 (33% fly ash) contained a blend of wood fly ash and Class C fly Ash. Mixture proportions are listed in Table 7. In proportioning mixtures, 50% of the wood ash content was used as sand because of its coarseness, and Class C fly ash was used as 1.25 times of the cement replaced. Therefore, in Table 7, cementitious content has been referred as “Equivalent Cementitious Content”. Of the three Mixtures C-2 (22% fly ash), C-3 (29% fly ash), and C-4 (33% fly ash) were developed to have wood fly ash contents of approximately 5%, 8%, and 12% of the total cementitious materials, as a partial replacement of cement. Concrete Mixtures C-2 (22% fly ash), C-3 (29% fly ash), and C-4 (33% fly ash) also contained Class C fly ash, 17% to 20% of the total cementitious materials. The Control Mixture (C-1) did not contain any wood ash but it contained Class C fly ash, 9% of the total cementitious materials. The slump of all concrete mixtures was maintained between 100 and 120 mm. The amount of water added to the concrete mixtures was varied to achieve the desired level of slump.

Manufacturing of Concrete Mixtures

Concrete ingredients were weighed and loaded in a rotating drum ready-mixed concrete mixer. All concrete mixtures were made in accordance with ASTM C 94. Before discharging the concrete mixture, slump (ASTM C 143) of the mixture was measured and additional water was added as required to achieve the desired slump of approximately 100 mm. Whenever additional water was added to obtain the specified fresh concrete characteristics, the concrete mixture was mixed for an additional three minutes.

Specimen Preparation and Testing

Fresh concrete properties including slump (ASTM C 143), air content (ASTM C 138), unit weight (ASTM C 138), and concrete temperature (ASTM C 1064) were measured and recorded for each mixture. Ambient air temperature was also measured and recorded. For each concrete mixture, test specimens were cast in accordance with ASTM C 192. Test specimens were cast for compressive strength (ASTM C 39), splitting-tensile strength (ASTM C 78), flexural strength (ASTM C 78), freezing and thawing resistance (ASTM C 666, Procedure A), and shrinkage (ASTM C 157) measurements.

RESULTS AND DISCUSSION

Fresh Concrete Properties

Mixture proportions and fresh properties of the concrete mixtures are shown in Table 7. The slump was recorded to be between 100 and 120 mm. The density of Control Mixture C-1 (without wood fly ash) was 2276 kg/m^3, whereas, it was 2297, 2207, and 2294 kg/m^3 for Mixtures C-2 (22% fly ash), C-3 (29% fly ash), and C-4 (33% fly ash), respectively. Air-content was between 5.8 and 10%. Even though Mixture C-3 (29% fly ash), produced high air-content, it was accepted as a field variation sometimes tolerated in ready-mixed concrete.

Compressive Strength

Compressive strength of mixtures was determined at 3, 7, 28, 91, 182, and 365 days, and the test results as a function of age are presented in Fig.1. The Control Mixture C-1 (22% fly ash) achieved a compressive strength of 22.7 MPa at the age of three days, 28 MPa at the age of seven days, 33.9 MPa at the age of 28 days, 38.6 MPa at the age of 91 days, 42.2 MPa at the age of 182 days, and 43.9 MPa at the age of 365 days. The compressive strength of the concrete mixtures containing wood fly ash ranged from 21 to 23.9 MPa at the age of three days, 28.1 to 4315 MPa at age of seven days, 32.7 to 33.3 MPa at the age of 28 days, 39.3 to 40.3 MPa at the age of 91 days, 41.3 to 42 MPa at the age of 182 days, and 42.5 to 46 MPa at the age of 365 days. Therefore, wood fly ash concrete of equivalent strength can be produced. It is evident from these results (Fig. 1) that inclusion of wood fly ash contributed to the strength development of concrete mixtures, even as the cement content was decreased by about 15%. This indicates pozzolanic contribution of wood fly ash.

Splitting-Tensile Strength

Splitting-tensile strength results are shown in Fig. 2. The Control Mixture C-1 (without wood fly ash) gained a splitting-tensile strength of 2.6 MPa at the age of three days, 3 MPa at the age of seven days, 3.8 MPa at the age of 28 days, 4.1 MPa at the age of 91 days 4.2 MPa at the age of 182 days, and 4.3 MPa at the age of 365 days. The splitting-tensile strength of the concrete Mixtures C-2 (22% fly ash), C-3 (29% fly ash), and C-4 (33% fly ash) containing wood fly ash varied between 2.5 and 2.9 MPa at the age of three days, 2.9 and 3.1 MPa at the age of seven days, 3.6 and 4 MPa at the age of 28 days, 3.7 and 4.5 MPa at the age of 91 days, 3.9 and 4.8 MPa at the age of 182 days, and 4.2 and 5.1 MPa at the age of 365 days. The splitting-tensile strength of the concrete mixtures containing wood fly ash generally followed the same pattern as that for the compressive strength. Therefore, equivalent splitting tensile strength concrete can be produced with wood fly ash.

Flexural Strength

Flexural strength of concrete mixtures was determined at the age of 7, 28, 91, and 365 days, and results are shown in Fig. 3. The Control Mixture C-1 (without wood fly ash) achieved a flexural strength of 3.1 MPa at the age of seven days, 4.1 MPa at the age of 28 days, 4.2 MPa at the age of 91 days, and 4.4 MPa at the ages of 365 days. The flexural strength of the concrete Mixtures C-2 (22% fly ash), C-3 (29% fly ash), and C-4 (33% fly ash) containing wood fly ash varied between 3.2 and 3.9 MPa at the age of seven days, 3.9 and 4.4 MPa at the age of 28 days, 4.3 and 5 MPa at the age of 91 days, and 4.3 and 5.3 MPa at the age of 365 days. Test results indicate that inclusion of wood ash enhanced the flexural strength of concrete mixtures due to pozzolanic contribution of the wood fly ash.

Drying Shrinkage

Drying shrinkage of concrete mixtures is shown in Fig. 4. Drying shrinkage of the Control Mixture C-1 (without wood fly ash) was - 0.00916% at 7 days, and - 0.05138% at 232 days. For concrete Mixture C-2 (22% fly ash), the shrinkage ranged from 0.1154% at 7 days to -0.0269% at 232 days. Shrinkage values for concrete Mixture C-3 (29% fly ash) were 0.01438% at 7 days, and -0.01289% at 232 days. Mixture C-4 (33% fly ash) had shrinkage between -0.00514% at 7 days and -0.04366% at 232 days.

Freezing and Thawing Resistance

Freezing and thawing resistance of concrete test specimens was determined by measuring their relative dynamic modulus, pulse velocity and percent change in length. Fig. 5 shows the variation of relative dynamic modulus versus number of freezing and thawing cycles.

