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A thermal analysis study of recycled portland cement concrete (RPCC) aggregates

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Abstract

It is shown that thermal analysis and XRD data can identify the component of RPCCA which may be hydrated cement or slag (generally considered as an aggregate component). The other coarse aggregates present may be gravel or limestone. The fine aggregate often referred to as sand may be quartz or limestone in origin. The limestone may be dolomite and/or calcite in nature. The TG reveals the extent of the hydration product portlandite [$Ca(OH)_2$] in the sample, the amount of $CaCO_3$ present, and the amount of dolomite. XRD studies confirm the presence of these materials. In old concrete samples, the portlandite may be partially carbonated. TG data in CO_2 allows the presence of dolomite to be identified. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Portlandite; Recycled portland cement concrete; Tufa formation

1. Introduction

Recycled portland cement concrete (RPCC) is used in pavement base layers. It is subject to leaching by water to produce calcium ions in solution [1,2]. In the presence of acidic rain (considered here to be carbon dioxide dissolved in water), the leaching of calcium ions can be relatively high. On drainage to an air–water interface, the calcium ions may be subsequently precipitated in the form of calcium carbonate called tufa. If the normal drainage systems are present there is a real danger of the drainage system being blocked by the formation of these tufa deposits. Obviously, if the base layers were of gravel, crushed stone or other non-calcite material there is no danger of tufa formation. The tufa or calcite precipitation also occurs in nature from limestone. The evidence is that tufa formation occurs from calcite based compounds in RPCC such as free lime (CaO) around 2–3%, or portlandite [$Ca(OH)_2$]. However, the $Ca(OH)_2$ can be carbonated by action of CO_2 to $CaCO_3$ and in old concrete and mortars a considerable amount of carbonation has been shown to occur. In concrete, the Ca^{2+} in the leachate may be traced as well to limestone used as fine or coarse aggregate.

Dolomite [$CaMg(C0_3)_2$] also used as fine or coarse aggregate is a further source of Ca^{2+} on leaching but Mg^{2+} would also appear in the leachate. The presence of acid water will cause the formation of $CaHCO_3$ which is undoubtedly the primary source of leachate supersaturated with Ca^{2+}.

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1.1. The chemical process of cement hydration in concrete

The cement clinker produced at the cement works is mixed with small amounts of gypsum ($CaSO_4{\cdot}2H_2O$), ground, and then with an aggregate added, is hydrated in the presence of water to form concrete. The aggregate may be quartz, limestone, dolomite, or slag. Some of these may react with the water by leaching out Ca^{2+} and/or Mg^{2+}, some may chemically react with water in a hydration process. The cement over the period of time will hydrate with water. The cement chemists have a special shorthand notation used in the present article. In this C=CaO; S=SiO_2; A=Al_2O_3; F=Fe_2O_3; H=H_2O; and S′=SO_3. The four main components of the Portland cement clinker are tricalcium silicate; C_3S, dicalcium silicate; β-C_2S, tricalcium aluminate; C_3A, and a ferrite solid solution of composition between C_2F and C_6A_2F often represented as C_4AF. An approximate representation of the hydration process for C_3S and C_2S is

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH \quad (1)$$

$$2C_2S + 4H \rightarrow C_3S_2H_3 + CH \quad (2)$$

The $C_3S_2H_3$ is often represented as C-S-H indicating its amorphous nature and variable composition. The hydration products of the other cement components — the calcium aluminosilicates are not generally described as producing CH.

Thermodynamic data indicates that the solubility of silicate compounds is much lower than these of carbonates and hydroxides. Thus CH may be the more likely Ca^{2+} donor then the C-S-H or the hydrated calcium aluminosilicates [1].

1.2. Solution chemistry of calcium ion dissolution

Rainwater generally contains dissolved CO_2.

$$CO_2\ (g) \rightarrow CO_2\ (aq) \quad (3)$$

The carbon dioxide dissolved in water can give rise to carbonic acid

$$CO_2\ (aq) + H_2O\ (l) \rightarrow H_2CO_3\ (aq) \quad (4)$$

The carbonic acid reacts with $CaCO_3$ to give calcium bicarbonate

$$CaCO_3\ (s) + H_2CO_3\ (aq) \rightarrow Ca^{2+}\ (aq) + 2HCO_3^-\ (aq) + H_2O\ (l) \quad (5)$$

The solubility of the calcium ions in the above environment is greatly increased. When the pH of the above leachate reverts back to neutral or beyond then the solution is supersaturated with respect to calcium ions and they are precipitated as $CaCO_3$ generally through nucleation from a suitable surface. This change of pH is liable to occur when the leachate reaches the ceramic or concrete structures of the drainage ‘pots’ at the side of the road. Such drainage systems provide a surface with suitable nucleation sites for the growth of adhering layers of tufa. In the present project RPCC materials from various localities are examined by thermal analysis [2–4].

2. Materials and methods

2.1. Materials

The runs were carried out on RPCC samples from many locations in Ohio. The samples reported here were choosen to cover various types of RPCC. They are listed in Table 1. For the thermal analysis experiments, the sample size used was between 25 and 30 mg. The samples were ground to a fine powder, passing sieve #200 for thermal analysis and XRD tests, and passing sieve #200 and retaining on sieve #230, then dried in the oven at 80°C for 1 h, and cooled in the dessicator for the ethylene glycol test [5].

