Environmental impact assessment for the recycling of phosphogypsum in alternative cementitious binders

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1. Introduction

Phosphogypsum (PG) is a by-product from the fertilizer production with a relatively low worldwide recycling rate owing to the presence of remnants of phosphoric acid, fluorides, metals, rare earth elements, organic substances and enhanced concentrations of naturally occurring radionuclides. The annual production amounts to about 215 million ton of which about 60-80 million ton is being recycled and the amount of PG at landfills is expected to reach 7-8 billion ton by 2040. [1]

Mainly owing to the large volumes in which OPC (ordinaire Portland cement) is produced, its use is accompanied by the exploitation of large volumes of natural resources, a water- and energy- intensive production and an important carbon footprint amounting to about 0.8 t CO_2 per ton clinker, almost 10% of the global CO_2 emissions which is primarily linked to the combustion of fuels and the decomposition of limestone. Therefore, alternative cementitious binders such as alkali-activated materials (AAMs) are under development that can enable the recycling of important fractions of mineral residues while using less energy-intensive production processes, allowing a significant reduction of CO_2 emissions and enabling an efficient immobilization of hazardous components. [2]

Phosphogypsum can be used to replace gypsum in various types of cementitious binders, concretes and mortars. However, its use can influence the mechanical properties of the matrix. For example, the introduction of phosphogypsum in concrete can introduce a delay in the setting time, a reduction in the workability of the concrete mix, a reduced mechanical strength of cements, mortars and concretes. The introduction of PG can result in negative effects on the drying shrinkage and the soundness expansion. The reported effects can depend on the type of PG that is used and the type of cementitious binder that is produced and more systematic research is required to evaluate the occurrence of these defects. The delay in the setting time is not in all cases a disadvantage, since PG could be used as a setting retardant. However, many of the other issues need to be addressed before recycling becomes possible. Washing steps using tap water, sulfuric acid or milk of lime can be introduced to target the impurity content of PG but in that case for example the produced waste water needs to be treated with a water treatment facility leading to increased water use. To increase the strength, a calcination pretreatment step can be used which comes with a thermal cost. By adding mineral or glass fibers, the flexural strength, freeze/thaw and water resistance of PG based cementitious binders and concretes could be improved. The density of PG is lower relative to the sand and cement that it replaces which provides options for producing lightweight bricks or plasters. [3]

The aim of the current research initiative is the development of alternative types of cementitious binders such as alkali-activated materials (AAMs) and ettringite binders that are then tailored to the properties of phosphogypsum originating from landfills and active production sites. Ideally, the incorporation of phosphogypsum provides an added value for the matrix and the recycle option includes an appropriate pretreatment step to deal with the heterogeneous presence of problematic (trace) elements that can -as discussed- negatively influence the properties of the cementitious binder matrix. The first phase of the project, for which the results are presented in the current contribution, aims to achieve a more systematic understanding of the impact of the variations in the (trace) elemental composition and their impact on the mechanical, radiological and environmental properties of the newly produced AAM and ettringite binders.

2. Materials and methodology

Alkali-activated and ettringite-based binders were developed via a combination of IAEA reference PG (reference material nr 434) phosphogypsum with respectively ground granulated blast furnace slag (GGBFS) and ladle slag (LS) as described in [4] and [5]. The mechanical and physico-chemical properties (strength, mineralogy, microstructure, porosity…) of the new binders were studied. An environmental impact assessment was implemented that focusses on the leaching analysis of various contaminants of potential concern (metals and naturally occurring radionuclides) using an up-flow percolation test following CEN/TC 16637-3 [6]. The evaluation of the presence of naturally occurring radionuclides from the ^{238}U and ^{232}Th decay chain was realized by gamma spectroscopy using a HPGe detector and radon exhalation/emanation measurements using the procedure described in [4].

