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# An examination of recycled Portland cement concrete rich in dolomite and low in calcite obtained from various locations in Ohio

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## Abstract

Thermal analysis is used to investigate 30 year old samples of concrete. In this study, thermal analysis data is combined with XRD data. The contents of these concrete samples are identified in terms of portlandite, calcite, dolomite, gypsum, and quartz. However, the calcium carbonate comes from the carbonation of the portlandite, from the fine and coarse aggregate used in the preparation of the concrete, and also from the second stage of the thermal decomposition of the dolomite. In the present study, samples of recycled Portland cement concrete are investigated which were low in calcite but high in dolomite content. The original presence of slag in these samples influences the long term leaching potential of the concrete. Leaching experiments reveal the presence of both calcium and magnesium ions in the leachate. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Samples of recycled Portland cement concrete (RPCC) aggregates utilized in pavement construction which were low in calcite but high in dolomite were examined. These samples were over 30 years old and formed part of a project on leaching organized by the Ohio Department of Transportation (ODOT). The RPCC has been subjected to leaching particularly from acid rain over years of existence. Here acid rain may be considered to be carbon dioxide dissolved in water. The carbonic acid increases the leaching of the calcium and magnesium ions from the solid matrix. The situation is reversed when the leachate reaches an air–water interface when the carbon dioxide is lost to the atmosphere, the pH change occurs and the solubility of calcium ions are drastically reduced. This causes precipitation of Tufa — a form of calcium carbonate. The leaching occurs from the calcium based components of RPCC such as free lime [CaO], portlandite [$Ca(OH)_2$], dolomite [$CaMg(CO_3)_2$], and calcite [$CaCO_3$]. The latter in the case of the samples studied here were very low. The first step in the decomposition of the dolomite would result in the formation of some of the this calcite

$$CaMg(CO_3)_2\,(s) \rightarrow MgO\,(s) + CO_2\,(g) + CaCO_3\,(s) \quad (1)$$

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The free lime would originally be present in the slag components of RPCC but the suppliers usually spray the slag with water for a considerable period to reduce the free CaO content. Over the years, the action of water will be to hydrate the free CaO. The reaction is simply

$$CaO\,(s) + H_2O\,(1) \rightarrow Ca(OH)_2\,(s) \tag{2}$$

but some will be carbonated to calcite

$$CaO\,(s) + CO_2\,(g) \rightarrow CaCO_3\,(s) \tag{3}$$

and

$$Ca(OH)_2\,(s) + CO_2\,(g) \rightarrow CaCO_3\,(s) + H_2O\,(l) \tag{4}$$

The net result is that over the 30 years of exposure the already low free CaO content will have been so diminished to make its contribution very little towards the leaching process. In hydrated cement there is a considerable amount of hydrated calcium silicate present. In the parlance of the cement chemists symbolism the portlandite is formed by the hydration of calcium silicate present in cement [1]

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH \tag{5}$$

and

$$2C_2S + 4H \rightarrow C_3S_2H_3 + CH \tag{6}$$

However, the above representation is approximate and the product is often referred to C–S–H indicating its amorphous nature and variable composition [1]. These silicate compounds have a much lower solubility than those of calcium hydroxide or calcium carbonate and can be considered as making a negligible contribution to the leaching of calcium ions into solution.

### 1.1. Chemistry of calcium and magnesium ions dissolution

Rain water containing dissolved carbon dioxide will precipitate calcite via the reactions:

$$CO_2\,(g) \rightarrow CO_2\,(aq) \tag{7}$$

$$CO_2\,(aq) + H_2O \rightarrow H_2CO_3\,(aq) \tag{8}$$

$$H_2CO_3\,(aq) + Ca^{2+}\,(aq) + 2OH^-\,(aq) \rightarrow 2H_2O\,(l) + CaCO_3\,(s)$$

From Eq. (8),

$$K_{CO_2} = \frac{[H_2CO_3]}{p_{CO_2}[H_2O]}, \qquad pK_{CO_2} = -\log K_{CO_2} \tag{10}$$

