METABOLISM OF TOXIC METALS IN INDUSTRIAL SYMBIOSIS IN THE CEMENT INDUSTRY – A GLOBAL REVIEW AND ANALYSIS

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Abstract

UNDER CONSTRUCTION
1 Introduction

Over the past three decades, the concept of industrial ecology has emerged as central to the development of resource efficiency and sustainability (e.g., Frosch & Gallopoulos, 1989; Chertow, 2000). With its comparable need to make efficient use of resources, industrial activity is analogous to a natural ecosystem, where a network of companies (organisms) must innovate (adapt) in response to market (environmental) pressures, and competition leads to survival of the fittest. In a natural ecosystem, resources are shared and cycled between members for mutual benefit in symbiotic relationships. In industrial symbiosis, the by-products of one industry become the raw materials for another.

Concrete is the most widely used material in the world and essential to much of our infrastructure. As well as consuming about 11% of global industrial energy, cement production consumed more than 5 Gt of non-fuel raw materials in 2011. More efficient management of the significant proportion of global resources consumed by the cement/concrete industry is therefore important to sustainability. As obtaining energy and materials resources at lower cost has always been good business, industrial symbiosis has occurred in the cement industry since long before the popularisation of industrial ecology. The most common practices have been: 1) co-processing of alternative fuels and raw materials (ARF), whereby a) wastes with high calorific value replace fossil fuels, and/or b) mineral wastes replace raw material feeds (limestone, clay and supplements), to the cement kiln, and 2) replacement of Portland cement clinker with pozzolanic wastes and diluents to produce blended cements. Minerals waste may also replace natural aggregate in concrete (Stegemann, 2014).

Many wastes contain elements or compounds that have the potential to interfere with cement chemistry or pollute the environment and the viability of utilising wastes in cement production requires that: 1) the manufacturing process is not adversely affected or can be adapted, 2) the technical characteristics of the final cementitious material are appropriate to its intended use, and 3) the risks of negative impacts on health or the environment from manufacturing and use of the cementitious material are unchanged or reduced (Stegemann, 2014). In general, there has been a high degree of conservatism and regulatory influence regarding the industrial by-products that are allowed to enter the cement production system, and the cement industry has promoted industrial symbiosis as a safe practice (e.g., Cembureau, 1997). However, when resources are more scarce and costly and waste builds up in an ecosystem at levels that are detrimental to its health, there is a greater incentive to evolve more efficient by-product utilisation in more specialised industrial-ecological niches. Consequently, there is increasing pressure for a wider range of waste types, including hazardous wastes, to be used in cement-based products.

The objectives of this review are therefore to:

1) to examine our present understanding of the fate and behaviour of heavy metals in co-processing, through the cement kiln, into clinker and air pollution control dusts, to hydrated Portland and blended cement pastes and the environment, and
2) identify areas where further research is needed to enable resource efficiency with concomitant protection of the environment from heavy metal pollution.
2 Approach

Review of the literature focussed on ...

3 Results

3.1 Co-processing of wastes containing heavy metals in the cement kiln as alternative fuels

(Geron & Brizio, 2008; Li, 2013a; Y.-M. Lin et al., 2011; Seyler et al., 2005)

3.2 Co-processing of wastes containing heavy metals in the cement kiln as alternative raw materials

(Alp et al., 2008, 2009; Bernardo et al., 2007; Y.-L. Chen et al., 2009, 2012; Chen, Jida; Liao, Shiguo; Xie, Bin; Zhang, Liwei; Wang & Jiang, 2011; Denise C R Espinosa & Tenorio, 2000; Gomes et al., 2013; Guan et al., 1998; Kapur & Kapur, 2004; Krammart & Tangtermsirikul, 2004; Lam et al., 2011; B. G. Ma, 2009; Medina et al., 2006; Pan et al., 2008; Qiu et al., 2011; Saikia et al., 2007; Taeb & Faghighi, 2002; Monica Adriana Trezza & Scian, 2009; Tsakiridis et al., 2004, 2008; L. Wang, Jin, Nie, et al., 2008; T. Zhang, Gao, Gao, Wei, & Yu, 2013; Zhu, Takaoka, Oshita, & Morisawa, 2011; Ziegler, Scheidegger, Johnson, Dahn, & Wieland, 2001)

3.3 Heavy metal content of commercial cements
3.4 Fate of metals in the cement kiln

3.4.1 Volatilisation and mineralogy of gas-entrained and condensed solid phases

3.4.2 Clinker formation and mineralogy

Stephan

(Andrade et al. 2003)
- Addition of 1% ZnO, Pb(NO3)2 and NH4VO3
- V has shown a preferential partition towards C2S. Zn appears in higher amounts in periclase, and C3S has higher Zn contents than C2S. Pb concentrates in minute spherules and partitions toward C3S in small amounts

