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VALORISATION OF WASTES BY ALKALI-ACTIVATION - PROGRESS, OPPORTUNITIES AND PITFALLS

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Introduction

Alkali-activation, as a pathway by which waste materials can be converted to cementitious binders, is rapidly gaining both academic and practical interest worldwide.¹⁻⁵ The combination of a solid aluminosilicate precursor, supplied in powder form, with an aqueous solution containing alkalis (e.g. sodium or potassium silicate or hydroxide), can induce a chemical reaction process^{3,6} which leads the material to set, harden and gain strength in a manner which is in an engineering sense analogous to the hydration of Portland cement, but without requiring the manufacture of a cement clinker via thermal processing. A hardened alkali-activated binder consists of an aluminosilicate skeleton, with a molecular structure which can be either 'zeolite-like' or 'tobermorite-like' depending on the calcium content. Low-calcium alkali-activated materials have an alkali-aluminosilicate structure which resembles a disordered form of a zeolitic framework.⁷ The addition of more calcium leads to the formation of a binding gel which resembles more closely the tobermorite-type calcium silicate hydrate structures formed through the hydration of Portland cement,⁸⁻¹⁰ although the higher levels of alkalis and aluminium present can lead to structural differences in terms of the nature of the ordering, degree of crosslinking and the content of interlayer species.¹¹⁻¹³ These gels can also coexist at intermediate calcium contents,^{14,15} and the combinations of engineering and durability properties which can be achieved through appropriate design of such blended binder systems^{16,17} are focusing significant interest in this area at present.

The current and planned large-scale production of alkali-activated binders is based mainly on the use of coal fly ash and metallurgical slags as the dominant solid aluminosilicate sources, as these are now the most widely available and inexpensive aluminosilicate waste materials which are amenable to alkali-activation.^{18,19} The use of calcined clays in alkali-activation is also attractive in a number of applications, and although the cost of such materials can be higher as they are manufactured products

rather than industrial by-products, the simplified supply-chain which results from the use of a primary resource is attractive in a commercial sense. The high rate of consumption of blast furnace slag and coal fly ash in blended Portland cements and concretes in many parts of the world does mean that the availability of these materials can be constrained – for example, the United Kingdom experienced a widely-reported shortage of fly ash which impacted concrete production in 2014, and some parts of the USA have also suffered shortages of suitable fly ash in the past several years. For this reason, although there are parts of the world where the common fly ash and/or blast furnace slag precursors are readily available (some parts of North America, China, Australia, South Africa, and elsewhere), there are other locations where the development of alkali-activated concrete mixes based on alternative raw materials (particularly those which are not suitable for blending with Portland cement) will be essential if this technology is to be deployed on an industrial scale.

Opportunities for alkali-activation of non-blast furnace slags

There are various non-blast furnace slags which have been tested as precursors for alkali-activation; these include:

- Phosphorus slag^{4,20-22}
- Copper slag^{23,24}
- Nickel slag²⁵
- Ferronickel slag²⁶⁻²⁸
- Silicomanganese slag²⁹
- Various steel slags^{4,30-32}
- Manganese slag³³
- Titaniferous slag³⁴
- Zinc slag^{35,36}
- Lead slag³⁷

Among these slags, an interesting case study is silicomanganese slag, approximately 10 million tonnes per annum is produced worldwide, with significant stockpiles already sitting in landfill due to very low historical utilisation rates.²⁹ Silicomanganese is an important reagent and intermediate in modern steelmaking processes, and its production results in the generation of a glassy slag which displays some pozzolanic properties.³⁸ The chemical composition of silicomanganese slag is to some extent similar to that of blast furnace slag (Table 1), although with a much higher manganese content and somehow lower calcium content, rendering it an acidic slag. Under Chinese standards specifying slag activity indices based on chemical composition, MnO is considered to reduce the activity of slags; for example, the ratio $(\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3)/(\text{SiO}_2 + \text{MnO} + \text{TiO}_2)$ is used to represent slag activity in

regulatory standards,⁴ indicating that the presence of Mn is classified as detrimental to the pozzolanic reaction of the slag.

