

Assessing, Understanding and Unlocking Supplementary Cementitious Materials

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Received: 16 June 2016 / Accepted: 08 July 2016 / Published online: 16 August 2016

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Abstract

The partial replacement of Portland clinker by supplementary cementitious materials (SCM) is one of the most popular and effective measures to reduce both costs and CO₂ emissions related to cement production. An estimated 800 Mt/y of blast furnace slags, fly ashes and other materials are currently being used as SCM, but still the cement industry accounts for 5-8% of global CO₂ emissions. If no further actions are taken, by the year 2050 this share might even rise beyond 25%. There is thus a clear challenge as to how emissions will be kept at bay and sustainability targets set by international commitments and policy documents will be met.

Part of the solution will be a further roll-out of blended cements in which SCMs constitute the main part of the binder to which activators such as Portland cement are added. Since supply concerns are being raised for conventional high-quality SCMs it is clear that new materials and beneficiation technologies will need to step in to achieve further progress. This paper presents opportunities and challenges for new SCMs and demonstrates how advances towards more powerful and reliable characterisation techniques help to better understand and exploit SCM reactivity.

Keywords: Supplementary Cementitious Material; Pozzolan; Blended Cement; Beneficiation; Activation

1 The sustainability challenge

The cement of the future, whether Portland or else, will be blended with tailored residues from other industries. At present, blended Portland cements containing one or more supplementary cementitious materials (SCMs) already make up the large majority of produced cementitious binders [1]. In 2010, the global clinker factor, the average Portland clinker fraction in the final cement, was estimated at 0.77 [2]. Considering a global 2015 cement production of 4200 Mt [3], this corresponds to at least 800 Mt of SCMs used in cement and concrete. To meet a growing demand for cement and concrete and at the same time reduce CO₂ emissions and exhaustion of primary resources, cement producers are looking at ways to use more SCMs without compromising performance and durability. If no actions are taken the share of cement production on global CO₂ emission is likely to increase substantially from 5-8% to 25% or more by 2050 [4]. With limited supplies of high-quality SCMs such as blast furnace slags (300-360 Mt/y) [5], future CO₂ emission reductions will need to depend on an expanded use of other SCMs such as coal combustion fly ashes [6], or natural pozzolans [7] and thermally activated clays [8]. Moreover, restructuring of the energy market towards renewables and increased recycling of energy-

intensive materials such as metals will lead to locally declining supplies of conventional SCMs (blast furnace slag, fly ash) [9]. New SCMs will therefore need to step in. Finally, the rising societal pressure towards sustainable waste management and resource efficiency in a more circular economy will keep on driving future expansion and diversification of SCM use, both in combination with Portland cement or in upcoming other cementitious materials.

Major technical barriers in the development of blended cements are usually related to physical or chemical incompatibilities between the SCMs and the (Portland) cement or activator. Common incompatibility issues that lead to unacceptable or undesirable properties are given in Table 1. In some cases these problems can be solved by applying physical or chemical pre-treatments or by introducing additives to the mix. Affordable physical treatments are applied quite commonly, for instance by fine grinding [10] or removal of unburnt coal from coal combustion fly ashes [11]. More costly chemical treatments or additives often require additional incentives, such as recovery of other valuable materials (e.g. metals), new functionality (e.g. self-compacting concrete), avoidance of landfilling taxes or important environmental impact reductions. In this respect, the assignment of

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environmental impacts can be a subject of controversy. For instance, once a residue becomes a useful by-product (e.g. blast furnace slag) it may be allocated part of the environmental impact of the related industrial process [12].

A large and steadily growing body of research papers, conferences and RILEM technical committees on the SCM topic clearly demonstrates a global interest in blended

cements. On the one hand this common effort has resulted in successful applications for a wide range of materials. On the other hand, for an even larger number of potentially interesting materials, it has demonstrated one or more technical challenges (cf. Table 1). An overview of the main investigated material types and their properties is given in Table 2.