(Barros et al. 2002)

(Gineys et al. 2011)
- maximum amount that could be incorporated into a standard clinker whilst reaching the limit of solid solution of its four major phases (C3S, C2S, C3A and C4AF).
- Threshold limit was considered to be reached when XRD showed new phases
- The threshold limits for Cu, Ni, Zn and Sn were respectively equal to 0.35, 0.5, 0.7 and 1 wt.%.
- beyond the threshold limits. Ni was associated with Mg as a magnesium nickel oxide (MgNiO2) and Sn reacted with lime to form a calcium stannate (Ca2SnO4).
- Cu changed the crystallisation process and affected therefore the formation of C3S. Indeed a high content of Cu in clinker led to the decomposition of C3S into C2S and of free lime. Zn, in turn, affected the formation of C3A. Ca6Zn3Al4O15 was formed whilst a tremendous reduction of C3A content was identified.

(Gineys et al. 2011)
- The threshold limit for Sn was affected by the Bogue content in interstitial phases.
- The threshold limit for Zn was affected by the Bogue content in C3S
- Cu was unaffected by any modifications of clinker composition

(Prodjosantoso & Kennedy 2003)
- solubility of Mg, Cd, Pb and Ba in Ca3Al2O6
- Mg cations are found to partially substitute for Ca2+, and structural refinements show that Mg preferentially occupies the smaller six-coordinate sites in Ca3 xMgxAl2O6.
- Ba preferentially occupies the larger eight- and nine-coordinate sites.
- X-ray microanalysis suggests that Pb and Cd are lost from the samples during the preparation process.

(Ract et al. 2003)
- Samples were prepared by additions from 0.25 to 5 wt.% of a galvanic sludge to an industrial clinker
- raw-material in a laboratory device
• up to 2 wt.% of a galvanic sludge containing 2.4 wt.% Cu and 1.2 wt.% Ni to clinker raw-
material do not affect the clinkering reactions and that these metals are totally incorporated
into the clinker.
• [this is only 480 mg/kg Cu, 240 mg/kg Ni!]

3.5 Fate of metals in the hydrated paste

3.5.1 Fundamental studies

Hydrated cement paste, whether Portland or blended, is composed of highly alkaline crystalline and
amorphous phases, including calcium silicate hydrate (C-S-H, at least 50% on a dry mass basis),
\( \text{Ca(OH)}_2 \) (up to 20% on a dry mass basis), as well as hydrated calciumalumino-ferrites and calcium
sulphoaluminates, including ettringite \([\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_12\cdot26\text{H}_2\text{O}]\). and monosulphate
\([\text{Ca}_2\text{AlSO}_4(\text{OH})_6] \cdot 12\text{H}_2\text{O} \) (e.g., Lothenbach et al. 2011). Heavy metals can be taken up into these
cement hydration products, or sorbed onto their surfaces, or form separate solid phases in the
alkaline conditions, as further discussed in an excellent review by Johnson (2002). Recent
fundamental and valuable studies in this area have also been undertaken by Wieland and co-
workers, who have used x-ray absorption spectroscopy (XAS) to study speciation of various metals
doped into C-S-H and hardened cement pastes.

It is thought that cation-exchange can occur in the CaO interlayer of C-S-H; replacement of \( \text{Ca}^{2+} \) by
\( \text{Mg}^{2+} \) has been reported (e.g., Massazza, 1998), which suggests that the potential for replacement by
other alkaline earth elements, such as Sr, exists. The crystalline calcium silicate hydrate mineral
tobermorite has been shown to have a high capacity for exchange of \( \text{Ca}^{2+} \) with \( \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+} \) and
\( \text{Mg}^{2+} \) (Johnson 2002). However, there is good evidence that \( \text{Zn} \) and \( \text{Pb} \) are incorporated as oxides in
the silicate layers of C-S-H, rather than exchanging for \( \text{Ca}^{2+} \) (Ziegler et al. 2001, Tommaseo and

Trivalent cations, such as \( \text{Cr}^{3+}, \text{Ni}^{3+} \) and \( \text{Co}^{3+} \), can also substitute for \( \text{Al}^{3+} \) or \( \text{Fe}^{3+} \) in ettringite, as
reported by Gougar and co-workers (1996), and possibly other hydrated calcium aluminate\ such as
hydrogarnet \([\text{C}_3\text{AS}_{12}\text{H}_{6-2x}] \) which has been shown to take up \( \text{Cr}^{3+} \) (Kindness et al., 199b). Gougar (1996)
also reviews reports that divalent cations, such as \( \text{Ba}^{2+}, \text{Cd}^{2+}, \text{Co}^{2+}, \text{Hg}^{2+}, \text{Ni}^{2+}, \text{Pb}^{2+}, \text{Sr}^{2+} \) and
\( \text{Zn}^{2+} \), can replace \( \text{Ca}^{2+} \) in ettringite minerals, but the evidence for this is not strong. As reviewed by Johnson
(2002), heavy metals that form oxyanions, such as As, Cr(VI), Mo, Sb, Se, Te, V and W can substitute
for sulphate in ettringite and monosulphate.