It can be seen from Fig. 5 that the relative dynamic modulus decreases very slightly with the increase in number of freezing and thawing cycles for all the four concrete mixtures. The decrease in initial dynamic modulus is not significant. For Mixture C-1 (without wood fly ash), relative dynamic modulus is 97.7% of the initial value (Zero cycle), whereas it is 95.7% for Mixture C-2 (22% fly ash), 97.8% for Mixture C-3 (29% fly ash), and 95.7% for Mixture C-4 (33% fly ash), at 300 cycles. It is evident that presence of wood fly ash did not have significant effect on the freezing and thawing resistance of concrete mixtures.

The pulse velocity of concrete mixtures is shown in Fig. 6. There is no significant effect from inclusion of wood ash on the pulse velocity of concrete mixtures. At 300 cycles, the pulse velocity of concrete Mixtures C-1 (without wood fly ash) was 17800 ft/sec, 17970 ft/see for Mixture C-2 (22% fly ash), 18225 ft/sec for Mixture C-3 (29% fly ash), and 17830 ft/sec for Mixture C-4 (33% fly ash).

Percent change in length of concrete mixtures is shown in Fig. 7. For Control Mixture C-1 (without wood fly ash), percent change in length was 0% at 32 cycles, and -0.00556% at 360 cycles. The percent change in length for Mixture C-2 (22% fly ash) was –0.003273% at 32 cycles and 0.01113% at 300 cycles, 0.002942% at 32 cycles and 0.00903% at 300 cycles for Mixture C-3 (29% fly ash), -0.000417% at 32 cycles and 0.01156% at 213 cycles for Mixture C-4 (33% fly ash).

CONCLUSIONS

1. Pozzolanic contributions of wood ash was found to be significant. Blending of wood fly ash with Class C fly ash resulted in improvement in performance of concrete.
2. Although wood ash did not conform to ASTM C 618 requirements for coal fly ash, it was found to be suitable for use in producing structural-grade concrete.
3. Compressive strength, splitting tensile strength, and flexural strength have continued to increase with age.
4. Concrete mixtures containing a blend of wood fly ash and ASTM C 618 Class C fly ash achieved equivalent compressive, tensile, and flexural strength with respect to Control Mixture.

5. Inclusion of wood fly ash in concrete mixtures did not affect freezing and thawing resistance and drying shrinkage of concrete mixtures.

REFERENCES

1. Etiegni, L., Wood Fly Ash Recycling and Land Disposal. Ph.D. Thesis, Department of Forest Products, University of Idaho at Moscow, Idaho, 174 pp., June 1990.
2. Etiegni, L. and Campbell, A. G., Physical and Chemical Characteristics of Wood Fly Ash, Bioresource Technology, Elsevier Science Publishers Ltd., England, Vol. 37, No. 2, pp.173-178, 1991.
3. National Council for Air and Stream Improvement, Inc. (NCASI), Alternative Management of Pulp and Paper Industry Solid Wastes. Technical Bulletin No. 655, NCASI, New York, 44 pp., Nov. 1993
4. Campbell, A. G., Recycling and Disposing of Wood Fly Ash. TAPPI Journal, TAPPI Press, Norcross, GA, Vol. 73, No. 9, pp.141-143, Sept. 1990.
5. Mishra, M. K., Ragland, K. W., and Baker, A. J., Wood Fly Ash Composition as a Function of Furnace Temperature. Biomass and Bioenergy, Pergamon Press Ltd., UK, Vol. 4, No. 2, pp. 103-116, 1993.
6. Steenari, B. M. and Lindqvist, O., Co-combustion of Wood with Coal, Oil, or Peat -Fly Ash Characteristics. Department of Environmental Inorganic Chemistry, Chalmers University of Technology, Goteborg, Sweden, Report No. ISSN 0366-8746 OCLC 2399559, Vol. 1372, pp. 1-10, 1998.

7. Steenari, B. M., Chemical Properties of FBC Ashes. Report No. ISBN 91-7197-618-3, Department of Environmental Inorganic Chemistry, Chalmers University of Technology, Goteborg, Sweden, 72 pp., Apr. 1998.

8. Naik, T. R., Tests of Wood Fly Ash as a Potential Source for Construction Materials," Report No. CBU-1999-09, UWM Center for By-Products Utilization, Department of Civil Engineering and Mechanics, University of Wisconsin - Milwaukee, Milwaukee, 61 pp., Aug. 1999.

9. Meyers, N. L. and Kopecky, M. J., Industrial Wood Fly Ash as a Soil Amendment for Crop Production. TAPPI Journal, TAPPI Press, Norcross, GA, pp. 123-130, 1998.

10. Nguyen, P. and Pascal, K. D., Application of Wood Fly Ash on Forestlands: Ecosystem Responses and Limitations. Proceedings, Conference on Eastern Hardwoods, Resources, Technologies, and Markets, Forest Product Society, Madison, WI, Apr. 21-23, 1997.

11. Bramryd, T. and Frashman, B., "Silvicultural Use of Wood Ashes – Effects on the Nutrient and Heavy Metal Balance in a Pine (Pinus Sylvestris, L.) Forest Soil, Water, Air and Soil Pollution. Proceedings, Fifth International Conference on Acidic Deposition: Science and Policy, Acid Reign '95, Part 2, Kluwer Academic Publishers, Dordrecht, Netherlands, V. 85, No. 2, pp. 1039-1044, Jun. 1995.

12. Naylor, L. M. and Schmidt, E. J., Agricultural Use of Wood Fly Ash as a Fertilizer and Liming Material. TAPP Journal, TAPPI Press, Norcross, GA, pp. 114-119, Oct. 1986.

13. Naik, T. R., Flowable Slurry incorporating Wood Fly Ash. Report No. CBU-2000-01, REP-367, UWM Center for By-Products Utilization, Department of Civil Engineering and Mechanics, University of Wisconsin - Milwaukee, 37 pp., Jan. 2000.

14. Mukherji, S. K., Dan, T. K., and Machhoya, B. B., Characterization and Utilization of Wood Fly Ash in the Ceramic Industry. International Ceramic Review, Verlag Schmid GmbH, Freiburg, Germany, Vol. 44, No. 1, pp. 31-33, 1995.

