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HYDRATION VERSUS STRENGTH IN A PORTLAND CEMENT DEVELOPED FROM DOMESTIC MINERAL WASTES — A COMPARATIVE STUDY

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ABSTRACT

Early age hydration studies on fresh pastes of a Type I cement produced from local mineral tailings have been conducted by using thermal techniques such as DTA and TGA and degrees of hydration at varying time intervals have been estimated in terms of non-evaporable water and free calcium hydroxide incorporated in the hydration products. The results are subjected to an earlier proposed expression which gives a direct correlation between strength and degree of hydration for a given hydrating cement paste except for the period of low reactivity, commonly referred to as the dormant period exhibiting very low heat evolution in a calorimetric plot, when cement remains plastic while still undergoing a certain degree of hydration. It is noticed that the critical degree of hydration at which strength starts developing is a function of hydration time and theoretically corresponds to the termination of the acceleration period when tricalcium silicates and dicalcium silicates in the cement have hydrated to produce enough hydration products to intermesh and initiate early strength. The experimental data are compared with those of a commercially available Type I cement and are interpreted in terms of strength development as a function of hydration.

INTRODUCTION

Vast deposits of copper–nickel and iron ores located in Northern Minnesota are capable of producing up to 150 Mtons of tailings every year [1]. These tailings frequently contain finely disseminated fibrous amphiboles as potential air and water pollutant, therefore presenting both disposal and environmental problems [2–4]. In an attempt to cope with this problem, the tailings have been used successfully as a raw feed component to produce a Type I Portland cement as reported elsewhere [4]. This cement, designated as the tailing cement, has exhibited better strength properties than the commercially available Type I Portland cement when tested under identical conditions as shown in the strength vs. time plot in Fig. 1. The improved strength properties may be ascribed to its chemical composition, especially of the tricalcium silicates and dicalcium silicates which are the primary

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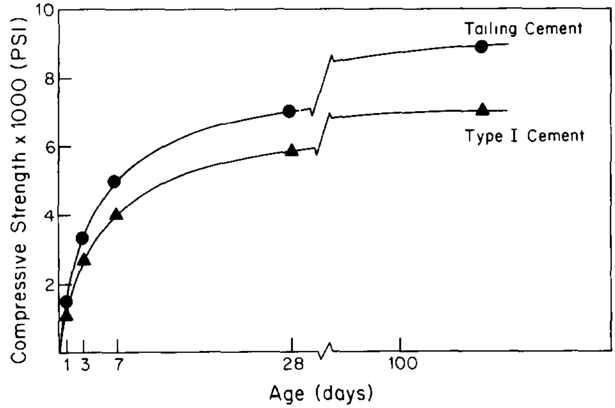

Fig. 1. Strength vs. curing time plot for the tailing and the Type I cements when cured under identical conditions.

sources of strength development in a hydrating cement paste. The major components of the tailing cement and those of an ordinary Type I Portland cement are given in Table 1. Comparative studies on the hydration behaviors of both these cements over longer curing periods have been conducted previously using thermal techniques such as DTA and TGA [5].

Present studies are focused primarily on very early hydration reactions in an attempt to demonstrate a critical hydration time as an index to the initial strength development in a cement paste. It is suggested that in hydrating cement–water systems the initial strength gain would occur when a sufficient amount of hydration products grow and begin intermeshing in sufficient quantities.

Although major cement compounds, i.e. the tricalcium silicates (C_3S) and dicalcium silicates (C_2S), when in contact with water, give similar hydration products, i.e. calcium silicate hydrate (also known as the C–S–H gel) and calcium hydroxide, their rates of formation are largely controlled by the nature and the amount of C_3S and C_2S present at the start of the hydration

TABLE 1

Compound compositions (wt.%) for the tailing cement and a Type I cement with their respective tri/dicalcium silicate ratios

Compounds	Tailing cement	Type I cement
Tricalcium silicate	56.00	47.25
Dicalcium silicate	17.00	26.00
Tricalcium aluminate	6.00	10.25
Tetracalcium aluminoferrite	14.00	7.50
Tricalcium silicate/ dicalcium silicate ratios	3.29	1.82

reaction. The formulation of the C–S–H gel is only approximate and varies with hydration time [6]. It is anticipated that the two cement–water systems under investigation, being different in compound composition, would undergo varying rates of hydration.

The investigations also include calorimetric studies to supplement data on heats of hydration of the cement pastes over given curing periods. The collected data are analyzed to derive a correlation between strength, curing time and the degree of hydration of individual cement–water systems.