Drever [2] noted that at 25°C, the partial pressure of $CO_2$ is $10^{-3.5}$ and $pK_{CO_2} = 1.47$ when

$$[H_2CO_3] = K_{CO_2}p_{CO_2} \approx 10^{-5.0} \tag{11}$$

Experimental observation [3] is that in the pore water of the sub-base containing RPCC, pH values of 11–12 can be realized accompanied by increased dissolution of calcium ions. If only $Ca(OH_2)$ is considered in pure water, then

$$K_{\mathrm{sol\,Ca(OH)_2}} = [Ca^{2+}][OH^-]^2 = 7.9 \times 10^{-6}$$

Bruinsma et al. [4] then showed that in an RPCC base-layer water closed to the atmosphere by overlying pavement structures pH values of 11–12 could be realized with high concentrations of carbonate species which would agree with experimental observation. They also showed that when such solutions reached the atmosphere the pH would drop to around a pH of 8 leading to Tufa precipitation. Their model is however based on the supposition that the origin of the calcium ions in solution would be portlandite but the possibility exists that the calcium ions could originate as well from dolomite and calcite leaching process. Taylor [5] points out that in the presence of carbon dioxide, calcium carbonate comes into equilibrium with the carbonic acid to produce the bicarbonate ions

$$CaCO_3\,(s) + H_2CO_3\,(aq) \rightarrow Ca(HCO_3)_2\,(aq) \tag{12}$$

when as much as 2.29 g of calcium carbonate will dissolve in 1 l of water. Dolomite will also dissolve in acidic conditions but the leaching is accompanied by the production of both $Ca^{2+}$ and $Mg^{2+}$ ions. It would appear unrealistic to ascribe the dissolution of $Ca^{2+}$ ions into solution as, due to portlandite alone particularly as in these aged aggregates, the amount of portlandite is very low (see Section 2). The present study comprises a group of RPCC samples investigated which were low in calcite content and rich in dolomite. The TG–DTA results are reported, together with XRD studies and dissolution data.

## 2. Experimental

### 2.1. Materials

The runs were carried out on RPCC samples that were low in calcite and rich in dolomite content. They came from many locations in Ohio. They are listed in Table 1. In their use for thermal analysis, the sample size used was between 25 and 30 mg. The samples were prepared as a fine powder by grinding and passing through (US standard) sieve #200. Samples used for the XRD, were passed through sieve #200 but retained on sieve #230. Samples prepared in this manner were dried in the oven at 80°C for 1 h. They were stored in a desiccator for use in the ethylene glycol test [6] that was adopted to detect free lime (CaO).

### 2.2. Methods

The samples were investigated using a simultaneous TG–DTA unit, model 2960, from TA Instruments. Samples were subjected to a carbon dioxide purge gas at a flow rate of 100 ml $\mathrm{min}^{-1}$. The temperature range investigated was from 35 to 1100°C at a heating rate of 10°C $\mathrm{min}^{-1}$. The samples were also examined to obtain X-ray powder diffraction data by the use of a Scintag XRD 2000 powder diffraction unit operating at 45 kV and 40 mA current at a Cu K$\alpha$ wavelength of 1.5406 Å. Leaching experiments were also carried out on the rubbelized RPCC where the aggregates were suspended in an equal volume of water and carbon dioxide was bubbled through the bed for 24 h. The leachate was examined using an Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP–AES), Perkin Elmer Plasma II Emission Spectrometer to determine the quantity of calcium and magnesium ions which have been leached into solution. The free calcium oxide present in the aggregates was determined using the ethylene glycol test.

## 3. Results and discussion

Figs. 1–6 show thermogravimetric (TG) and differential thermal analysis (DTA) plots selected from the thermal analysis experiments on the samples listed in Table 1. The first event was loss of adsorbed water in the region 100–150°C and there is a continuous loss of water as a background in the region from 150 to 400°C. This is due to loss from the hydrated calcium