Table 1: Compositions of slags used in this work, in wt.%, as determined by X-ray fluorescence. All components are represented as oxides, although it is probable that some elements are present in the slags in reduced redox environments.

Oxide component	Blast furnace slag	Silicomanganese slag ²⁹
SiO ₂	35.8	42.6
Al ₂ O ₃	10.9	12.2
CaO	41.2	25.2
Fe ₂ O ₃	0.8	1.0
MgO	7.8	4.2
MnO	0.4	9.9
Na ₂ O	>0.1	0.4
K ₂ O	0.4	2.2
TiO ₂	0.6	0.4
SO ₃	1.6	0.1

Nonetheless, there is interest in valorising this material due to its relatively high availability in some locations, and its low cost compared to blast furnace slag in those locations where it is available, as it is essentially a material which is diverted from landfill. There are some concerns associated with the toxicity of manganese in high concentrations, particularly when inhaled or ingested,³⁹ thus the possible leaching of manganese from products based on Mn-rich slags must be investigated and controlled. Nonetheless, if slags from silicomanganese processing can be successfully valorised, this may be of significant industrial interest, as indicated by the existence of a standard for alkali-activated silicomanganese slag-based materials in the former USSR standardisation system.⁴⁰ Kumar et al.²⁹ demonstrated that the mechanical activation of silicomanganese slag through very high energy milling is desirable in terms of achieving a high-reactivity precursor for production of alkali-activated binders with high strength (> 100 MPa at 28 d, Figure 1), whereas a standard ball milling process for particle size reduction yielded a less reactive material, and less than 25% of the compressive strength for the final product. Mechanochemical activation through high-energy milling has been shown to induce chemical reactivity in otherwise unreactive phases such as halloysite⁴¹ and quartz,⁴² and it is likely that a similar effect will also be observed in the silicomanganese slag.

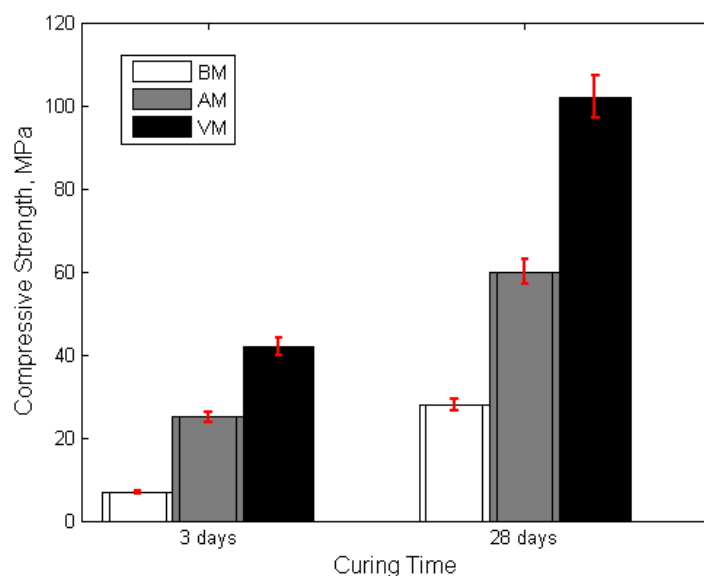


Figure 1: Compressive strength data for alkali-activated silicomanganese slag, milled in a ball mill (BM), attrition mill (AM) and vibratory mill (VM).

The AM and VM samples were of very similar particle size distribution, with d_{50} of 5 μm and 100 % passing 40 μm , while the BM sample had a d_{50} of 30 μm and 100 % passing 200 μm . The alkali-activator used for all samples was 6 M sodium hydroxide, added at a liquid/slag mass ratio of 0.35. Samples were 70 mm paste cubes, cured under sealed conditions at 27 °C.²⁹

Considering the cost and energy input required for high-energy milling of metallurgical slags – which tend to be harder and more difficult to grind than Portland cement, for example – it may be that these processes involving very fine grinding are less environmentally friendly - or cost-efficient than a less-fine grinding of the slag followed by its use in a blended binder system.