Table 1. Challenging SCM properties for blended cements

| Physical incompatibility | Effect on concrete properties | Contingency |
|---|---|--|
| Very high fineness | Excessive water demand | Superplasticisers, thermal treatment (sintering) |
| Insufficient fineness | Lowered performance | Grinding |
| High water absorption (porous components) | Excessive water demand | Selective removal, grinding,... |
| Intense colour (red, black, brown...) | Undesirable colour change | Selective removal of coloured components, redox treatments |
| Chemical incompatibility | | |
| Low reactivity | Low early strength | Activators, grinding, thermal activation |
| Expansive components (CaO, MgO, Al, ...) | Volume instability, cracking, pop-outs | Maturation by hydration, carbonation, oxidation... |
| Corrosive components (Cl, ...) | Corrosion of steel reinforcement | Cl removal (washing), alternative/no reinforcement |
| Durability impairing components (soluble alkalis, sulfate, ...) | Long term expansion/cracking, efflorescence | Wet chemical pre-treatment |
| Environmental quality | Leaching of contaminants | Immobilisation/removal by beneficiation pre-treatments |

Table 2. Overview of materials used or considered as SCMs: chemical composition, volume estimates and comments regarding application as SCM.

| Material | Chemistry | Volume est. (Mt/y) | In Use | Comments |
|-------------------------------|-------------------|--------------------|--------|---|
| Blast furnace slag | Ca-Si-Al | 300-360 | Y | Nearly fully used, latent hydraulic |
| Coal fly ash – Si rich | Si-Al | 600-900 | Y | Subject to limitations on carbon content, reactivity |
| Coal fly ash – Ca rich | Si-Ca-Al | 100-200 | Y | Subject to limitations on C, CaO, MgO content; latent hydraulic |
| Natural pozzolans | Si-Al | 75 | Y | Large variety/variability, often high water demand |
| Silica fume | Si | 1-2.5 | Y | Used in high-performance concrete |
| Calcined clays | Si-Al | 2-3 | Y | Metakaolin performs best, often high water demand |
| Limestone | CaCO ₃ | 300 | Y | Cementitious contribution in combination with reactive aluminates |
| Biomass ash | Si | 100-140 | N | Competition with use as soil amendment, high water demand |
| MSWI bottom ash | Si-Al-Ca | 30-60 | N | Expansive and corrosive components, leaching issues |
| Steel slag | Ca-Si-Fe | 170-250 | N | Various types, can contain expansive components (CaO) or leachable heavy metals (Cr,...). Low reactivity. |
| Copper slag | Fe-Si | 30-40 | N | Low reactivity, leaching of heavy metals, more research needed |
| Other non-ferro slag | Fe-(Si)-(Ca) | 5-15 Mt/y each | N | Low reactivity, leaching of heavy metals, more research needed |
| Bauxite residue | Fe-Al-Si | 100-150 | N | High alkali content, low reactivity, colour |
| Waste glass | Si-Na-Ca | 50-100 | N | Glass recycling preferable, high alkali content |

Many materials can be added to cement in modest amounts (up to 10-15%) without significant performance loss. At these low replacement levels filler effects can easily compensate for dilution effects, even in case of largely inert materials such as quartz powders [13]. To reach the desired higher replacement levels (beyond 30%) triggering SCM reactivity is key. Identifying the parameters that control SCM reactivity in blended cements is not trivial due to the often complex interplay of reactions. The purely empirical testing approach focusing on macroscopic performance has delivered a quite fragmented chemical understanding of SCM reactivity, even for widely used blastfurnace cements [14]. Analytical, more fundamental approaches have made considerable progress as of lately, as for instance demonstrated by the successful application of equilibrium thermodynamics in predicting hydrate assemblages of various blended Portland cements [15]. However, more

effort is required to further establish reliable test systems and models that can link SCM properties and reactivity in cementitious systems. This letter offers a vantage point to some of the latest advances in assessing and understanding SCM reactivity and gives perspectives on unlocking the highly needed new SCMs of the future.

