This is a repository copy of *A discussion of the papers "Impact of hydrated magnesium carbonate additives on the carbonation of reactive MgO cements" and "Enhancing the carbonation of MgO cement porous blocks through improved curing conditions", by C. Unluer & A. Al-Tabbaa*.

White Rose Research Online URL for this paper:
http://eprints.whiterose.ac.uk/92252/

Version: Accepted Version

eprints@whiterose.ac.uk
https://eprints.whiterose.ac.uk/

1   **A discussion of the papers "*Impact of hydrated magnesium carbonate additives on the**
2   *carbonation of reactive MgO cements*" and "*Enhancing the carbonation of MgO cement porous**
3   *blocks through improved curing conditions*", by C. Unluer & A. Al-Tabbaa**

4   Sam A. Walling, John L. Provis*

5   *Immobilisation Science Laboratory, Department of Materials Science & Engineering, University of Sheffield, Sheffield,*
6   *S1 3JD, United Kingdom*
7   *corresponding author: email: j.provis@sheffield.ac.uk, Tel: +44 114 222 5490*

8   **Abstract**

9   This paper is a discussion of two recent papers by Unluer & Al-Tabbaa [1, 2] which analysed accelerated
10 carbonation of reactive MgO blocks. We suggest that the authors have incorrectly analysed key data, leading
11 to overstated claims of MgO carbonation. Based on reassignment of their X-ray diffraction data, it is proposed
12 that little MgO carbonation occurred in the samples discussed in those papers, with $CaCO_3$ instead forming
13 during accelerated carbonation. We also draw attention to the thermodynamic instability of nesquehonite
14 under ambient conditions, which calls into question the long-term stability of these binders.

15 **Discussion**

16 Cements containing reactive magnesia are of great interest as alternative binders, as they have been
17 proclaimed to embody potentially lower CO_2 emissions during manufacture and service. Two recently
18 published papers by Unluer and Al-Tabbaa [1, 2] have added to the body of literature on these cements,
19 studying the effect of hydrated magnesium carbonate (HMC) addition and curing conditions, respectively, on
20 the properties and structure of porous reactive MgO cement blocks exposed to accelerated carbonation
21 conditions. We will focus the discussion here on the first of these two papers, as the results presented in the
22 second are largely an extension of the first, and contain similar points requiring re-analysis.

23 In these papers the authors claim to carbonate MgO to form a range of magnesium carbonates which
24 constitute their binding phases; this is a key aspect of the 'green' credentials proposed for these alternative
25 cements. Unfortunately, we are unable to reach the same conclusions made by the authors, based on our
26 own analysis of the data presented in their papers. In our opinion, the scientific discussion in these two
27 papers is based upon poorly-assigned X-ray diffraction patterns, which have led to incorrect interpretations
28 of thermal analysis data, and consequently erroneous claims of high levels of carbonation.

29 In the paper "Impact of hydrated magnesium carbonate additives on the carbonation of reactive MgO
30 cements" [1], the authors produce blocks containing natural aggregates, pulverised fuel ash (PFA) as filler,
31 and MgO as the key anhydrous precursor, with hydrated magnesium carbonates (HMCs) added to some of
32 the mixes. The combination of hydration and carbonation is proposed to lead to the formation of additional
33 hydrated magnesium carbonates as binding phases, when cured under either natural or accelerated
34 carbonation conditions. The authors achieved some interesting strength data, exceeding 20 MPa in
35 compression in some instances, which shows that their methodology is of some interest.

36 However, there are several apparent discrepancies in the peak assignments in the two XRD patterns used by
37 the authors to identify hydration products after accelerated carbonation (Fig. 7 in [1]). This graphic is
38 reproduced here as Figure 1, with our suggested peak assignments for their first set of XRD patterns overlaid
39 on the original data. The authors of [1] mis-assign the major calcite peak at 29.4° 2θ (PDF # 005-0586),
40 labelling it as nesquehonite and dypingite (both magnesium carbonate phases). Additional calcite reflections
41 can be seen at 23°, 39.4°, and 48.5° 2θ, confirming its presence in these samples. Nesquehonite (PDF # 020-
42 0669) typically exhibits its highest intensity peak at 13.7° 2θ, with a much lower intensity reflection at 29.5°