Table 1
The RPCC samples low in calcite but high in dolomite content used in the project

| Sample ID | Mix design/Sources | | | | |
|---|---|---|---|---|---|
| | Coarse aggregate | | | Fine aggregate | Cement |
| | Gravel | Lime | Slag | | |
| 1 | #3 Gr. Am Aggregate | | | Am Aggregate | Universal |
| 2 | #3 Gr. Am Aggregate | | | Am Aggregate | Huron |
| 3 | #3 & 4 Gr. Am Aggregate | | | Feuton Const Co Fine | Universal & Miami |
| 4 | #3 Gr. Am Aggregate | | | Feuton Const Co Fine | Alternate Universal/Miami |
| 5 | #3 Gr. Am Aggregate | | | Feuton Const Co Fine | Universal |
| 6 | | | #57 Slag | Fine Sand & Gravel | Unknown |
| 7 | | #3 Limestone | | Ohio Gravel | Miami |
| 8 | | #3 Limestone | | Ohio Gravel | Miami & Universal |
| 9 | #3 Gr. Ohio Aggregate | | | Ohio Fine Aggregate | Peninsular |
| 10 | | #3 Limestone | | Fine Sand & Gravel | Universal, Medusa, Huron |
| 11 | | #3 Limestone | | Fine Sand & Gravel | Medina |
| 12 | | #3 Limestone | | Fine Sand & Gravel | Miami |
| 13 | | | #3 Slag Aggregate | Fine Sand & Gravel Aggregate | Standard |
| 14 | | | #4 & 6 Slag and US Steel | Fine Sand & Gravel | Medusa |
| 15 | | | #3 Slag Cleveland | Natural Sand & Gravel | Standard |

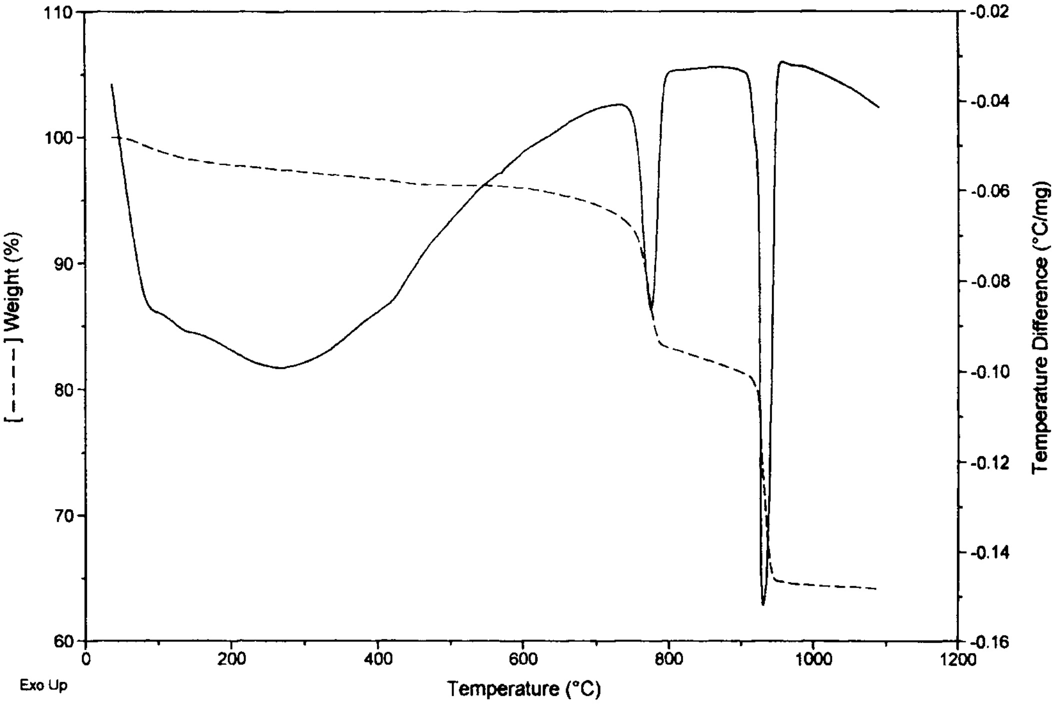

Fig. 1. The TG–DTA curves for RPCC aggregate in the flowing atmosphere of $CO_2$ for sample #1.