MATERIALS AND METHODS

Neat pastes of both the tailing cement and a Type I Portland cement were prepared with deionized water at a water–cement ratio of 0.49. The pastes were cast in 1-in. cube molds and kept for varying curing times (i.e. 1, 3, 6, 10, 15, 20, 24 h) at 21 ± 1°C. After a given curing time (and unless the specimen became hard enough to be demolded and smashed for strength measurements) fractions of samples required for thermal analysis were collected and partially dried in a nitrogen-purged cabinet. The samples were then dried at 105°C to a constant weight in an oven to drive off the unbound moisture and subjected to thermal analysis by heating at a constant rate of 20°C min^{-1} from ambient to 1000°C in a Stanton-Redcroft thermoanalyzer (series 780) equipped with simultaneous DTA, TGA and temperature recorder. The runs were carried out in nitrogen atmosphere flowing at 50 $\text{cm}^3\ \text{min}^{-1}$.

A separate set of experiments was conducted to record heats of hydration for both cements using a calorimeter under isothermal conditions.

RESULTS AND DISCUSSION

In an ordinary Portland cement, the compounds tricalcium silicate and dicalcium silicate, when brought into contact with water, give rise to the following hydration products:

$$2(3CaO \cdot SiO_2) + 6H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca(OH)_2 \tag{1}$$

$$3(2CaO \cdot SiO_2) + 4H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + Ca(OH)_2 \tag{2}$$

The compound $3CaO \cdot 2SiO_2 \cdot 3H_2O$ is also known as the C–S–H gel. It is regarded as the binder and primary strength developer in a cement paste and is present by more than 60% by weight in a fully hydrated cement paste [7]. The composition $3CaO \cdot 2SiO_2 \cdot 3H_2O$ is only approximate, since it is non-stoichiometric and poorly crystalline and more than one variety of C–S–H is formed upon hydration [6]. As hydration proceeds, the ratio C/S

TABLE 2

Weight losses during various decompositon regions

Curing time (h)	Weight losses (%) during			Actual water loss (%) (Ldh + Ldx)	Ignition loss (%) (Ldh + Ldx + Ldc)
	Dehydration 105–440 °C (Ldh)	Dehydroxylation 440–580 °C (Ldx)	Decarbonation 580–1000 °C (Ldc)		
Tailing cement					
1	0.50	0.20	0.35	0.70	1.05
3	0.65	0.35	0.40	1.00	1.40
6	1.90	0.70	0.75	2.60	3.35
10	2.50	1.00	0.95	3.50	4.40
15	3.90	2.00	1.00	5.90	6.90
20	4.50	2.50	1.00	7.00	8.00
24	5.00	4.20	1.80	9.20	11.00
Type I cement					
1	1.80	0.20	3.00	2.00	5.00
3	2.20	0.30	3.00	2.50	5.50
6	2.30	0.40	3.00	2.70	5.70
10	2.70	0.60	3.20	3.30	6.50
15	3.10	0.80	3.30	3.90	7.40
20	3.20	0.90	3.40	4.10	7.50
24	3.60	1.20	3.60	4.80	8.40

in the aqueous phase changes from 1.5 to as high as 3.0 towards the end of the dormant period, when the leaching of calcium ions into the solution is optimum [8,9]. The C/S ratio decreases soon after nucleation of $Ca(OH)_2$ in the aqueous phase when the reactants again come into contact to assume hydration leading to the onset of initial setting of the paste [7]. The C–S–H gel incorporates chemically bound water which controls the process of hydration and determines the rate of strength attainment [10]. Degrees of hydration and the amounts of free calcium hydroxide precipitating in the pores are estimated on the basis of weight lossses recorded in the TGA plots. Calculated values are given in Tables 2 and 3. The following expressions have been used in these calculations [11].

$$\text{Chemically bound water} = (\text{Ldh} + \text{Ldx}) + 0.41(\text{Ldc}) \tag{3}$$

$$\text{Free calcium hydroxide} = 4.11\ (\text{Ldx}) + 1.68(\text{Ldc}) \tag{4}$$

where Ldh, Ldx and Ldc are weight losses on TGA and DTA plots during dehydration of the C–S–H gel which occurs between 105 and 440 °C, dehydroxylation of the calcium hydroxide between 440 and 580 °C and decarbonation of the carbonates formed during exposure to the air, between 580 and 1000 °C, respectively [12]. Typical TGA and DTA plots for both the cements are given in Figs. 2, 3 and 4. Data on simultaneous strength developments are given in Table 4.