43 2θ. Dypingite (PDF # 029-0857) has several reflections in the low-angle region, with strong reflections
44 observed at 8.2°, 13.7° and 15° 2θ (elsewhere noted as 5.7°, 8.5°, 14° and 15.1° 2θ [3]). The absence of these
45 reflections in the data leads us to conclude that dypingite is not in fact present in these samples. The presence
46 of only a small reflection for nesquehonite at 13.7° proves that the peak at 29.4° must be mostly due to
47 calcite, with only a very small quantity of nesquehonite present.
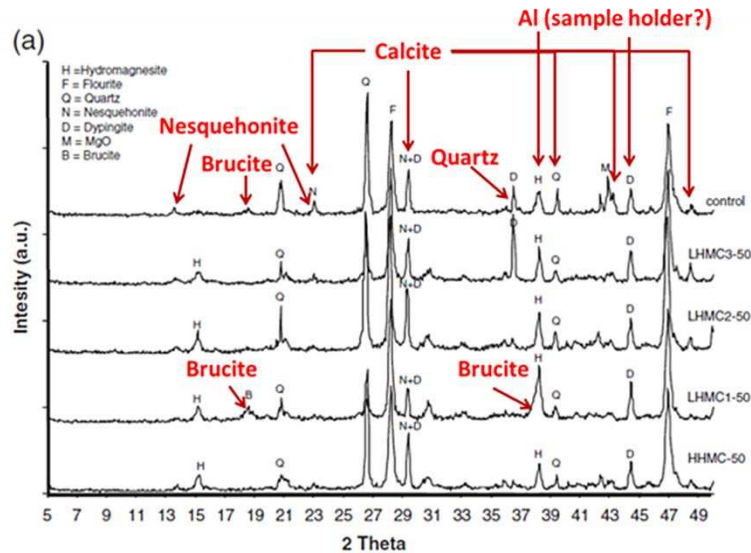
48
49 **Figure 1.** XRD patterns (Fig 7a of [1]), with our suggested peak assignments labelled with arrows above the authors'
50 original assignments

51 The authors also mis-assign the reflection at ~36.5° 2θ to dypingite. There is a dypingite reflection listed in
52 PDF card 029-0857 at this angle, but this is a minor reflection compared to many of the other dypingite
53 reflections, which should be more intense, but are absent from the diffractograms. We tentatively assign this
54 reflection to quartz (110), although this is also a relatively weak reflection of this phase. The other labelled
55 quartz peaks at ~21° and ~26.7° 2θ vary greatly in intensity from sample to sample, possibly as a result of
56 inclusion of differing amounts of the fine aggregates from the concrete specimens during the preparation of
57 each sample for XRD analysis, which would be expected to be relatively coarse particles within the samples
58 and thus potentially subject to preferred orientation issues. It is therefore unsurprising to find a quartz peak
59 at ~36° 2θ in two of the samples, but not the others. The authors also label a peak at ~44.5° 2θ to dypingite.
60 The PDF card for dypingite does show peaks around 44.6° 2θ, but due to the lack of other dypingite reflections
61 in the diffractograms, this is most likely an aluminium (200) reflection from the XRD sample holder.

62 There is another peak at 38.3° 2θ which is labelled by the authors as hydromagnesite, and does correspond
63 to the $(\bar{2}23)$ reflection of this phase, but this peak should only be around $1/6^{th}$ of the intensity of the
64 hydromagnesite (011) peak at 15.3° 2θ. Major reflections for brucite (PDF # 044-1482) and aluminium (PDF
65 # 004-0787, potentially from a sample holder as mentioned above) are located very close to this angle. The
66 major reflections for hydromagnesite (PDF # 025-0513) are 15.3° and 30.8° 2θ, which were observed in the
67 four samples containing added HMCs (but not the control). Several minor reflections exist for this phase,
68 including around ~38° 2θ, however all have significantly lower intensity than the two major reflections, so
69 are unlikely to contribute to the peak observed here. This peak in the data set for the control sample was
70 also incorrectly labelled as hydromagnesite, however this is more likely to be brucite (due to the absence of
71 added HMCs in this sample) and potentially aluminium. This is also likely true of the HMC-containing samples.

