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1 Advances in understanding alkali-activated 2 materials

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9 Abstract

10 Alkali activation is a highly active and rapidly developing field of activity in the global research and
11 development community. Commercial-scale deployment of alkali-activated cements and concretes is
12 now proceeding rapidly in multiple nations. This paper reviews the key developments in alkali-
13 activated materials since 2011, with a particular focus on advances in characterisation techniques
14 and structural understanding, binder precursors and activation approaches, durability testing and
15 design, processing, and sustainability. The scientific and engineering developments described in this
16 paper have underpinned the on-going scale-up activities. We also identify important needs for
17 future research and development to support the optimal and appropriate utilisation of alkali
18 activated materials as a component of a sustainable future construction materials industry.

19 **Keywords:** Alkali-activated material (D); binder precursor; structural characterization (D); durability
20 (C); sustainability

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31 **1. Introduction**

32 The keynote paper dedicated to the 13th International Congress on the Chemistry of Cement held in
33 Madrid in 2011 focused on the chemistry of alkali-activated and hybrid binder systems [1]. The aim
34 of this paper is not to provide a detailed overview of all aspects of the history, chemistry and
35 engineering of alkali-activated materials (AAMs), which can be found in references [2-6]. Nor does it
36 aim to summarise in detail the extensive published work in validating the use of different sources of
37 fly ash, blast furnace slag and metakaolin in AAMs, a topic which comprises a very large percentage of
38 the publications in this field. Rather, it is intended to review and highlight the key recent scientific
39 developments in the development, characterisation, durability, processing and environmental
40 assessment of AAMs since the last Congress.

41 **2. Advances in characterisation**

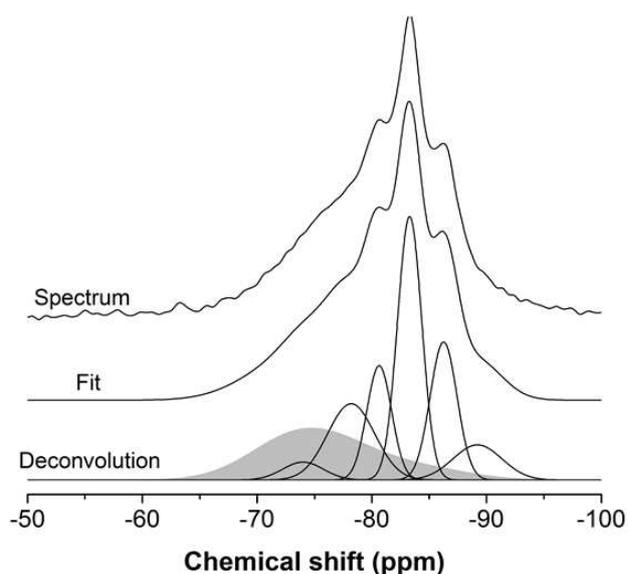
42 The characterisation of cementitious materials is well known to present significant challenges when
43 applying most common materials science techniques. The disordered, chemically complex, multiphase
44 nature of the key strength-giving components of cementitious materials means that the parameters
45 controlling their structure have only recently been understood in detail. This is further complicated by
46 the fact that most precursor materials used in AAMs are also structurally disordered, being either
47 glassy (e.g. fly ash; blast furnace slag) or thermally disrupted layer structures (e.g. metakaolin and
48 other calcined clays). This means that the contribution of unreacted precursors to an observed
49 spectrum or diffractogram, which must be accounted accurately in any truly quantitative analysis, is
50 often difficult to identify and delineate [7, 8]. This remains probably the most significant outstanding
51 problem in the structural analysis of AAMs. The advances in both in situ and ex situ characterisation
52 techniques during the past several years have brought a much deeper understanding of both the
53 nanostructure and the microstructure of AAMs. This section summarises application of these
54 techniques to the study of AAMs.

55 **2.1 Nanostructural characterisation**

56 The nanostructure of AAMs is strongly dependent on the available calcium content of precursors; a
57 high-calcium system such as alkali-activated blast furnace slag is dominated by a calcium
58 aluminosilicate hydrate (C-A-S-H) gel with a tobermorite-like (mostly Q², some Q¹ and Q³) structure [3,
59 9], while low-calcium systems such as those based on metakaolin or fly ash tend to generate an alkali
60 aluminosilicate (N-A-S-H) gel with a highly crosslinked (mainly Q⁴), disordered pseudo-zeolitic
61 structure [3, 10, 11]. These gels can coexist in binders based on blends of high-calcium and low-calcium
62 precursors [12-14], although the stability of the gel coexistence at high alkalinity is still the subject of
63 some discussion[5, 15, 16]; Garcia-Lodeiro et al. [16] found a tendency towards C-A-S-H gel as the final
64 stable product when the pH remained >12 in mixtures of synthetic C-S-H and N-A-S-H gels.

65 The key spectroscopic techniques which are used in analysis of AAMs include Fourier transform
66 infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy. The majority of published NMR
67 studies of AAMs investigate ²⁷Al and ²⁹Si nuclei by a magic angle spinning (MAS) approach, which yields
68 information about the coordination states of Al and the connectivity of Si (to non-bridging oxygen
69 sites, or bridges to Si or Al). Such information has been instrumental in building a deeper
70 understanding of the network structures of both C-A-S-H and N-A-S-H gels in AAMs [8, 17-19]. Many
71 attempts have been made to quantify the contributions of component sub-peaks to measured NMR
72 spectra of AAMs using mathematical deconvolution processes. However, it is essential to note that
73 unless the contribution of the remnant unreacted precursor is taken correctly into account – either

74 through selective isotopic labelling of the binder [20], or through subtraction of a scaled component
75 spectrum for the remnant precursor during the deconvolution process (Figure 1) [8, 18, 21] – the
76 quantification of the spectra will not yield an accurate representation of the binder chemistry.



77

78 **Figure 1.** ^{29}Si MAS NMR spectrum of a sodium metasilicate-activated blast furnace slag paste cured for 14 days, with
79 deconvolution into component peaks. The fit is the sum of the deconvoluted peaks, and the dark grey band represents
80 the contribution of the remnant anhydrous slag. Adapted from [18].

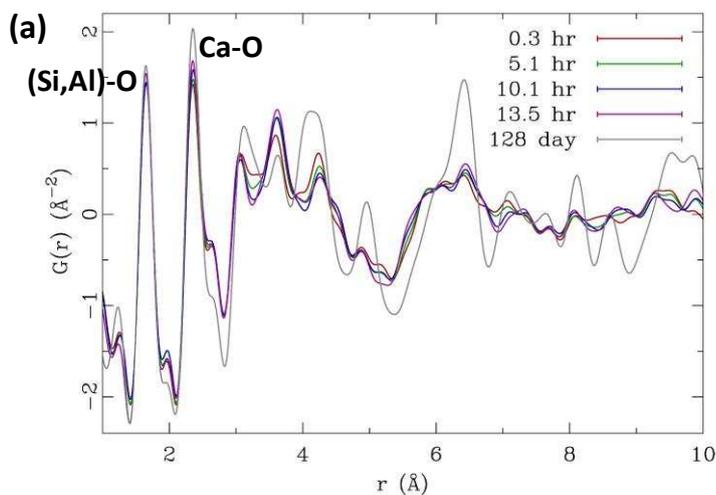
81 Two-dimensional NMR approaches such as multiple quantum MAS NMR, probing quadrupolar nuclei
82 including ^{17}O , ^{23}Na and ^{27}Al [20, 22, 23], are starting to bring additional insight into the details of the
83 bonding environments within the N-A-S-H gel in particular, and appear to offer significant scope for
84 future advances in the understanding of AAMs. Less common nuclei such as ^{43}Ca , ^{39}K and ^{25}Mg can
85 also yield useful information if studied at sufficiently high magnetic field [24-26], although
86 interpretation of the spectra is not always straightforward. The significant Fe content of most fly ashes
87 can limit the resolution and spectral quality achievable for those materials, but spectra of excellent
88 quality are in general able to be obtained for materials based on slags and metakaolin.

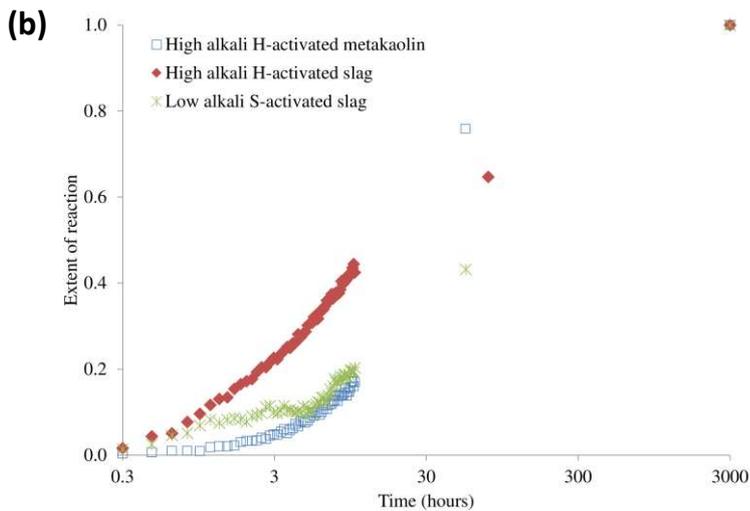
89 Infrared spectroscopy is a key technique for the analysis of AAMs, particularly for low-calcium systems
90 where it can probe the connectivity within Si-O-(Si,Al) frameworks via shifts in the peak corresponding
91 to the asymmetric stretch of that bond [27-29]. Recent developments in the application of infrared
92 spectroscopy have involved the use of in situ time-resolved FTIR spectroscopy, where spectra are
93 collected as often as every minute during a reaction process [30, 31], and also infrared microscopy
94 (often conducted using a synchrotron beamline source), which enables collection of spatially-resolved
95 infrared data for polished samples[31]. The combination of time-resolved and spatially resolved
96 infrared spectroscopy has also provided powerful new insight into the influence of the availability of
97 the binder-forming species silica [32] and alumina [33] on gel structures. The theory of an initial Al-
98 rich binder gel (described as “Gel 1”) forming at early age, and then evolving to a more Si-rich structure
99 (“Gel 2”), which was developed from ex-situ analysis of the gel evolution [27], has also been refined.
100 As FTIR spectroscopy measures bond vibrations rather than the actual nuclei, the distinction between
101 ‘Al-rich’ and ‘Si-rich’ gels is related to connectivity rather than bulk composition: the ‘Gel 1’ stage
102 involves a high degree of formation of Si-O-Al bonds relative to the bulk Si/Al ratio, because the
103 formation of crosslinks involving Al atoms joining between Si sites is rapid. This leads to a gel which
104 has a relatively high concentration of Si-O-Al bonds. Later, the ongoing gel structural evolution

105 involves condensation reactions between the Si-OH groups remaining within the immature gel, giving
106 an increase in the effective Si/Al ratio of the gel as measured by FTIR[5]. This explains why the gel
107 formed by the reaction between a solid aluminosilicate precursor (e.g. fly ash) and a silicate activator
108 – which has a very high Si/Al ratio in the solution phase at early age – can appear relatively ‘Al-rich’ to
109 FTIR spectroscopy at early age, when bulk chemical considerations would indicate that the Si/Al ratio
110 should decrease throughout the reaction process as Al is gradually released from the fly ash particles,
111 and the additional Si supplied by the activator is consumed.