2.2. Methods

The thermal analysis was carried out using a simultaneous TG/DTA unit, model SDT 2960 from TA Instruments. The samples were also examined using X-ray powder diffraction data obtained from a Scintag XRD2000 powder diffractometer operating at (the Cu Kα wavelength of 1.5406 Å) 45 kV and 40 mA. Leaching experiments were also carried out in the rubbelized RPCC in which the aggregates were suspended in an equal volume of water and carbon dioxide was bubbled through the bed for 24 h. The amount of calcium and magnesium ions in the solution leached from this unit were determined using a Perkin Elmer Plasma II Emission Spectrometer. Free calcium oxide present in the recycled portland cement concrete aggregate (RPCCA) was measured using the ethylene glycol test.

Table 1
The RPCCA used in the present project

Sample ID	Pavement date	Mix design				
		Coarse aggregate			Fine aggregate	Cement
		Gravel	Lime	Slag		
1	October 66	#3 Gravel aggregate	–	–	Queen City Gravel	Miami
2	May 66	#3 Gravel aggregate	–	–	Ohio Fine aggregate	Kosmos
3	July 64	#3 Gravel aggregate	–	–	Ohio Fine aggregate	Dundee
4	October 63	–	#3 Limestone	–	Ohio Gravel	Miami
5	June 64	–	#3 Limestone	–	Ohio Gravel	Miami universal
6	September 64	–	–	#3 Cleveland slag	Fine Sand & Gravel	Columbia
7	July 65	–	–	#3 Cleveland slag	Fine Sand & Gravel	Columbia
8	October 66	–	–	#57 Cleveland Slag	Fine Sand & Gravel	Bessemer
9	November/ December 67	–	–	#57 Cleveland Slag	Fine Sand & Gravel	Huron & Dundee

3. Results and discussion

Figs. 1–9 show the thermogravimetric and differential thermogravimetric analysis plots (TGA and DTG) for the nine samples listed in Table 1. The experiments were carried out in a flowing atmosphere of carbon dioxide (flow rate 100 ml min^{-1}) at a heating rate of 10°C min^{-1}.

In carbon dioxide, the first event on the TG will be the dehydroxylation of any portlandite present.

$$Ca(OH)_2\ (s) \rightarrow CaO\ (s) + H_2O\ (g) \qquad (6)$$

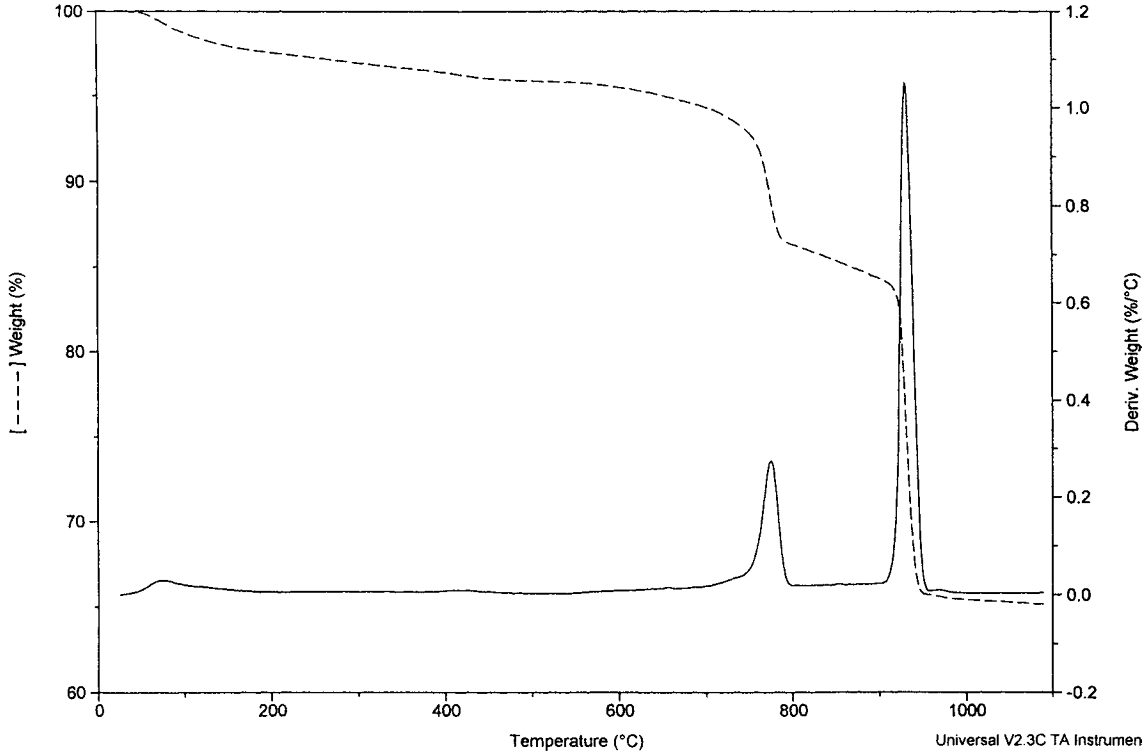

Fig. 1. TG and DTG for RPCCA sample #1 carried out in a flowing atmosphere of CO_2 (100 ml min^{-1}) at a heating rate of 10°C min^{-1}.