72　This mistaken identification led the authors of [1] to infer that 100 % of the brucite has carbonated, when it
73　is in fact much more difficult to determine how much has reacted, as will be discussed below in the context
74　of the TGA data also presented in [1].

75　The authors of [1] then used the Reference Intensity Ratio method to quantify from the XRD patterns the
76　degree of carbonation. However, as the reflection assignments were incorrect, with the diffractograms in
77　fact potentially demonstrating very little carbonation of $MgO/Mg(OH)_2$, the calculated figures cannot be
78　considered reliable, particularly where 100% carbonation is claimed for samples with visible residual brucite
79　peaks in the diffractograms. The authors of [1] also used an 'acid digestion' method to determine carbonation
80　of MgO, but the results obtained by this technique must be considered questionable due to (a) unrecognised
81　$CaCO_3$ formation within the samples, and (b) the inability of the reader to understand or reproduce the
82　experimental protocol from the details provided.

83　The errors introduced in analysis of the XRD patterns were also carried over to the TG/DTA analysis (Fig. 8 in
84　[1]), where the decomposition of $Mg(OH)_2$ at ~400 °C and $CaCO_3$ decomposition at ~780 °C were confused
85　with the signals of magnesium carbonate decompositions. This confuses attempts to quantify the amount
86　and type of magnesium carbonates formed, making this section of analysis unreliable.　The strong
87　endothermic peak and mass loss in the temperature range corresponding to $Mg(OH)_2$ decomposition in all
88　samples shown in Figure 8 of [1] must be related, at least in part, to the presence of this phase.

89　In our opinion, the authors have in fact largely carbonated the CaO impurities within the raw MgO (2 wt. %
90　CaO from XRF analysis), or the CaO content of the PFA (6.8 wt.% CaO from XRF analysis) during accelerated
91　carbonation, forming calcite ($CaCO_3$), rather than generating hydrous magnesium carbonates from the MgO.
92　The mortars were made using 85 % aggregate, 5 % PFA, and 10 % magnesia-based cement (different blends
93　of MgO and HMCs), which leaves ample ash available for carbonation, and it has previously been
94　demonstrated that low calcium ashes can be induced to carbonate under elevated CO_2 conditions [4, 5]. We
95　therefore believe that the accelerated used conditions in this paper (20 °C, 70-90% relative humidity, 20 %
96　CO_2) could have caused carbonation of the PFA.

97　Due to these issues in the data analysis, the conclusions drawn in [1] regarding the use of HMC in reactive
98　MgO blocks do not definitively demonstrate the full or effective carbonation of MgO in these specimens. The
99　subsequent publication, [2], essentially follows the same route in data analysis, and suffers from the same
100　inconsistencies in peak assignments and phase analysis. We will not recapitulate our arguments in detail
101　regarding this specific paper, other than to say that the discussion presented above is also relevant to the
102　conclusions presented in [2] regarding phase analysis by X-ray diffraction and thermal analysis.

103　As a side note, we are also concerned that the authors claim to be producing stable and durable construction
104　materials involving nesquehonite as a key binding phase, when this phase is known to be thermodynamically
105　unstable with respect to hydromagnesite under normal environmental conditions [6, 7], decomposing by
106　release of water and CO_2 at room temperature and normal ambient humidities over a period of several years.
107　This does not appear to have been considered, and could have significant consequences in terms of the
108　longer-term behaviour of the materials produced by this method.

109　A recent thermodynamic study [8] of magnesium carbonates has determined that nesquehonite has a narrow
110　range of stability. Although relatively easily formed under laboratory conditions using elevated CO_2
111　concentrations, it is actually thermodynamically unstable with regard to both hydromagnesite and magnesite
112　at ambient temperature, relative humidity and partial pressure of CO_2. The free energy diagram in Figure 2
113　is adapted from reference [8], and beneath this is shown the unit cell volume per mole of Mg atoms for the
114　relevant phases. Conversion from nesquehonite to magnesite would entail a >60% reduction in density per

115   mole of Mg, though slow growth kinetics of magnesite are likely to inhibit this process during the service life

116   of a porous block. Conversion directly to hydromagnesite is, however, more kinetically favourable, and yields