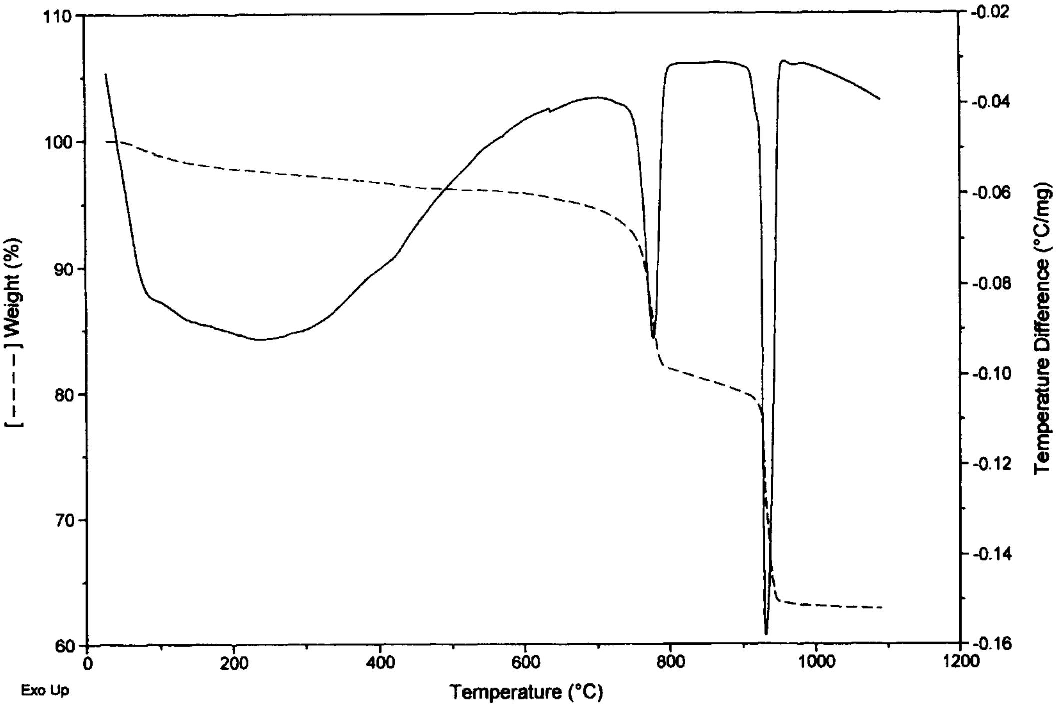

Fig. 2. The TG–DTA curves for RPCC aggregate in the flowing atmosphere of $CO_2$ for sample #3.

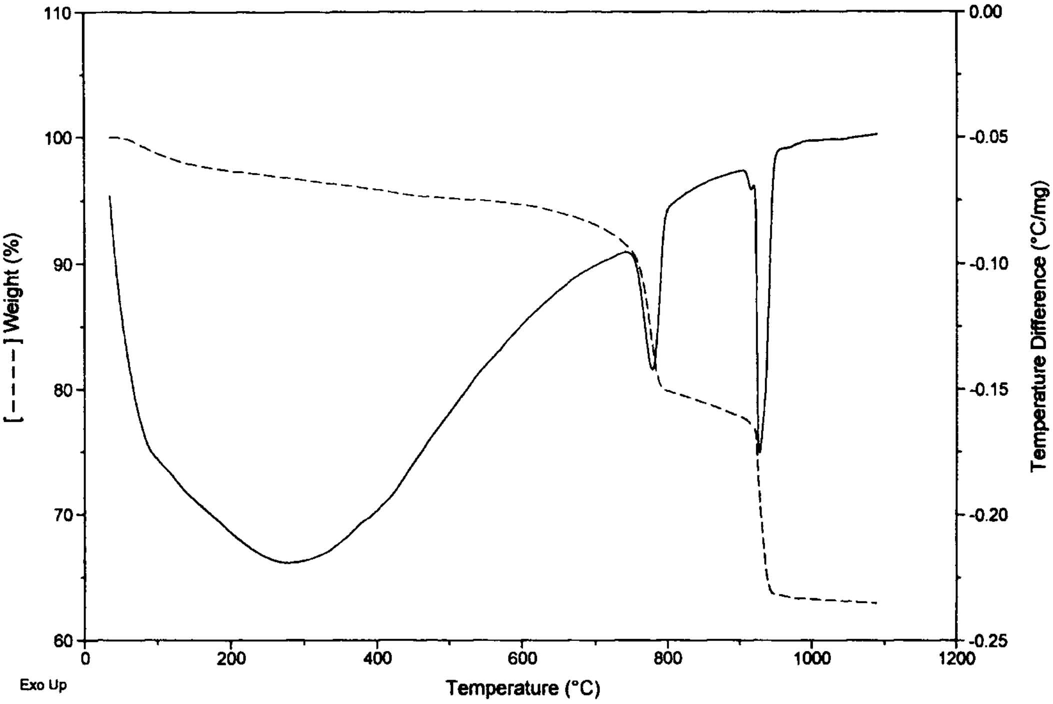

Fig. 3. The TG–DTA curves for RPCC aggregate in the flowing atmosphere of $CO_2$ for sample #6.