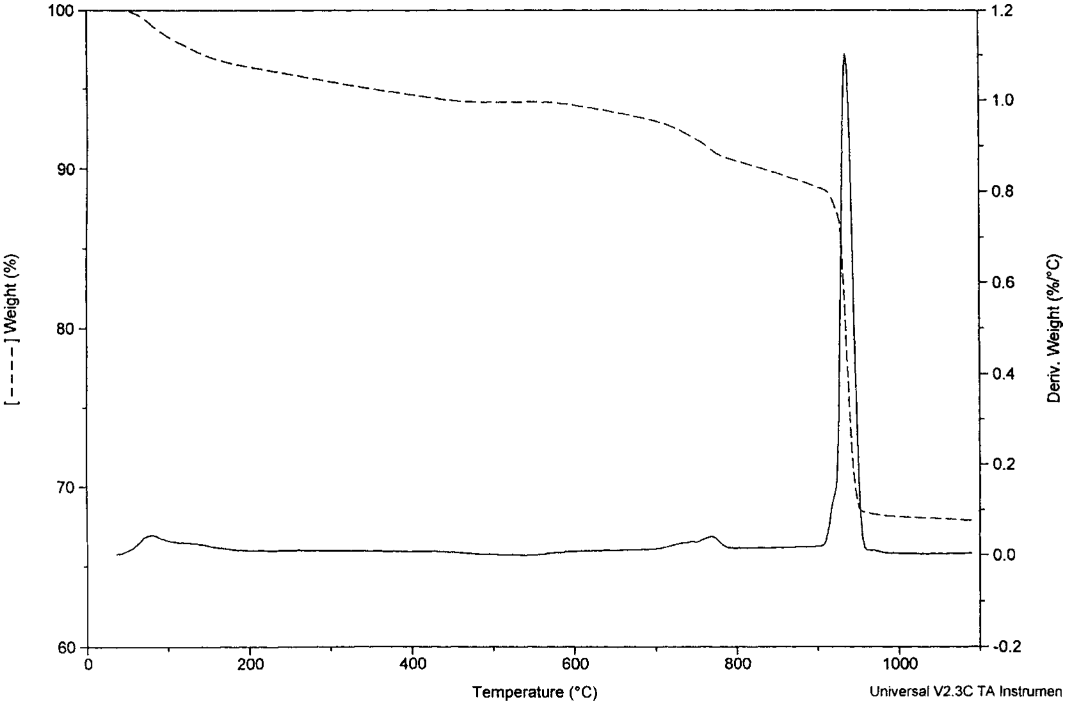

Fig. 2. TG and DTG for RPCCA sample #2 carried out in a flowing atmosphere of CO_2 (100 ml min^{-1}) at a heating rate of 10°C min^{-1}.

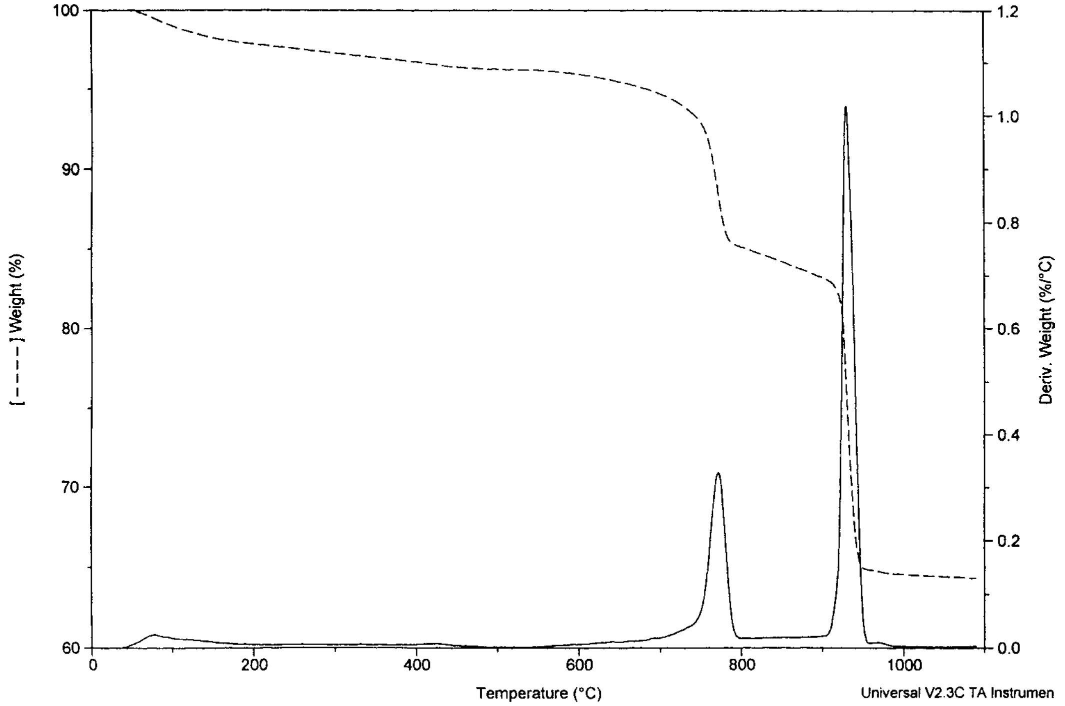

Fig. 3. TG and DTG for RPCCA sample #3 carried out in a flowing atmosphere of CO_2 (100 ml min^{-1}) at a heating rate of 10°C min^{-1}.