117   a reduction in density of more than 40% per mole of Mg. Such a change in density, with expulsion of water,

118   is liable to destabilise a binder relying on nesquehonite for its strength. We feel that significant caution is

119   required when relying on a binder that is so unstable under normal temperature variations.
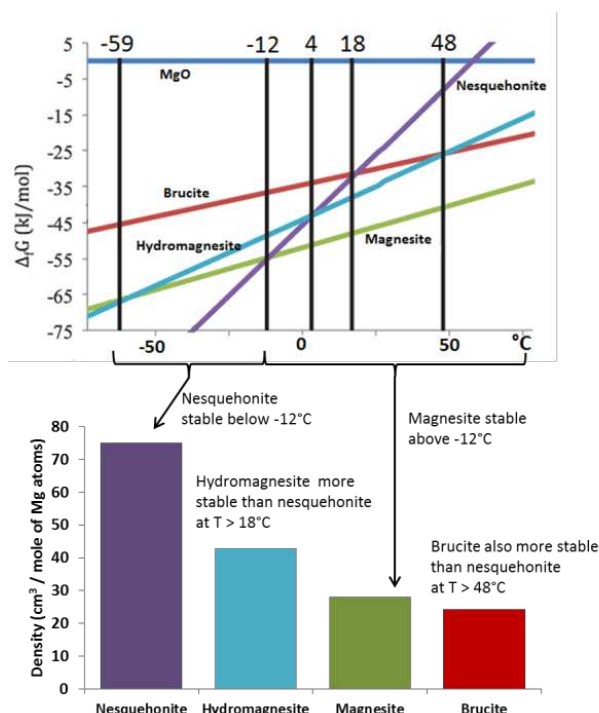
120

121   **Figure 2.** Free energy phase diagram for hydrous magnesium carbonates calculated by Chaka and Felmy [8], under

122   conditions of pCO_2 = 400 ppm and pH_2O = 32 mbar (saturation vapour pressure at 298 K), along with the density per

123   mole of Mg atoms of stable magnesium phases (data from Webmineral.com)

Acknowledgements

References

128   [1] C. Unluer, A. Al-Tabbaa, Impact of hydrated magnesium carbonate additives on the carbonation of reactive MgO
129   cements, Cem. Concr. Res., 54 (2013) 87-97.

130   [2] C. Unluer, A. Al-Tabbaa, Enhancing the carbonation of MgO cement porous blocks through improved curing
131   conditions, Cem. Concr. Res., 59 (2014) 55-65.

132   [3] J.H. Canterford, G. Tsambourakis, B. Lambert, Some observations on the properties of dypingite,
133    $Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$, and related minerals, Miner. Mag., 48 (1984) 437-442.

134   [4] H.Y. Jo, J.-H. Ahn, H. Jo, Evaluation of the CO_2 sequestration capacity for coal fly ash using a flow-through column
135   reactor under ambient conditions, J. Hazard. Mater., 241–242 (2012) 127-136.

136   [5] G. Montes-Hernandez, R. Pérez-López, F. Renard, J.M. Nieto, L. Charlet, Mineral sequestration of CO_2 by aqueous
137   carbonation of coal combustion fly-ash, J. Hazard. Mater., 161 (2009) 1347-1354.

138   [6] R.A. Robie, B.S. Hemingway, The heat capacities at low-temperatures and entropies at 298.15 K of nesquehonite,
139    $MgCO_3 \cdot 3H_2O$, and hydromagnesite, American Mineralogist, 57 (1972) 1768-1781.

140   [7] Y. Xiong, A.S. Lord, Experimental investigations of the reaction path in the $MgO–CO_2–H_2O$ system in solutions with
141   various ionic strengths, and their applications to nuclear waste isolation, Appl. Geochem., 23 (2008) 1634-1659.

142   [8] A.M. Chaka, A.R. Felmy, Ab initio thermodynamic model for magnesium carbonates and hydrates, J. Phys. Chem. A.,
143   118 (2014) 7469-7488.

144   [9] L.J. Vandeperre, A. Al-Tabbaa, Accelerated carbonation of reactive MgO cements, Adv. Cem. Res., 19 (2007) 67-79.