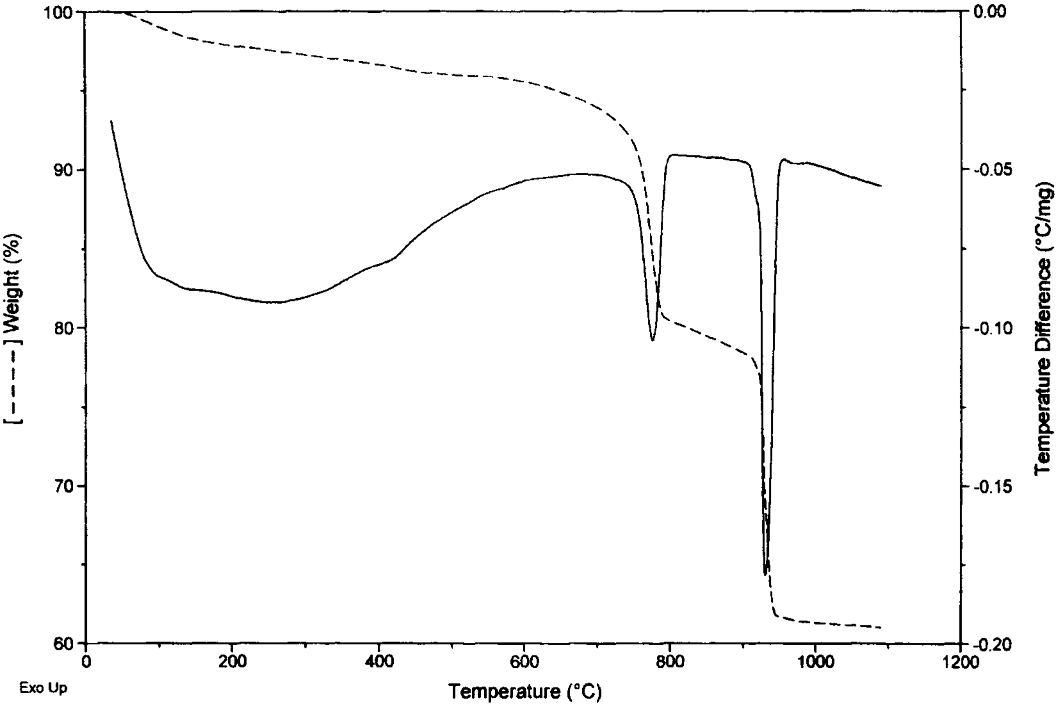

Fig. 4. The TG–DTA curves for RPCC aggregate in the flowing atmosphere of $CO_2$ for sample #9.