112 Pair distribution function (PDF) analysis, as reviewed by Meral et al.[34], involves the calculation of
113 interatomic distance correlations for disordered materials from ‘total scattering’ data. The use of X-
114 ray and neutron PDF analysis in the study of AAMs has continued to provide unparalleled new insight
115 into the formation and structure of the gels which dominate these materials [35]. *In situ* PDF analysis
116 (Figure 2) provides direct insight into the molecular-scale structural development of the disordered
117 binder phases on a timescale which can be as short as 3 minutes when using a synchrotron beamline
118 source [36], or 15 minutes for a high-intensity neutron scattering instrument [37]. *Ex situ* analysis of
119 as-synthesised and thermally-treated samples has also provided new understanding of the structure
120 of metakaolin and the products of its alkali-activation [38, 39], and the differences between the C-A-
121 S-H gels formed by hydration of Portland cement and in alkali-activation of blast furnace slag [40].

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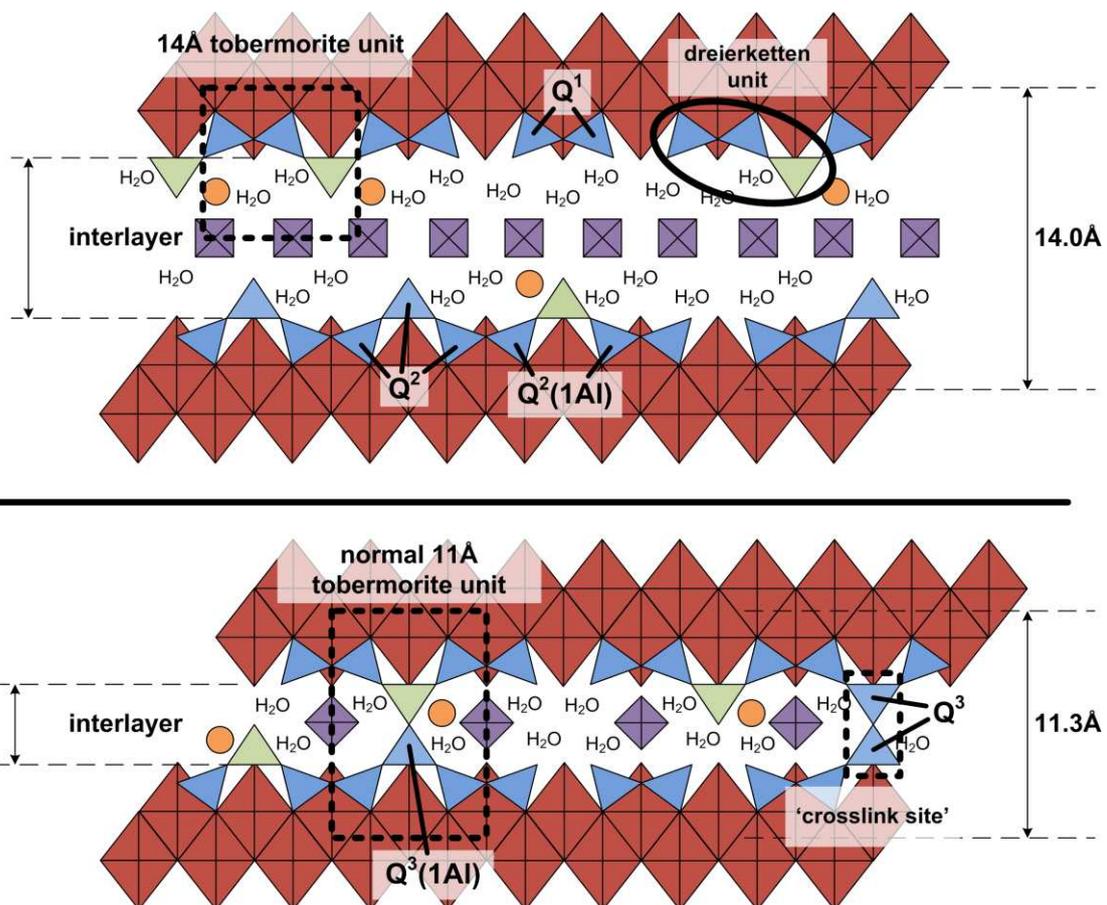




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132 Figure 2. (a) X-ray PDF data for sodium silicate activation of slag, collected *in situ* at times as marked, and with the atomic
 133 interactions responsible for the nearest-neighbour peaks identified; (b) quantification of the *in situ* PDF data collected for
 134 sodium hydroxide ('H') and sodium silicate ('S') activation of metakaolin and slag, normalised to 100% extent of reaction
 135 at 128 days (approx. 3000 hours) for all systems. Adapted from [36].

136 Recent developments in the understanding of the C-A-S-H gel in alkali-activated blast furnace slag
 137 binders have been focused on the construction of a realistic structural description of the silicate chain
 138 structures in this gel, which can differ significantly from those formed in the C-S-H produced by
 139 Portland cement hydration [40-42]. This is mainly attributed to the low Ca/Si ratio and high Al content
 140 of the gel produced by alkali activation of blast furnace slag, which opens the possibility of cross-linking
 141 between the *dreierketten* chains of the tobermorite-like gel [19, 41], Figure 3.



142

143 **Figure 3.**Schematic of structural features, silicate and aluminate site environments, cross-linking, and interlayer sites in
144 tobermorite-like C-N-A-S-H. Adapted from [41].

145 The question of whether the alkali metal cations in AAMs can become structurally incorporated into
146 C-A-S-H, or are mainly sorbed onto its surface, is yet to be fully resolved. This is partially related to the
147 difficulty in defining what exactly is the ‘surface’ of such a small (a few nanometres) particle, and
148 partially also due to challenges in distinguishing ion-exchangeable interlayer sites from ion-
149 exchangeable surface sites via currently-available analytical techniques. However, the determination
150 of pore solution chemistry in alkali-activated slag, and its comparison with solubility measurements
151 carried out in more dilute solutions, show that alkali uptake by the gels is a function of gel chemistry
152 rather than being dominated by the available surface area [43]. This shows that the incorporation of
153 the alkalis into the gel structure is significant, and may provide at least a partial explanation for recent
154 PDF analysis results which showed that the C-A-S-H gel in alkali-activated binders is structurally distinct
155 from the C-S-H product of C₃S hydration, and specifically appears more disordered[40]. If
156 incorporation of alkali cations in the interlayer of C-A-S-H is inducing additional structural disorder,
157 both by reducing the periodicity of the interlayer and by reducing the regularity of the stacking of the
158 layers through differences in ionic size, this could link these nanostructural and chemical observations.

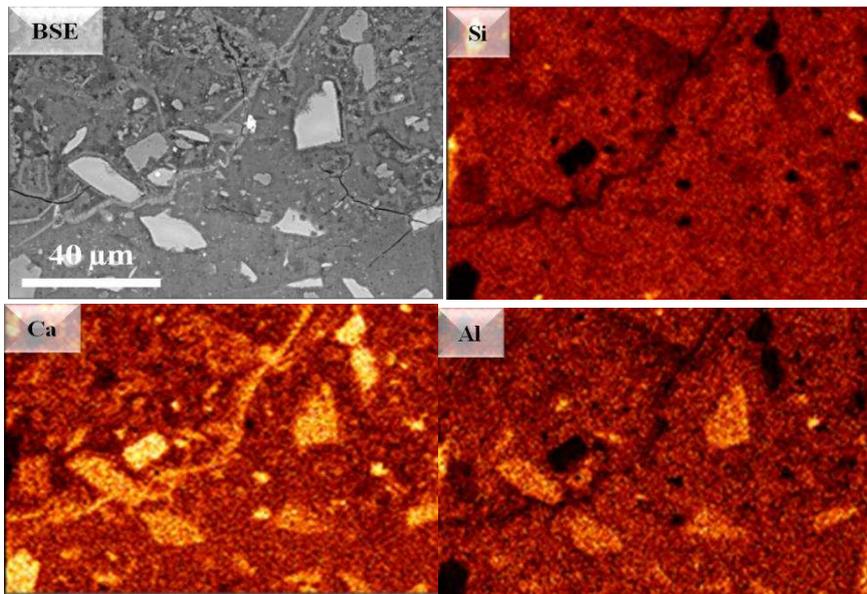
159 **2.2 Microstructural characterisation**

160 The most widely used tool for microstructural analysis of AAMs is scanning electron microscopy (SEM).
161 In this context, the advances which have been made regarding analytical methods and
162 instrumentation applied to Portland cement-based materials are also of value in the analysis of AAMs.
163 The ability to collect hundreds or thousands of spot analyses per sample using energy-dispersive
164 spectroscopy (EDS) via automated data collection systems is bringing vast improvements in the ability
165 to identify, quantify and analyse specific binder components and unreacted precursors, and most of
166 the data reduction and processing algorithms which have been demonstrated for Portland cement-
167 based materials [44, 45] should be quite readily transferable to the analysis of alkali-activated binder
168 systems. The higher-spatial resolution compositional analysis which is made possible by the use of
169 transmission electron microscopy (TEM) is also of value in the analysis of the nanostructured and
170 closely intermixed phases which coexist within alkali-activated binders, and nanoindentation may also
171 prove to be of value in this regard [46].

172 Quantitative analysis of disordered phases, e.g. metakaolin and N-A-S-H gel in a low-calcium AAM,
173 has also been demonstrated using more traditional X-ray diffraction methods coupled with the ‘partial
174 or no known crystal structure’ (PONKCS) algorithm, validated and supported by SEM-EDS analysis [7],
175 and this methodology appears to offer significant potential for future application.

176 As the field of alkali-activation matures as a research area, it is also becoming possible to analyse
177 the microstructural features of relatively older samples which have been held under controlled
178 conditions for longer periods of time. Such analysis of aged alkali-activated blast furnace slag-based
179 samples [47, 48] has provided insight into the ongoing and cyclic nature of the alkali-activation
180 reaction process, as the alkalis which remain in the pore solution can contribute to a very extended
181 process of continuing reaction and microstructural development within the hardened material. In
182 some instances (e.g. Figure 4), partial crack closure can be observed as a result of these processes,
183 which offers interesting scope for future optimisation and development.