Table 1- Physical Properties of portland Cement

Test	Type I Cement used	ASTM C 150 specification for Type I cement
Compressive strength, (MPa)		
3-day	17.7	12.4
7-day	26.6	19.3
28-day	38.8	27.6
Autoclave expansion, (%)	0.055	0.8 max.
Fineness, % (Retained on No. 325 sieve	4.0	-
Fineness: specific surface (air-permeability test), (m^2/kg)	340	280 min.
Air content of mortar, (%)	11.0	12 max.
Vicat time of setting, (min)		
Initial	275	45 min.
Final	365	375 max.
Specific gravity	3.15	-

Table 2.- Chemical Composition of portland Cement

Analysis Parameter	Type I Cement (%)	ASTM C 150, Type I cement (%)
SiO_2	21.9	-
Al_2O_3	4.9	-
Fe_2O_3	3.0	-
CaO	64.1	-
MgO	2.4	6.0 max.
TiO_2	0.0	-
K_2O	0.5	-
Na_2O	0.1	-
SO_3	1.4	3.5 max.
LOI (1000^{o}C)	1.7	3.0 max.
Moisture	0.9	-
Available Alkali, Na_2O	0.88	-

Table 3- Physical Properties of Fine and Coarse Aggregates (ASTM C 33)

	Unit Weight, (kg/m^3)	Bulk Specific Gravity	SSD Bulk Specific Gravity	Apparent Specific Gravity	SSD Absorption, (%)	Percent Void	Fineness Modulus	Material Finer than #200 Sieve (%)	Clay Lumps and Friable Particles, (%)	Organic Impurity for Fine Aggregate
ASTM Test Designation	C 29	C 127/C 128				C 29	C 136	C 117	C 142	C 40
Sand (Fine Aggregate)	1762	2.64	2.67	2.72	1.3	38.0	2.7	0.6	0.0	Passes
Stone (Coarse Aggregate)	1564	2.66	2.67	2.70	0.7	41.2	6.7	0.0	0.0	N.A.

Table 4 - Gradation of Fine and Coarse Aggregates (ASTM C 136)

Fine Aggregate*			Coarse Aggregate*		
Sieve Size	% Passing	ASTM C 33 % Passing	Sieve Size	% Passing	ASTM C 33 % Passing
3/8" (9.5-mm)	100	100	1" (25.4-mm)	99.2	100
#4 (4.75-mm)	100	95 to 100	3/4" (19-mm)	90.9	90 to 100
#8 (2.36 mm)	88.7	80 to 100	1/2" (12.7-mm)	55.6	-
#16 (1.18 mm)	73.5	50 to 85	3/8" (9.5-mm)	30.8	20 to 55
#30 (600 micron)	49.9	25 to 60	#4 (4.75-mm)	2.3	0 to 10
#50 (300 micron)	18.9	10 to 30	#8 (2.36-mm)	1.0	0 to 5
#100 (150 micron)	3.4	2 to 10	#16 (1.18-mm)	-	-

* Values reported for % passing are an average of three tests

Table 5 - Physical Properties of Wood Fly Ash and Class C Fly Ash

Test Parameter	Wood Ash	Class C Fly ash	ASTM C 618 Specifications		
			Class C	Class F	Class N
Retained on No.325 sieve, (%)	90	10	34 max	34 max	34 max
Strength Activity Index with Cement, % of Control					
3-day	102*	109.2			
7-day	83.3*	110.8	75 min	75 min	75 min
28-day	78.7*	104.7	75 min	75 min	75 min
Water Requirement, % of Control	115*	95	105 max	105 max	115 max
Autoclave Expansion, (%)	-0.63*	0.08	±0.8	±0.8	±0.8
Unit Weight, (kg/m^3)	1374	1082	-	-	-
Specific Gravity	2.6	1.9	-	-	-

* Materials passing, No. 100 (150 µm) sieve was used for this test

Table 6 - Chemical Composition of Wood and Class C Fly Ash

Analysis Parameter	Wood Ash	Class C Fly Ash	ASTM C 618 Requirements		
			Class C	Class F	Class N
SiO_2	61.4	36.6	-	-	-
Al_2O_3	6.2	19.5	-	-	-
Fe_2O_3	2.6	5.9	-	-	-
$SiO_2 + Al_2O_3 + Fe_2O_3$	70.2	61.0	50 min	70 min	70 min
CaO	12.3	26.1	-	-	-
MgO	2.9	6.4	-	-	-
TiO_2	0.57	1.4	-	-	-
K_2O	3.3	0.5	-	-	-
Na_2O	1.4	2.2	-	-	-
SO_3	0.8	1.2	5 max	5 max	4 max
LOI (1000^0C)	8.4	0.4	6 max	6 max*	10 max
Moisture	10.5	0.2	3.0 max	3.0 max	3.0 max
Available Alkali, Equ. Na_2O, (ASTM C-311)	0.8	2.8	1.5 max	1.5 max	1.5 max

* The use of Class F pozzolan containing up to 12% loss on ignition may be approved by the user if either acceptable performance records or laboratory test results are made available

Table 7 - Mixture Proportions and Fresh Concrete Properties

Mixture Number	C-1	C-2	C-3	C-4
Cement, C, (kg/m^3)	302	285	261	264
Wood Fly Ash, A1, (kg/m^3)	-	20	31	48
Class C Fly Ash, A2, (kg/m^3)	30	61	77	80
Equivalent Cementitious Content, Ceq. (kg/m^3)	326	344	338	352
SSD Fine Agg., (kg/m^3)	838	823	781	808
SSD Coarse Agg., (kg/m^3)	971	983	953	974
Water, W, (kg/m^3)	137	155	144	137
% Class C + Wood Fly Ash*	9	22	29	33
% Wood Fly Ash**	-	5	8	12
W/Ceq.	0.42	0.45	0.43	0.39
MRWRA, (ml/m^3)	1316	1355	1336	1316
AEA, (ml/m^3)	166	166	325	194
Slump, (mm)	115	120	115	100
Air Content, (%)	7.0	5.8	10.0	5.7
Air Temperature, (°C)	16	19	19	16
Concrete Temperature, (°C)	21	20	22	21
Fresh Concrete Density, (kg/m^3)	2276	2297	2201	2294

* (A1+A2)/(C+A1+A2) ** A1/(C+A1+A2)

