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**Alkali-Activated Materials for Sustainable Construction  
Applications**

An Experimental Investigation of Dredged Sediment-Based Binder Systems

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## Abstract

The construction industry faces many environmental challenges, but this thesis focuses on two main ones. The first is the CO<sub>2</sub> emissions from making ordinary Portland cement (OPC). The second is the increasing amount of sediment that needs to be removed from hydroelectric reservoirs. This research explores whether alkali-activated materials (AAMs) made from dredged sediment can address both issues simultaneously by providing a low-carbon, waste-based alternative binder that reduces CO<sub>2</sub> emissions.

We used two main types of sediment: one from the Perrères Dam (Valle d'Aosta) and one from the Poggia Dam (Brescia). Both were analyzed for their elements, minerals, and particle sizes using X-ray fluorescence (XRF), X-ray diffraction (XRD), and laser granulometry. We tested the sediments in both raw and heat-treated forms (at 700 °C). In total, we prepared 37 alkali-activated mortar mixes, grouped into 9 experimental series based on the additional materials added, including calcium hydroxide, mullite, gypsum, OPC, and LUKOSIL M130 silicone resin. These mixes also helped us study the effects of heat treatment and the type of activator used. We cured the samples at 60 °C for 14 days and then measured water absorption, leachate pH, compressive strength, and flexural strength.

Of all the mixes we tested, MIX11, which used calcined sediment, had the highest compressive strength, but it required additional energy for heat treatment. MIX15, made from raw sediment, exhibited the best mechanical performance without thermal pretreatment. This mix, which included 10 grams of LUKOSIL M130 and a binary alkaline activator, reached a compressive strength of 17.93 MPa and a flexural strength of 9.64 MPa without heat treatment. Throughout the study, the finer Perrères sediment was more reactive than the coarser Poggia sediment, resulting in better mechanical performance. Of the extra materials we tried, mullite mainly worked as a micro-filler by improving particle packing, rather than changing the Si/Al ratio as we first thought. A first look at sustainability showed that a resin-free sediment binder could lower CO<sub>2</sub> emissions by about 30% by weight compared to ordinary Portland cement (OPC). However, this benefit is reduced when you consider the extra resin in the best-performing mix and the energy used for curing. Most of the remaining carbon emissions came from the alkaline activator rather than the sediment.

The findings indicate that dredged reservoir sediment can serve as a binder for non-structural and low-load precast products. Future research should prioritize quantitative microstructural analysis, long-term durability, and leaching behavior.



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## List of Abbreviations and Symbols

- AAM — Alkali-Activated Material
- BSE — Backscattered-Electron (imaging)
- C-A-S-H — Calcium (Alumino)silicate Hydrate
- C-S-H — Calcium Silicate Hydrate
- CEN — European Committee for Standardisation
- EDS — Energy-Dispersive X-ray Spectroscopy
- EN — European Norm (European Standard)
- GGBFS — Ground Granulated Blast Furnace Slag
- GWP — Global Warming Potential
- ICDD — International Centre for Diffraction Data
- IEA — International Energy Agency
- ISO — International Organisation for Standardisation
- LCA — Life Cycle Assessment
- LOI — Loss On Ignition
- MK — Metakaolin
- N-A-S-H — Sodium Aluminosilicate Hydrate
- OPC — Ordinary Portland Cement
- PDF-4+ — Powder Diffraction File (ICDD reference database)
- PDMS — Polydimethylsiloxane
- PSD — Particle Size Distribution
- PVA — Polyvinyl Alcohol (XRF pellet binder)
- RILEM — Int. Union of Laboratories and Experts in Construction Materials
- SCM — Supplementary Cementitious Material
- SDS — Safety Data Sheet
- SE — Secondary Electron (imaging mode)
- SEM — Scanning Electron Microscopy
- UNEP — United Nations Environment Programme
- VOC — Volatile Organic Compound
- WD-XRF — Wavelength-Dispersive X-Ray Fluorescence
- XRD — X-Ray Diffraction
- XRF — X-Ray Fluorescence

## Symbols and Chemical Notation

- $D_{[4,3]}$  — Volume-weighted mean particle diameter ( $\mu\text{m}$ )
- $f_c$  — Compressive strength (MPa)
- $f_f$  — Flexural strength (MPa)
- $\bar{\sigma}_c$  — Mean compressive strength over failing half-specimens (MPa)
- $\bar{\sigma}_f$  — Mean flexural strength (MPa)
- $\sigma_f/\sigma_c$  — Flexural-to-compressive strength ratio