3. Results and discussion

3.1 Mechanical and physico-chemical analysis

The influence of 10 wt% IAEA reference PG addition in GGBFS based AAMs was compared to GGBFS based AAMs without PG. Dependent on the activator used, the compressive strength of AAM samples incorporating 10 wt% was reduced (for example by 33.1% at 28 days when using a sodium silicate activator) or improved (for example up to 89,0% at 28 days) when using a sodium hydroxide activator. For each of the synthesized binders, PG completely dissolved taking part in the hydration product formation. For each sample a detailed mineralogical analysis was performed. The strength reduction was observed for samples that displayed a lower amorphous content. A more detailed evaluation of the impact of PG addition on the AAM, strength development and final matrix properties in function of the activator used can be found in [7]. For ettringite binders, when replacing gypsum by reference PG (30 wt%) a 60% increase in compressive strength is observed. [7] Additionally, the impact of using different types of PG with a very different elemental composition relative to reference PG on the mechanical properties is investigated dependent of the type of PG leading to an increase or decrease in compressive strength.

3.2 Radiological evaluation

The measured activity concentration of the different radionuclides from the ^{238}U and ^{232}Th are lower than 1000 Bq/kg and the activity concentration of ^{40}K is lower than 10000 Bq/kg for all investigated types of PG and, therefore, the byproducts are not considered as Naturally Occurring Radioactive Materials (NORM) following the Euratom Basic Safety Standards (EU-BSS). In accordance with the EU-BSS the activity concentration index (ACI) was used to evaluate the use of PG in concrete. The ACI needs to be below 1 and this criterion was met for incorporation of 10 wt% reference PG in AAM based concretes and 30 wt% reference PG in ettringite-based concretes. For the incorporation of reference PG, the radon emanation factor of alkali activated pastes using different molarities (2 – 6 M) of sodium silicate and sodium hydroxide activators was lower than 3.8 ± 0.6 % while a much higher emanation factor (50,7 ± 2.9 %) was found for ettringite-based pastes. This large difference cannot be interpreted purely in terms of the increased PG wt%. The significantly increased radon exhalation is attributed to the water-filled needle-like structure of ettringite. A more detailed discussion of results obtained for reference PG can be found in [7] and these results are compared with other types of PG. The AAMs based on PG provide a more efficient radon immobilization matrix in comparison to ettringite binders.

3.3 Leaching assessment

The leaching assessment is focused on the leaching of naturally occurring radionuclides and non-radiological elements. For GGBFS and reference PG (10 wt%) based AAMs a very strong retention of ^{238}U, ^{226}Ra, ^{210}Pb and ^{228}Ra was observed while for ^{232}Th and ^{40}K the release is dependent on the used activator. 19,9 ± 2,0% release (the highest release) of ^{232}Th was observed for a sodium silicate activator while 75,8 ± 14,1% release (the highest release) of ^{40}K was observed for a sodium hydroxide activator. ^{40}K demonstrated a similar leaching behavior as the elements Na and S where releases of respectively 59-88 % and 71-87% were observed. The leaching behavior can be interpreted in terms of the formation of several leachable and non-leachable complexes and is strongly related to the porosity. Ladle slag and reference PG (30 wt% PG) based ettringite based mortars demonstrated a very high immobilization potential at lab-scale level since the immobilization degree for several PG related contaminants (Ce, Mn, P, Ti, Fe and Mg) was nearly 99-100 % and more than 90 % for Sr. The ettringite based mortars demonstrated particularly low micro-and mesoporosity in comparison to OPC (1.5-25 m2/g) their specific surface areas were relatively speaking 20-30 times lower. In the current contribution, the results obtained for IAEA reference PG (described in more detail in [7]) are compared to results for other types of PG.

4. Conclusion

Step by step, more systematic research is implemented to evaluate the use of PG in cementitious binders. The current study demonstrated the advantages and limitations of using PG in AAMs and ettringite binders. Ettringite binders demonstrate a good immobilization potential for several trace elements but the radon exhalation can be increased. A lower radon release is observed for AAMs but the added value of incorporating PG in the binder needs further research. From the performed experiments it is clear that dependent of the elemental composition of PG there can be an important difference in properties between the synthesized AAMs and ettringite binders.

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