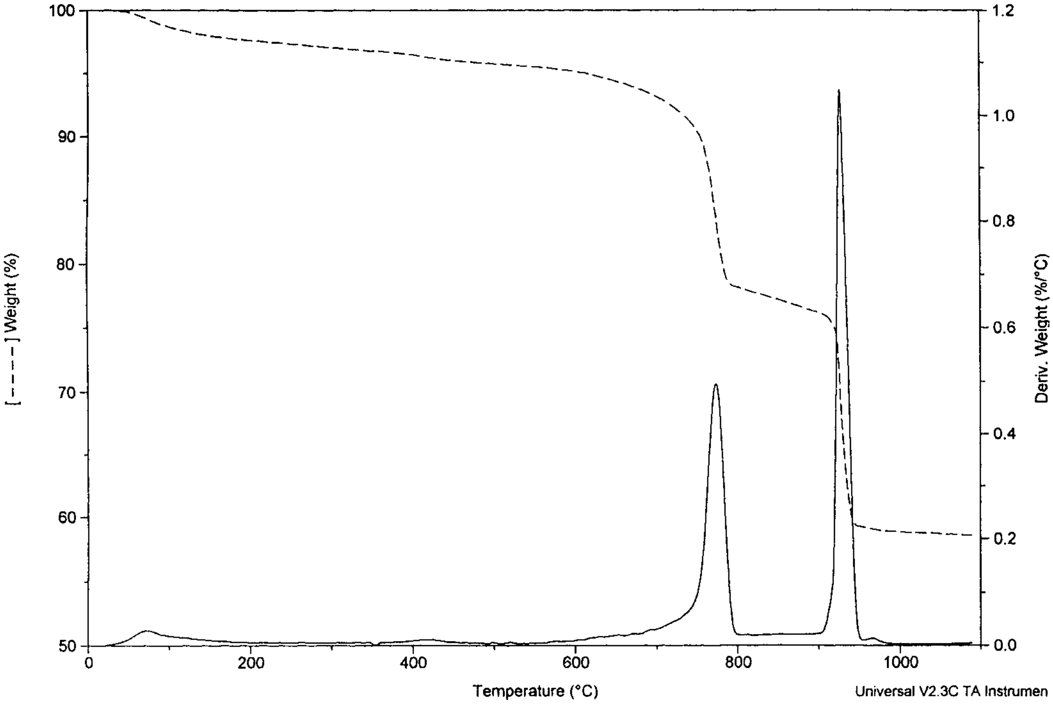

Fig. 4. TG and DTG for RPCCA sample #4 carried out in a flowing atmosphere of CO_2 (100 ml min^{-1}) at a heating rate of 10°C min^{-1}.

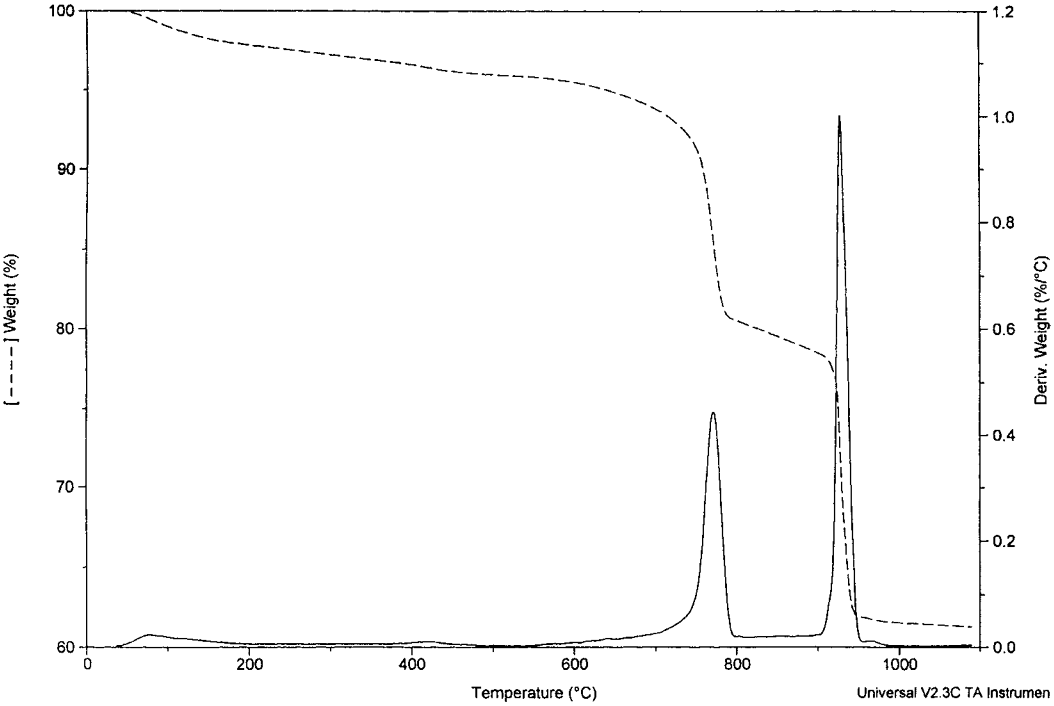

Fig. 5. TG and DTG for RPCCA sample #5 carried out in a flowing atmosphere of CO_2 (100 ml min^{-1}) at a heating rate of 10°C min^{-1}.

