Toxicity of cement-based materials

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Abstract. Clinker production represents a high percentage of global CO₂ emissions and a significant decrease by 2030 is mandatory. Therefore, there is a permanent search for innovative and sustainable cement-based construction materials (CBM) around the world. The increased development and demand of sustainable construction solutions pushed the incorporation of non-traditional raw materials in CBM mixes. Due to the insufficient knowledge on the use of these components, it is fundamental to perform studies to assess their toxicological effects on the relevant environmental compartments. Some studies are found in the literature that analysed the environmental impacts of new CBM but there are not many that include a toxicity analysis. The procedures followed in the latter are varied since there were no specific recommendations to analyse construction materials until 2017, and the results were obtained following different standards or directives. Therefore, the direct comparison of the results of these studies is generally not possible. In that year, a guidance on the use of ecotoxicity tests on construction products was published - technical report CEN/TR 17105:2017 (Construction products - Assessment of release of dangerous substances). Nevertheless, the process to evaluate the potential toxicity of construction materials is complex, but fundamental. In fact, there is no direct correlation between existing metals’ concentration in one product and leached metals’ concentration, which makes it difficult to know the toxicity level. The aim of this paper is to review and present available CBM toxicity information, including standards, databases or labels. The tools that already exist to support the evaluation of the toxicity risks of CBM will also be analysed. Based on this, an approach for the toxicity evaluation of CBM is proposed in order to provide researchers with real-time support for the development of sustainable CBM with reduced risks associated with toxicity.

1. Introduction

There is a permanent search for innovative and sustainable cement-based construction materials (CBM) around the world. For a long time, the development of CBM relied solely on the assessment of mechanical resistance and durability. This type of studies normally applies a methodology that tests a high number of samples that represent different mixes with different raw materials proportions in order to find the optimized solution. The high personnel costs and resources investment involved are a considerable handicap of this approach.

The increase on sustainable construction solutions’ development and interest pushed up the incorporation of non-traditional raw materials in CBM mixes. Due to the insufficient knowledge on the use of these non-traditional materials, it is fundamental to assess their toxicological effects on the
relevant environmental compartments by doing toxicity studies, as part of the Life Cycle Assessment (LCA) or as an individual evaluation, thus contributing to the sustainable development goal of responsible consumption and production of materials (SDG 12). This paper presents an approach to address the toxicity of CBM.

2. Toxicity databases

It is possible to collect environmental impact or toxicity information on raw and construction materials in open access databases or in Environmental Product Declarations (EPDs). Databases consist of data collected from several sources and, according to their purpose, are based on different calculation methods. Therefore, different databases can provide different environmental impact results. Thus, it is recommended to use databases that are appropriate, with high transparency and reliability, and that present an explicit description and a regular updating [1, 2]. There are several free or commercial databases available. Some of the toxicological databases that present information about construction materials and chemical substances are briefly described in Table 1.

Table 1. Toxicity databases

| Database       | Country of origin | Publisher/Developer                      | Substances | Single chemical | Chemical compound | Cost            | Access          |
|----------------|-------------------|------------------------------------------|------------|----------------|------------------|-----------------|-----------------|
| ECHA [3]       | Europe            | European chemicals agency                | +90,000    | yes            | yes              | free            | online          |
| Ecotox [4]     | USA               | EPA                                      | -          | +11,700        |                  | free            | open access     |
| ToxCast [5] [6]| USA               | EPA                                      | +4,700     | yes            | yes              | free            | online          |
| Toxnet [7]     | USA               | U. S. National Library of Medicine       | -          | yes            | yes              | free            | online          |
| eChemPortal [8]| France            | OECD                                     | -          | yes            | yes              | free            | online          |
| Pharos CML [9] [10]| USA         | Healthy Building Network                 | +160,000   | yes            | yes              | license needed  | online          |
| CPCat [11][12] | USA               | EPA                                      | +43,000    | yes            | yes              | free            | open access     |

3. Toxicity tools

There is an ever increasing concern about the toxicity of chemicals and their effects. The United States Environmental Protection Agency, U.S. EPA, started to develop the Design for Environment (DfE) program, to support the evaluation of the added value, in terms of toxicity, of chemicals replacement and, subsequently, several other tools with similar objective appeared. Toxicity tools provide the potential to identify chemicals or materials that are of concern, regulated or not yet regulated [13][14]. Table 2 summarizes a non-exhaustive list of toxicity tools that could be applied to assess cement-based materials and their components.