- $M_s$  — Silicate modulus,  $\text{SiO}_2/\text{Na}_2\text{O}$  molar ratio
- $\text{Si}/\text{Al}$  — Silicon-to-aluminium molar ratio
- $\text{Na}/\text{Si}$  — Sodium-to-silicon molar ratio
- $\text{Si}/\text{Ca}$  — Silicon-to-calcium molar ratio
- $w/b$  — Water-to-binder ratio
- $WA$  — Water absorption (%)
- $\rho$  — Apparent density ( $\text{g}/\text{cm}^3$ )
- $2\theta$  — Diffraction angle, XRD (degrees)
- $\lambda$  — X-ray wavelength ( $\text{\AA}$ )



# Chapter 1: Introduction

## 1.1 Background and global context

Construction shapes nearly everything about how we live — our cities, our buildings, the infrastructure that makes daily life possible. Sustaining that role is environmentally expensive. The UN Environment Program reports that the built environment accounts for about 40% of global energy-related CO<sub>2</sub> emissions each year [1]. Much of this impact comes from one material: cement.

Cement holds concrete together, and concrete is still the most widely used construction material in the world. Global production now exceeds 4 billion tonnes per year [2] and continues to increase. Making Portland cement clinker always creates a lot of carbon for two main reasons. First, the raw materials must be heated to about 1,450°C, which uses a lot of fossil fuel. Second, limestone releases CO<sub>2</sub> as it breaks down, regardless of the energy source used. Together, these two sources put every tonne of clinker at roughly 0.66–0.82 tonnes (660–820 kg) of CO<sub>2</sub> [3], which adds up to an estimated 5–7% of global greenhouse gas emissions — around 2 billion tonnes of CO<sub>2</sub> annually [4, 5]. Left on its current trajectory, with production potentially reaching 6 billion tonnes by 2050 [2, 22], this trend sits uneasily against the targets set by the Paris Agreement [7].

All of this has pushed researchers to look hard for alternatives, and one of the more promising is alkali-activated materials (AAMs) — binders made by reacting an aluminosilicate precursor with an alkaline activator solution, skipping the high-temperature clinker firing that makes ordinary cement so carbon-intensive. The precursor is usually an industrial by-product or waste material. Reported CO<sub>2</sub> reductions for AAMs run to 40–80% against conventional cement concrete, depending on precursor type and where the life-cycle assessment draws its system boundary [10, 18] — numbers substantial enough to explain why the field has drawn so much interest over the past two decades.

Davidovits established the scientific foundation for this field in the 1970s through his pioneering research on geopolymers [8]. Since then, the field has continued to grow. Most of what we know about how AAMs work, how to make them, and where they can be used comes from a few main sources. These include the RILEM State-of-the-Art Report [12], Provis and Bernal’s review [13], and the handbook edited by Pacheco-Torgal et al. [14]. Some industries have begun using AAMs outside the lab [11, 15, 16], but challenges remain, including differences in raw materials, sensitivity to activator chemistry, and the lack of widely accepted design standards. This thesis addresses one aspect of that variability problem directly: whether dredged reservoir sediment, a locally available waste material, can serve as a viable AAM precursor.