TABLE 3

Calculated values of "free" and chemically bound water, free calcium hydroxide and degree of hydration

Curing time (h)	Free water lost at (~105 °C) (wt.%)	Chemically bound water (wt.%)	Free calcium hydroxide (wt.%)	Degree of hydration (%)	
				By extrapolation	By eqn. (5)
Tailing cement					
1	45.00	0.85	0.82	4.05	3.54
3	39.95	1.17	1.44	5.57	4.90
6	31.88	2.91	2.88	13.85	12.13
10	19.74	3.89	4.11	18.53	16.21
15	25.56	6.31	8.22	30.05	26.29
20	20.90	7.41	10.28	35.29	30.88
24	12.59	9.94	17.26	47.33	41.42
Type I cement					
1	46.94	3.23	0.82	15.38	13.46
3	41.71	3.73	1.23	17.76	15.54
6	35.70	3.93	1.64	18.71	16.38
10	32.75	4.61	2.47	21.95	19.21
15	29.87	5.25	3.67	25.00	21.88
20	26.05	5.49	3.91	26.14	22.88
24	18.55	6.28	4.97	29.90	26.17

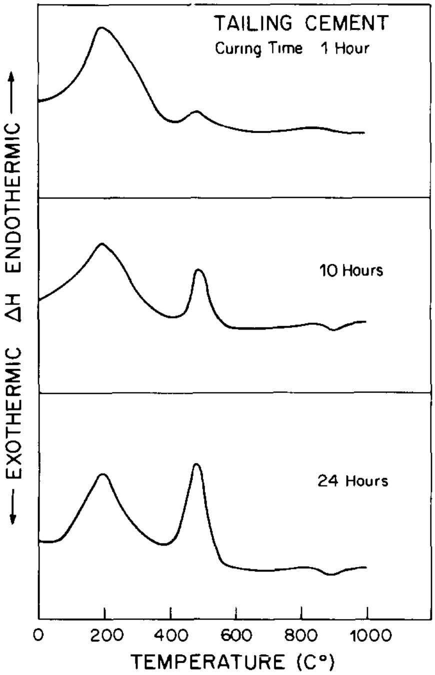

Fig. 2. Typical DTA plots for the tailing cement.

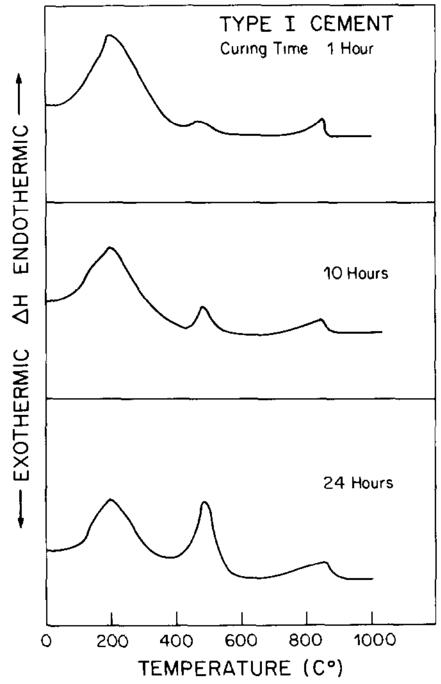

Fig. 3. Typical DTA plots for the Type I cement.

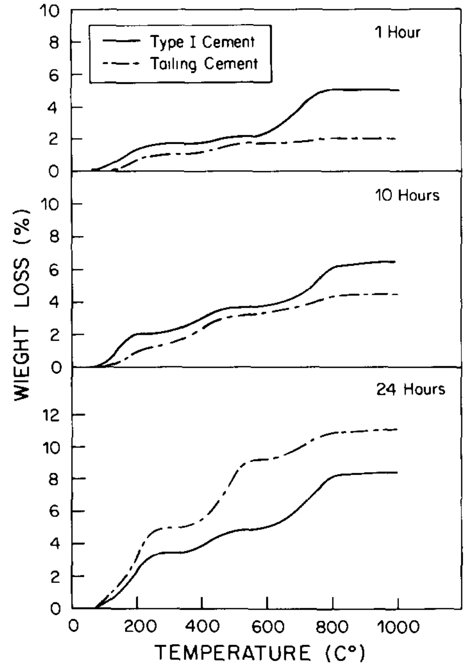

Fig. 4. TGA plots for the tailing and the Type I cements.

