

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47

HIGHLIGHTS & BREAKTHROUGHS

Safe long-term immobilization of heavy metals: looking at natural rocks

MAARTEN A.T.M. BROEKMANS*

Geological Survey of Norway – NGU, Department of Mineral Resources & Metals
PO Box 6315 Sluppen, N-7491 TRONDHEIM, Norway

Abstract

Portland cement clinker is primarily used in building and construction, with a global annual production of ~4 billion tonnes. Part of it is also used for immobilization of hazardous materials (eg. industrial slurries, harbor bottom sludge, shredded tyres), notably those containing toxic metals like eg. zinc, cadmium, barium (Trezza & Scian 2000). Limited amounts may be added to the raw meal and get incorporated into the clinker minerals upon burning (Taylor 1997), assuming they remain immobilized in the high-pH concrete or mortar environment after hydration and setting of the cement. Extensive laboratory tests seem to confirm effective mobilization, but are generally of limited duration for reason of practicality. Access to sample materials from centennia- or millennia-old structures is limited for reasons of cultural heritage preservation, and none of these structures were originally designed for environmental reasons. The paper by Khoury et al (2015a) analyzes uncommon combustion-metamorphic rocks from Jordan closely resembling cement-immobilized waste, exposed to supergene weathering and alteration over time-spans far exceeding experimental practicality.

Keywords: combustion metamorphism, impure chalk-marl, lime-monteponite series, portlandite, weathering, alteration, cadmium, immobilization.

The paper by Khoury et al (2015a) merges scientific disciplines that usually live their own day-to-day lives in practice, without being overly concerned about the one or the other. The authors describe the discovery of a mineral of nearly exactly intermediate composition in the lime-monteponite (CaO-CdO) series, occurring naturally in rocks in the Mottled Zone Complex, Levant, at approximately 60km SSE from the center of the city of Amman in Jordan. The area is arid and challenging to access, and its mud volcanoes and gas flares have already been described since antiquity (eg. Sokol & Kokh 2010).

The Belqa Group marine sediments consist of impure limestones, shales and marls that have enjoyed combustion metamorphism, through natural ignition of the bituminous matter they contain. The combustion metamorphism took place ~100ka ago; since then, the rocks have been exposed to ‘weather and climate’ at ambient surface conditions.

The oxidative burning at high temperature produced minerals normally ‘rock-forming’ in industrial Portland clinker used for cement production (eg. Taylor 1997; also see Table 1 in Sokol et al 2014), but otherwise occurring rarely in nature and typically associated with calcareous xenolithic enclaves in lavas (see eg. Hentschel 1983). Metal-sulfide minerals present in trace amounts in the precursor were metamorphically transformed into a number of unnamed Ca-U oxides (Khoury et al 2015b) and other less common mineral species, including the lime-monteponite intermediates referred to here. Some of the original Cd was

* maarten.broekmans@ngu.no

48 lost during the combustion-metamorphic ‘clinkering’, as shown by the Zn/Cd ratios relative to
49 non-metamorphosed precursor (note: Cd is much less refractory than Zn).

50 The (Ca,Cd)O grains are ~50µm small and were initially tentatively identified by
51 composition only in SEM-EDS (SDD). Subsequently, as more and more samples were
52 assessed (over one thousand altogether), these intermediate grains were found to represent a
53 common accessory in the combustion-metamorphic marbles across the area. X-ray diffraction
54 on extracted single grains confirms their identity as a lime-monteponite intermediate with a
55 cubic NaCl-type structure, without signs of ordering of Ca and/or Cd. Detailed analysis by
56 EPMA confirms individual grains are homogeneous without detectable zoning, with CdO
57 contents ranging from 58-73wt% (=36-55% **apfu**), with trace contents of Zn and Fe.

58 The potential of these rocks as an alternative bulk raw material for ‘green’ Portland
59 clinkering with reduced CO₂-emission has been recognized (Taylor 1997, Justnes 2012).
60 Meanwhile, the incorporation of (heavy) metal species in Portland cement upon clinkering
61 (Trezza & Scian 2000, Prodjosanto & Kennedy 2003, Shih et al 2005; also compare Rankin et
62 al 1987), as well as hydration during cement setting and leaching of heavy metals from the
63 fully set product (eg. Sprung & Rechenberg 1988, Alunno Rosetti & Medici 1995, Asavapisit
64 et al 1997, Hillier et al 1999, Deja 2002, Halim et al 2004, Belebchouche et al 2015), has been
65 subject of extensive study for its possible environmental repercussions (eg. Pöllmann 2010).
66 Thus, long-term behavior of hydrated Portland clinker products is a most relevant and highly
67 actual issue for environmentalists and related disciplines.