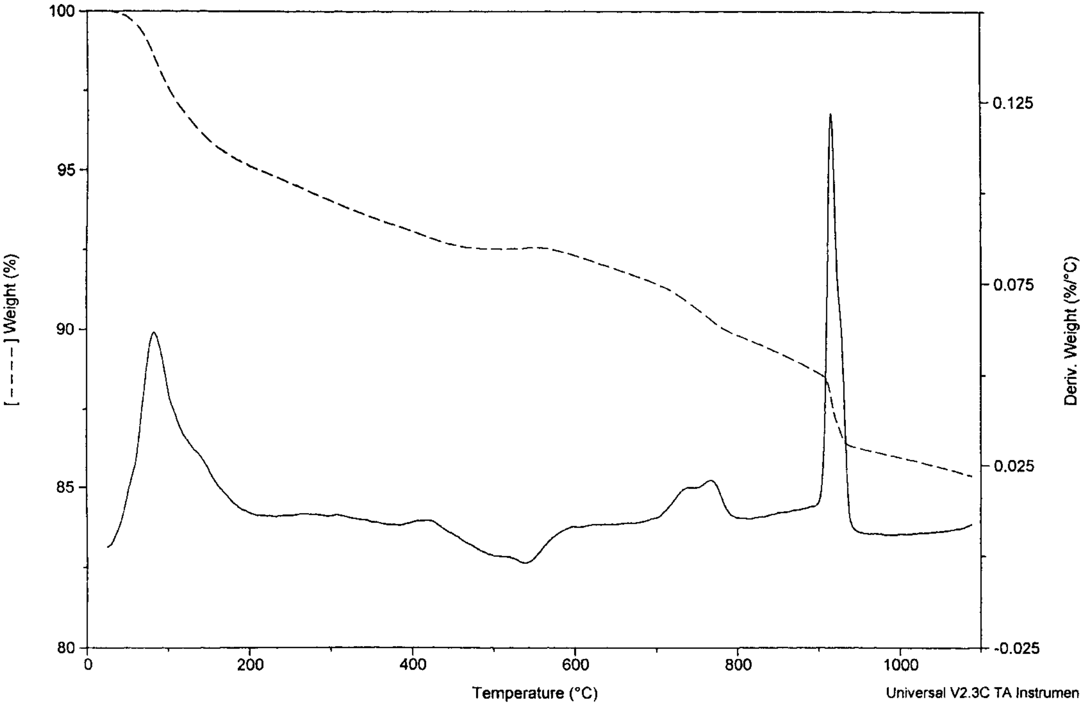

Fig. 6. TG and DTG for RPCCA sample #6 carried out in a flowing atmosphere of CO_2 (100 ml min^{-1}) at a heating rate of 10°C min^{-1}.