To explore this possibility, Figures 2 and 3 present analytical data for the production of an alkali-activated binder based on ground granulated blast furnace slag, replaced by up to 20 wt. % silicomanganese slag. The silicomanganese slag was crushed in a laboratory ring mill, which is a moderately high intensity milling technique, to reach a d_{50} of 20 μm and with all particles passing 100 μm . The alkali-activator used was sodium metasilicate, added at a dose of 5 g per 100 g of total slag precursors, and with a water/slag mass ratio of 0.42. All alkali-activated binder samples were cured under sealed conditions at 20 °C.

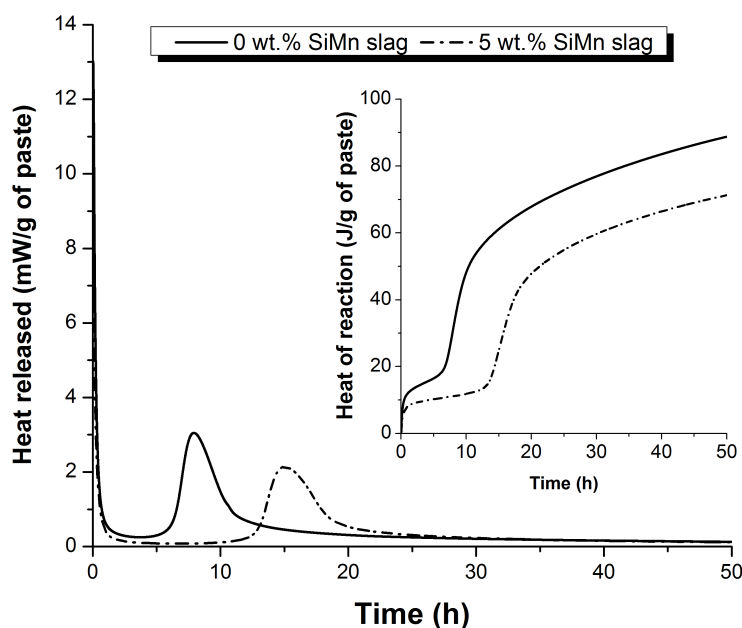


Figure 2: Isothermal calorimetry data for alkali-activated blast furnace slag, blended with 0 and 5 % silicomanganese slag. The alkali-activator used was sodium metasilicate, added at a dose of 5 g per 100 g of slag precursors, and with a water/slag mass ratio of 0.42.

The isothermal calorimetry data in Figure 2 show a retarding effect upon inclusion of silicomanganese slag – even at a dose as low as 5 %, and much more than would be expected if the slag was unreactive. This indicates a hitherto unknown chemical effect, potentially due to the release of manganese from the silicomanganese slag as it starts to dissolve, which is influencing the setting and hardening of the blast furnace slag. Manganese nitrate is known to retard the setting of Portland cement,⁴³ but its role in alkali-activation processes is much less well understood, and requires further investigation.

Figure 3 presents X-ray diffraction data for the alkali-activated blended blast furnace slag-silicomanganese slag binders at 7 and 28 days, where there is little evident mineralogical difference between the samples at either age; the only notable difference between the samples is in the peaks. Manganese is known to substitute onto both the Mg and Al sites in hydrotalcite-group minerals,⁴⁴ and thus may participate in the formation of this phase in these blended binder systems. The role of hydrotalcite in enhancing the carbonation resistance of alkali-activated slag-based binders has been identified and described,⁴⁵ and so it remains to be seen whether this characteristic can also be enhanced through the incorporation of

silicomanganese slag, or other waste materials containing available transition metal cations which can participate in the formation of hydrotalcite-group phases.