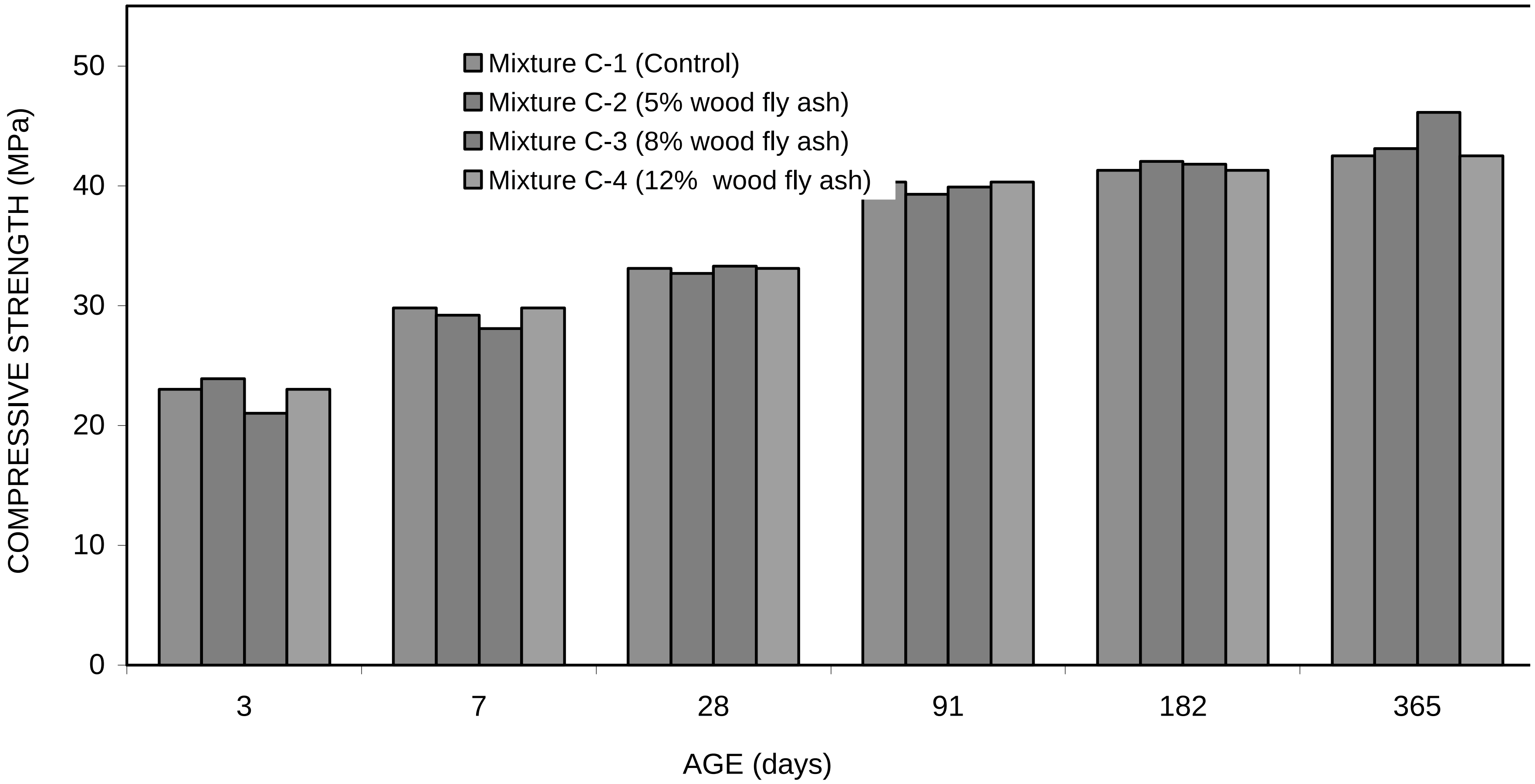

Fig. 1 Compressive strength of concrete mixtures

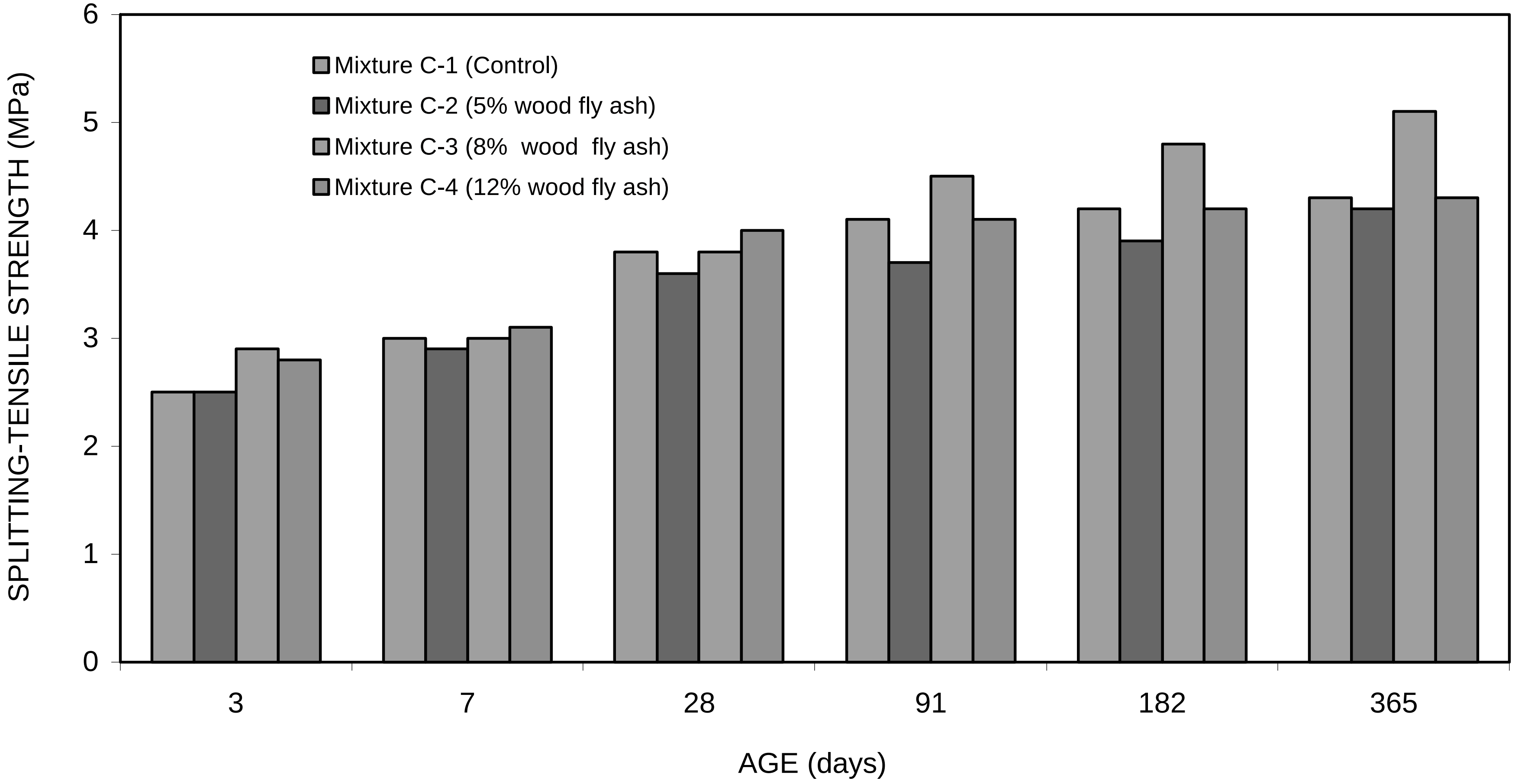

Fig. 2 Splitting-tensile strength of concrete mixtures