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Figure 4. SEM image of the paste within a 7-year old sodium silicate-activated slag concrete, showing the deposition of calcium-rich reaction products around and inside microcracks in the paste. Reproduced from [48], copyright Elsevier B.V.

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190 Another key tool which is gaining popularity and interest is tomography. This can be applied on both
191 nanometre [49] and micrometre [50] length scales using X-rays, or on a nanometre scale using
192 electrons in a transmission electron microscope [51], to provide three-dimensional insight into the
193 geometry of the pore and solid components of AAMs.

194 The alkali-activation reaction process has also been better understood through rheological and
195 surface-chemical analysis of these AAMs. The nature of the very early-age reaction products in the
196 alkali-silicate activation of metakaolin has been elucidated through the combination of rheological
197 measurements with small-angle scattering and other spectroscopic techniques [52-55]. Precursor
198 particle surface chemistry has also been invoked as an explanation for the various dispersing effects,
199 or lack thereof, achieved by the addition of polymeric dispersants to AAMs [56], as well as explaining
200 the differing influences of silicate and hydroxide activators on the rheology of alkali-activated slag [57]
201 and alkali-activated fly ash [58] pastes.

202 The electrical properties of a porous material are closely related to its pore structure and the
203 chemical composition of pore solution, and so alternating current (AC) impedance spectroscopy
204 provides information regarding the microstructural development during hydration of cement-based
205 materials [59]. Figure 5(a) is a typical impedance spectrum of a cement-based material. It has a high
206 frequency arc and a low frequency arc, characterising the bulk material effect and polarisation effect
207 of the electrode/specimen respectively, and Figure 5(b) shows examples of the data collected for
208 alkali-activated slag pastes at different ages. The high frequency arc in impedance spectroscopy is
209 closely related to the microstructural characteristics of cement-based materials. Three key features,
210 the high frequency resistance (R_1), depression angle (α) and bulk resistance (R_b), can be obtained from
211 the spectra.

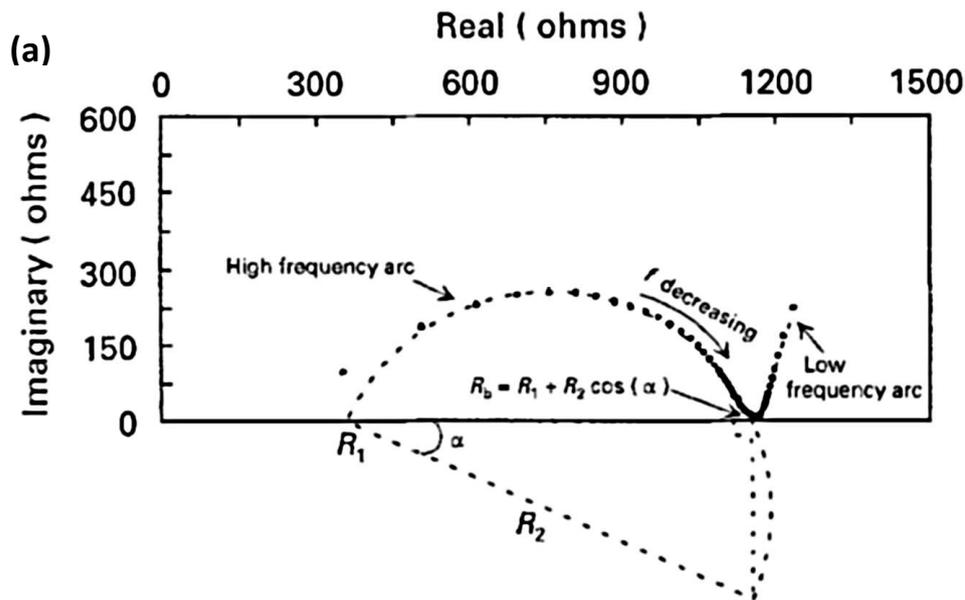
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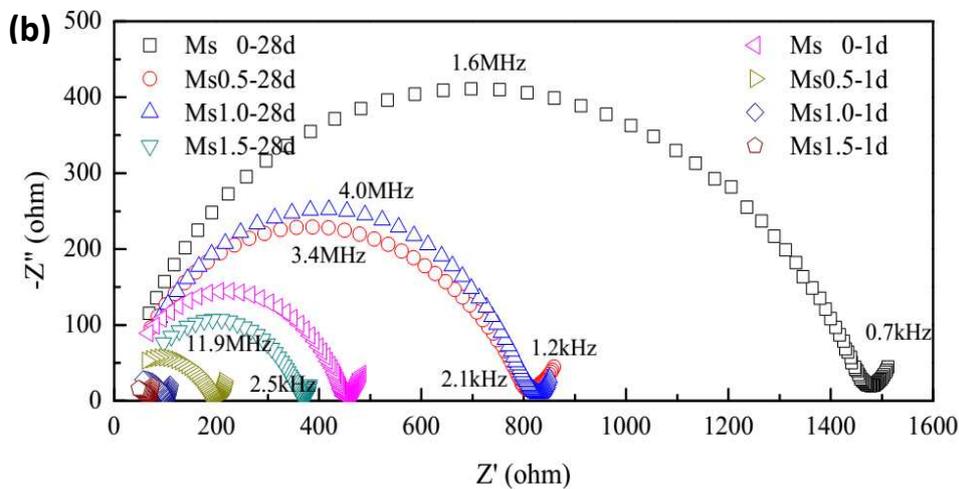
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Figure 5.(a) Typical impedance spectrum of a cement-based material with key features identified; adapted from[60]; (b) impedance spectra of waterglass-activated slag with different activator moduli (Ms) at ages of 1 and 28 d; data from [61].The high frequency resistance (R_1), depression angle (α) and bulk resistance (R_b) can be obtained from the spectra; Z' and Z'' represent the real and imaginary parts of the impedance response respectively.

231 McCarter et al. [62] studied the early hydration kinetics of alkali-activated slag by using impedance
232 spectroscopy over the frequency range 1-100 kHz; from the capacitance and conductance response,
233 a number of distinct regions can be identified, corresponding to the stages of hydration, thus giving
234 information about the chemical activity and changes in rigidity of the mixture. Hanjitsuwan et al.[63]
235 found that the dielectric constant of alkali-activated high calcium fly ash pastes decreased
236 substantially with increasing frequency, although this was less notable at higher NaOH concentration.
237 The relaxation peak height decreased and the peak position shifted towards a higher frequency,

238 because the samples contained less unreacted fly ash and were denser than those formulated with
239 lower NaOH concentrations.

240 An equivalent circuit model is an important conceptual bridge which can be used to connect the
241 measured AC impedance spectrum with the real microstructure of the materials. Ravikumar and
242 Neithalath [64] measured the electrical response of alkali silicate powder activated slag concretes
243 before and after standard chloride transport tests using a proposed equivalent circuit model. They
244 found that the resistance of the connected pores extracted from the fits of the circuit model decreased
245 after the rapid chloride permeability test (RCPT), but increased after the non-steady state migration
246 test (NSSMT). They ascribed this to microstructural damage imposed by the higher voltage and
247 associated temperature increase during the RCPT, and the formation of additional chloride binding
248 products during the NSSMT.

249 Liu et al. [61] proposed an equivalent circuit model to quantitatively characterize the ion
250 concentration and pore structure of waterglass-activated slag cement during hydration. This included
251 two parts: one describing the bulk material effect, and another to represent the electrode polarisation
252 effects. The properties of continuous and discontinuous conductive paths, solid-solution interfaces,
253 and interlamellar spaces between C-S-H gel could be obtained. Bulk resistance decreased with
254 increasing dosage and modulus of waterglass due to the increase in the volume of hydration products
255 and the decrease of ionic concentration in the pore fluid.

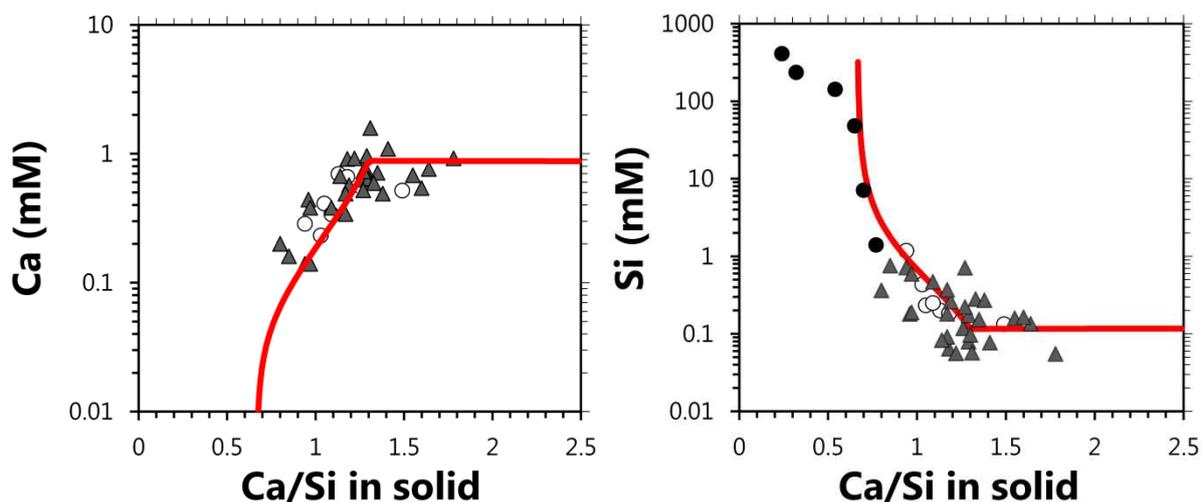
256 **2.3 New modelling approaches**

257 One rapidly growing area in cement science during the past several years is mathematical modelling
258 of the kinetics and mechanisms of reaction during hydration, and the structure of the resulting
259 hydrates in the hardened state [65, 66]. Puertas et al. [42] developed an atomistic structural model for
260 C-A-S-H in alkali-activated slags using a force field-based approach, by analogy to the extensive work
261 which has been published related to the application of this technique to C-S-H gels. Their model
262 incorporated Na to charge-balance Al sites, and predicted crosslinking of the tobermorite chains
263 within the C-A-S-H gel, consistent with the observation of a $Q^3(1Al)$ site environment in the NMR
264 spectra of many alkali-activated slag binders. To reflect this structural feature in a detailed structural
265 chemical model for tobermorite-like C-A-S-H gels, the need for the extension of the 'substituted
266 general model' of Richardson [67] to crosslinked tobermorite structures was identified. Myers et al.
267 [41] provided a structurally rigorous implementation of the calculation of crosslinking degrees in
268 tobermorite-like structures, and Richardson [68] also provided a crystal chemical model with a focus
269 on the description of layer spacing in these gels. Models such as these are essential in enabling the
270 correct interpretation of ^{29}Si MAS NMR spectra for C-A-S-H gels, as they provide structural constraints
271 which may be used to guide and validate the complex process of spectral deconvolution for
272 quantification of individual sites, thus enabling the accurate calculation of structural parameters such
273 as $Ca/(Al+Si)$ ratios and mean chain lengths from appropriately deconvoluted spectra [19, 69].