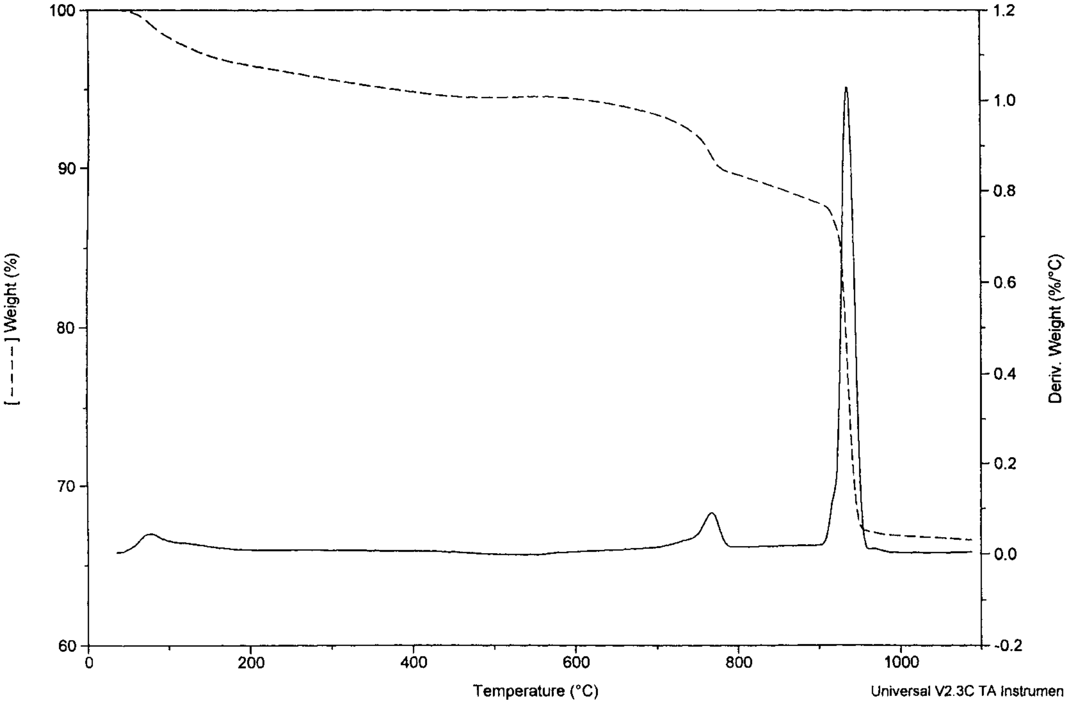

Fig. 7. TG and DTG for RPCCA sample #7 carried out in a flowing atmosphere of CO_2 (100 ml min^{-1}) at a heating rate of 10°C min^{-1}.

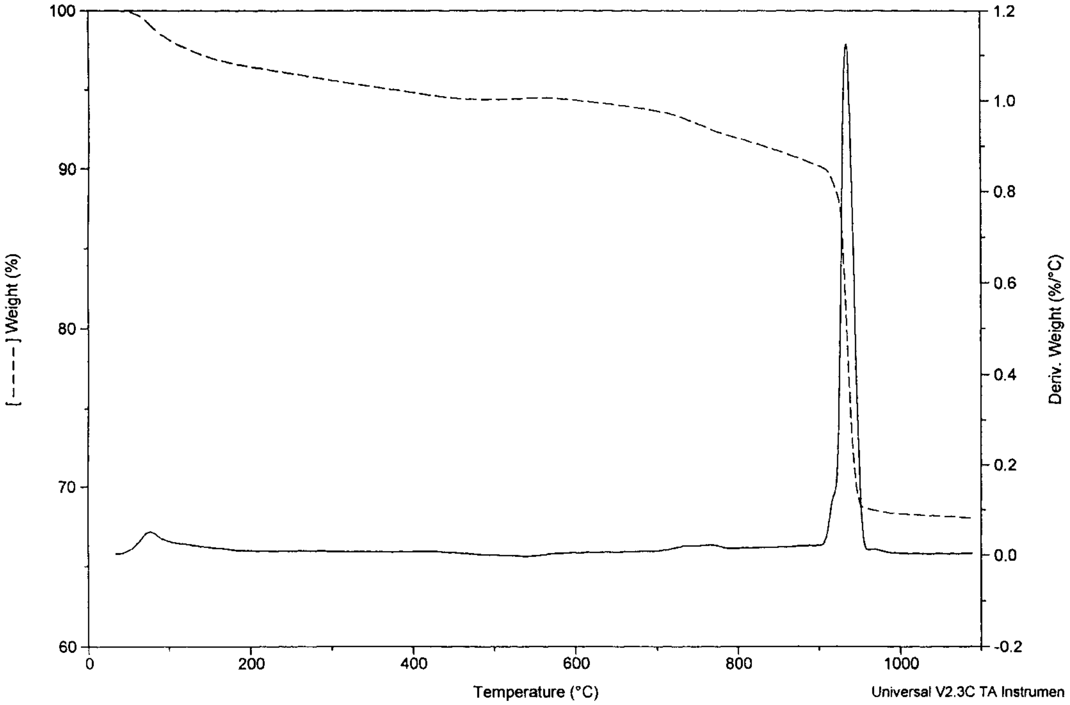

Fig. 8. TG and DTG for RPCCA sample #8 carried out in a flowing atmosphere of CO_2 (100 ml min^{-1}) at a heating rate of 10°C min^{-1}.