2 Assessing SCMs: new developments in characterisation

Since most SCMs are by-products from other processes their quality as SCM has traditionally been subordinate to the efficiency of the main industrial activity. This has often resulted in situations of sub-optimal SCM quality and considerable variability between sources and over time. The

complexity of many, both new and existing, by-product materials poses a clear challenge to existing standards and analytical techniques that often fail to explain marked differences in behavior.

The complexity of SCMs is related to their often multi-component nature, of which one or more amorphous materials are the reactive components of interest next to a range of non-reactive materials as exemplified by electron microscopy data on a class C fly ash in Figure 1 [16]. Recent developments in EDX detector technologies have opened up new avenues for image analysis based on multi-element mappings. Adapted algorithms have been developed to detect and quantify different phases in raw SCMs, and have been successfully applied to follow the reaction of each in both model systems [17] and cement pastes [18]. This approach delivered unprecedented detail in the characterisation and description of reaction kinetics of compositionally heterogeneous SCMs such as fly ashes. Drawbacks are that the technique is inherently limited by the spatial resolution of the EDX interaction volume (1-2 μm) and that the sample preparation requires expertise and resources. The application of the technique may very well find its way to many new systems (slags, ashes, etc.) [19], provided that there are clear chemical contrasts between reactive/unreactive and reacted/non-reacted materials.

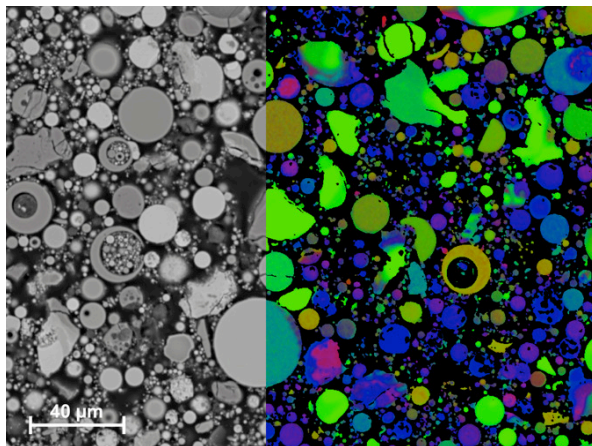


Figure 1. Image analysis based on BSE and EDX mapping data used to segment a class C fly ash in compositionally different populations. More Ca-rich fly ash particles (blue) are more reactive than Si-rich particles (green). Modified after [16].

X-ray powder diffraction (XRD) is one of the most commonly applied characterisation techniques in cement chemistry. The last decade has seen the spread of the Rietveld method to quantify the crystalline phase composition of Portland cement. One important limitation of the classical Rietveld method is that it requires starting crystal structure models to calculate and fit a simulated XRD scan to the experimental scan. Unidentified or X-ray amorphous phases are thus disregarded in the calculation of the composition. This problem is partially overcome by introducing the measurement of reference materials, either as internal standard mixed into the sample, or as separately measured external standard. This way the sum of all amorphous and/or

unknown phases can be back-calculated. A new hybrid quantification method called PONKCS (Partial Or No Known Crystal Structure) goes one step further and combines Rietveld refinement for crystalline phases with previously calibrated profiles for amorphous phases [20]. The method was first introduced for in-situ cement hydration studies to account for the formation of C-S-H [21] and was subsequently applied to blended cements [22, 23]. Promising results were reached for anhydrous blends containing multiple amorphous phases as in Figure 2. For hydrated cements reports are mixed, extensive peak overlap between an evolving C-S-H profile and blast furnace slag may cause parameter correlation and bias of the results if too few constraints can be built into the analysis code. In systems that show less overlap between reactants and products the results show satisfactory correspondence with independent measurements. Drawbacks of the method are the need for careful calibration of the component materials and the relatively high detection limits of 5-10 wt.% [23]. Moreover, typical XRD accuracy intervals of 2-3 wt.% translate into quite large uncertainties in the quantification of the degree of reaction of SCM fractions. Further progress is possible through a deeper understanding and contingency of parameter correlation in the fitting.