274 The description and prediction of phase assemblages through either volume-based or mass balance-
275 based models has also become a key technique in modern cement science [70, 71], and has been
276 applied to the study of calcium-rich AAMs [72, 73], where the coexistence of C-A-S-H phases and
277 important secondary products such as hydrotalcite plays a major role in determining material
278 properties including strength and durability [74]. However, uncertainty was introduced into such
279 models by the lack of an explicit description of the roles played by alkali metals and by aluminium in
280 the structure of the C-(N)-A-S-H gel; this has recently been resolved through the development of a

281 thermodynamic model entitled CNASH_{ss} [43] which describes this phase as an ideal solid solution
282 between eight end-members containing different degrees of Al and alkali substitution, and gives an
283 accurate description of solubilities in the quaternary CaO-Na₂O-Al₂O₃-SiO₂ aqueous system as well as
284 relevant ternary (Figure 6) and binary subsystems.

285



286

287 **Figure 6.** Comparison of CNASH_{ss} model predictions (lines) against experimental data (points) in the CaO-Na₂O-SiO₂
288 system at NaOH concentrations between 0.3-0.8 mol/L. Points of different shapes relate to different sources of data:
289 Points marked ○ are from [75], ▲ from [76], and ● from [77]. Reproduced from [43], copyright Elsevier B.V.

290

291 It is notable, however, that such models are not yet available for N-A-S-H type gels. The
292 thermodynamics of this type of gel are less well defined, and although some work based on analogies
293 with the thermochemistry of zeolites has begun to give promising results in describing calorimetric
294 data [78, 79]. Šmilauer et al. have also developed a volumetric description of alkali-activated
295 metakaolin binders based on analogies with the Powers model for water environments in Portland
296 cement [80]. At a chemical level, probably the most promising approach to the description and
297 simulation of N-A-S-H gels is multiscale modelling, whereby results from an atomistic simulation (e.g.
298 using density functional theory [81, 82]) are coarse-grained and used in a larger-scale simulation such
299 as a Monte Carlo model of gel nanostructure [83]. This has proven successful for alkali-aluminosilicate
300 gels, but there is not yet a published multiscale model which can describe the influence of calcium on
301 these gels, and the computational demands of this approach remain high. However, it is expected that
302 this will be an area of continuing development in coming years, as both theoretical descriptions of
303 AAM chemistry and available computational resources continue to improve.

304 **3. Advances in binder development**

305 **3.1 New precursors**

306 Early studies and applications of AAMs mainly used precursors such as blast furnace slag (BFS),
307 fly ash, and metakaolin; the chemical and physical characteristics of these precursors, and the
308 materials derived from them, are well described in the literature including [2, 3]. Recent studies have
309 greatly widened the sources and types of precursors, as briefly described in this section.

310 **3.1.1 Silico-manganese (SiMn) slag**

311 Silico-manganese slag is a discharge from the smelting of silicomanganese. It consists of irregular
312 porous amorphous particles, somewhat lower in calcium content than blast furnace slags, and
313 contains a significant content (~10 wt.%) of manganese within its glassy phase. This reduces its
314 reactivity compared to the more basic blast furnace slag. Kumar et al. [84] used sodium hydroxide as
315 an activator for high-energy milled silico-manganese slag, and obtained alkali activated cement pastes
316 with strength up to 101 MPa after 28 days of sealed curing at 27±2°C. However, the high-energy
317 milling was seen to be important in achieving this performance, as the strength achieved through this
318 process was more than three times the strength achieved through alkali-activation of the same slag
319 processed through a regular ball-milling process.

320 **3.1.2 Mineral processing tailings**

321 **3.1.2.1 Coal gangue**

322 Coal gangue is a mineral waste discharged during coal excavation and washing. It is
323 aluminosilicate in nature, and its major mineralogical components are kaolin, quartz and feldspars.
324 The amount of coal gangue accumulated in China has already reached 3.8 billion tons; the disposal of
325 such a large quantity of waste requires a lot of land and has caused many serious environmental
326 problems [85]. AAMs can be prepared using calcined coal gangue with high amorphous aluminosilicate
327 content, in combination with and chemical activators. Zhang et al. [86] found that the compressive
328 strength of sodium silicate-activated calcined coal gangue pastes could reach 42.5 MPa after 24 h of
329 curing at 90°C.

330 **3.1.2.2 Red mud**

331 Red mud, also known as bauxite residue, is a waste generated during alumina extraction from
332 bauxite ores via the Bayer process. It consists mainly of SiO₂, Al₂O₃ and Fe₂O₃, with main mineral phases
333 of quartz, zeolites containing sodium and calcium, as well as clays, hematite, and others. All these
334 components are suitable raw materials for AAM production [87], although sometimes thermal
335 pretreatment is beneficial [88, 89], and red muds from highly efficient refineries which are low in Al₂O₃
336 tend to be relatively unreactive in alkali-activation. He et al. [90] used red mud and rice husk ash to
337 prepare AAMs with compressive strengths of up to 20.5 MPa; prolonged curing significantly increased
338 the compressive strength and Young's modulus, but reduced ductility.

339 **3.1.2.3 Mine tailings**

340 In China, more than of 87% the vanadium resources exist in hard coal. The tailings which remain
341 after vanadium extraction from the coal consist mainly of quartz, feldspar, zeolites and sodium silicate
342 [91]. Jiao et al. [92] activated a blend of ground vanadium tailings and fly ash with sodium silicate, with
343 the aim of producing a fire-resistant product; the mechanical performance was retained after
344 exposure to temperatures as high as 900°C, and no apparent microstructural damage was observed
345 below 600°C. Zhang et al. [93] also used class F fly ash to adjust the Si/Al ratio of copper mine tailings
346 to an appropriate level for use in alkali-activation, and used NaOH solution as the activator to prepare
347 AAMs with appropriate physical properties for use as a regular construction material.

348 **3.1.3 Catalyst residues**

349 Petroleum refineries worldwide process crude oil in fluid catalytic cracking (FCC) units, and
350 160,000 tonnes of spent FCC catalyst residue are thus produced every year. The spent catalyst is
351 essentially an agglomeration of zeolite (faujasite) crystals held together by an aluminosilicate matrix
352 including amorphous silica and clays. Tashima et al. [94] studied the synthesis and mechanical

353 properties of geopolymer mortars produced from FCC catalyst residue, which yielded a compressive
354 strength of about 68 MPa after 3 days of curing at 65°C. Rodríguez et al. [95] also synthesised AAM
355 pastes using FCC catalyst residue and sodium silicate solutions to form a highly dense and crosslinked
356 aluminosilicate type gel. However, in using this type of residue as a precursor in alkali-activation, it is
357 important to consider the significant heavy metal content of the catalysts, particularly nickel,
358 vanadium and/or lanthanum, as these may impact the performance of the geopolymer materials, and
359 are also potentially leachable under some conditions. Catalysts from different sources and processes
360 also differ in composition and reactivity, meaning that this is rather a diverse class of materials which
361 can provide alkali-activated products with a range of performance levels [96].

362 **3.1.4 Coal bottom ash**

363 Coal bottom ash (CBA) is a by-product of coal combustion which is collected at the bottom of
364 furnaces that burn coal for the generation of steam, the production of electric power, or both; fly ash
365 is produced from the same process, but is instead captured at the top of the furnace. CBA tends to be
366 coarser than fly ash, with grain sizes spanning from fine sand to fine gravel [97], and so needs to be
367 milled before use in alkali-activation. It contains only a small amount of semi-spherical particles and
368 less glass than fly ash, and so tends to result in AAMs with lower strength. However, because bottom
369 ash is generally not accepted in Portland cement blends due to its lower reactivity and often significant
370 heavy metal content, it is becoming popular as a potential precursor for alkali-activated binder
371 production, at least on a laboratory scale. The morphology, particle size, surface properties, and
372 amorphous phase content of CBAs will influence their ability to react in synthesis of alkali-activated
373 binders. Sathonsaowaphak et al. [98] found that strengths of up to 58 MPa could be achieved when
374 the material was ground to a sufficient fineness and combined with sodium silicate at an appropriate
375 modulus, while Donatello et al. [99] used coal bottom ash as a high-volume component of hybrid
376 alkaline cements.

377 **3.1.5 Rice husk ash**

378 Rice husk ash (RHA) is a waste generated through burning rice husk primarily for the generation
379 of electricity or for other purposes. The main component of the ash is silica (>90–95 wt.%), existing
380 predominantly in amorphous and partly in crystalline phases, in high-surface area particles, with
381 residual carbon as the major impurity (depending on combustion conditions) and other trace elements
382 such as K and Ca. The amorphous silica in RHA is reactive and can be used as a pozzolan; its use in
383 alkali-activation requires a secondary source of aluminium, as the Al content of RHA is close to zero.
384 Detphan and Chindaprasirt [100] used coal fly ash and RHA to prepare AAMs using NaOH and sodium
385 silicate as activators, and found that the optimum burning temperature of RHA for making FA-RHA
386 AAMs was 690°C. The compressive strengths ranged up to 56 MPa, depending on the ratio of FA/RHA,
387 the RHA fineness, and the activator modulus. Bernal et al. [101] also used RHA as an alternative silica
388 source for the production of low-cost silicate activating solutions from aqueous NaOH, which gave
389 equivalent or better performance when compared with a commercial waterglass but with both
390 environmental and financial benefits.

391 **3.1.6 Palm oil fuel ash**

392 Palm oil fuel ash (POFA) is a by-product from the palm oil industry produced in massive amounts
393 in many parts of the world, and has particularly become of interest to researchers in south-east Asia
394 for use as a pozzolanic additive for PC concretes as well as in alkali-activation [102]. Salih et al. [103]
395 used POFA in combination with sodium silicate and sodium hydroxide to prepare alkali-activated
396 binders, achieving a compressive strength of up to 32.5 MPa after 28 days of curing at 60 °C. Other

397 workers have also utilised POFA with other aluminosilicate materials, such as slag and rice husk ash,
398 to make alkali-activated pastes or mortars with improved performance [104].