Some of the presented tools apply Green Screen method to identify toxicity hazard levels. Green Screen method is divided into two processes: Green Screen List Translator (GSLT) and Green Screen full assessment. Both of them start to characterize the hazard levels as very high (vH), high (H), medium (M), low (L) or very low (vL) [15]. Green Screen assessment assigns, to each parameter, a hazard level using data from scientific literature, standardized tests, analogs, and models. The quality of this assignment is characterized by a confidence level depending on data quality or analog strength (low or high confidence).

GSLT returns the highest hazard level assigned by the most authoritative lists that are characterized by high confidence.

4. Certifications and labels of CBM

Table 3 briefly presents some environmental certifications and labels with toxicological criteria that are already applied to CBM. All labels and certifications referred are voluntary and third-party verified, allowing a transparent process for their award.
### Table 2. Toxicity tools

| Tool                                      | Focus                  | Impact                  | Year | Data                     | Method                      | Sponsor or company          | Cost                                      |
|-------------------------------------------|------------------------|-------------------------|------|--------------------------|-----------------------------|-----------------------------|------------------------------------------|
| Chemical Hazard Data Commons              | x                      | x                       | x    | x                        | x                           | Pharos and Data Commons     | HBN expense varies by chemical or requires annual subscription free |
| P2OASys [16]                              | x                      | x                       | x    | x                        | various                    | The Toxics Use Reduction Institute | free                                     |
| QCAT [13]                                 | x                      | x                       | x    | x                        | various                    | Washington Dept. of Ecology | free                                     |
| Scivera Lens [17][18]                     | x                      | x                       | x    | x                        | x                           | Scivera LLC                 | expense varies by chemical or requires annual subscription license needed |
| Toxnot [19]                               | x                      | x                       | x    | x                        | x                           | Toxnot                      | Toxnot license needed                  |

1 Globally Harmonized System of Classification and Labelling of Chemicals (see section 5).

### Table 3. Certifications and labels of CBM

| Certifications / labels         | Owner / sponsor               | Country                              | Year |
|--------------------------------|--------------------------------|--------------------------------------|------|
| Blue Angel [20]                | BMU1                           | Germany (also used in most of EU, Australia, Japan, Korea, New Zealand, Norway, USA, Switzerland, and South Africa) | 1978 |
| BRE Global Certified Environmental Profiles [21] | BRE Group                      | UK (also used in the Czech Republic, Denmark, France, Netherlands, and in the USA) | 1999 |
| Cradle to Cradle Certified [22] | Cradle to Cradle Products Innovation Institute | Netherlands (also used in France, Germany, Spain, Switzerland, and in the USA) | 2005 |
| Ecoplatform EDP [23]           | 20 founding members including AENOR2 and IBU3 | Belgium (recognized in Europe) | 2014 |
| Greenguard [24]                | UL Environmental               | USA (used in 37 countries, including Portugal) | 2001 |

1 Federal Ministry for the Environment, Nature Conservation, and Nuclear Safety

2 Spanish Association for Standardisation and Certification

3 Institut Bauen und Umwelt e.V.

### 5. Approach for the toxicity evaluation of CBM

To better understand the proposed approach, it is important to take into account some aspects presented in the following subsections.

#### 5.1. GHS, REACH, CLP, and POP Regulations

Globally Harmonized System of Classification and Labelling of Chemicals (GHS) is a non-legally binding international system that harmonises criteria for communication elements and classifying hazardous chemical substances and mixes using their physical, environmental, and health and safety information (include production, handling, transport, and use stages) [25].

REACH Regulation (Registration, Evaluation, Authorisation and Restriction of Chemicals) intends to improve the protection of human health and the environment from the risks that can be posed by the chemical substances that are produced and marketed in the European Union. This Regulation defines for EU companies the steps needed to collect information on the properties and assess the risk of chemical substances. REACH also avoids duplication of information, allowing companies to work...
together to define chemicals information, and intends to help the market to use safer substances to the detriment of substances with higher risks.

In order to allow free movement of substances and mixes between the European Union Member States, ensuring consistency and safeguarding the health and the Environment, a new classification, labelling and packaging (CLP) system was issued in Regulation 1272/2008 [26][27]. CLP Regulation safeguards that workers and consumers in the EU are unambiguously aware of the hazards presented in chemicals by defining hazard statements [28][27]. It was enforced on 20 January 2009 and is directly applicable to all industrial sectors in the EU. This regulation modified the Dangerous Substances Directive (67/548/EEC) [29], the Dangerous Preparations Directive (1999/45/EC) [30] and the REACH Regulation 1907/2006/EC [31] since 1 June 2015. CLP is also based on the Globally Harmonized System (GHS) allowing the classification and labelling of substances and mixes using pictograms and signal words for every hazard class and category. Physical, health, environmental and additional hazards are the hazard classes covered by this regulation [32][27].