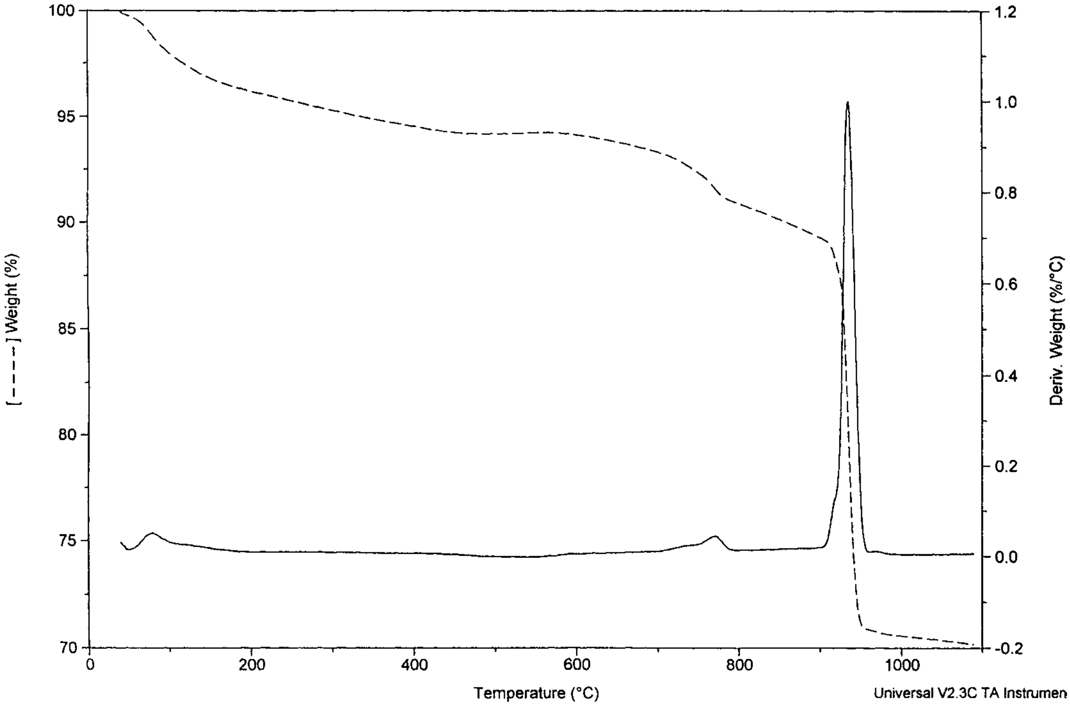

Fig. 9. TG and DTG for RPCCA sample #9 carried out in a flowing atmosphere of CO_2 (100 ml min^{-1}) at a heating rate of 10°C min^{-1}.

In practice, the sample will have lost water around 100–150°C, and will show a continuous loss from 150–400°C at a slow rate when around 400°C the portlandite dehydroxylation can be observed. This is usually a small amount particularly in old concrete and cement samples as the portlandite initially formed will largely undergo carbonation over many years [6].

$$Ca(OH)_2\ (s) + CO_2\ (g) \rightarrow CaCO_3\ (s) + H_2O\ (l) \quad (7)$$

The purpose of carrying out the TG in CO_2 is because it separates out the dolomite dissociation into two steps. Dolomite [$CaMg(CO_3)_2$] in N_2 decomposes in a single step [7].

$$CaMg(CO_3)_2\ (s) \rightarrow CaO\ (s) + MgO\ (s) + 2CO_2\ (g) \quad (8)$$

However, in CO_2 at atmospheric pressure the dissociation takes place in two stages.

$$CaMg(CO_3)_2\ (s) \rightarrow MgO\ (s) + CaCO_3\ (s) + CO_2\ (g) \quad (9)$$

The second stage at a higher temperature is the dissociation of the $CaCO_3$. The first step in the dissociation takes place around 780°C and enables the dolomite present to be estimated. The dissociation of $CaCO_3$ takes place around 910°C.

$$CaCO_3\ (s) \rightarrow CaO\ (s) + CO_2\ (g) \quad (10)$$

The dissociation of portlandite (Eq. (6)) allows the calculation of the amount of $Ca(OH)_2$ present. If the CaO is produced with a very small particle size then recarbonation with a small increase in mass can be observed. The dissociation of the dolomite at 780°C allows the composition of the dolomite present to be calculated. Dolomite present must come from either the coarse or fine aggregate (see Table 1). The final loss in weight at 910°C is due to $CaCO_3$ dissociation (see Eq. (10)). However, some of this comes from the presence of dolomite and this can be subtracted from the total present. The remaining $CaCO_3$ comes from two sources — the carbonation of the portlandite over a 30-year period and calcite present as an aggregate in the RPCCA. Data on the %portlandite, the %dolomite, and %calcite present in the samples is shown in Table 2. The % free CaO is also shown in Table 2. A typical XRD pattern showing the presence of dolomite, calcite, and quartz is shown in Fig. 10 for sample #3. The quartz can also be indicated on the DTA runs performed on the simultaneous TG-DTA unit. Data based on the XRD is also shown in Table 2.

The ethylene glycol test [5] showed only trace quantities of free CaO. This is not surprising as the RPCCA samples are over 30-years old (Table 1) and any free CaO would have weathered by either hydration or carbonation

$$CaO\ (s) + H_2O\ (l) \rightarrow Ca(OH)_2\ (s) \quad (11)$$

$$CaO\ (s) + CO_2\ (g) \rightarrow CaCO_3\ (s) \quad (12)$$

Likewise, the TG data on portlandite was lower than might be expected, being in the range from 2.0–3.9%. Values of 10–20% might have been expected for uncarbonated cement paste [6]. The value would be

Table 2
Data on various RPCC samples[a]

Sample ID	% Free CaO	% Portlandite	% Dolomite	% $CaCO_3$	XRD results (assessment of quantity)
1	0.20	2.84	40.69	20.84	D>CC>Q
2	0.35	2.42	15.58	43.19	CC>Q>D
3	0.01	2.71	47.16	21.62	D>CC>Q
4	–	3.86	75.16	3.58	D≫CC>Q
5	–	3.41	65.63	7.97	D≫CC>Q
6	–	3.00	11.67	2.02	Q>D, no CC
7	–	2.01	20.41	41.72	CC>Q>D
8	–	2.84	13.35	47.80	CC>Q>D
9	–	2.71	13.86	39.72	CC>Q>D

[a] Free GaO determined by ethylene glycol test [5]; % Portlandite, dolomite, and $CaCO_3$ determined from TG/DTG experiment; D: Dolomite; CC: $CaCO_3$; Q: Quartz.