399 **3.1.7 Waste glass**

400 The recycling of waste glasses from consumer utilisation and industrial processes poses a major
401 problem for municipalities worldwide. Tashima et al. [105] investigated the properties and
402 microstructure of alkali-activated glass fibre waste using NaOH and KOH solution as activators. The
403 mortar samples showed compressive strengths of up to 77 MPa after 3 days of curing at 65°C when
404 10mol/L NaOH solution was used as activator. Balaguer Pascual et al. [106] used metakaolin (MK) to
405 replace a part of the glass powder in order to introduce Al and also to stabilise alkali ions in the system.
406 Compressive strength of the mortars increased with MK content up to 8%. In contrast, without MK or
407 with less than 3% MK content, the compressive strength decreased with time. The need for additional
408 aluminium sources is relatively common in the alkali-activation of waste glasses, as few commercial
409 glass systems contain sufficient Al to produce a stable AAM.

410 Bajare et al. [107] investigated the use of a combination of dross from aluminium recycling,
411 calcined kaolin clay, and lead-silica glass (LSG) from recycled fluorescent lamps, to prepare foamed
412 alkali activated binders. The residual aluminium metal in the dross generates hydrogen when reacting
413 with the sodium silicate activator, leading to a low-density material (460 - 550 kg/m³), with a total
414 porosity of 82 - 83 %, and compressive strengths from 1.1 MPa to 2.3 MPa. One of the interesting
415 points of novelty in this work was the use of a waste material as foaming agent; this offers potential
416 commercial and environmental benefits compared to the use of finely divided metal powders,
417 peroxides, or surfactant-based foaming methods.

418 Puertas and Torres-Carrasco [108] activated blast furnace slag with three activators: commercial
419 waterglass, a NaOH/Na₂CO₃ mixture, and the solutions resulting from dissolving waste glass in
420 NaOH/Na₂CO₃. The compressive strength was over 60 MPa at 28 days when NaOH/Na₂CO₃ mixture
421 and glass waste mixed solution were used as activators, indicating that this glass was potentially useful
422 as a supplementary silica source in place of commercial silicate solutions.

423 **3.1.8 Waste ceramic**

424 Ceramic waste is produced in the demolition of masonry buildings, and as a by-product of
425 porcelain and whitewares production or disposal. The ceramic waste consists mainly of SiO₂ and Al₂O₃,
426 with the major crystalline phases of quartz (SiO₂) and albite (NaAlSi₃O₈), in addition to a glassy phase.
427 A conceptual model for metakaolin could possibly be used to describe the alkali-activation of ceramic
428 wastes, although the ceramics are usually fired at a higher temperature than is required for
429 metakaolin formation, and so the reactivity of the material is not as high. In a study by Reig et al. [109],
430 waste ceramics were first ultrasonically cleaned to remove contaminants such as paper scraps, metal,
431 plastic, or other organic matter, then dried and pulverised to an average particle size (d₅₀) of around
432 30 µm. NaOH and sodium silicate solution were used as activators, yielding pastes with a maximum
433 compressive strength of 41 MPa after 7 days of curing at 65°C.

434 **3.1.9 Incineration products of sludges**

435 **3.1.9.1 Paper sludge ash**

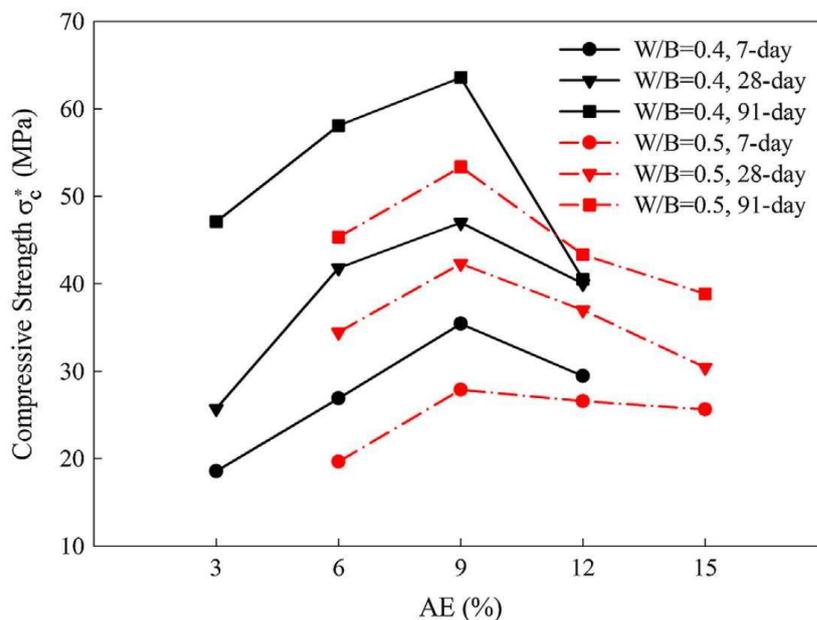
436 Significant residual waste streams are produced in pulp and paper mills; the solid wastes resulting
437 from pulp production and paper mill operations are moist and contain some combustible fractions
438 including organic wood or recycled paper fibres from which energy can be recovered (and so are

439 burned as recycled fuels), but also chlorinated organics, significant amounts of ash in the form of
440 calcite and kaolinite clays, as well as trace quantities of heavy metals. Combustion of paper sludge at
441 700–800°C can generate an ash with a high content of highly reactive aluminosilicate components
442 resembling metakaolin, which exhibits good pozzolanic properties [110], and can be effectively alkali-
443 activated [111]. However, it is important to understand the composition of a paper sludge ash when
444 using these materials in alkali-activation, as there is a very wide range of compositions among the
445 paper sludge ashes available worldwide, ranging from materials which are mostly aluminosilicate in
446 nature, through to some which contain mainly calcite and very little aluminosilicate material, and this
447 must be considered carefully in any mix design process.

448 3.1.9.2 Sludges resulting from water treatment

449 Reservoir sludge is comprised of the components of surface rock from a water catchment area
450 that accumulate as loose particles aggregation at the bottom of a reservoir; this material is removed
451 from reservoirs on a regular basis, and generally requires disposal in landfill. It is mainly composed of
452 smectite clays such as montmorillonite. In a study [112], reservoir sludge was crushed, ground and
453 calcined at 850°C for 6 h. A mixture of 30% blast furnace slag and 70% calcined reservoir sludge powder
454 was activated by mixing with different alkaline solutions of water, sodium hydroxide and sodium
455 silicate, resulting in compressive strengths of up to 63 MPa, as shown in Figure 7 .

456



457

458 **Figure 7.** Effect of water/binder ratio (W/B) and Na₂O-equivalent alkali dose (AE, as a percentage of the solid powder
459 content) on compressive strengths of alkali-activated mixtures of 30% blast furnace slag and 70% calcined reservoir sludge
460 powder after different durations of curing at ambient temperature. From [112], copyright Elsevier B.V.

461

462 Guo et al. [113] also produced AAMs from water treatment residuals, which are a combination
463 of the suspended solids (largely clay) removed from drinking water during its treatment, and the
464 flocculants used to achieve its removal. Calcination of the water treatment residuals at 900°C yielded
465 a material rich in reactive calcium, which could be blended with a fly ash-based AAM to provide
466 improved strength.

467 3.1.10 Natural minerals

468 Feng et al. [114] synthesised one-part geopolymers by thermal activation of albite with sodium
469 hydroxide and sodium carbonate. Albite powder blended at different ratios with NaOH or Na₂CO₃ was
470 heated at temperatures between 850 and 1150°C, then rapidly cooled to room temperature and
471 pulverised, yielding a powder which was X-ray amorphous and highly reactive. The ground powder
472 was added water to prepare paste samples, then cured at 25°C. When albite was calcined with 50%
473 NaOH at 1000°C, the main mineral phase was identified as a disordered zeolitic/feldspathoid type
474 compound, and the hardened paste showed a compressive strength of 44.2MPa at 28 days. There was
475 a tendency towards efflorescence due to the very high alkali content which was used to achieve
476 activation under such conditions, but the work does demonstrate, as a proof of concept, that the
477 production of one-part AAMs from feldspars is possible.

478 Volcanic ashes, which were the original pozzolans used in Roman concretes [115], are also
479 amenable to alkali-activation; pumice-type ashes from Iran have shown value as precursors for alkali-
480 activated binders in combination with sodium silicate solutions, although the incorporation of a small
481 quantity of calcium aluminate cement was found to be important in reducing efflorescence due to the
482 low reactive alumina content of the volcanic ash [116, 117]. Cameroonian natural pozzolans have also
483 been shown to be of value in production of both dense and porous AAMs, in studies by a number of
484 different research groups [118-120].

485

486 3.2 Hybrid binder systems

487 The replacement of Portland cement with supplementary materials usually result in long setting
488 time and lower early strength, but the addition of an extra alkali source to accelerate the reaction can
489 result in a useful hybrid cement. Chapter 8 of reference [2] summarised previous publications on
490 hybrid alkali-activated cements. The alkali can be supplied either via the use of a strongly alkaline
491 solution instead of mixing water, or as a solid or dissolved Na/K compound which can react with the
492 PC clinker to generate alkalinity *in situ*.

493 The reactivity of fly ash in hybrid alkaline cements is much faster than in the absence of added
494 alkalis, depending on the reaction conditions, particle shape, mineralogy and granulometry. The
495 reactivity of fly ash increases with increasing vitreous content [121] and the reduction of particle
496 size [122, 123], as well as with increasing alkalinity generated by the activator. Garcia Lodeiro et al.
497 [124] analysed hybrid cements activated with solutions of different alkalinity, and found that while
498 the type of alkaline activator impacted reaction kinetics and the formation of secondary reaction
499 products (particularly carbonates and AF_m phases), it did not appear to have any material effect on
500 the nature of the main cementitious gels formed. The thermodynamically stable majority product was
501 a mix of cementitious gels that formed irrespective of the activator used; however, the proportions of
502 these gels will be significantly affected by the type of activator. While a highly concentrated alkali
503 promotes the reaction of the fly ash and the precipitation of a (N,C)-A-S-H type gel, the use of
504 activators of moderate alkalinity favours the formation of C-A-S-H type gels [124]. Bernal et al. [125]
505 also showed that the combination of Na₂SO₄ with calcined clays, white Portland cement and limestone
506 results in a mixture of AF_m, AF_t, C-A-S-H and N-A-S-H phases in varying proportions depending on the
507 mix design.