TABLE 4

Variation of strength with degree of hydration at given curing times

Curing time (h)	Tailing cement		Type I cement	
	Degree of hydration (%)	Strength (psi)	Degree of hydration (%)	Strength (psi)
1	4.05	–	15.38	–
3	5.57	–	17.76	–
6	13.87	–	18.71	–
10	18.53	–	21.95	–
12	24.81	200	22.88	–
15	30.05	500	25.00	200
20	35.20	900	26.14	300
24	47.33	1600	29.90	650

Initial strength development in a cement paste takes place at a critical degree of hydration when the hydration products are accumulated in sufficient amounts to interlock and to exhibit adequate strength. Based on values of "free" water, bound water and free calcium hydroxide, the rate of strength gain for the tailing cement is higher than the ordinary Type I cement. Higher estimated values of "free" water for the Type I cement indicate that smaller proportions of water remain available for hydration to effectively proceed with time. For instance, at 20 h hydration, the amount of free water for Type I cement is 26.05% as compared to 20.90% for the tailing cement, whereas bound water incorporated in the C–S–H gel is 5.49% as compared to 7.41% in the tailing cement. The corresponding degrees of hydration for Type I and the tailing cement are 26.14 and 35.29% and the compressive strength values 300 (psi) and 900 (psi), respectively.

The degree of hydration is the percentage ratio between the chemically bound water of a given cement paste to that of a completely hydrated paste. The values of the degrees of hydration for both the cements, given in Table 3, are calculated by employing the extrapolated value of bound water for completely hydrated pastes, which is 0.21 for both the cements under investigation. Another method of calculating the degree of hydration is by using the following equation:

$$\text{Degree of hydration } (\%) = \frac{W_c}{0.24} \times 100 \qquad (5)$$

where W_c is the chemically bound water. When cement is fully hydrated, i.e. at 100% degree of hydration, 0.24 parts of chemically bound water are combined with each part of cement [7]. Degrees of hydration calculated by using eqn. (5) are also given in Table 3.

Calorimetric plots given in Fig. 5 show similarities in the early strength gain for both the cement pastes. The deceleration period in a calorimetric

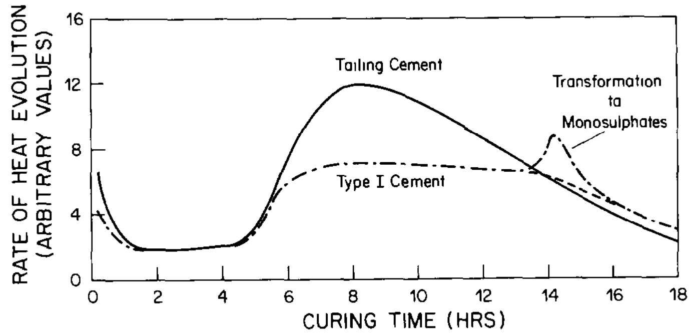

Fig. 5. Variation in heat evolution with curing time in calorimeteric plots for the tailing and the Type I cements.

plot of a hydrating cement paste indicates the continued formation of the hydration products and relevency to the rate of early strength gain [7]. It may be noted that although the amount of bound water and therefore the degree of hydration for the Type I cement are higher in the very early stages (up to ~ 10 h), the initiation of strength for both the cements takes place at virtually the same "critical" degree of hydration (i.e. at ~ 22.5%), as shown in Fig. 6. This corresponds to about 14 and 11 h of curing time for the Type I and the tailing cements, respectively. These times on the calorimeteric curves, Fig. 5, fit reasonably well in the deceleration region, which marks the onset of early stiffening in a cement paste.

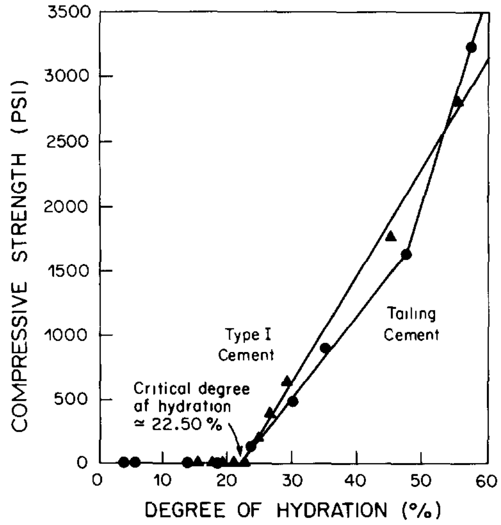

Fig. 6. Plots of compressive strength vs. degree of hydration for the tailing and the Type I cements.