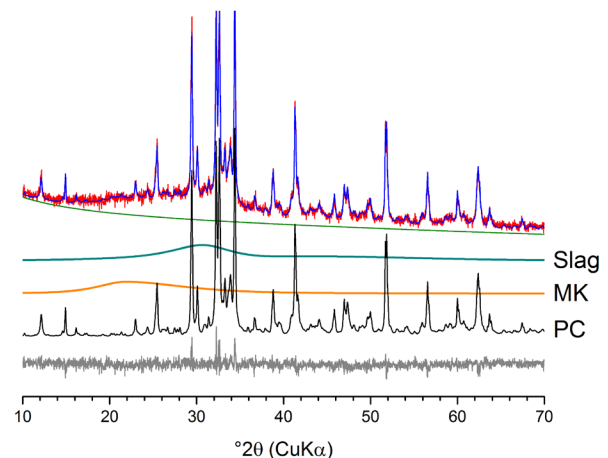


Figure 2. Decomposition of the XRD pattern of a blend of 25% blast furnace slag (Slag), 25% metakaolin (MK) and 50% Portland cement (PC) blend. Quantification of the individual amorphous fractions by the PONKCS method.

In more applied environments such as production or quality control it is not practically possible to carry out a detailed SCM characterisation. More direct screening methods are then required to assess the quality of a potential SCM. Standard practice is to carry out compressive strength testing of blended cement mortars to determine the strength activity index. In case of blended cements this has the important drawback that many SCMs react slowly and clearly contribute to the strength development only at ages of 28 or 90 days. In response, more rapid chemical tests have been developed. These tests track properties of model mixes containing the SCM and one or more reactants that trigger a pozzolanic or hydraulic reaction. Properties that are commonly followed are $\text{Ca}(\text{OH})_2$ consumption, bound water,

sample volume, heat flow and solution composition. A common flaw of these methods is that correlation with compressive strength development is not necessarily straightforward for a wide range of SCMs [24]. Recent efforts have therefore focused on establishing more relevant, reliable tests that deliver an assessment of the SCM contribution to strength development rapidly. One such development successfully related the heat release of model mixes of calcined clays, portlandite and alkali sulfate to the strength development of mortar bars containing the corresponding 30% calcined clay blended cements (Figure 3) [25]. Equally promising correlations for similar systems were established for other properties of model systems such as bound water content as well. Critical evaluation and further development of rapid, reliable and relevant SCM reactivity tests will be carried out in an extensive experimental programme coordinated by the recently created RILEM TC-TRM (Tests for Reactivity of supplementary cementitious Materials).

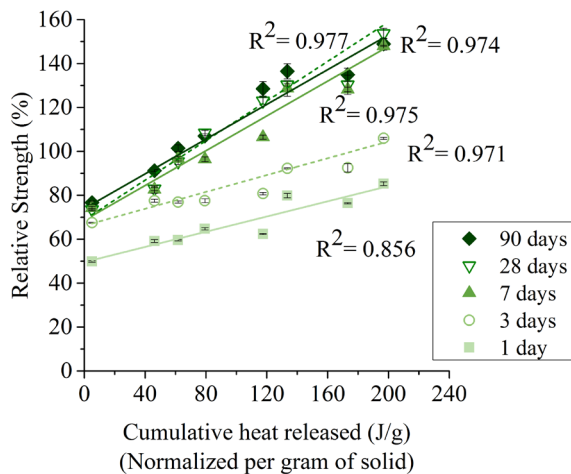


Figure 3. Plot of cumulative heat release at 1 day in $\text{Ca}(\text{OH})_2$ – calcined clay model systems cured at 40 °C versus the relative strength of a calcined clay blended cement mortar (30% replacement) prepared and tested according to EN 196-1 at 1 to 90 days of hydration. Beyond 1 day of hydration there is a close correlation between the reactivity of the calcined clay and the contribution to compressive strength. Modified after [25].