## 1.2 The environmental problem of dredged sediments

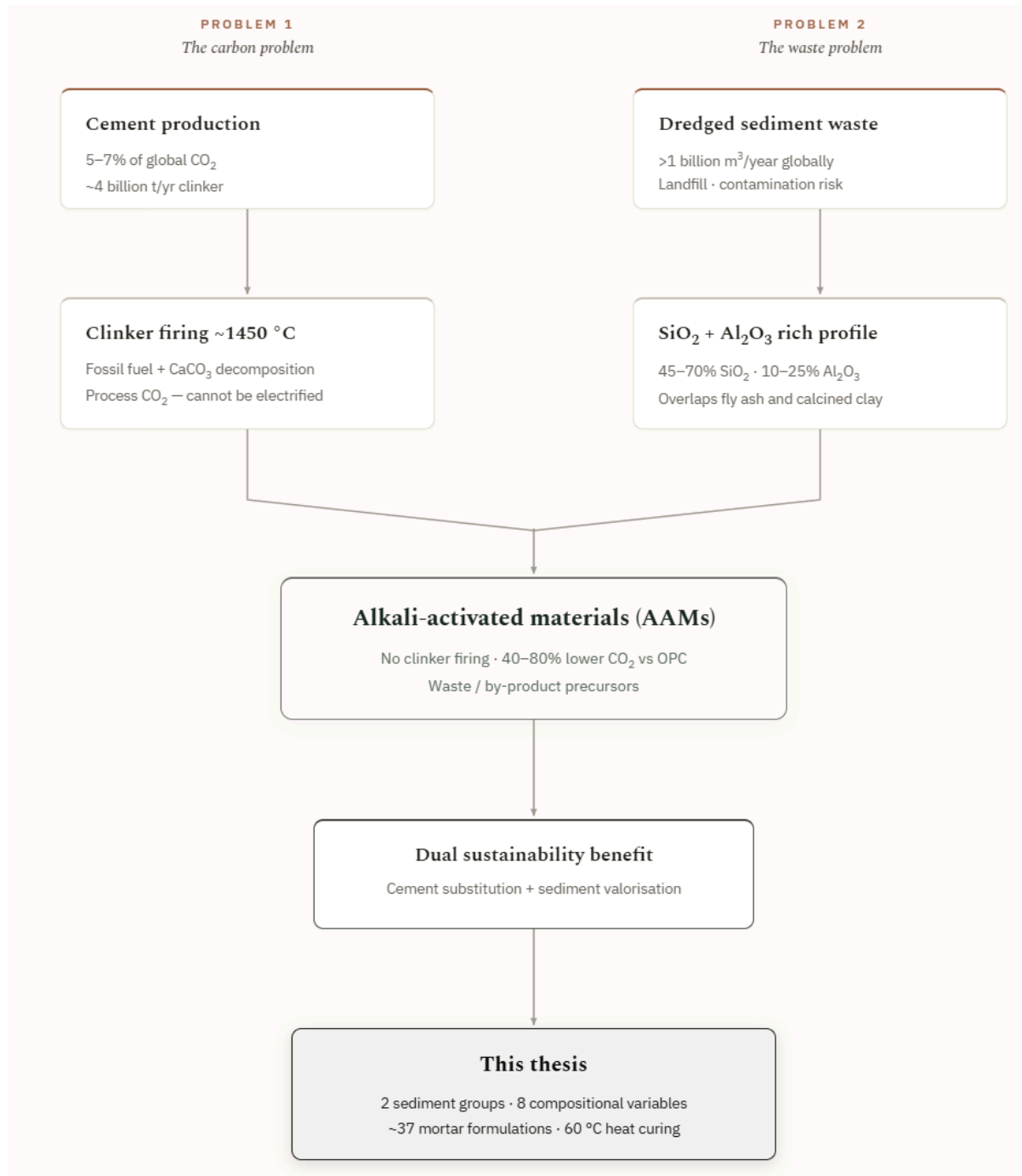
Alongside the cement problem, there is another environmental issue in the construction and infrastructure sector that gets far less attention: what to do with dredged

sediments. Rivers, lakes, hydroelectric reservoirs, and ports all accumulate fine material over time — sand, silt, and clay carried in by water and deposited on the bed. In hydroelectric reservoirs, this gradual build-up reduces storage capacity and can affect the safety and efficiency of dam structures. Globally, more than one billion cubic meters of sediment are dredged annually [17], making sediment management one of the largest material-handling challenges in the infrastructure sector.

The difficulty is not just in removing the sediment — it is in deciding what to do with it afterward. The most common options are landfilling, releasing it back downstream, or storing it in containment areas. None of these is straightforward. Each carries economic costs and environmental consequences: land use, contamination risk, and disruption to aquatic ecosystems [18, 19]. In Italy, the situation is particularly pressing. Many hydroelectric reservoirs were built in the mid-twentieth century and are now showing the effects of decades of sediment accumulation. At the same time, regulations on downstream re-emission have become increasingly strict, leaving operators with fewer and fewer viable options [20].

There is real potential in this waste stream. Instead of being just inert fill, dredged sediment usually contains high levels of silica ( $\text{SiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ), iron oxides, and calcium compounds [17, 20]. This chemical composition is very similar to that of fly ash and slag, which are commonly used in AAM research. This similarity is supported by a 2025 review of 32 experimental studies, which found that our mechanically activated sediments can be used to produce binders with 28-day compressive strengths ranging from 15 to 40 MPa [17]. While the lower end of this range may not be suitable for structural applications, this work focuses on formulations at the higher end that resemble low-strength concrete. The same review found that these binders also resist sulfate attack, freeze–thaw cycles, and carbonation. Life-cycle assessments support these benefits: Habert et al. [18] showed that most standard geopolymers have a lower global warming impact than similar OPC concrete, but they also noted that sodium silicate production is an important factor in the overall environmental impact.