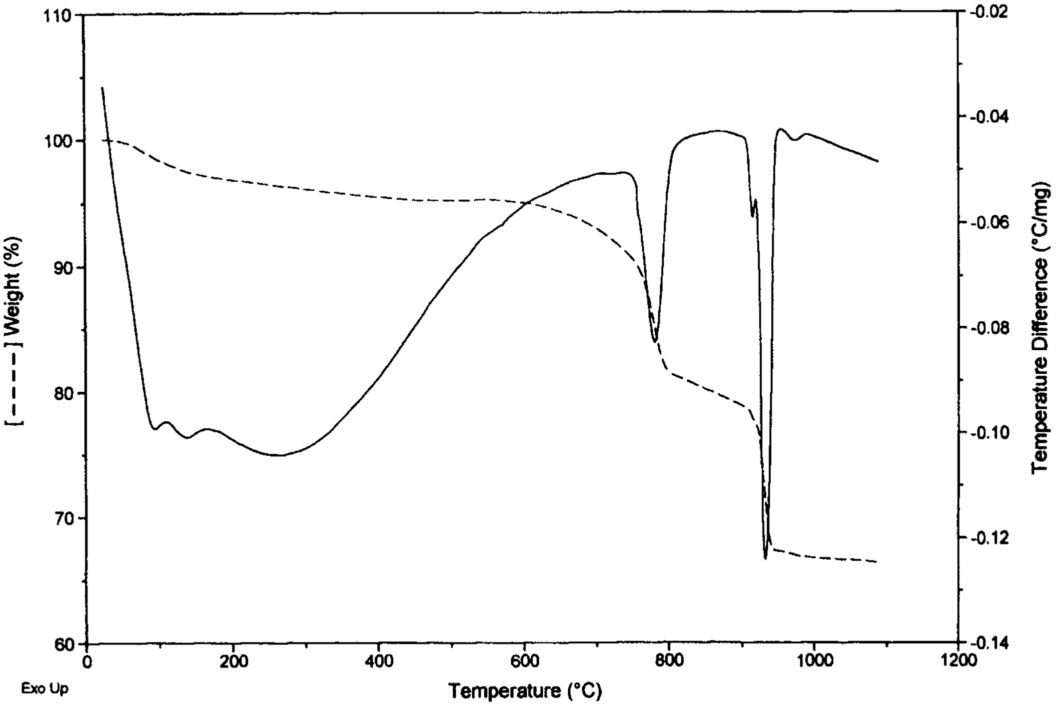

Fig. 5. The TG–DTA curves for RPCC aggregate in the flowing atmosphere of $CO_2$ for sample #13.

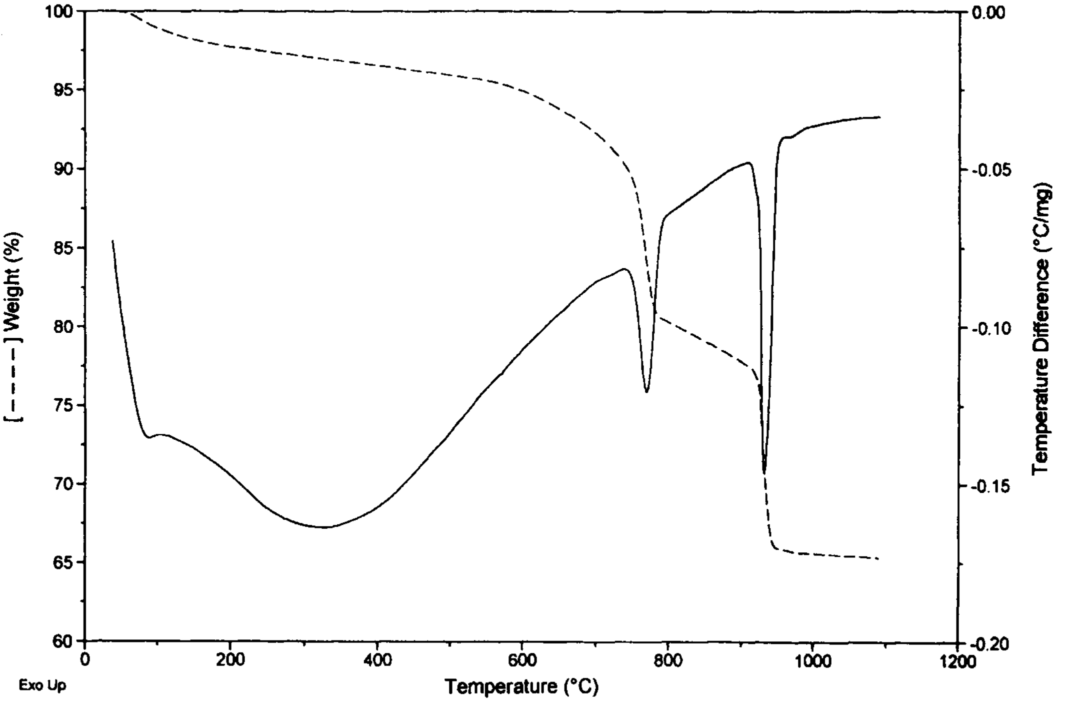

Fig. 6. The TG–DTA curves for RPCC aggregate in the flowing atmosphere of $CO_2$ for sample #14.

silicates present in the concrete. In the region around 400°C, portlandite dissociation takes place

$$\mathrm{Ca(OH)_2\,(s) \rightarrow CaO(s) + H_2O\,(g)} \qquad (13)$$

and as explained in the earlier paper [7] this can be used as the basis for estimating the % portlandite present. The TG was carried out in carbon dioxide because the dolomite present decomposes in two stages [8]. The first stage (see Eq. (1)) occurs at 780°C and can be seen on the TG plot. On the assumption that this step is due to dolomite, the amount of dolomite present can be calculated.