68 Long-term stability of concrete was addressed by Jackson et al (2013) in an excellent
69 article also published in this journal, highlighted by Elsen et al (2013). They attributed the
70 proven durability of Roman-time concrete against immersion in seawater for over 2ka to its
71 high Al-content, initially inherited from pozzolanic volcanic ashes mixed in with the binder,
72 sustained by coarser particles used for aggregate. The value of ancient built cultural heritage
73 for long-term durability studies was also recognized by Roy & Langton (1983, and references
74 therein), but is essentially limited to anthropogenic construction history. This is where the
75 presently highlighted paper by Khoury et al (2015a) represents a breakthrough, by tapping
76 into the geological record comprised by a rather uncommon lithology serving as a natural
77 analog to modern-day belite sulfoaluminate cements (Sokol et al 2014), that have been
78 exposed to supergene conditions.

79 SEM-BSE imaging reveals that the (Ca,Cd)O lime-monteponite grains are partially
80 altered along the periphery to (Ca,Cd)[OH]₂ (or alternatively ‘Cd-bearing portlandite’), as
81 confirmed by Raman spectroscopy and single-grain XRD. Also other ‘clinker minerals’
82 present in the metamorphic rock samples are partially altered, confirming that alteration is
83 pervasive, though somewhat variable with lithology grain size. Nevertheless, element
84 mapping reveals that the cadmium remains strictly confined to the anhydrous core and the
85 hydrated rim, as confirmed by their preserved Ca/Cd-ratios. By contrast, alteration of sample
86 #TH-72 also involved chloride and fluoride, replacing original lime-monteponite grains
87 partially with fluorite surrounded by haloes of Cd-bearing hydration products *s.l.*, illustrating
88 mobility of Cd in presence of dissolved Cl (note: CdCl₂ is highly soluble in water).

89 Middle to Late Quaternary paleo-climate reconstructions back to 350ka of the southern
90 Levant indicate humid periods 350-290ka, 220-190ka, and 142-109ka. During latter period,
91 the combustion metamorphic rocks also enjoyed alteration by alkaline fluids circulating along
92 a fracture-fault system at repeated instances. Despite the overall pervasive and long-lasting
93 alteration, Cd is retained provided F and especially Cl are absent, confirming and extending
94 state-of-the-art experimental laboratory work to geologically-long time spans.

95 The authors merge detailed petrography and advanced mineralogical characterization
96 with paleoclimatology, Portland cement clinkering, and environmental science, enabling them
97 to draw conclusions not readily accessible otherwise. This cross-fertilization shows the power

98 of trans-disciplinary research, and in particular of the capability of ‘mineralogy for society’ to
99 resolve real life issues. The paper should inspire scientists and engineers committed to
100 research within the fields mentioned above, and hopefully outside as well. The Jordanian
101 rocks investigated here are undoubtedly best known for the geological curiosity they
102 represent, however, they also deserve recognition as an indispensable resource of very useful
103 long-term information, for a broad range of scientific disciplines that can benefit from mutual
104 inspiration.