When the sorption or exchange capacity of cement hydration products is exceeded, metals will form
new solid phases. Due to the alkaline nature of cement hydration products, with a typical pH of
12.3, and a possible range from about 10 to 14, the most likely anion to form a metal-bearing salt is
the hydroxide ion, \( \text{OH}^- \). Metals may form single-metal hydroxides, but may also form other phases
such as calcium zinctate, or other mixed hydroxides (e.g., Scheidegger et al. 2000, Johnson 2002).
Oxyanions may also precipitate with calcium (Johnson 2002)

Wieland and coworkers - significant uptake of stannate and uranate \([\text{Sn(IV)} \text{ and } \text{U(VI)}] \) by C-S-H and a
structural model of the binding mechanism has been proposed on the basis of X-ray absorption
spectroscopy studies.
An important difference between heavy metals introduced by co-processing of wastes, as compared with those introduced by blending of mineral wastes with blended cements, is that the former are likely to be more intimately mixed with cement phases and may have undergone a change in speciation, whereas the latter may be associated with waste particles. However, inorganic encapsulated particles are likely to react with the cement matrix to some degree. Depending on reaction kinetics, soluble species such as chlorides and sulphates may dissolve during or soon after mixing of cement powder with water, releasing metals for other interaction with the cement hydration products, whereas species such as oxides may dissolve more gradually and participate in secondary reactions during cement hardening and curing, and some aluminosilicates may retain their original form in the waste in the long term.

3.5.2 Portland cement from co-processing

3.5.3 Blended cements with mineral wastes

Hsaio et al. (2001) observed respeciation of soluble CuCl2 to precipitated Cu(OH)2, and also oxidation of Cu+ to Cu2+ in municipal waste incinerator fly ash solidified with Portland cement.

4 Leaching of metals from cement pastes

Hydrated cement paste provides a dense physical matrix of low permeability, which constitutes a physical barrier to leaching.

AsO$_4^{3-}$ and MoO$_4^{2-}$ are known to form calcium salts of low solubility at high pH, whereas the solubility of calcium salts of AsO$_3^{3-}$, CrO$_4^{2-}$, SeO$_3^{2-}$, SeO$_4^{2-}$ is higher, and that of Sb and V salts is unknown (Johnson 2002).

The measured porewater or leachate concentrations of metal contaminants are often found to be lower than the solubilities of their hydroxide (Johnson, 2002). If the total contaminant concentration in the product is lower than the capacity of the matrix for uptake of the contaminant, the leachate concentration is controlled by partitioning between the solid and liquid, rather than metal hydroxide solubility. This phenomenon is evident for Pb, whose solubility is an order of magnitude lower than the solubility in equilibrium with hydroxide at pH 10 to 13.5, and several orders of magnitude lower at more acidic pHs (Johnson, 2002). However, Pb remains by far the most soluble metal in the alkaline environment provided by a cement matrix.

Based on leaching data alone, it is difficult to know the mechanism by which the matrix takes up contaminants. It is assumed that surface sorption is responsible at lower contaminant concentrations, and uptake into the hydration products through solid solution occurs as contaminant concentrations increase and surface sorption sites are saturated.

5 Fate of heavy metals in demolition of cement-based structures
- use of: electric arc furnace dust (EWC code 10 02 07*) as iron supplement by St Lawrence Cement, air pollution control (APC) residues from energy-from-waste (EFW) plants, which are classified as hazardous wastes under EWC code 19 01 07*, in cement-based products by Cenin (cenin.co.uk) and Lignacite (www.lignacite.co.uk); other proposals include utilisation of leaded cathode ray tube glass (EWC code 16 02 13*/15*) ....

6 Discussion

6.1 Research Requirements

7 Conclusions

8 References [UNDER CONSTRUCTION; NEEDS SORTING AND SOME ADDITIONS, E.G., CLINKER PAPERS]


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Yang LY, Lei L, Ma JT. Study on leaching behavior of heavy metals and properties of combustion residue of municipal solid waste Portland cement. Concrete. 2012(3): 12-14. [In Chinese]


5 General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China and National Standardization Management Committee of China （2013） Technical specification for co-processing of solid waste in cement kiln (draft for approved).