508 Sanchez Herrero et al. [126, 127] have provided evidence for different mechanisms of hydration of
509 calcium aluminates and calcium silicates depending on the pH of the medium (higher than 12-13) and

510 on the ionic species involved in the hydration reactions. The presence of either Na_2SO_4 or Na_2CO_3
511 improves the mechanical strength development of synthetic tricalcium aluminate by favouring
512 calcium carboaluminate (from Na_2CO_3) or sulfoaluminate (from Na_2SO_4) formation. Carboaluminate
513 formation is favoured over the precipitation of cubic and hexagonal hydrates. Na_2SO_4 stimulates the
514 formation of the U-phase [128], which, being morphologically similar to calcium monosulfoaluminate,
515 contributes to strength development in the matrix by densifying the material. Hydrating both C_3S and
516 C_2S with an 8 M solution of NaOH favours the precipitation of portlandite, leading to more rapid
517 hydration and a higher degree of reaction in both C_3S and C_2S , but particularly the latter [129]. Given
518 the low initial activity of C_2S under normal hydration, this finding has implications for the possible
519 creation of a new family of belite cements. It was also demonstrated that the non-hydraulic polymorph
520 $\gamma\text{-C}_2\text{S}$ can be alkali-activated [130, 131], which offers further scope for developments in C_2S -based
521 cements.

522 Fernández-Jiménez et al. [132] also demonstrated the use of solid Na_2CO_3 and K_2CO_3 as activators
523 to obtain a hybrid cement from a blend of 20 % clinker + 40 % blast furnace slag + 40 % metakaolin.
524 The use of solid carbonate activators is very attractive from a commercial perspective as these are less
525 expensive to procure, and much less difficult to handle, than aqueous silicate or hydroxide solutions.
526 The highest mechanical strength values were obtained with 5 % Na_2CO_3 as activator, which yielded a
527 mix of (N,C)-A-S-H and C-A-S-H cementitious gels as the main reaction products, along with metastable
528 calcium monocarboaluminate, which later evolved into the calcite or vaterite forms of calcium
529 carbonate.

530 Arbi et al. [133] combined blast furnace slag or diatomite with an alkaline activator in the presence
531 of reactive aluminium sourced from calcium aluminate cement (CAC). The main reaction product was
532 a cementitious gel that precipitated with crystalline phases such as ettringite, the U-phase, and
533 katoite. While the slag-blended binder reacted to generate a C-(A)-S-H-like gel under moderately
534 alkaline conditions, diatomite reactivity proved to be very low under such conditions. The greater
535 reactivity of both slag and diatomite at high pH (high alkalinity) favoured their interaction with CAC.

536 **4. Advances in durability**

537 **4.1 Durability and thermodynamics**

538 The countless examples in nature of the presence of alkalis, and particularly of alkaline
539 aluminosilicates, in rocks stand as geological and consequently thermodynamic proof that these
540 compounds, appropriately proportioned and combined with network-forming elements, are highly
541 stable (insoluble). Moreover, the temperatures and pressures needed to manufacture AAMs are
542 similar to the conditions prevailing in some of the processes involved in sedimentary rock formation.
543 Residual soils often contain low-temperature forming sedimentary zeolites such as phillipsite
544 $[(\text{K}_2,\text{Ca})\text{Al}_2\text{SiO}_{12}\cdot 4.5 \text{H}_2\text{O}]$, scolecite $[\text{CaAl}_2\text{Si}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}]$, analcime $[\text{NaAlSi}_2\text{O}_6\cdot \text{H}_2\text{O}]$, mordenite
545 $[(\text{Ca},\text{Na}_2,\text{K}_2)\text{Al}_2\text{Si}_9\text{O}_{22}\cdot 6\text{H}_2\text{O}]$ or natrolite $[\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}]$ [134, 135].

546 Analcime, for instance, tends to form on certain temperate seabeds (temperatures of under 30 °C),
547 an outcome of the interaction between volcanic ash and alkaline metals dissolved in the seawater.
548 The sole determinants of its formation, and that of other zeolites, are the concentration of the
549 elements in the seawater in contact with the ash, and the water temperature. While in high calcium

550 media, calcium-bearing zeolites are the varieties most prone to precipitation, when the alkali
551 concentration is high, sodium or potassium partially or wholly replace the alkaline-earth cations [135].
552 The result is an alkaline metal-rich precipitate, which is entirely compatible with the presence of
553 alkaline-earth metal zeolites.

554 Resistance to decay is clearly more effective in alkaline aluminosilicate hydrates such as muscovite
555 and paragonite than in calcium aluminosilicates. The existence of these sodium- and potassium-
556 bearing minerals in nature further supports the excellent durability of compounds similar to the
557 products of alkaline activation. Krivenko et al. [3, 136] built a flowchart of sedimentary rock formation
558 from the products of rock weathering, which was then used as a basis for modelling artificial minerals.

559 Processes such as silicate condensation and polymerisation, then, with the attendant changes in
560 the respective mineral phases, all exhaustively studied under laboratory conditions, also take place in
561 the Earth's crust. That would appear to constitute irrefutable evidence of the thermodynamic stability
562 of the reaction products, and provides positive indications regarding the long-term durability of AAMs.

563

564 **4.2 Testing for durability**

565 Most previous studies have focused on the process of alkali activation and mechanical properties
566 of alkali-activated cements and concretes, with less emphasis on durability aspects until recently. A
567 host of standards with respect to durability testing have been well established and widely applied to
568 Portland cement concretes, but their applicability for AAMs remains to be addressed. The two books
569 [2, 3] summarise previous studies on durability of AAMs; this section outlines some recent relevant
570 publications and presents some important arguments with respect to durability testing of AAMs.

571 **4.2.1 Chloride ingress and binding**

572 Chloride ingress and binding in concrete are very important in defining the time taken to initiate
573 corrosion of steel in reinforced concrete structures and elements. Douglas et al. [137] used the RCPT
574 method to measure the charge passed by alkali-activated slag cement concretes, and obtained results
575 corresponding to the values expected for a low water/cement ratio Portland cement concrete.
576 Mercury intrusion measurement of corresponding mortar specimens indicated that Na_2SiO_3 -activated
577 slag mortars exhibited much lower porosity and finer pore structure than Na_2CO_3 -activated and NaOH -
578 activated slag mortars. However, the RCPT results indicated that Na_2SiO_3 -activated slag mortars
579 exhibited a much higher charge passed, particularly at early age, while those activated by NaOH or
580 Na_2CO_3 showed little change in charge passed from 3 to 90 days. It is speculated that the chemistry of
581 the pore solution appears to contribute more to the electrical conductivity or the charge passed than
582 does the pore structure, for alkali-activated slag cement mortars and concretes. These problems
583 become much more severe when different AAMs are compared[3]. Bernal et al. [138] studied the
584 resistance of alkali-activated concretes to chloride permeability by RCPT and direct diffusion tests, and
585 found that the correlations between the chloride diffusion coefficient resulting from the two methods
586 were weak, which further reveals the limitations of the RCPT in analysis of alkali-activated concretes.
587 It seems that the nature of the alkali-activated gel hydration products strongly influences chloride
588 ionic transport [139], but a full description of these processes has not yet been published. In high-Ca
589 alkali-activated systems, the C-A-S-H reduces porosity, while in low-Ca systems the N-A-S-H, which is
590 more porous[50], appears to contribute significantly to higher chloride binding [139].

591 The RCPT method is based on the measurement of electrical conductivity, which determined by

592 both pore structure and solution chemistry. Thereby the results from this method may be misleading
593 if the pore chemistry becomes dominant in the measurement [140]. The pore chemistry becomes
594 more complicated due to the addition of an alkali activator, which can buffer the pore chemistry at
595 very high pH during hydration [141]. So, it has become attractive to apply alternative accelerated
596 chloride migration tests such as the NordTest method NT Build 492[142], or ponding tests such as
597 ASTM C1543 [143], which use the colour change induced by application of silver nitrate solution to a
598 split sample surface to determine the chloride penetration depth, and thus chloride diffusion
599 coefficients. Such tests provide a more evident correlation to field performance because chloride
600 movement is measured directly. However, it should be noted that the alkalinity and volume of pore
601 solution of cement-based materials, and the concentration and volume of sprayed AgNO₃ solution all
602 influence the chloride concentration at the colour change boundary in the silver nitrate colorimetric
603 method [144, 145]. This may cause some variation in the test results [146], particularly for AAMs.

604 4.2.2 Carbonation

605 Carbonation of cements through uptake of CO₂ from the atmosphere causes a decrease in the
606 alkalinity of concrete, increasing the susceptibility to corrosion of steel reinforcement. This
607 depassivation of the steel in alkali-activated concretes can take place either directly due to reduced
608 pH [147, 148], or coupled with chloride attack [149]. The mechanism of carbonation in AAMs is
609 obviously different from that which takes place in Portland cement[150]. In Portland cement pastes,
610 atmospheric CO₂ dissolves in the pore solution and reacts rapidly with portlandite to form CaCO₃, and
611 then with C-S-H gel to form CaCO₃ and silica gel[151]. In contrast, the carbonation of alkali-activated
612 slag paste occurs directly in the C-A-S-H gel because of the lack of portlandite, leaving an alumina-
613 containing remnant siliceous gel in addition to CaCO₃ [18, 152]. Carbonation can also induce a loss of
614 strength and an increase in pore volume in alkali-activated concretes [153]. The hydrotalcite-group
615 phases produced as a secondary product in most alkali-activated slag binders are also observed to play
616 a significant role in binding carbonate ions and retarding the progress of carbonation [74]. The
617 carbonation of low-calcium alkali-activated binders appears mainly to involve conversion of the alkali-
618 rich pore solution to carbonate or bicarbonate salts [154], with little nanostructural alteration
619 identifiable in the binder gel itself (as the N-A-S-H gel cannot undergo decalcification processes)[18],
620 but the mechanisms of strength loss induced by carbonation of such materials still require further
621 investigation.

622 Another key determining factor for carbonation processes is relative humidity (RH), where an
623 intermediate humidity is required to enable uptake of CO₂ from the atmosphere, which is slow under
624 either very dry or saturated conditions. Most accelerated carbonation tests use relative humidities
625 between 50-70% [155], where the majority of concretes (including alkali-activated slags) are
626 carbonated at the fastest rate [156]. However, exposure of immature samples to lower relative
627 humidities during accelerated carbonation tests can result in significant drying shrinkage, and
628 subsequently induce microcracks [156], which certainly contributes to the rapid carbonation of AAMs
629 in accelerated tests.

