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USE OF THERMAL ANALYSIS IN THE HYDRATION STUDIES OF A TYPE 1 PORTLAND CEMENT PRODUCED FROM MINERAL TAILINGS

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ABSTRACT

A high-strength Type 1 cement produced from raw taconite and copper–nickel tailings of Minnesota is the subject of hydration studies by using thermal methods such as TGA and DTA. Hydration is measured in terms of hydration product formation and the amount of bound water and free calcium hydroxide incorporated in them. When cured under identical conditions, the Type 1 "tailing" cement, compared to an ordinary Type 1 Portland cement, exhibits better hydration properties. This is attributed to its higher tricalcium silicate content, a component that hydrates faster and also contributes much to the strength development. Correlation between the degree of hydration and strength is suggested and a simple mathematical expression relating these parameters proposed.

INTRODUCTION

In ordinary Portland cement the compounds tricalcium silicate and dicalcium silicate are the primary strength developers and are present to an extent of 70–80% by weight [1]. Upon their hydration, the formation of calcium silicate hydrate, known as the C–S–H gel, provides the necessary cementing properties in the hardening of cement pastes and essentially contributes towards the ultimate strength. Tricalcium silicate, being more reactive under hydraulic conditions, dominates the first four weeks of hydration after which dicalcium silicate starts to have an influence until the hydration is effectively complete.

The present investigation outlines some initial observations on the hydration of a high-strength Type 1 cement produced from mineral tailings which, as has been reported elsewhere [2], exhibits strength values almost twice the required ASTM specifications for an ordinary Type 1 Portland cement. Detailed compound composition of the tailing cement, given in Table 1, indicates that the presence of relatively higher tricalcium silicate may be critical in determining its hydration and eventually the strength-gaining behavior.

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TABLE 1

Major compound compositions (wt. %) for an average Type 1 and the tailing cement with their respective tri/dicalcium silicate ratios

Compounds	Type 1 cement	Tailing cement
Tricalcium silicate	47.25	56.00
Dicalcium silicate	26.00	17.00
Tricalcium aluminate	10.25	6.00
Tetracalcium aluminoferrite	7.50	14.00
Tricalcium silicate/ dicalcium silicate ratios	1.82	3.29

Methods of studying the hydration behavior of cement–water systems are numerous [3] and they include references to thermal analysis, such as DTA and TGA [1,4–13]. These methods are essentially based on the estimation of calcium hydroxide and bound water incorporated in the C–S–H gels which, being very nearly amorphous [14], are often not effectively detected by analytical methods other than DTA and TGA [11].

Hydration of tricalcium silicate and dicalcium silicate

Tricalcium silicate and dicalcium silicate, when brought into contact with water, give rise to similar hydration products, i.e., calcium silicate hydrate and calcium hydroxide. The reaction occurs as follows

$$\underset{\text{Tricalcium silicate}}{2(3\,CaO\cdot SiO_2)+6\,H_2O} \rightarrow \underset{\text{Calcium silicate hydrate (C–S–H gel)}}{3\,CaO\cdot 2\,SiO_2\cdot 3\,H_2O} + 3\,Ca(OH)_2 \qquad (1)$$

$$\underset{\text{Dicalcium silicate}}{2(2\,CaO\cdot SiO_2)+4\,H_2O} \rightarrow \underset{\text{Calcium silicate hydrate (C–S–H gel)}}{3\,CaO\cdot 2\,SiO_2\cdot 3\,H_2O} + Ca(OH)_2 \qquad (2)$$

Rates of these reactions and the formation of relevant amounts of hydration products depends on various factors such as hydration temperatures, surface areas of starting materials and water–cement ratios [11]. At a given temperature and water–cement ratio, tricalcium silicate hydrates faster than dicalcium silicate and forms three times as much calcium hydroxide per molecule of original silicate (see eqn. 1). Hydration products contain bound water incorporated within the calcium silicate hydrate gel and free calcium hydroxide that remains unreacted to the atmospheric carbon dioxide; both of which are widely regarded as a measure of the degree of hydration for a given cement paste at a given time [7,8,11]. At normal temperature, hydration products have a very low degree of crystallinity and are best detected by DTA and TGA which, because of their ability to detect the chemical changes occurring during hydration, are extensively used in cement hydration analysis. The aim of the present work is therefore to make use of these techniques to monitor hydration of the tailing cement as a guide to its strength development and to evaluate the results by comparing with those of ordinary Type 1 Portland cement.