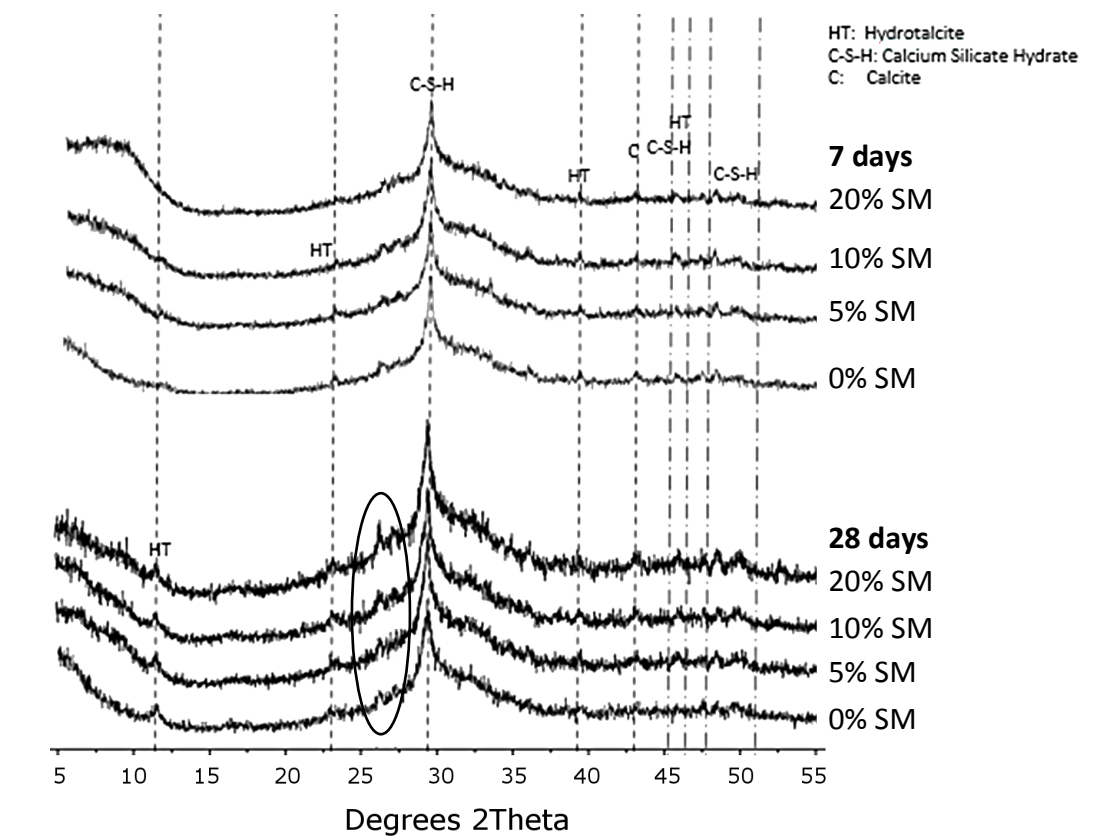


Figure 2: X-ray diffractograms (Cu K α radiation) for alkali-activated blast furnace slag, blended with 0, 5, 10 and 20 % silicomanganese (SM) slag, cured for 7 and 28 days. Circled peaks are due to the aragonite and calcite polymorphs of calcium carbonate.

The development of the ability to control the setting and hardening rate of alkali-activated blast furnace slag binders is an area of active research at present, and thus any additive which offers a reliable and predictable retarding or accelerating effect in this system without a detrimental effect on the final binder is of interest in this regard. These data indicate that the silicomanganese slag may be able to play such a role, which could be of interest both in terms of partial replacement of (increasingly scarce) blast furnace slag with other metallurgical industry wastes, and also in terms of developing ways by which the early-age behaviour of alkali-activated slag binders may be more precisely controlled. Questions regarding leachability of manganese (or

similarly chromium or lead from other metallurgical slags) obviously remain to be answered, but this does appear to be a promising pathway for the valorisation of currently underutilised sources of slags.