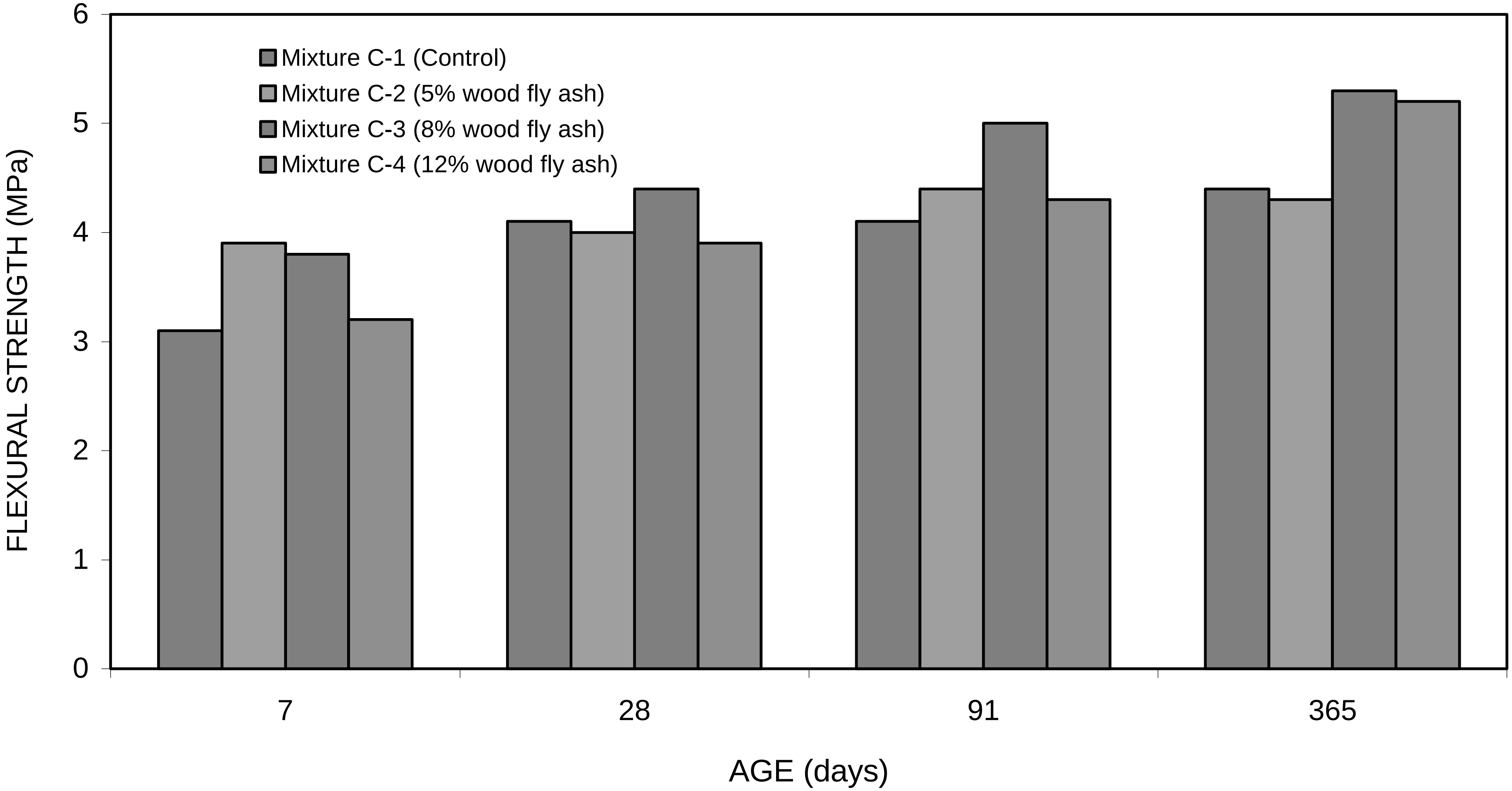

Fig. 3 Flexural strength of concrete mixtures

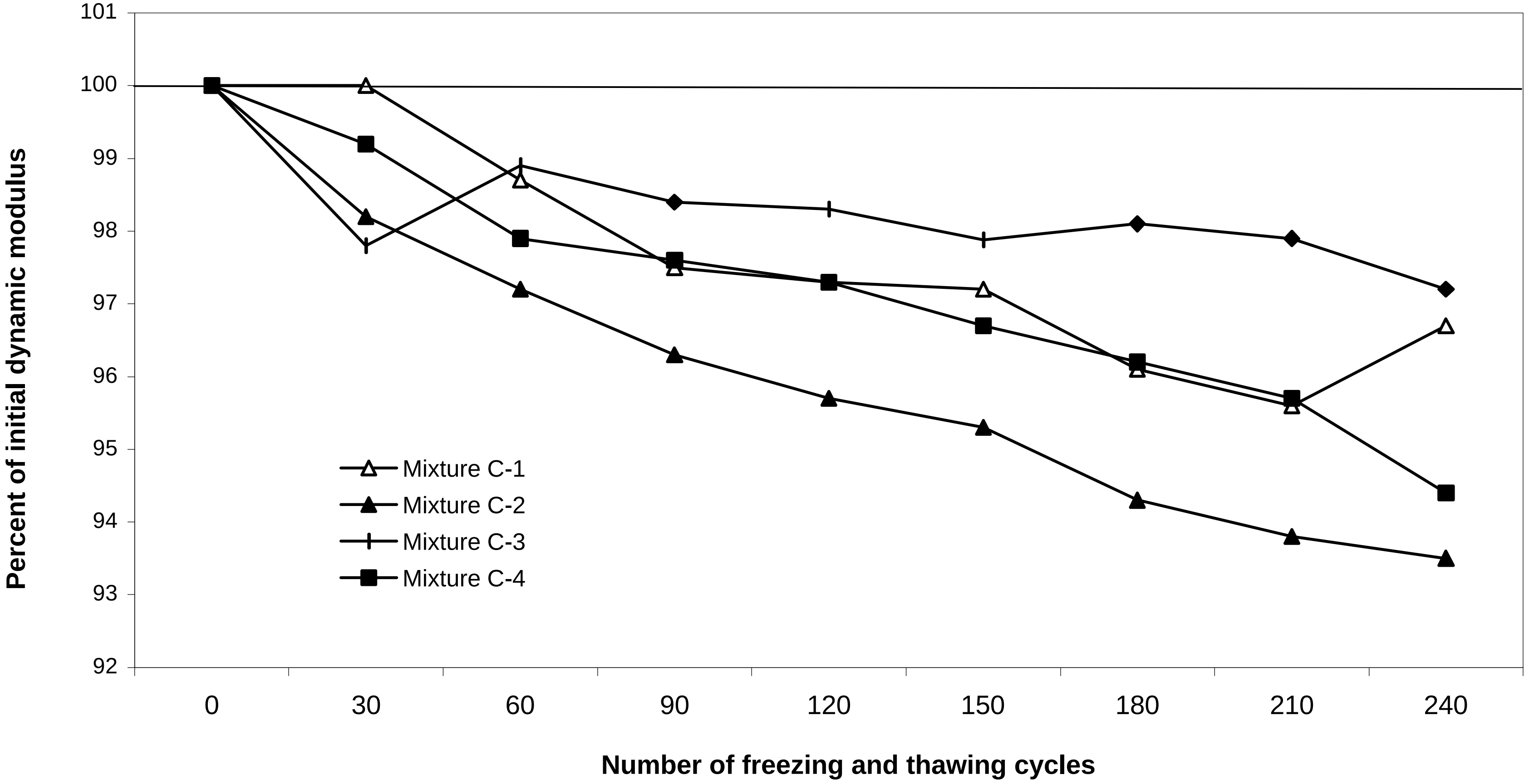

Fig. 5 Freezing and thawing cycles versus