MATERIALS AND METHODS

Neat pastes of both the tailing cement and ordinary Type 1 Portland cement were prepared by mixing with deionized water at water–cement ratios of 0.49. The pastes were cast in sealed Perspex moulds and kept overnight at 21 ± 1°C, demoulded and kept for varying curing times (i.e., 1, 3, 7, 28, 120, 200 days) in a 100% relative humidity chamber, also controlled at 21 ± 1°C. After given curing times the specimens were smashed and fractions of samples required for thermal analysis collected. These samples were partially dried and ground to −200 mesh in a nitrogen purged cabinet. The samples were dried again at 105°C to a constant weight in a standard oven to drive off the unbound moisture and subjected to thermal analysis by heating at a constant rate to 1000°C in a Stanton-Redcroft thermobalance (Series 780) equipped with simultaneous DTA, TGA and temperature recorders. The experiments were conducted in a static atmosphere of carbon dioxide-free nitrogen flowing at 50 cm^3 min^{-1}. The heating rate was kept at 15°C min^{-1} from ambient to 1000°C.

RESULTS AND DISCUSSION

Typical DTA plots for hydrated tailing cement and Type 1 Portland cements are shown in Fig. 1. For simplification, these plots can be divided into three broad temperature regions giving major decomposition reactions as follows.

(i) An endotherm occurs between 105 and 440°C showing a dehydration reaction ascribed mostly to the loss of water by calcium silicate hydrates. The peak in this region is less well defined and may also include dehydroxylation and some desorption [8,9].

(ii) Between 440 and 580°C an endotherm occurs exclusively due to the dehydroxylation of calcium hydroxide formed by the hydrolysis of the calcium silicates originally present. The peak in this region is well defined and any other reactions are unlikely to contribute here.

(iii) Between 580 and 1000°C, decarbonation of calcium carbonate, formed during exposure to air, occurs together with possible solid–solid phase transitions [12].

Weight losses associated with these decomposition regions are derived

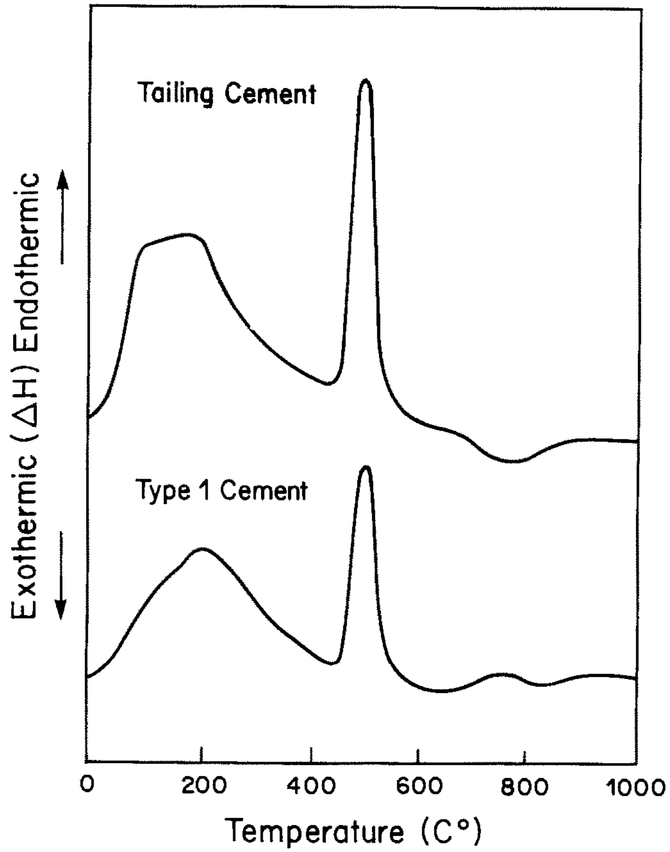

Fig. 1. Typical DTA plots for hydrating tailing cement and Type 1 cement. Seven-day-old pastes at a water/cement ratio of 0.49.

from TGA plots and are typically shown in Fig. 2. Respective weight losses estimated from the TGA plots for both the tailing and Type 1 cements cured at varying times are given in Table 2.