At around 910°C any calcite present will decompose

$$\mathrm{CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)} \qquad (14)$$

This step can also be seen in the TG plot. The total amount of calcite present at this stage can therefore be determined. The amount can be adjusted to account for the dolomite present. The remaining calcite can originate from two sources: (i) the amount of calcite present as aggregate and (ii) the amount of calcite originating from carbonation of the portlandite over a period of 30 years. The portlandite will gradually carbonate over such a period at room temperature (see Eq. (4)). The amounts of portlandite, dolomite, and calcite present in the samples are listed in Table 2. The amounts of portlandite and calcite present are small. It is reasonable to suppose that all or most of the calcite present could have resulted from the carbonation of the portlandite. A final column in Table 2 expresses this as total % portlandite originally present. It can be seen that the values for such an estimate vary between 2.01 and 12.15%. In the earlier publication [9] it was pointed out that values between 10 and 20% were to be expected in ordinary cement paste so these results seem plausible. Free CaO might have been present in the samples originally containing slag in the aggregate. However, over 30 years the free lime (CaO) would have been carbonated (see Eq. (3)). The ethylene glycol test showed negligible amounts of free calcium oxide which would seem to confirm this supposition. The XRD data indicated the presence of gypsum as a minor constituent in all samples and this is to be expected.

The presence of quartz could be seen in many of the samples from both the DTA data as a very small endothermic transition [10] at 573°C and from the XRD pattern. The XRD data also indicated the presence of portlandite, dolomite, and calcite (see a typical XRD pattern for these samples in Fig. 7). The XRD patterns for all the samples is shown as relative quantities in Table 2, being a qualitative estimate of dolomite, calcite, and quartz present.

The relevant leachate experiments are given in Table 3. It can be seen that the ratio of Ca/Mg is

Table 2
Analysis data on the various RPCC samples investigated

| Sample ID | From TG data | | | XRD results/assessment of quantity | Total % portlandite originally present |
|---|---|---|---|---|---|
| | % Portlandite | % Dolomite | % CaCO3 | | |
| 1 | 2.92 | 55.18 | 12.46 | $D \geqslant C = Q$ | 12.15 |
| 2 | 4.27 | 69.12 | 5.41 | $D \geqslant C > Q$ | 8.28 |
| 3 | 2.84 | 61.01 | 9.45 | $D \geqslant C \geq Q$ | 9.84 |
| 4 | 3.70 | 62.86 | 8.24 | $D \geqslant Q = C$ | 9.81 |
| 5 | 3.82 | 57.48 | 0.26 | $D \geqslant Q > C$ | 4.01 |
| 6 | 4.56 | 65.21 | 2.47 | – | 6.39 |
| 7 | 3.86 | 75.16 | 3.58 | $D \ggg C > Q$ | 6.51 |
| 8 | 3.41 | 65.63 | 7.92 | $D \geqslant C > Q$ | 9.28 |
| 9 | 3.82 | 65.80 | 8.03 | $D \ggg Q = C$ | 9.77 |
| 10 | 4.40 | 69.12 | 2.89 | $Q > D \geqslant C$ | 6.54 |
| 11 | 3.58 | 65.00 | 7.85 | $D \ggg C \geqslant Q$ | 9.40 |
| 12 | 5.06 | 66.55 | 3.76 | – | 7.85 |
| 13 | 1.69 | 60.00 | 0.57 | $D \geqslant Q > C$ | 2.11 |
| 14 | 2.01 | 67.06 | 0.00 | – | 2.01 |
| 15 | 3.62 | 57.74 | 1.08 | $Q > D \geqslant C$ | 4.42 |