Progress in the application of alkali-activation technology

In the past decade, alkali-activation has grown from a field which was predominantly the domain of a limited number of research laboratories, to the current situation where it is the topic of both commercial and regulatory progress on multiple continents, as well as a very large number of research organisations. Commercial progress and large-scale applications of alkali-activation technology have been described in a recent RILEM State of the Art report,⁴⁶ including deployment in eastern and western Europe, China, Australia and the Americas. Recent developments include the construction of infrastructure elements,⁴⁷ airport facilities⁴⁸ and public buildings⁴⁹ from alkali-activated concretes in Australia, as well as scale-up leading to production of alkali-activated binders and concretes by a rapidly increasing number of countries worldwide. Standardisation efforts by organisations including ASTM International⁵⁰, VicRoads⁵¹ and SIA⁵², in addition to prescriptive standards which are in place in nations such as Ukraine^{53,54} and China⁵⁵ demonstrate explicit regulatory acceptance of alkali-activated binders. These materials also fall within the scope of performance-based standards such as ASTM C1157⁵⁶ which do not specify a particular type of binder chemistry.

This standardisation and regulatory approval process in various jurisdictions worldwide is paving the way for much more widespread usage of these materials in large-scale applications, as many legal and liability issues related to the specification and construction processes are much more straightforward when it is possible to specify materials according to a regulatory standard. There exist both prescriptive and performance-based approaches to the specification of alkali-activated materials;⁵⁷ the performance-based methodology is certainly the pathway which is more amenable to the valorisation of a wide variety of slags, but relies on the availability of appropriate testing methods, which is not always the case. Conversely, a prescriptive approach based on the specification of a particular mix design and combination of precursors would arguably provide more confidence for the consumer, but is much more cumbersome in terms of requiring the testing and validation of each specific formulation to be included in the standard. It is undoubted that a mixture of the two approaches will continue to be utilised worldwide, and both approaches offer valuable pathways for the uptake and utilisation of alkali-activated materials.

Possible pitfalls and areas for caution

In developing any new material for large-scale deployment, it is essential to ensure that there is a sufficient, and robust, supply chain in place. This is particularly critical in the construction materials industry because of the enormous volumes of cement and concrete which are produced and used worldwide; a modern cement kiln will usually process several thousand tonnes per *day* of material, by comparison with most process industries where this sort of figure could easily represent an *annual* throughput. The cement and concrete industry, and the extractive metallurgy industry, are arguably the only process sectors which are equipped to handle a such a large volume of solids as both precursor and product, and this raises important questions when analysing a potential new route to market, or a new product. Fundamentally, when defining whether a particular alkali-activated binder formulation (or application for these materials) will be worthy of commercial attention, the key question often becomes: is it actually possible to make enough of this material for the project to be commercially viable? There is a large number of academic studies, conducted and published every year, which describe the production of an alkali-activated binder system from particular combinations of industrial wastes and chemical feedstocks. However, if a particular waste material is available only in quantities of a few tens of tonnes per day from a given location, it will be very difficult to produce a sufficient volume of alkali-activated concrete using this as the main precursor, to provide a commercially viable source of materials for general construction or infrastructure applications.

This means that, in essence, the majority of alkali-activated concretes based on waste streams of lower to moderate volume (including most slags arising from non-ferrous metallurgy) will require a driver other than simply the production of a low-cost, standard-performance concrete to enable their use in a practical and profitable context.¹⁹ Specific environmental or cost benefits which can arise from the use of a particular solid waste material (through diversion from landfill) or source of waste alkalis (replacing some of the costly sodium silicate which is usually used in large-scale alkali-activated concrete production)

Conclusions

Valorisation of a wide variety of metallurgical slags can be achieved through the use of these materials as precursors for alkali-activated binders and concretes. Most alkali-activated mixes are currently based on ground granulated blast furnace slag or on fly ash, with alternative metallurgical slags generally used in lower volumes. Blending of these slags as minor constituents of a mix based on blast furnace slag or fly ash can offer a lower-risk and potentially highly attractive path to their utilisation,

as the quality control and metals leachability issues which are often associated with such slags are reduced through dilution. The specific chemistry of various slags derived from non-ferrous metallurgy can also be of value in manipulating the engineering properties of the blended binder formulation, either at early or later age. Standardisation and large-scale commercial deployment of alkali-activation technology is taking place rapidly in many jurisdictions worldwide, and although most of the mixes now being used at scale are based on a smaller selection of precursors, a performance-based approach to standardisation does certainly offer scope for the utilisation and valorisation of a much wider range of silicate and aluminosilicate slags as precursors for the production of alkali-activated concretes.

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