Estimation of chemically bound water

The actual water loss between 105 and 1000°C is given by the sum of dehydration (L_{dh}) and dehydroxylation (L_{dx}) losses, and is less than the total ignition loss, as it also accounts for the decarbonation loss in the temperature region 580–1000°C (see Table 2 for the comparison of these values). From these values, estimation of bound water can be carried out by the following expression [8,9].

$$\text{Chemically bound water} = (L_{dh} + L_{dx}) + 0.41(L_{dc}) \qquad (3)$$

where (L_{dc}) is the decarbonation loss and the factor 0.41 corrects for water loss equivalent to that of decarbonation occurring in this region, assuming

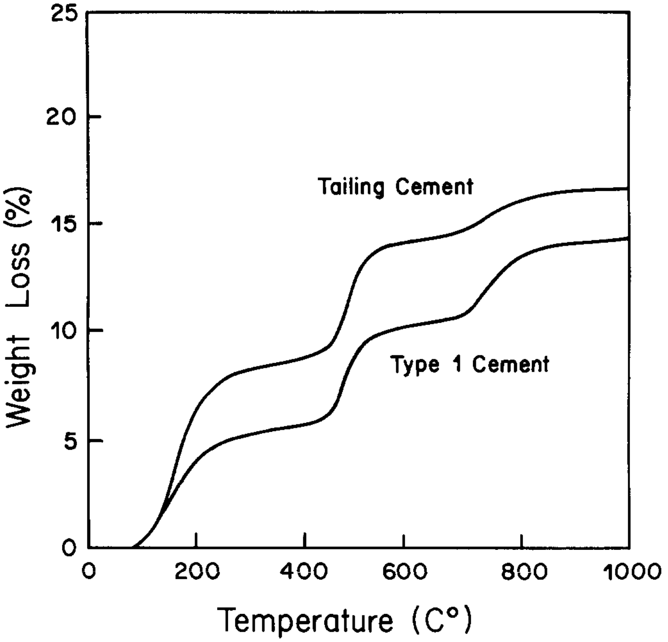

Fig. 2. Weight losses derived from the TGA plots for seven-day-old tailing cement and Type 1 cement pastes.

TABLE 2

Weight losses during various decomposition regions and values of total water loss and ignition loss derived from TGA plots of both the tailing cement and Type 1 cement cured for varying times

Curing time (days)	% Weight loss during			Actual water loss ($L_{dh}+L_{dx}$)	Ignition loss ($L_{dh}+L_{dx}+L_{dc}$)
	Dehydration 105–440°C (L_{dh})	Dehydroxylation 440–580°C (L_{dx})	Decarbonation 580–1000°C (L_{dc})		
Tailing cement					
1	5.0	4.2	1.8	9.2	11.0
3	6.7	4.5	2.0	11.2	13.2
7	9.1	5.2	2.0	15.0	17.0
28	10.8	6.0	2.5	16.8	19.3
120	12.0	6.2	3.4	18.2	21.6
200	12.4	6.5	3.8	18.9	22.7
Type 1 cement					
1	3.6	1.2	3.6	4.8	8.4
3	5.6	2.4	3.9	8.0	11.9
7	7.0	3.2	4.0	10.2	14.2
28	9.4	4.2	4.4	13.6	18.0
120	10.0	4.6	4.7	14.6	19.3
200	10.5	5.0	5.0	15.5	20.5

that the carbonate is formed by carbon dioxide reacting with calcium hydroxide present during hydration. Calculated values of bound water are given in Table 3.