percent of intial dynamic modulus

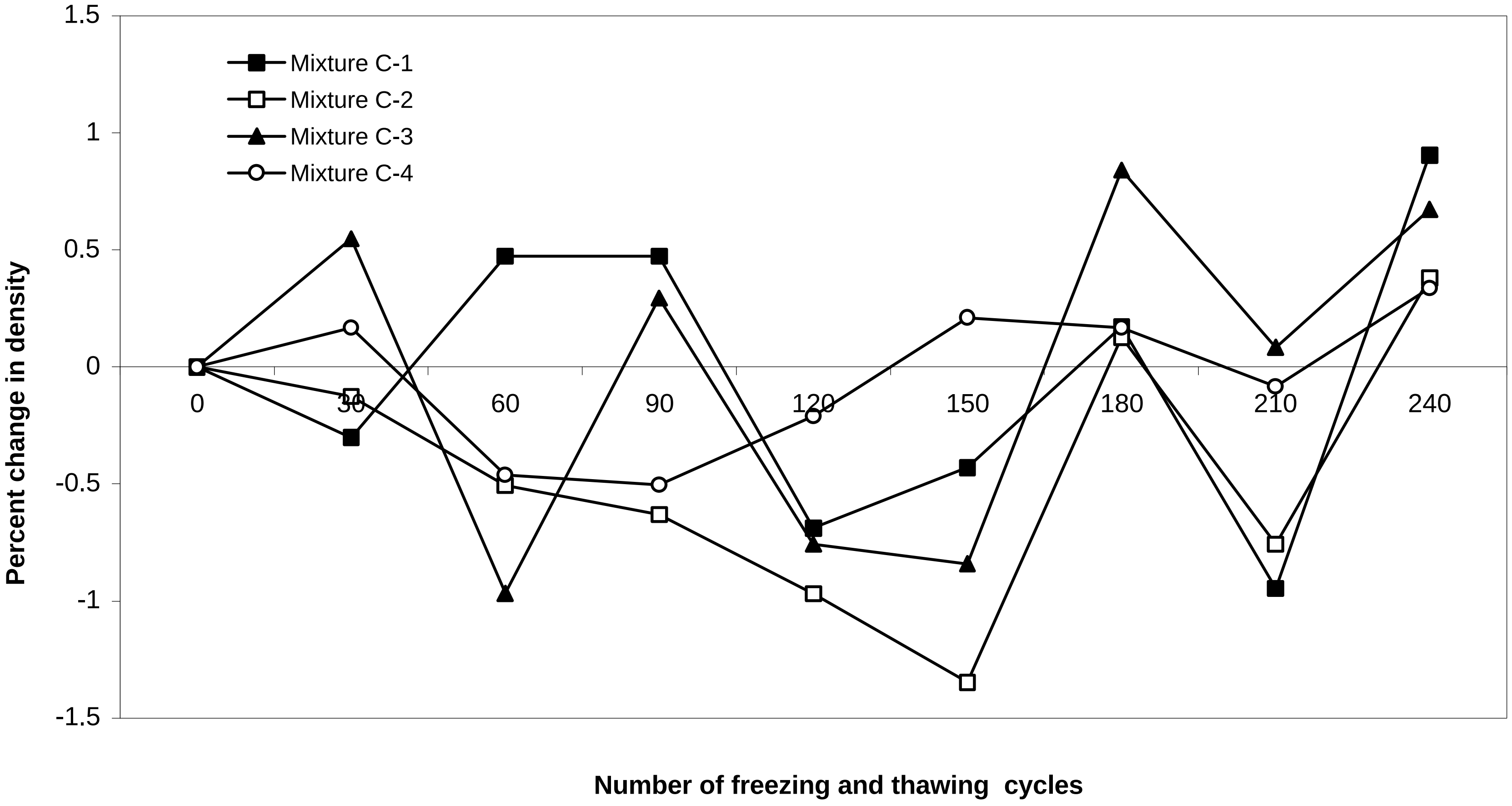

Fig. 6- Freezing and thawing cycles versus percent change in density

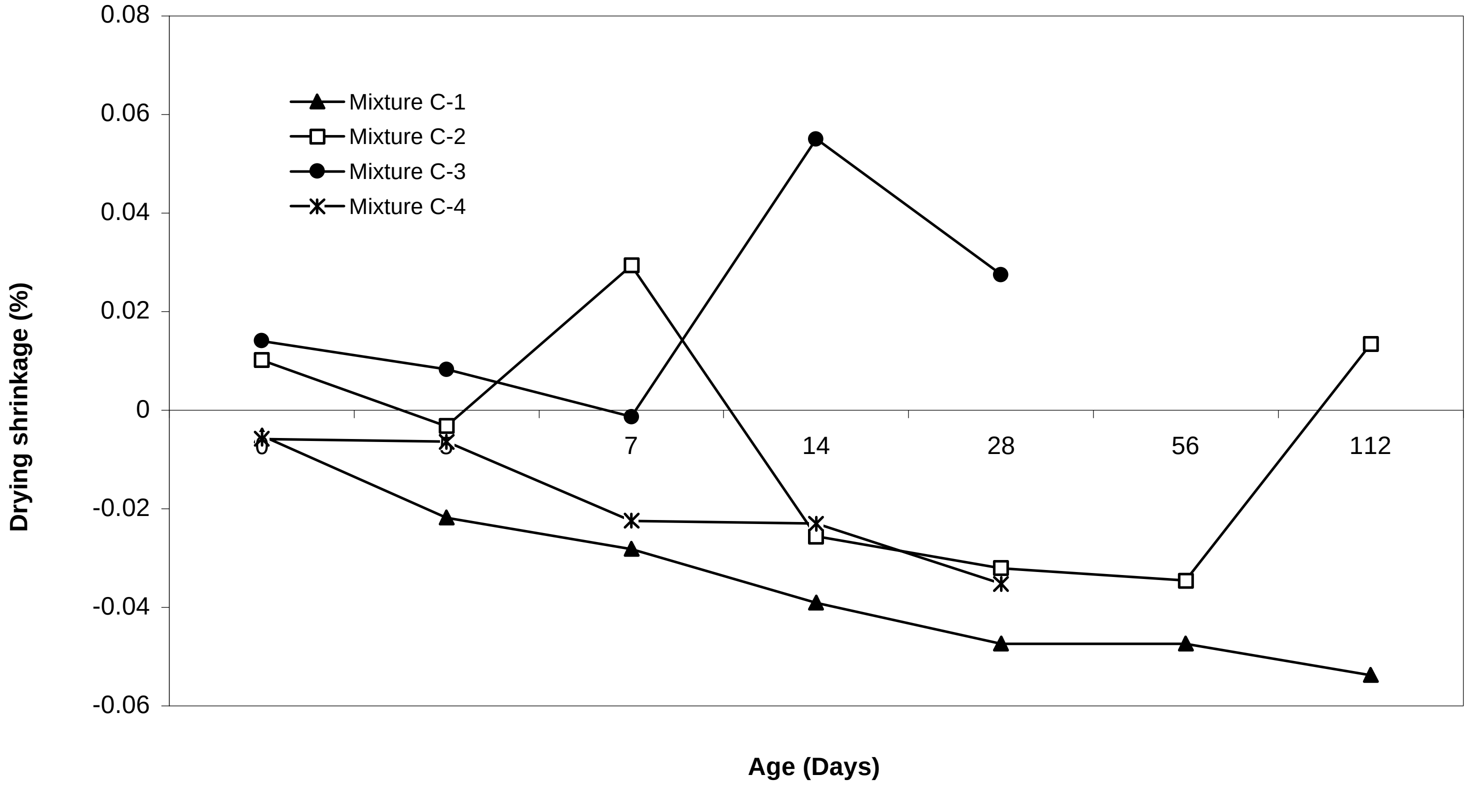