630 A complication in this discussion is that accelerated carbonation testing of alkali-activated binders,
631 carried out at elevated CO₂ concentrations, has been shown to provide results which are unlikely to
632 represent the behaviour of the products under actual service conditions, due to changes in alkali
633 carbonate phase equilibria when the CO₂ concentration is increased [153, 157]; the tests are highly
634 aggressive to alkali-activated binders, meaning that assessment based on test results may
635 overestimate the risk of carbonation of these materials in the field. Under natural CO₂ conditions, the

636 excess alkalis present in the pore solution of an alkali-activated binder will quite possibly maintain the
637 internal pH at a level which is sufficiently high to protect steel in a passive state [157]. Carbonation at
638 early age is expected to reduce the achievable extent of reaction by limiting the availability of alkalis,
639 and extremely high pH, which are needed for the reaction process to continue, and so this may be
640 damaging to the performance of the material. The influence of carbonation on the mechanical
641 integrity of the binder phases also needs to be examined, as there are indications that a loss of
642 strength may take place during carbonation [138], but the mechanisms involved in this change in
643 mechanical performance still require further investigation. Given that the currently testing methods
644 are excessively aggressive, but a relatively high degree of acceleration is required to make the slow
645 natural carbonation processes observable on a laboratory timescale, how can an appropriate and
646 reliable test be designed and implemented? This also requires further attention.

647 **4.2.3 Sulfate attack**

648 Deterioration of concrete due to sulfate attack is generally attributed to reactions of calcium-rich
649 cement hydration products with sulfates to form expansive reaction products after hardening, which
650 produces internal stress and a subsequent expansive disruption of the concrete[158]. Due to differences
651 in phase chemistry of the hydration products, and specifically the absence or low concentrations of
652 AFm phases in AAMs, the mechanisms of sulfate attack observed in alkali-activated concrete are
653 notably different from those in Portland cement. Shi et al. [2] and RILEM TC 224-AAM [3] summarised
654 earlier research on the sulfate attack resistance of alkali-activated slag; the conclusion was that AAMs
655 appear to be superior to regular Portland cement under exposure to most sulfate solutions, and even
656 superior to sulfate-resistant Portland cement when exposed to sodium sulfate solutions. This particular
657 aspect of the performance of AAMs is brought about because Na_2SO_4 can actually be used as an
658 activator in higher-Ca AAMs [159], and thus would favour the structural evolution of the binding
659 phases and densification of the system [2]. However, when AAMs containing any significant level of
660 calcium are immersed in MgSO_4 solutions, significant loss of compressive strength occurs due to
661 decalcification of the C-A-S-H, gypsum and/or ettringite can be formed [160-162]. There has been little
662 detailed investigation of the sulfate resistance of calcium-free alkali-activated binders, as the
663 expansive processes which take place in calcium-rich materials are unlikely to be replicated in the
664 absence of significant contents of calcium in the binder.

665 The other important aspect of the interaction between cementitious materials and sulfates is
666 related to internal sulfate attack, whereby sulfates included in the original mix can cause expansive
667 processes at later ages. This is of particular interest in the context of nuclear waste immobilisation,
668 where different methodologies including direct incorporation of sulfates into metakaolin-based
669 binders [163], and the use of $\text{Ba}(\text{OH})_2$ as an additive in slag-based binders containing Na_2SO_4 , to
670 simultaneously bind sulfate as BaSO_4 and generate alkalinity for slag activation [164], have recently
671 been demonstrated.

672 **4.2.4 Acid Attack**

673 Hydrated cement paste is an alkaline material and can be attacked by acidic solutions, where the
674 removal of calcium leads to structural damage and loss of performance. Many studies have
675 demonstrated that AAMs can show better acid corrosion resistance than Portland cement pastes due
676 to the differences in the nature of their hydration products. The dissolution of $\text{Ca}(\text{OH})_2$ and calcium
677 sulfoaluminates from Portland cement, and the decalcification of high Ca/Si ratio C-S-H, either leaves
678 a very porous corroded layer or simply removes the specimen surface. Conversely, the low initial
679 permeability of alkali-activated slag specimens, along with the low CaO/SiO_2 ratio typical of the C-A-S-

680 H in such binders, leaves a coherent layer of aluminosilicate gel even after decalcification [165, 166].
681 This can hinder the further ingress of acids, contributing to the high acid resistance of AAMs [166,
682 167]. Pu et al. [168] also noted that for AAMs based on different slags, the less-basic slags yielded
683 binders with better acid resistance.

684 Corroded depth and mass loss are often used to characterise the acid induced degradation of
685 cements and concretes. Lloyd et al. [166] found that the corroded depth was a more sensitive
686 measurement of the progress of attack on AAMs than change in mass, because acid attack on N-A-S-
687 H gels leads to the formation of an apparently intact, but porous and low-strength, reaction product
688 layer on the sample surface, rather than actual dissolution of the binder. Shi and Stegemann [169]
689 found that the corroded depth of alkali-activated slag paste was about 1.3 mm, compared to 2.5 mm
690 for Portland cement paste after 580 days of immersion in pH 3 nitric acid solutions, and its resistance
691 to corrosion in HCl and H₂SO₄ was also higher than that of Portland cement paste [169]. However, the
692 dealumination of N-A-S-H gel has been identified in HCl solution, along with the destruction of the
693 zeolites formed in alkali-activated fly ash binders, independent of the type of activator used [170].

694 **4.2.5 Alkali-aggregate reactions**

695 As was mentioned in section 4.1, AAMs usually contain a very high content of alkalis, meaning that
696 potential alkali-aggregate reactions (AAR) become a concern in infrastructure applications [171].
697 Based on the relationships between alkali-silica reaction expansion and slag content of Portland-slag
698 cement, it seemed that deleterious expansion would not happen when the slag content was higher
699 than 80% and alkali content over 4% [2, 172]. It has been argued that this is because replacement of
700 Portland cement with high volume blast furnace slag and/or fly ash will result in C-S-H with a low Ca/Si
701 ratio and significant Al content, that can bind more alkali ions than that with a higher Ca/Si ratio, and
702 so inhibit AAR [172]. Many researchers have confirmed that AAR does in fact happen in alkali-activated
703 slag-based materials [173-176], with significant amounts of AAR reaction product observable under
704 electron microscopy [176], but the expansion was in almost all cases smaller than that of conventional
705 Portland cement-based materials tested in parallel. Among these studies, a trend was identified that
706 as the replacement of blast furnace slag with low calcium fly ash or metakaolin in an alkali-activated
707 binder increased, the expansion of the specimens decreased, and alkali-activated fly ash or metakaolin
708 materials, even with alkali-reactive aggregates, demonstrated very small or negligible expansion [175,
709 177, 178]. The low availability of calcium in the pore solution of the alkali-activated binders is also
710 likely to contribute to restricting the expansive processes [179], as is the binding of pore solution
711 alkalis by incorporation into aluminosilicate reaction products.

712 The accelerated mortar bar test method (ASTM C1260 [180]) has been most widely used for
713 screening alkali-reactive aggregates and evaluating the effectiveness of supplementary cementing
714 materials in suppressing AAR. In this testing procedure, the mortar bars are cured for only 24 h, then
715 submerged in water for 24 h, and afterwards in 1 M NaOH solution at 80°C. Immersion in water at
716 such early age can result in a severe problem for AAMs, as the leaching of alkalis is damaging to the
717 maturity development of the binder [3]. Thus, AAM mortars are often cured in steam, rather than in
718 water at 80°C, before immersion in NaOH solution, but this does render the test strictly non-compliant
719 with the ASTM standard. Another consideration is that the alkali concentration in the immersion
720 solution, 1 M NaOH, is designed to test AAR in Portland cement mortars, but is lower than the intrinsic
721 alkali content of most alkali-activated binders [181], and thus the contribution of the external alkalis
722 may actually be very limited. Also, expansion measurement of the mortars in this test starts only 48 h
723 after mixing, when the binders, especially with low calcium aluminosilicate glass precursors, are not

724 yet well hydrated. This might be problematic since a significant overlap of chemical shrinkage and AAR
725 expansion could take place, resulting in a reduced or non-observable expansion of the specimens
726 [182].

727 Shi [2, 183] also used an autoclave method to examine the alkali-silica reaction in alkali-activated
728 phosphorus slag cement, but found that this test was not suitable because the alkali aggregate
729 reaction might happen before the raw material was fully activated. Thus, both the AAR mechanisms
730 and testing methods need further detailed studies.

731 **4.3 Predicting durability**

732 The prediction of in-service performance, and specifically service life, of a reinforced concrete
733 element based on laboratory test results remains essentially a 'holy grail' for much of the field of
734 cement and concrete science. There are relatively well-defined approaches to this problem for plain
735 Portland cement concretes, where a suite of largely validated testing methodologies are used to
736 obtain information regarding the physicochemical characteristics of concretes, and these
737 characteristics are then used as the inputs of predictive models based on given exposure conditions,
738 cover depths and other parameters. For AAMs where, as was noted above, the applicability of various
739 testing methods for Portland cement is questionable at best [3], such an approach is prone to errors
740 [4]. The interactions between different degradation mechanisms, e.g. binder carbonation and chloride
741 corrosion of steel, are likely to differ between alkali-activated and Portland cement binders [147, 157],
742 but there is still a significant degree of work required to fully understand and validate the description
743 of these interactions.

744 **5. Advances in processing**

745 Alkaline activation, from its rapid upswing in popularity in the scientific and technical scene since
746 the 1990s, has experienced a very high level of scientific advancement; the quantity and the quality
747 of fundamental knowledge generated in the last decades around the materials synthesised by alkaline
748 activation is notable. Many interesting concepts supported by the chemistry of alkali activation of
749 aluminosilicates have opened up a range of possibilities for the development of new materials:
750 electronic composites with carbon nanotubes, photoactive composites with oxide nanoparticles,
751 bioactive materials, drug delivery agents, dye carrying media, novel chromatography media,
752 precursors for oxide or non-oxide ceramics, fluorescent materials, novel catalysts, solid-state
753 hydrogen storage media, nanoporous materials, fibre-reinforced composites, and others [184].

754 Production of alkaline concrete, which has already been successfully applied with slag-based
755 mixtures in the second half of the 20th century [185] and with fly ash-based mixtures from the
756 beginning of the 21st century [186], has evolved over time based on objectives of 'sustainability'
757 (maximum use of industrial waste), 'economy' (concrete cheaper than Portland cement concrete) and
758 'durability'. The preparation of ready-mixed or precast concrete using alkaline formulations is
759 probably the processing technology in the field of the alkaline activation which has developed most
760 rapidly in the last few years.