There is still not much research focused on sediments from hydroelectric reservoirs, compared to studies on maritime or river dredging. In Italy, the most relevant studies were done by Molino et al. [20] and Ferone et al. [21]. They looked at making geopolymer binders from clay sediments taken from Italian reservoirs. Their work showed that using these materials is technically possible and highlighted that calcination temperature and the type of activator are important factors for performance. This thesis builds on that body of knowledge, extending the experimental program to a broader range of sediment sources, formulation variables, and activator compositions. The overall conceptual framework of the thesis — linking the two environmental problems through alkali-activated materials to a combined sustainability benefit — is summarised in Figure 1.1.



**Figure 1.1** — Conceptual framework linking the two parallel environmental problems addressed in this thesis (cement CO<sub>2</sub> emissions and dredged sediment waste) through alkali-activated materials (AAMs) to a dual sustainability benefit, and defining the specific scope of the experimental program.

### 1.3 Research motivation and novelty

What motivates this thesis is fairly direct: there is a lot of dredged sediment, it is a genuine disposal headache, and its chemistry appears promising for binder production. Even replacing some conventional cementitious materials would be a real benefit for both ecological sustainability and waste management. The problem is that sediment sources are never the same. Their composition changes depending on where they come from, how they

were deposited, and any pre-treatment they receive. This variability is one of the main reasons clear design guidelines for sediment-based AAMs have been slow to emerge.

This research tackles that challenge by studying two distinct sediment groups side by side under identical experimental conditions. The first group consists of fractions 1C, 2C, 3C, and 4C sampled from Perrères Dam, Valtournenche, Valle d'Aosta, blended together in equal proportions. The second group includes sediments SUD and INVASO, which were collected from Poglia Dam in Cedegolo, Brescia, and combined in the same way. Using this parallel method makes it possible to directly observe how the origin of the materials affects the results when following a single mix-design protocol. While using only two sources does not allow for a full separation of the effects of fineness, mineralogy, and bulk chemistry—since these factors change together in the groups—the comparison still shows that both where the sediment comes from and how fine the particles are have a strong impact on performance. A study with just one source could not show this.

Beyond the sediment comparison, this thesis investigates eight categories of compositional variables, explored across 37 distinct mortar formulations — each with a unique combination of constituent proportions. The study examined several variables: water-to-binder ratio, calcium hydroxide addition, thermal pre-treatment of the sediment by calcination, gypsum addition as a sulfate source and possible setting modifier, LUKOSIL M130 methylsilicone resin as a hydrophobic modifier, mullite as a reactive aluminosilicate corrector, Ordinary Portland Cement as a hybrid binder, and a combined cement-and-silicone resin addition. The water-to-binder ratio was not set beforehand. Instead, extra water was added to each mix as needed to make it workable. Because of this, it is considered an uncontrolled process parameter rather than a true experimental variable. Section 5.2 explains how this affects the comparison between mixes. Most mixes used a basic NaOH and Na<sub>2</sub>SiO<sub>3</sub> activator. In Series I-III, sodium aluminate (NaAlO<sub>2</sub>) was also added to increase the available aluminum during geopolymerisation. These eight categories of compositional variables are summarised in Table 1.1.

*Table 1.1 — Eight Compositional Variable Categories*

| No. | Variable Category       | Component Investigated / Modifier                         | Intended Function / Role                                     |
|-----|-------------------------|-----------------------------------------------------------|--------------------------------------------------------------|
| 1   | Binder Ratio            | <i>Water-to-binder ratio</i>                              | Baseline mix parameter — recorded, not controlled (see note) |
| 2   | Base Activator          | <i>NaOH + Na<sub>2</sub>SiO<sub>3</sub> binary system</i> | Baseline alkalinity and silica supply                        |
| 3   | Supplementary Activator | <i>Sodium aluminate (NaAlO<sub>2</sub>)</i>               | Increase early aluminium availability                        |
| 4   | Calcium-based Additive  | <i>Calcium hydroxide Ca(OH)<sub>2</sub></i>               | Promote C-A-S-H gel development                              |

| No. | Variable Category       | Component Investigated                               | / Modifier | Intended Function / Role                    |
|-----|-------------------------|------------------------------------------------------|------------|---------------------------------------------|
| 5   | Hybrid Binder Component | Ordinary Portland Cement (OPC)                       |            | Parallel hydration and early strength       |
| 6   | Mineral Modifier        | Mullite                                              |            | Reactive aluminosilicate corrector          |
| 7   | Setting Modifier        | Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) |            | Sulphate source / exploratory setting agent |
| 8   | Hydrophobic Modifier    | LUKOSIL M130 resin                                   |            | Reduce water absorption and leaching        |