Fig.4 Drying shrinkage of concrete mixtures

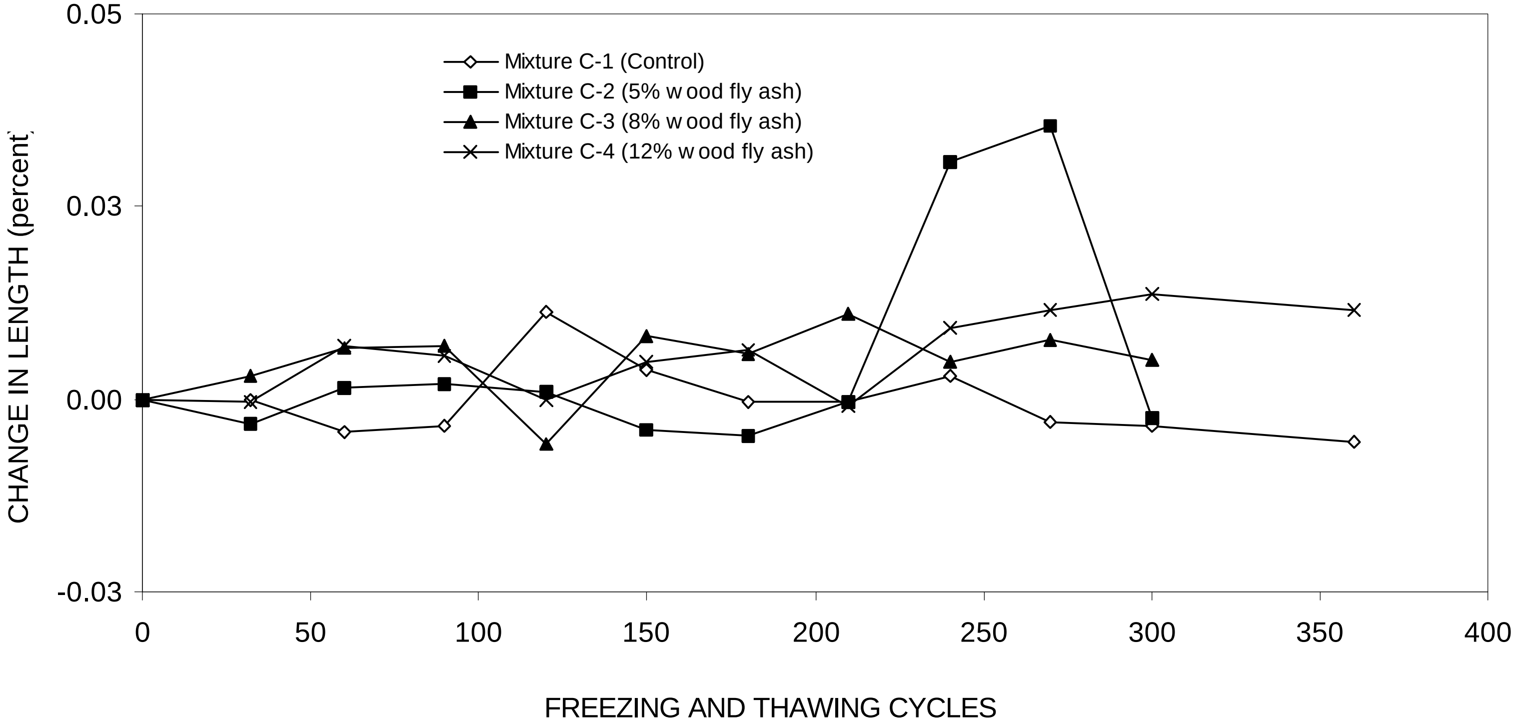

Fig. 7 Percent change length versus freezing and thawing cycles of concrete mixtures