3 Understanding SCMs: recent insights into reactivity

The cement reaction mechanism is a through-solution process that can be divided into two balanced parts occurring simultaneously: the dissolution of the anhydrous reactants (clinker, SCMs, precursors) and the precipitation of the reaction products. While predictions of SCM blended cement hydrate assemblages has greatly benefitted from recent advances in thermodynamic modelling, only very little data on dissolution kinetics of even common SCMs such as blast furnace slag is available. In response, recent simple dissolution experiments have clearly shown that SCM dissolution rates in alkaline solutions are 2-4 orders of magnitude lower than C_3S and C_2S [26-28]. This strokes well

with the generally lower reactivity of SCMs. The dissolution experiments showed that SCM reactivity can be rationalized following well-known concepts from glass chemistry such as available reactive surface area and glass polymerization [18, 26, 29]. Interestingly, dissolution experiments have also shown strong rate dependencies on solution composition, i.e. pH, solution saturation, and presence of activators or inhibitors such as dissolved Al species [26, 30]. These insights are instrumental in better understanding SCM reactivity and can be exploited by engineering solid SCM properties and/or solution composition.

Coupling between dissolution and precipitation is key to SCM reactivity in a variety of systems. Here the solution acts as reaction medium and plays a central role. In most cementitious systems it can be assumed that the solution composition is set by the reaction product assemblage and directly drives dissolution kinetics. Adjusting the product assemblage is an indirect but effective way of activating SCMs. Applying this *solution controlled dissolution* concept to a number of diverse cases puts SCM activation and reactivity in a different light:

Activation of (Al-rich) blast furnace slag cements by calcium sulfate in supersulfated cements. The addition of a Ca-sulfate source results in the precipitation of ettringite as major product [31]. Because of the low solubility of ettringite, the Al activity in the pore solution is much reduced and the slag dissolution rate is enhanced.

Adding carbonates to blended cements leads to the formation of monocarboaluminate and ettringite, again reducing Al activity in solution and thus increasing the dissolution of SCMs such as metakaolin. This feedback mechanism can at least partly explain the higher reaction rate of metakaolin in ternary limestone-calcined clay blended cements compared to binary calcined clay blended cements [32].

The formation of hydrotalcite reaction products during reaction of Mg-rich blast furnace slag enables to keep dissolution rates high. This contrasts with the previously known very low dissolution rate of Mg-silicate minerals at high pH. In the case of Mg-silicates this is explained by slowly dissolving Mg-O complexes/layers formed at the glass surface at pH above 12 [33]. In the case of slag, the availability of Al enables the precipitation of hydrotalcite-like phases which reduces solution saturation. This increases dissolution rates as demonstrated for nuclear glass in the case of smectite [34] and M-S-H [35] precipitation. Moreover, this may help to explain much lower reactivities of Mg-rich, Al-poor steel slags [36].

Calcium aluminosilicate glass dissolution is strongly enhanced at high pH. The increasing glass dissolution rates with pH correlate with the dissolution process becoming congruent. At high pH the glass decomposition rate becomes similar to the rate of outward diffusion of cations that produces a leached layer at lower pH. In consequence, the recombination of silica and alumina in the leached layer to form a passivation layer is avoided and further dissolution can proceed unhampered [37].

The glass composition itself exerts a dual effect on glass reactivity. On the one hand higher contents in alkaline earths weaken the aluminosilicate network, while on the other hand dissolved alkaline earths increase the solution pH, which then again increases dissolution rates. This positive feedback mechanism between the SCM and the solution explains how in closed systems differences in intrinsic glass dissolution rates become strongly enlarged.

Sustained dissolution will raise solution ionic concentrations and finally give rise to hydrate precipitation. Nucleation and growth of hydrates lowers ionic concentrations in solution and results in renewed dissolution that keeps pace with hydrate growth [38]. Precipitation of reaction products may thus lead to a resumption of dissolution. This mechanism is particularly important in the case of calcium-aluminosilicate SCMs where dissolution rapidly leads to a high pH and massive precipitation of lowly soluble calcium (alumino) silicate hydrates. The coupling of dissolution and precipitation thus increases the overall reaction rate and renders the SCM hydration reaction self-sustainable. This mechanism lies at the base of the so-called hydraulic behavior, i.e. the auto-catalytic formation of an insoluble cementitious binder by the reaction of water with clinker minerals or Ca-rich SCMs such as blast furnace slags. At the same time it becomes clear why pozzolanic materials require a source of calcium to react to a significant extent. The precipitation of calcium aluminate or silicate hydrates enables to maintain the solution undersaturated towards the pozzolan and thus drives further dissolution.