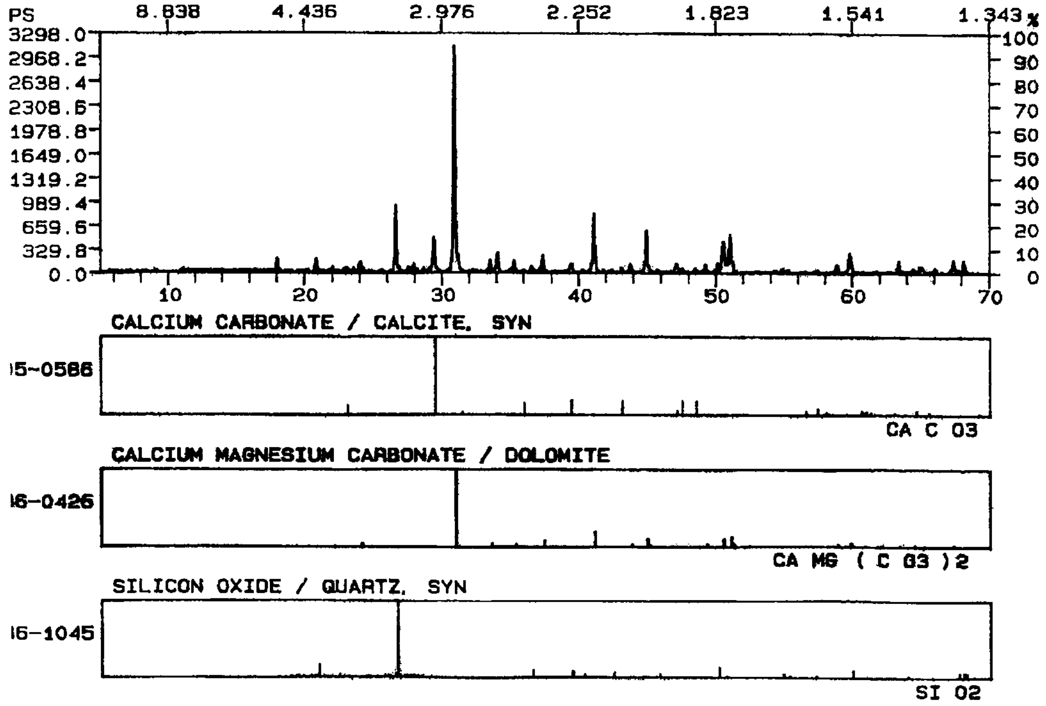

Fig. 7. Typical XRD pattern for sample #13.

between 1.3 and 5.5 but the results are mainly clustered around 1.55. The ratio of Ca/Mg in dolomite is 1.65. Taking regard of the fact that dolomite might not dissolve out in the ratio of their existence in the solid phase it would however seem likely that most of the leached ions originated from the dolomite. This leaching process under acidic conditions (carbon dioxide dissolved in water for 24 h) would also certainly cause leaching from the calcite and portlandite present. This would be a reason why the ratio of Ca/Mg that did not exactly correspond to the ratio present in the solid phase of dolomite.

Table 3
Results of ICP tests on leachates from the packed beds of the various samples when $CO_2$ was passed through the bed for 24 h

| Sample ID | Mg (ppm) | Ca (ppm) | Ca/Mg |
|---|---|---|---|
| 1 | 251.84 | 724.53 | 2.88 |
| 2 | 408.57 | 540.11 | 1.32 |
| 3 | 295.77 | 502.88 | 1.70 |
| 4 | 267.25 | 423.59 | 1.58 |
| 5 | 342.57 | 486.57 | 1.40 |
| 6 | 130.78 | 716.12 | 5.48 |
| 14 | 370.20 | 646.90 | 1.75 |
| 15 | 132.15 | 607.90 | 4.60 |

## 4. Conclusions

Taking into account the low values for portlandite in RPCC aggregates rich in dolomite but low in calcite it can be concluded that any calcite detected arises from carbonation of portlandite originally formed over the life span of these samples (30 years). The ratio of calcium ions to magnesium ions in the leachate would suggest the dolomite is a dominant factor in the leaching process from acidic water. It would also seem in view of the low values for the portlandite and calcite content that their role in the dissolution process is minor.

## Acknowledgements

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