761
762 Heat treatment has also opened new possibilities of alkaline activation in relation to new
763 products. For example, high-purity leucite [187] and pollucite [188] have been prepared by heating
764 metakaolin-based geopolymers, containing potassium and caesium respectively, and with designed
765 Si/Al ratios. These are technologically valuable ceramics, leucite as a dental material, and pollucite

766 because of its low thermal expansivity. Kuenzel et al. [189] transformed metakaolin-based AAM
767 mortars into polycrystalline nepheline/quartz ceramics with relatively high compressive strength
768 (~275 MPa) and high Vickers hardness (~350 HV). The application of appropriate thermal treatments
769 or chemical admixtures can also lead to special products such as lightweight cements or foams [190-
770 192].

771 The manufacture of bricks for construction has also been the object of attention in the field of
772 alkali activation; in Malaysia [193], the USA [194] and India [195], various brick-making processes
773 have been adapted to the use of alkali-activated binders instead of firing bricks in a kiln.

774 **6. Quantification of sustainability**

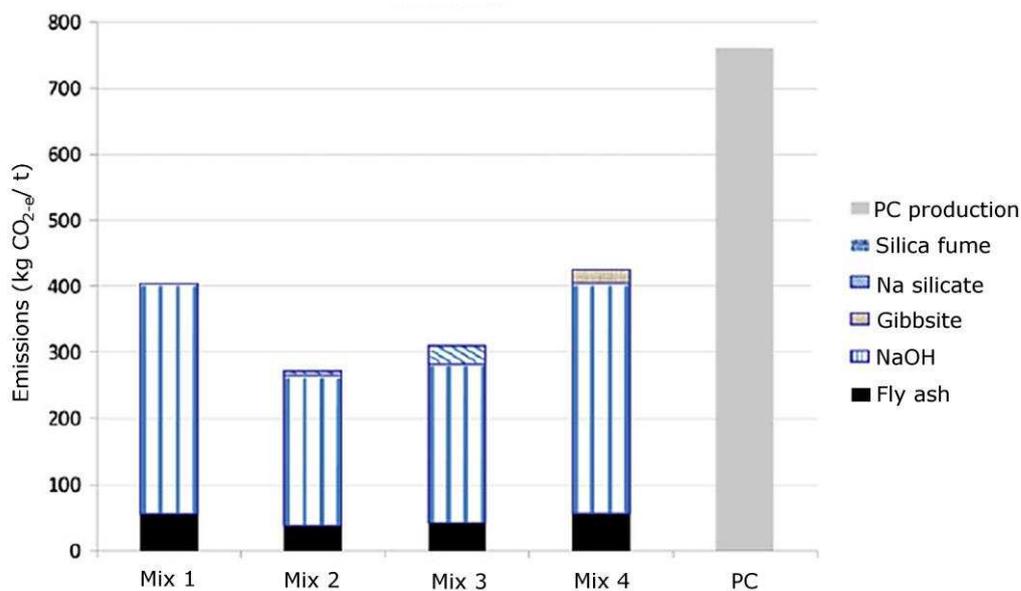
775 The raw materials related to Portland cement, such as limestone and clay, are non-renewable
776 resources. The production of one tonne of Portland cement consumes 3-6 GJ of energy and releases
777 about 0.85 tons of CO₂ [196]. The precursors of AAM are mainly industrial byproducts or wastes.
778 Some of them can be used directly, some of them may need grinding and some of them may need
779 calcination or thermal activation at 700-900°C. Thus, it has been identified that AAMs should have
780 advantages in sustainable development over conventional Portland cement, even when the
781 emissions associated with the production of the activator are taken into consideration.

782 Many of the published studies which aim to assess the environmental footprint of AAMs
783 attempt to take a holistic view on a worldwide (or continent-wide) basis – but in doing so, any
784 opportunities for precision in terms of describing the actual production, transport and utilisation of
785 specific materials in a given location, are lost. It is precisely this level of detail which is required, if a
786 meaningful comparison with currently-used technologies is to be drawn. For this reason, any broad
787 statement that AAMs offer the possibility to save a certain percentage of CO₂ emissions compared to
788 ‘Portland cement’ is prone to inaccuracy, unless the full system is precisely specified: the location,
789 the source of every material component, the functional unit (whether this is defined by volume of
790 concrete, mass of paste, normalised to compressive or flexural strength, or by some other method),
791 the mix design of the alkali-activated material, and the mix design of the reference Portland cement
792 mix (based on the understanding that different blended cements now dominate the market in many
793 parts of the world, and in some places the use of a non-blended Portland cement in concrete
794 production is becoming rather unusual). When this is done with care, e.g. [197-199], valuable results
795 can be obtained, but there is still a strong need for further, detailed, comparative life-cycle studies of
796 alkali-activated and Portland cement-based concretes, based on validated input and inventory data,
797 and in specific locations to account accurately for energy generation mixes, supply-chain and
798 transport considerations. It is only through the availability of such information that the
799 environmental performance of AAMs can be accurately assessed, and the current status of research
800 in this area does not yet in general provide the necessary level of specificity.

801 It has been identified that the most critical factor determining the environmental footprint of
802 an alkali-activated concrete is the activator dose, particularly when silicate or hydroxide activators
803 are used [200]; this is also likely to be the most expensive component of any alkali-activated
804 concrete mix, which means that a producer has dual incentives to design an efficient mix design with
805 minimal activator content. Habert et al. [199] used life cycle assessment methodology to analyse the
806 environmental impacts of AAM concretes made with fly ash, blast furnace slag and metakaolin based
807 on published results. A calculation based on an average of 49 mix designs published in the scientific

808 literature (and thus produced without the intention to minimise either cost or environmental
809 footprint) indicated that fly ash based geopolymer mixtures released 45% less CO₂ than an average
810 Portland cement concrete mixture. Granulated blast furnace slag based binders showed lower
811 emissions, but metakaolin-based geopolymer showed higher global warming effects than Portland
812 cement, due to the high activator doses used in such mixes in most laboratory studies. Additionally,
813 calcination of metakaolin at 800°C consumes around 50% of the energy, and generates about 33% of
814 the CO₂ emissions, compared to the production of Portland cement [201]. Figure 8, derived from the
815 work of McLellan et al. [198], exemplifies the importance of the activator in the emissions
816 calculations for several fly ash-based AAM formulations; the vast majority of the emissions are
817 attributed to the activator component, while the transport of the fly ash is also a significant
818 contributor in the context of that country. This highlights the importance of efficient and economic
819 mix design in ensuring the environmental credentials of any particular alkali-activated binder
820 system: these materials are not intrinsically or fundamentally ‘low-CO₂’ unless designed effectively
821 to achieve such performance, but when mix design and raw materials selection are carried out with
822 a view towards optimisation of environmental performance, the outcomes can result in very
823 significant savings.

824



825

826 **Figure 8.** Calculated CO₂-equivalent emissions of four different fly ash-based AAM paste mix designs, each with target
827 strength 40 MPa, compared to a typical Portland cement, incorporating transport and electricity emissions calculated
828 using typical Australian data. Adapted from [198].

829 7. Conclusions and perspectives

830 The development and use of AAMs as an alternative to Portland cement-based materials for
831 construction and other applications, has advanced extremely rapidly in the past several years. These
832 materials are now deployed on a commercial scale in multiple nations around the world, in
833 infrastructure, general construction and paving, nuclear waste immobilisation, and various other
834 niche applications. Hybrid binder formulations, making use of concepts and components from both
835 alkali-activation and Portland cement chemistry, are also becoming appealing due to their potential
836 to offer a more robust and less expensive pathway to AAMs.

837 The science required to underpin the large-scale utilisation of this class of materials has been
838 developed based on both bottom-up and top-down analytical procedures and design protocols.
839 There are still a number of areas which require attention, from both scientific and technological
840 perspectives, and particularly including the control of setting time and rheology. The development
841 and optimisation of alkali-activated binder formulations from an increasingly diverse range of waste-
842 derived precursors has become the focus of efforts from many research teams worldwide, often
843 with a focus on locally-available or problematic materials. This diversification both highlights the
844 versatility of the alkali-activation process, and also raises significant scientific questions related to
845 materials characterisation and optimisation, which would be required for legislative acceptance and
846 standardisation of the AAMs produced in this way. Appropriate and meaningful testing and
847 description of both durability and environmental sustainability is essential in ensuring the future role
848 of alkali-activated binder systems in the future global construction industry, and advanced
849 processing methodologies will be of value in enabling the true value of this class of materials to be
850 unlocked and realised.

851 It is also essential to develop AAM formulations, and new activators (sole components or
852 combinations) which provide desirable early- and late-age properties, while minimising the
853 environmental footprint of the material as a whole. The large-scale utilisation of commercially-
854 produced sodium silicate as an activator will face limitations in terms of scalability, cost, practical
855 handling issues and the environmental cost of this product. Thus, it is essential to develop
856 appropriate alternatives. Advances in the development of processing routes which enable the more
857 efficient use of activators with reduced doses for equivalent performance will also be important.

858 The scientific and technological maturity of the field of alkali-activation is rapidly increasing.
859 These materials are now genuinely moving from the laboratory into the field, and generating
860 opportunities for improvements in environmental sustainability and engineering performance (and
861 thus also profit) which are attracting the interest and support of industry, specifiers and regulatory
862 authorities worldwide. Some key aspects require detailed research attention in future years:

- 863 • Defining in detail the links between the physicochemical properties of complex precursors,
864 selected activators, and the performance of the resulting binder. recommendations for
865 improved characterisation of the precursor materials themselves, which are mineralogically
866 complex, heterogeneous, and often span a broad range of particle sizes and shapes;
- 867 • to seek new information through the use of analytical tools which have been under-utilised,
868 or not used at all, in the study of AAMs (e.g. Raman spectroscopy, confocal microscopy, X-
869 ray photoelectron spectroscopy);
- 870 • development of selective chemical attack methods for the separation of phases and
871 remnant precursors, and accurate quantification of the extent of reaction of aluminosilicate
872 precursors in AAMs;
- 873 • to synthesise pure products from chemical reagents, simulating the chemistry of 'real' alkali-
874 activated binder gels, to enable characterisation and comparison between pure products
875 and geopolymers from real precursors, and understanding of the structural and chemical
876 effects of minor elements;
- 877 • new activators should be investigated in order to contribute to fabrication of inexpensive
878 binder systems, sustainable processes, and non-hazardous handling;
- 879 • methods for the characterisation of particle surface chemistry under high ionic strength,
880 chemically aggressive conditions prevailing within AAMs;

- 881 • the thermodynamic description of N-A-S-H gel for its incorporation into geochemical-type
882 models;
883 • identification and modelling of rheological characteristics of alkali activated pastes and
884 concretes, including the effects of different families of chemical additives on the rheological
885 properties: new water reducers, shrinkage controllers, foaming agents, and others;
886 • characterisation of transitional zones between aggregate-paste or reinforcement-paste
887 within AAMs.

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