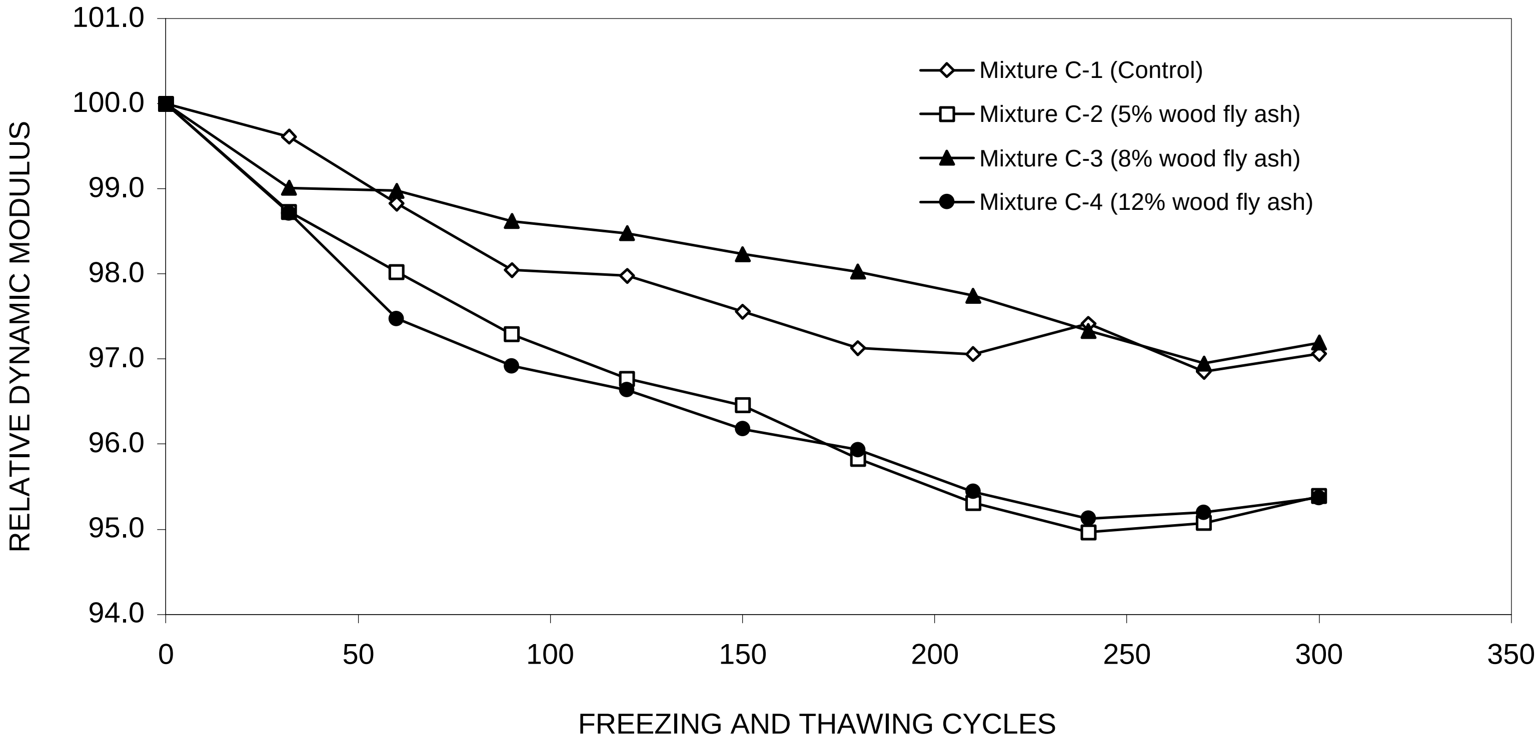

Fig. 5 Relative dynamic modulus versus freezing and thawing cycles of concrete mixtures

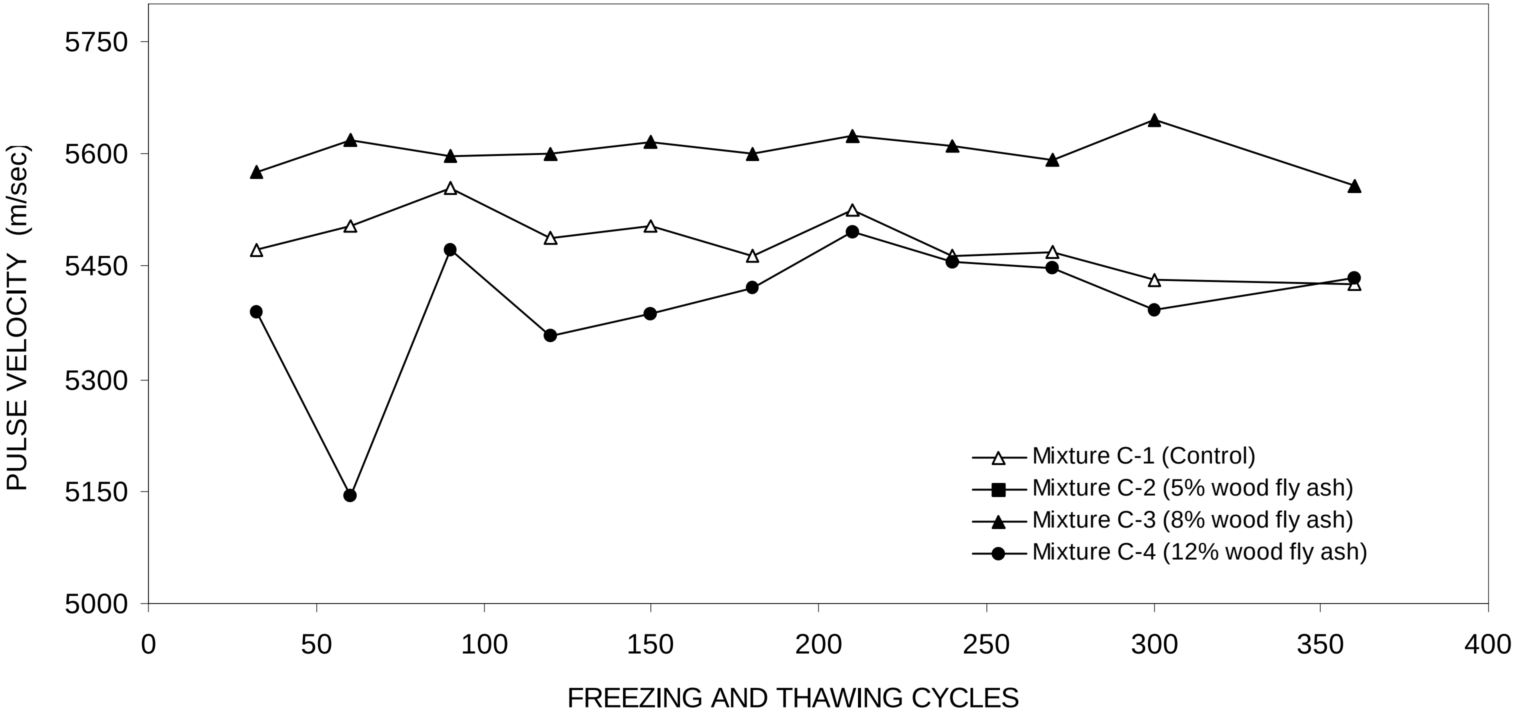

Fig. 6 Pulse velocity versus freezing and thawing cycles of concrete mixtures