105
106

107 REFERENCES CITED

108

- 109 Alunno Rosetti, V., and Medici, I. (1995) Inertization of toxic metals in cement matrices: effects on hydration, setting and
110 hardening. *Cement & Concrete Research*, 25/6, 1147-1152.
- 111 Asavapitit, S., Fowler, G., and Cheeseman, C.R. (1997) Solution chemistry during cement hydration in the presence of metal
112 hydroxide wastes. *Cement & Concrete Research*, 27, 1249-1260.
- 113 Belebchouche, C., Moussaceb, K., Tahakourt, A., and Ait-Mokhtar, A. (2015) Parameters controlling the release of
114 hazardous waste (Ni^{2+} , Pb^{2+} and Cr^{3+}) solidified/stabilized by cement-CEM I. *Materials & Structures*, 48, 2323-2338.
- 115 Deja, J. (2002) Immobilization of Cr^{6+} , Cd^{2+} , Zn^{2+} and Pb^{2+} in alkali-activated slag binders. *Cement & Concrete Research*,
116 32, 1971-1979.
- 117 Elsen, J., Cizer, O., and Snellings, R. (2013) Lessons from a lost technology: the secrets of Roman concrete. *American*
118 *Mineralogist*, 98, 1917-1918.
- 119 Gross, S. (1977) The mineralogy of the Hatrurim Formation, Israel. *Geological Survey of Israel Bulletin*, 70, 1-80.
- 120 Halim, C.E., Amal, R., Beydoun, D., Scott, J.A., and Low, G. (2004) Implications of the structure of cementitious wastes
121 containing Pb(II), Cd(II), As(V), and Cr(VI) on the leaching of metals. *Cement & Concrete Research*, 34/7, 1093-
122 1102.
- 123 Hentschel, G. (1983) Die Mineralien der Eifelvulkane. Christian Weise Verlag, München/DE. Lapis Monographie: pp152.
- 124 Hillier, S.R., Sangha, S.M., Plunket, B.A., and Walden, P.J. (1999) Long-term leaching of toxic trace metals from Portland
125 cement concrete. *Cement & Concrete Research*, 29/4, 515-521.
- 126 Jackson, M.D., Chae, S.R., Mulcahy, S.R., Meral, C., Taylor, R., Li, P., Emwas, A.M., Moon, J., Yoon, S., Vola, G., Wenk,
127 H.R., and Monteiro, P.J.M. (2013) Unlocking the secrets of Al-tobermorite in Roman seawater concrete. *American*
128 *Mineralogist*, 98, 1669-1687.
- 129 Justnes, H. (2012) Alternative low- CO_2 ‘green’ clinkering. *Reviews in Mineralogy & Geochemistry*, 74, 83-99.
- 130 Kakali, G., and Parissakis, G. (1995) Investigation of the effect of Zn oxide on the formation of Portland cement clinker.
131 *Cement & Concrete Research*, 25/1, 79-85.
- 132 Khoury, H.N., Sokol, E.V., Kokh, S.N., Seryotkin, Y.V., Kozmenko, O.A., Goryainov, S.V., and Clark, I.D. (2015)
133 Intermediate members of the lime-monteponite solid solutions ($\text{Ca}_{1-x}\text{Cd}_x\text{O}$, $x=0.36-0.55$): discovery in natural
134 occurrence. *American Mineralogist*, 100, xxxx-xxxx.
- 135 Khoury, H.N., Sokol, E.V., and Clark, I.D. (2015) Calcium uranium oxide minerals from Central Jordan: assemblages,
136 chemistry, and alteration products. *Canadian Mineralogist*, pp22 (DOI: 10.3749/canmin.1400071)
- 137 Pöllmann, H. (2010) Mineralisation of wastes and industrial residues. Shaker Verlag, Aachen/DE: pp478.
- 138 Prodjosantoso, A.K., and Kennedy, B.J. (2003) Heavy metals in cement phases: on the solubility of Mg, Cd, Pb and Ba in
139 $\text{Ca}_3\text{Al}_2\text{O}_6$. *Cement & Concrete Research*, 33, 1077-1084.
- 140 Rankin, A.H., Miller, M.F., and Carter, J.S. (1987) The release of trace elements and volatiles from crinoidal limestone
141 during thermal decipitation. *Mineralogical Magazine*, 51, 517-525.
- 142 Roy, D.M., and Langton, C.A. (1983) Characterization of cement-based ancient building materials in support of repository
143 seal materials studies. Battelle Memorial Institute, Office of Nuclear Waste Isolation. BMI/ONWI-523: pp 146.
- 144 Shih, P.H., Chang, J.E., Lu, H.C., and Chiang, L.C. (2005) Reuse of heavy metal-containing sludges in cement production.
145 *Cement & Concrete Research*, 35, 2110-2115.
- 146 Sokol, E.V., Kokh, S.N., Vapnik, Y., Thiéry, V., and Korzhova, S.A. (2014) Natural analogs of belite sulfoaluminate cement
147 clinkers from Negev Desert, Israel. *American Mineralogist*, 99, 1471-1487.
- 148 Sokol, E.V., and Kokh, S.N. (2010) Reflections on eternal flames. *People & Environment*, ?, 92-111.
- 149 Sprung, S., and Rechenberg, W. (1988) Einbindung von Schwermetallen in Sekundärstoffen durch Verfestigen mit Zement.
150 Wischers, G. (Ed) *Betontechnische Berichte 1986-1988*, Forschungsinstitut der Zementindustrie, Düsseldorf/DE:
151 143-158.
- 152 Taylor, H.F.W. (1997) *Cement chemistry*. 2nd edition. Thomas Telford, London/UK: pp 459.
- 153 Trezza, M.A., and Scian, A.N. (2000) Burning wastes as an industrial resource: their effect on Portland cement clinker.
154 *Cement & Concrete Research*, 30/1, 137-144.