With the objective of protecting the Environment and the human health from persistent organic pollutants (POPs), regulation 850/2004/EC [33] was published. POPs are chemical substances that can bioaccumulate and persist in the environment leading to a risk of causing adverse effects to Environment and human health. Afterwards, the amendments commission regulation 757/2010/EC [34] and 756/2010/EC [35] was enforced in 2010, including more dangerous chemical substances banned or with high restrictions in the EU [36].

5.2. Laboratory assessment of CBM’s toxicity

There are two different methodologies to estimate the toxicity: chemical analyses and biological tests. Technical report CEN/TR 17105:2017 [37] presents the biological approach to analyse construction materials ecotoxicity and outlines that, for complex materials of unknown composition, the chemical analyses may not be the most appropriate means of estimation of toxicity for individual substances. When a chemical analysis approach is applied, a toxicity estimate is achieved by comparing the results from leaching tests with limit values. Conservatively, if the chemical composition (CC) of the eluate is not available, one can consider the CC of the material itself.

For the application of biological toxicity tests, it is necessary, in a first step, to obtain an eluate. For that purpose, technical report CEN/TR 17105 [37] indicates the use of leaching tests according to CEN/TS 16637-2 [38] or CEN/TS 16637-3 [39], although other tests can be used. The first technical report corresponds to a horizontal dynamic surface leaching test and the second one to horizontal up-flow percolation test. CEN/TS 16637-2 [38] is more suitable for monolithic construction materials and the CEN/TS 16637-3 [39] is more appropriate, for example, to road bases aggregates analysis. In a second step, it is necessary to expose, at least, organisms from three different trophic levels to a diluted eluate. The aquatic ecotoxicity, expressed as the effective concentration value that causes the death to 50% of test organisms (EC50), is obtained for the following test species: luminescent bacteria (ISO 11348-3 [40]), algae (ISO 8692 [41]) and Daphnia magna (ISO 6341 [42]).

Since CEN/TR 17105 [37] is very recent, most of the existing studies are based on results of leaching tests carried out according to other procedures.

5.3. Limit values

To assess the toxicity potential, it is necessary to compare the released contents of the relevant substances with the legal limits defined in national or European Union legislation. Council Decision 2003/33/EC [43] defines leaching limit values for waste acceptable in landfills for inert, non-hazardous and hazardous waste at different liquid to solid ratios (L/S). CLP regulation [26] present concentration limits of substances in a mix that triggers a classification of the mix for a particular hazard. These limits are defined by weight percentage of the mixture, in the case of solids.

5.4. Admixtures

According to EN 934-2 [44], admixtures for concrete, mortar and grout cannot be added in a quantity
higher than 5% by mass of the cement content, and are divided into eleven groups, including water reducing/plasticizing, air entraining, and hardening acceleration.

Deutsche Bauchemie is the main association of the manufacturers of construction-chemical products [45] that includes Sika, BASF, Mapei and Weber. One of its state-of-the-art reports from 2016 [46] indicates that admixtures are safe. The reasons why are, among others, that admixtures: are added in very low content; are bound into the cement paste matrix; are negligible or not detectable in hardened concrete; and may act as an anchor group.

5.5. Organic and inorganic compounds
When analyzing the CC eluate results, it is important to know whether the tested material is an organic or an inorganic compound. This is due to the complexity of dissolved organic matter (DOM) that leads to incorrect CC results of the eluate [47].

5.6. Methodology for the toxicity assessment of CBM
In view of the above described information, it is possible to sketch a new approach (Figure 1) to maximize the efficiency of resources by minimizing the number and complexity of toxicity tests. It is important to define that, in case of doubt or any suspicion that some material may have a toxicity level of concern, it is recommended to apply toxicity tests accordingly to subsection 5.2.

After identifying each concrete or mortar constituent, it is important to check whether there is any risk associated with the handling and use of the listed constituents. This type of information is available at GHS, REACH, CLP, and POP regulations. Subsequently, it is essential to predict the effects of the constituents in the mix assuming that they do not interact and compare with the observed values. Such analysis starts to be focused on the material itself but gradually is becoming a more general approach instead of material-oriented. In the absence of reliable data, depending on whether an organic or an inorganic compound is being verified, the chemical characterization of the material or of its eluate will be needed. When analyzing an organic compound, it is not acceptable to exclude the possibility of toxicity hazard if the compound is not rapidly degradable and has the capacity to bioaccumulate. Obtained or available results should be compared with concentration limits values to check the toxicity of each constituent. When an admixture is listed, this constituent is set automatically as non-toxic according to subsection 5.3. As background it is important to have access to several databases, but the specific information that the researcher can obtain always takes priority over available data. Each constituent should be analysed through this approach. At the end, the output should be a list where each constituent and its mixture could be associated to one of three options: “acceptable toxicity level”, “insufficient data”, or “final product/material may have a toxicity concern level”. This classification results from the application of an adaptation of the “summation method” specified in CLP regulation [29].