Estimation of free calcium hydroxide

The amounts of calcium hydroxide produced during the hydration of tricalcium and dicalcium silicates in the cements are derived from both the dehydroxylation and decarbonation losses by using the following expression [8,9].

$$\text{Calcium hydroxide} = 4.11(L_{\mathrm{dx}}) + 1.68(L_{\mathrm{dc}}) \qquad (4)$$

Factors 4.11 and 1.68, respectively, correct for calcium hydroxide formed during hydroxylation and decarbonation. The first part of eqn. (4) gives the amount of free calcium hydroxide formed during hydration, their calculated values are also quoted in Table 3.

Analysis of data

Higher values of both the chemically bound water and free calcium hydroxide obtained in the case of the tailing cement predict it to be a better hydrating cement than the Type 1 Portland cement when cured under identical conditions. For instance, a one day old tailing cement shows the formation of 9.94 and 17.26% by weight of chemically bound water and free calcium hydroxide, respectively, as compared to the corresponding values of 6.28 and 4.93% for Type 1 cement. These products develop faster for both the cements during the early age of hydration forming respective values of 15.12 and 21.37, and 11.64 and 13.15% by weight for tailing and Portland cement in a week; the rate of development slows down after this initial period. Figure 3 illustrates the mode of formation of these products for both the cements. Higher values of these products in tailing cement may be attributed to its relatively higher tricalcium silicate content (56.00 compared to 47.25% by weight for Type 1 cement) and also to its high tricalcium silicate-to-dicalcium silicate ratio of 3.29 compared to 1.82 for a Type 1 cement (see Table 1 for individual compound composition). Tricalcium silicate hydrates faster, giving rise to larger amounts of hydration products, particularly the free calcium hydroxide content which, in the case of tailing cement, has formed up to 17.26% by weight in one day. Hydration of dicalcium silicates, however, becomes effective later (after 28 days) in the process [14,15].

Also, according to Copeland et al. [4], the presence of excessive tetracalcium aluminoferrite (in the tailing cement, 14.00%) may cause both tricalcium silicate and dicalcium silicate to hydrate rapidly. This, however, holds true for pure compounds or mixtures of pure compounds which, at

TABLE 3

Calculated values of chemically bound water, free calcium hydroxide and degree of hydration; using eqns. (3) and (4)

Curing time (days)	Tailing cement			Type 1 cement		
	Chemically bound water (wt. %)	Free calcium hydroxide (wt. %)	Degree of hydration (%)	Chemically bound water (wt. %)	Free calcium hydroxide (wt. %)	Degree of hydration (%)
1	9.94	17.26	47.33	6.28	4.93	29.90
3	12.02	18.50	57.24	9.64	9.86	45.95
7	15.12	21.37	72.00	11.64	13.15	55.43
28	17.83	24.66	84.90	15.36	17.26	73.14
120	19.59	25.48	93.33	16.53	18.91	78.21
200	20.46	26.72	97.62	17.55	20.55	83.57

present, may not be the case as both tricalcium silicate and dicalcium silicate and even tetracalcium aluminoferrite may not exist in pure form, and that the presence of tricalcium aluminate and other minor compounds in the system may, to some extent, affect the hydration reaction.