4 Unlocking SCMs by beneficiation and activation

As illustrated in the previous sections, an extension of cement reaction mechanisms with kinetic aspects such as in the coupled dissolution and precipitation model is instrumental in rationalizing SCM reactivity. Moreover, these insights can also be used to develop new binders, or to tailor waste streams into SCMs and thus unlock much needed resources for a more sustainable cement industry. An adequate response to this challenge will inevitably need to come from local synergies between residue/SCM/precursor suppliers and binder producers. Tailored binders based on locally available resources will need to rely on flexible “toolboxes” that enable to combine a sweep of beneficiation and activation treatments.

From the list of secondary resources in Table 2 many materials require a beneficiation pre-treatment before they can be used in combination with a classical Portland cement binder. In beneficiation treatments potentially problematic compounds such as free lime, carbon or leachable contaminants are either removed or converted into harmless compounds. For instance removal of (coarse) carbon from coal combustion fly ashes is possible by tribo-electrostatic treatments [11], while pre-hydration/washing and carbonation are common ways to reduce free lime, chloride and metal leaching of MSWI bottom ashes [39, 40]. Classical magnetic and density separation treatments may

be used to separate reactive and non-reactive fractions in complex residues. Also more advanced technologies based on electrofragmentation or microwave heating are being investigated as a means to upgrade residues to SCMs [41-43]. Finally, a range of pyrometallurgical treatments, such as (flash) calcination [44], incineration or plasma treatments [45] are being considered as means to recover valuables (e.g. molten metals), remove undesirable components (e.g. VOCs) and render the matrix material more suitable as resource for binders. Obviously, there should be clear value in the materials, be it as fuel, source of valuable (metal) components or avoided landfill tipping cost, before costly treatments can be considered.

Activation by grinding is commonly applied to condition SCMs [46, 47]. Co-grinding with Portland clinker at cement plants is most common in Europe, blending at concrete batching plants is more common in North America [48]. Since pozzolanic reactions are strongly enhanced by temperature (higher activation energy) [49], many pre-cast concrete production plants use curing at elevated temperature (40-80°C) to speed up production.

Simultaneously, a large body of research is very actively looking at activating SCMs in ways other than blending with Portland cement. Alkali-activation with alkali hydroxides or alkalisilicates has attracted most attention in this area [4], but may actually represent just one of multiple options. The use of tailored residues as SCM in calcium sulfoaluminate cements [50], as raw material for mechanically activated cements [51] or as precursor for carbonate-bonded materials [52] may well represent viable options depending on local availability of resources and infrastructure.

Conclusions

Future economies will see efficiency measures in material use and re-use for energy-intensive products such as cement. This will involve tangible shifts in construction design and practice, but will also intensify links between waste management and construction material production. It is clear that the present impetus towards less carbon-intensive and more circular economies are setting the scene for a diversified future of localized sustainable binders. In an innovation-friendly environment the many possible combinations of materials and treatments will see cements other than Portland emerge and gain acceptance. However, it should be noted that in the development of each new cementitious binder costs and benefits will need to be carefully balanced. Dedicated and sustained research, development and engineering efforts will be required to prove new materials at all levels ranging from mechanical performance over technical durability, environmental quality to overall sustainability in order to finally bring viable ideas into practice. In this respect the identification of new opportunities will strongly benefit from advances in characterisation methods and a more generalized understanding of reaction mechanisms for cementitious binders.

Acknowledgement

The support and advice of Karen Scrivener, Nele De Belie and Jan Elsen were greatly appreciated. Much of this work greatly benefitted from discussions with peers in the RILEM TC-SCM and TC-TRM committees and with many colleagues at VITO, EPFL, UGent and KU Leuven.

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