6. Conclusions
This article was written with the purpose of raising awareness towards the toxicity of CBM. It is important to know what information is already available and the existing standards and regulations that should be applied to know CBM’s toxicity. With the goal of supporting the search for sustainable CBM, existing toxicity tools are identified and a new approach for toxicity evaluation of CBM is presented.

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Figure 1. Approach for the toxicity evaluation of CBM
References

[1] A. Takano, S. Winter, M. Hughes, and L. Linkosalmi, “Comparison of life cycle assessment databases: A case study on building assessment,” Build. Environ., 2014.

[2] E. C. Peereboom, R. Kleijn, S. Lemkowitz, and S. Lundie, “Influence of Inventory Data Sets on Life-Cycle Assessment Results: A Case Study on PVC,” 1998.

[3] ECHA, “European Chemicals Agency,” 2018. [Online]. Available: https://echa.europa.eu/. [Accessed: 08-May-2019].

[4] EPA, “Ecotox - Ecotoxicology knowledgebase,” 2018. [Online]. Available: https://cfpub.epa.gov/ecotox/. [Accessed: 02-Apr-2019].

[5] USEPA, “ToxCast & Tox21 Summary Files from invitrodb_v2,” 2015. [Online]. Available: www2.epa.gov/chemical-research/toxicity-forecaster-toxcasttm-data. [Accessed: 04-May-2019].

[6] USEPA, “Toxicity Forecasting,” 2019. [Online]. Available: www.epa.gov/chemical-research/toxicity-forecasting. [Accessed: 17-Dec-2019].

[7] Toxnet, “Toxicology data network,” 2018. [Online]. Available: https://toxnet.nlm.nih.gov/.

[8] eChemPortal, “The global portal to information on chemical substances,” 2018. [Online]. Available: https://www.echemportal.org/echemportal/index.action. [Accessed: 19-Feb-2019].

[9] HBN, “Pharos,” 2019. [Online]. Available: www.pharosproject.net/. [Accessed: 30-Jan-2019].

[10] Pharos, “Chemical & Material Library (CML),” Tech. Rep. Full Syst. Descr., 2018.

[11] K. L. Dionisio et al., “Exploring consumer exposure pathways and patterns of use for chemicals in the environment,” vol. 2, pp. 228–237, 2015.

[12] EPA, “Learn About the Safer Choice Label,” 2019. [Online]. Available: https://www.epa.gov/saferchoice/learn-about-safer-choice-label. [Accessed: 11-Mar-2019].

[13] A. Stone, “Quick Chemical Assessment Tool - Version 2.0,” Tech. Rep. Washing. State Dep. Ecol., 2016.

[14] GC3, “Retailer Tools for Safer Chemistry,” 2019. [Online]. Available: https://greenchemistryandcommerce.org/resources/retailer-tools/retailer-tools/. [Accessed: 12-Mar-2019].

[15] Data Commons, “Overview of GreenScreen Method,” 2019. [Online]. Available: https://commons.healthymaterials.net/overview-of-greenscreen-method. [Accessed: 31-Jan-2019].

[16] TURI, “P2OASys Tool to compare materials,” 2018. [Online]. Available: https://www.turi.org/Our_Work/Research/Alternatives_Assessment/Tools_and_Methods/P2OASys_Tool_to_Compare_Materials. [Accessed: 26-Feb-2019].

[17] L. Kenny, S. Tisdale, and C. Robertson, “iNEMI Project on Alternative Materials Assessment,” 2015.

[18] J. H. Allen and A. Dinno, “Leadership in sustainable chemicals policy: opportunities for Oregon,” no. June, 2011.

[19] Sustainable Brands, “Toxnot. ILFI Team Up to Scale Product Transparency,” 2018. [Online]. Available: https://sustainablebrands.com/read/chemistry-materials-packaging/toxnot-ilfi-team-up-to-scale-product-transparency. [Accessed: 02-Sep-2019].