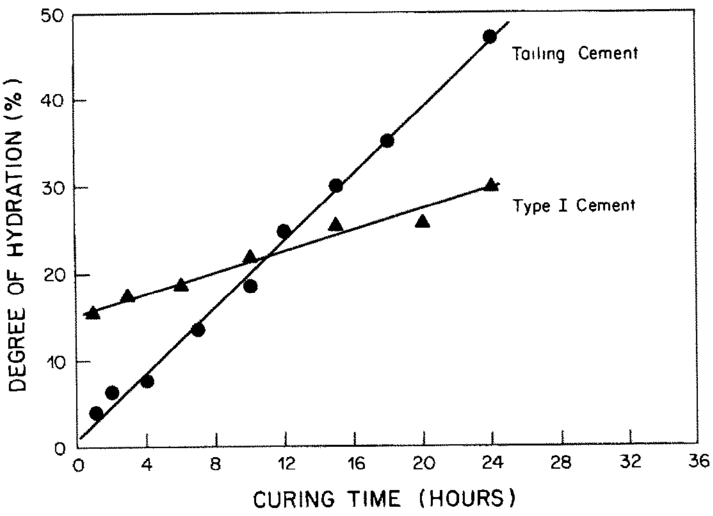

Fig. 7. Degree of hydration vs. curing time. The hydration rates calculated from the slopes of the plots are 1.04 for the tailing cement as compared to 0.65 for the Type I cement.

An exothermic hump in the deceleration region of the calorimeteric plot of the Type I cement most probably indicates the transformation of the compound ettringite to monosulfate. Ettringite forms when tricalcium silicate (C_3A) in the cement reacts with sulfate ions provided by the gypsum

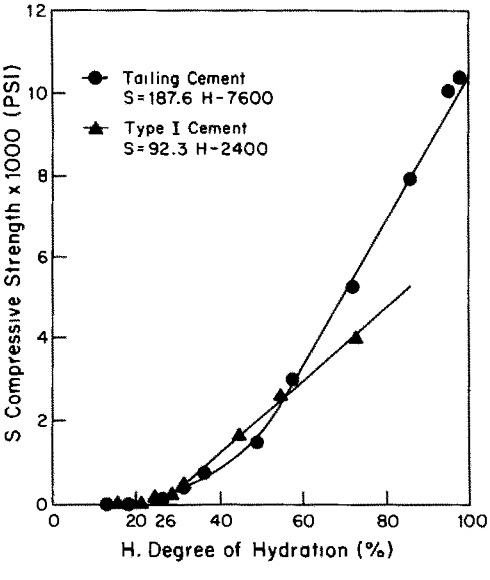

Fig. 8. Correlation plot between the compressure strength and degree of hydration for the tailing and Type I cements when cured for longer durations.

added as set regulator to avoid flash set and it is stable only if an adequate supply of sulfate ions is maintained. Upon the depletion of sulfate ions the ettringite transforms to monosulfate. The Type I Portland cement contains an excess of C_3A (10.25% compared to 6.00% in the tailing cement) and may not have enough gypsum present to maintain a regular supply of sulfate ions in the aqueous phase.

The fact that the hydration and the strength gains for the Type I cement are higher in the very early age, as shown in Fig. 6 and 7, does not reveal any complexities as the tailing cement eventually gains both in hydration and in strength. The rate of hydration for the tailing cement calculated from the degree of hydration vs. curing time plot, as in Fig. 7, is 1.04, which is 1.6 times higher than the Type I cement value of 0.65 when cured under identical conditions. This may be attributed to the higher tricalcium silicate compounds and indeed the higher tri/dicalcium silicate ratio in the tailing cement (3.29 compared to 1.82 for Type I cement) as given in Table 1. Tricalcium silicate contributes to early strength development whereas dicalcium silicate determines the ultimate strength [6]. In Fig. 8 are also shown the rates of strength attainment with time and direct correlations between strength and degree of hydration when both the cements are cured for longer periods. Rate of gain in the strength of the tailing cement is 187.6 which is more than twice the rate of 92.3 for the Type I cement.

CONCLUSIONS

The onset of strength development in hydrating cement–water systems takes place at a critical degree of hydration when the hydration products are formed in sufficient amount to exhibit interlocking. The rate to achieve this degree of hydration may differ for different types of Portland cements and could be largely controlled by the variations in their compound compositions, given that the other contributing factors such as water–cement ratios and curing conditions are not changed.

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