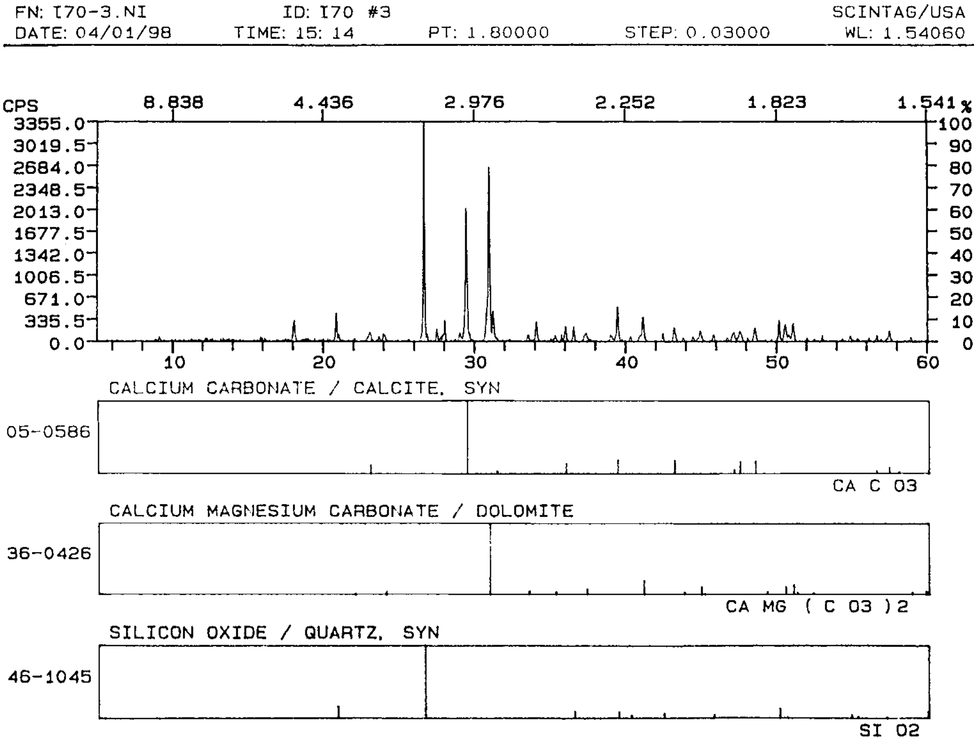

Fig. 10. XRD data for sample #3 showing presence of Quartz, Dolomite, and Calcite.

less for RPCCA because of the addition of fine and coarse aggregates and carbonization of the portlandite over 30-years (see Eq. (7)).

It is possible to make a rough calculation of the amount of cement paste available in the concrete. This calculation is based on the observation that sample #4 contains only carbonate aggregate leaving 21.42% that must be the amount of cement paste. If, therefore, the values for portlandite are multiplied by factor of 21.42/3.86(=5.55) for all the samples we have a measure of the amount of cement paste that went into the production of the concrete. An examination of the results shown in Table 3 and assuming that the '% other materials' are mainly quartz shows that the results of XRD data is in agreement with the TG results.

A further point can be made based on the observation of Dubberke and Marks [3] that the slope of the line before the first transition can be related to service life. They quote percent weight loss prior to the transitions. No relationship can be found from the present results but there is a loss of weight between 150 and 400°C varying from 1.5 to 3.0% according to the samples.

In the leachate experiments, the presence of acidic water (CO_2 in H_2O) dissolved out supersaturated quantities of Ca^{2+} (600 ppm or greater) and Mg^{2+}

Table 3
Approximate evaluation of RPCC samples composition

Sample ID	% Cement paste	% Carbonates	% Other materials[a]
1	15.76	61.53	22.71
2	13.43	58.77	27.80
3	15.04	68.78	16.18
4	21.42	78.58	0.00
5	18.93	73.60	7.47
6	16.65	13.69	69.66
7	11.16	62.13	26.71
8	15.76	61.15	23.09
9	15.04	53.58	31.38

[a] % Other materials is assumed to be mainly quartz.

(85 ppm or greater) ions at a pH of around 6.4 but upon exposure to air and loss of dissolved CO_2 the tufa was reprecipitated between the aggregates, the pH rose to between 9.0–11.5 and Ca^{2+} concentration dropped to around 20 ppm while the Mg^{2+} concentration dropped to around 10 ppm. Such experiments were difficult to control.

4. Conclusion

It is seen that TG-DTG data allows the composition of RPCCA to be established in terms of %portlandite, %dolomite, and %calcite. The origins of these materials can be established. Some reasonable assumptions allow an estimate to be made of quartz content. The consensus of opinion from various references is that "RPCCA base layers containing a higher percentage of fine material have a larger amount of surface area with which to react and therefore, result in an increase in calcite precipitate formation" [1]. The calcium content from the carbonate residues used as aggregate would seem to be another factor in calcite deposition from the leachate. The small quantity of portlandite present would not seem to make this material a significant factor in calcite precipitation.

Acknowledgements

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