[20] Blue Angel, “What is behind it?,” 2019. [Online]. Available: https://www.blauer-engel.de/en/blue-angel/what-is-behind-it. [Accessed: 01-Apr-2019].

[21] BRE Global, “Environmental Profiles,” 2019. [Online]. Available: http://www.greenbooklive.com/search/scheme.jsp?id=9. [Accessed: 26-Mar-2019].

[22] Cradle to Cradle Products Innovation Institute, “Get Cradle to Cradle Certified,” 2019. [Online]. Available: https://www.c2ccertified.org/get-certified/product-certification. [Accessed: 02-Apr-2019].

[23] U. Pannuti, “Epd & Eco Platform, a successful story,” 2016. [Online]. Available: https://www.epdindia.in/2016/10/13/epd-eco-platform-a-successful-story/. [Accessed: 11-Sep-2019].

[24] SPOT, “Products Catalog,” 2019. [Online]. Available: https://spot.ul.com/main-app/products/catalog/. [Accessed: 01-Apr-2019].

[25] United Nations, Globally Harmonized System of Classification and Labelling of Chemicals (GHS). 2011.

[26] Regulation (EC) No 1272/2008, of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006, vol. 1. 2008.

[27] European Chemicals Agency, “Understanding CLP,” 2019. [Online]. Available: https://echa.europa.eu/web/guest/regulations/clp/understanding-clp. [Accessed: 22-Nov-2019].
[28] EPA, “CLP Regulation (in Portuguese),” 2012.
[29] Council Directive 67/548/EEC, of the 27 June 1967 on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances, 1967.
[30] Directive 1999/45/EC, of the European Parliament and the Council of 31 May 1999 concerning the approximation of the laws, regulations and administrative provisions of the Member States relating to the classification, packaging and labelling of dangerous preparations THE, no. April 1993. 1999.
[31] Regulation (EC) No 1907/2006, of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Re. 2006.
[32] European Commission, “The classification, labelling and packaging of chemical substances and mixtures,” 2019. [Online]. Available: https://ec.europa.eu/environment/chemicals/labelling/index_en.htm. [Accessed: 22-Nov-2019].
[33] Regulation (EC) 850/2004, of the European Parliament and of the Council of 29 April 2004 on persistent organic pollutants and amending Directive 79/117/EEC. 2004.
[34] Commission Regulation 757/2010, of 24 August 2010 amending Regulation (EC) No 850/2004 of the European Parliament and of the Council on persistent organic pollutants as regards Annexes I and III. 2010.
[35] Commission Regulation 756/2010, of 24 August 2010 amending Regulation (EC) No 850/2004 of the European Parliament and of the Council on persistent organic pollutants as regards Annexes IV and V. 2010.
[36] European Commission, “POPs - Persistent Organic Pollutants,” 2019. [Online]. Available: https://ec.europa.eu/environment/archives/pops/index_en.htm. [Accessed: 15-Dec-2019].
[37] CEN, CEN/TR 17105 - Construction products - Assessment of release of dangerous substances - Guidance on the use of ecotoxicity tests applied to construction products. 2017, pp. 1–6.
[38] CEN, CEN/TS 16637-2 - Construction products - Assessment of release of dangerous substances. 2014.
[39] CEN, CEN/TS 16637-3 - Construction products - Assessment of release of dangerous substances - Part 3: Horizontal up-flow percolation test. 2016.
[40] CEN, ISO 11348-3 - Water quality - Determination of the inhibitory effect of water samples on the light emission of Vibrio fischeri (Luminescent bacteria test) - Part 3: Method using freeze-dried bacteria, vol. 2007, no. 911002522. 2007.
[41] ISO, “ISO 8692 - Water quality - Fresh water algal growth inhibition test with unicellular green algae,” vol. 2008, 2012.
[42] ISO, ISO 6341 - Water quality - Determination of the inhibition of the mobility of Daphnia magna Straus (Cladocera, Crustacea) - Acute toxicity test, vol. 2012. 2012.
[43] Council Decision 2003/33/EC, of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC. 2003.
[44] EN 934-2:2009, Admixtures for concrete, mortar and grout. Part 2: Concrete admixtures - Definitions, requirements, conformity, marking and labelling.
[45] Deutsche Bauchemie, “71 Years of Deutsche Bauchemie,” 2019. [Online]. Available: https://deutsche-bauchemie.com/home. [Accessed: 08-Nov-2019].
[46] Deutsche Bauchemie, Concrete Admixtures and the Environment. 2016.
[47] A. Nebbioso and A. Piccolo, “Molecular Characterization of Dissolved Organic Matter (DOM): a critical review,” no. September, 2013.