The degree of hydration, calculated as ratio of chemically bound water to

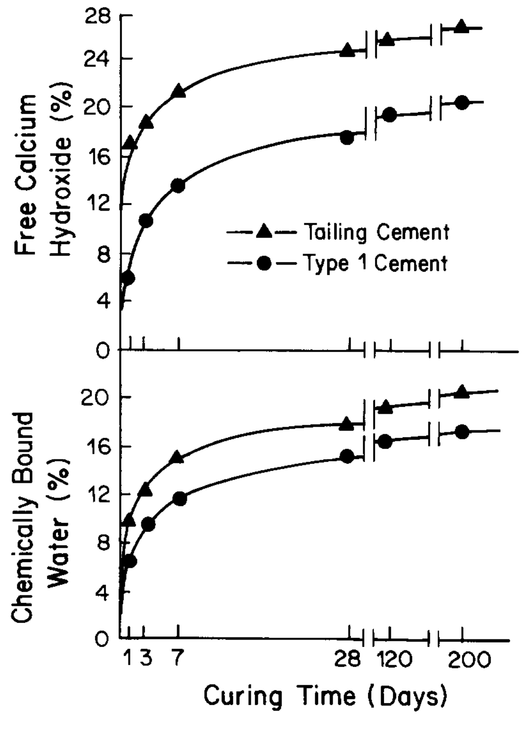

Fig. 3. Formation of chemically bound water and free calcium hydroxide with curing time for both the tailing and Type 1 cements.

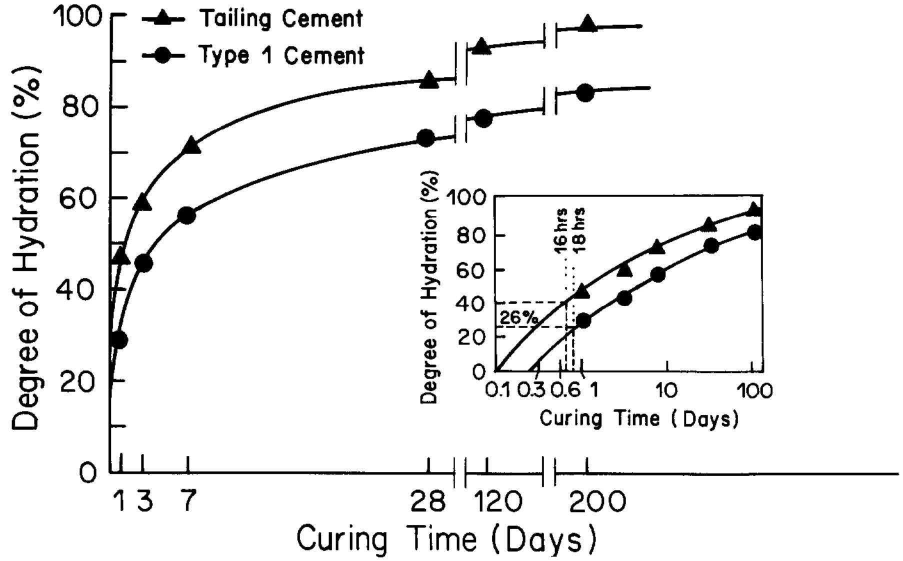

Fig. 4. Degree of hydration as a function of curing time. Inset showing the time for threshold values of degree of hydration for both the tailing and Type 1 cements.

the corresponding values at complete hydration [11] for both cements are given in Table 3. Bound water at complete hydration of tailing cement is estimated to be 21.00% by extrapolation and is taken as the reference value in calculating degrees of hydration. This value is in general agreement with the value of 21.74% calculated by Copeland et al. for a year-old cement cured at a water–cement ratio of 0.40 [4]. The degree of hydration as a function of time is shown in Fig. 4. Quantitatively, the tailing cement undergoes faster hydration showing a 75.33% degree of hydration in a week

TABLE 4

Data on compressive strength as a function of curing time for both the tailing and Type 1 cements

Curing time (days)	Compressive strength (psi)	
	Tailing cement	Type 1 cement (ASTM C150-83a minimum requirement)
1	1600	–
3	3250	1800
7	5100	2800
28	8150	4000
120	10350	–
200	10500	–

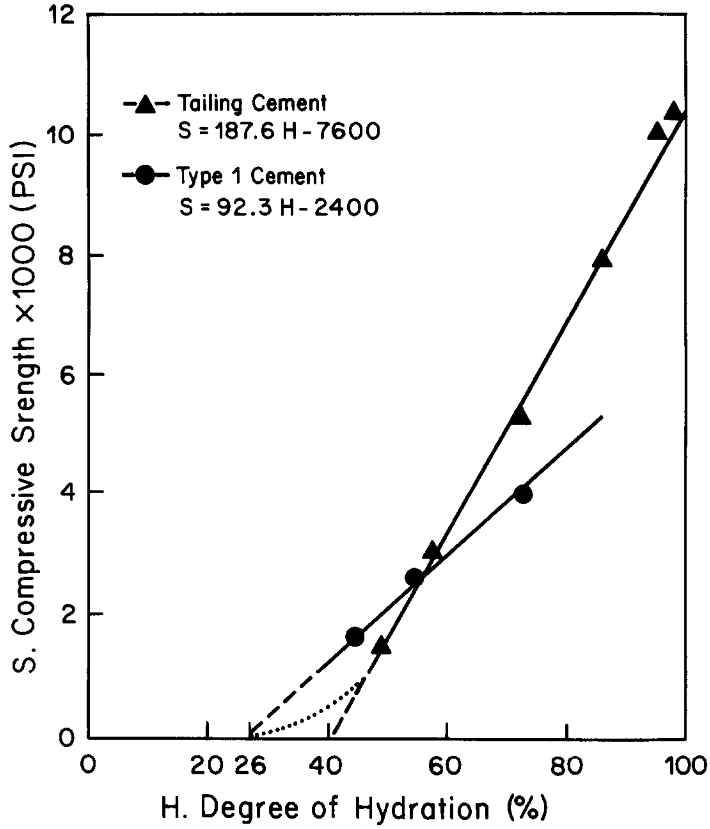

Fig. 5. Correlation between the compressive strength and degree of hydration for tailing and Type 1 cements.

which is 35.84% more than the recorded value of 54.43% for the Type 1 cement.

For both cements, the variation in the degrees of hydration and strength development shows parallel behavior and can be correlated as the straight line plots shown in Fig. 5. Strength data is given in Table 4. The correlation can also be expressed by the following equations

For tailing cement

$$S = 187.6H - 7600 \tag{5}$$

For the Type 1 cement

$$S = 92.3H - 2400 \tag{6}$$

where S = strength (psi) and H = degree of hydration (%).

The plots indicate that in hydrating tailing cement, significant strength does not develop until it gains up to a 40% degree of hydration, whereas in

Type 1 cement, strength starts developing at a 26% degree of hydration, though at a rate 2.03 times as slow. It may, however, be noted that the time to acquire these threshold values of degrees of hydration is nearly the same, i.e., 16 and 18 h for the tailing and Type 1 cements, respectively (see inset in Fig. 4 for the estimation of these values).

If the assumption is made that the tailing cement might be acquiring some strength at degrees of hydration below 40%, the lower portion of the plot in Fig. 5 may be modified to an extent shown by the dotted line. Verification of this point would, however, require further investigation.

Generally, hydration and strength do not develop immediately after cement is brought into contact with water. The system undergoes an initial rapid reaction controlled mainly by hydrolysis and dissolution of calcium ions leaching into the solution. This is followed by a relatively inactive phase known as the "dormant" period where a slow rise in calcium ion concentration [16] continues and the paste remains plastic for several hours [15]. By the end of the "dormant" period an acceleration period starts when both tricalcium silicate and dicalcium silicates react to initiate the hydration reaction forming calcium hydroxide crystallizing from the solution and the calcium silicate hydrate depositing into the available water-filled spaces [16]. This continues until the end of the accelerated period at which time the early hardening has begun [14]. The rate of reaction again slows down until reaching a steady state when hydration and strength progress simultaneously.

Complete hydration effectively means a 100% degree of hydration and would correspond to maximum attainable strength. Using eqns. (5) and (6), values of 11 160 and 6830 psi have been calculated as maximum strength values for the tailing and Type 1 cements, respectively.

CONCLUSIONS

As compared to ordinary Type 1 Portland cement, the tailing cement, because of its higher tricalcium silicate content, exhibits a better hydration behavior in terms of bound-water-free calcium hydroxide and degree of hydration.

Degree of hydration and the strength development in the hydrating cement pastes might be linearly correlated and can be expressed in simple mathematical relationships, which may differ for cements with different hydration behaviors.

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