*The eight compositional variable categories were examined across the 37 mortar formulations, each tested in both the Perrères (1C–4C) and Poglia (SUD–INVASO) sediment groups under identical experimental conditions.*

## 1.4 Research objectives

This thesis is built around five main objectives:

(1) To characterise dredged sediments from both groups, fractions 1C, 2C, 3C, and 4C blended as one precursor and sediments SUD and INVASO were blended as a second, in both raw and thermally pre-treated (calcined) states, using X-ray fluorescence spectroscopy (XRF) elemental analysis, X-ray diffraction analysis (XRD) for mineralogical characterisation, and laser granulometry for particle size distribution determination.

(2) To design and produce 37 distinct alkali-activated mortar formulations, each with a unique combination of constituent proportions, structured around eight categories of compositional variable including binder composition, supplementary materials, activator dosage, and water-to-binder ratio.

(3) To assess the durability behaviour of hardened specimens through 24-hour water immersion after oven curing, measuring water absorption and the pH of the immersion water as indicators of alkaline leaching from the binder matrix.

(4) After the samples are completely dried, their compressive and flexural strengths are measured. The mix variables and sediment groups that most improve mechanical performance are also identified.

(4) Published carbon data help estimate the cradle-to-gate carbon footprint of the best-performing mixes. The main sources of emissions are identified, and the best ways to reduce emissions compared to ordinary Portland cement (OPC) are suggested. A brief overview is provided regarding the potential for reusing dredged sediment and its role within a circular economy. It should be noted that this analysis represents an initial screening rather than a comprehensive 1.5 Scope and Limitations.

## 1.5 Scope and limitations

This study is based on laboratory testing of small mortar samples and focuses exclusively on dense paste and mortar systems. Lightweight, foamed, or fiber-reinforced mixes are not included. All sediment samples were collected from hydroelectric reservoirs in

northern Italy. Therefore, these results are specific to this region and should not be applied to very different sediments without more research.

The experimental program uses XRF and XRD to analyze the starting materials. Scanning electron microscopy (SEM) is used to examine the grain shape of the raw sediment powders. Water absorption and pH are measured after immersing hardened samples in water for 24 hours. Once the samples are completely dry, their compressive and flexural strength are tested. Qualitative SE-mode SEM of the fracture surfaces of the three best-performing hardened mixes is included (Section 5.3); detailed microstructural analysis of the gel network — EDS phase identification, porosity quantification and reaction-product identification — falls outside the scope of this work and is recommended for future investigation.

Fresh-state workability (e.g., flow table or mini-slump) was not measured in this study. All specimens were cured at 60°C; ambient-temperature curing was not investigated. The results are therefore primarily relevant to heat-cured precast applications. More testing under normal curing conditions is needed before these results can be used in real-world settings.

This study did not address important areas such as long-term durability, leaching, ecotoxicology, full life-cycle analysis, economic feasibility, or large-scale production. Future research should look into these topics.

## **1.6 Thesis structure**

The thesis is organized into six chapters. This opening chapter has introduced the environmental context, the CO<sub>2</sub> burden of cement production and the management challenge of dredged sediments, along with the motivation for the research, its specific objectives, and its scope. Chapter 2 surveys the relevant literature on alkali-activation fundamentals, dredged sediment as an AAM precursor, alkaline activator design, and supplementary materials used to modify performance. Chapter 3 covers the materials used, including dredged-sediment precursors, supplementary additives, and the activator system. Chapter 4 describes the experimental program and the testing methods used. Chapter 5 presents the results, including analyses of mechanical performance, water absorption, and pH response for each series and both sediment groups. This chapter also identifies the variables that produced optimal results and provides scanning electron microscopy (SEM) analysis of the best-performing samples to investigate their microstructure and its correlation with mechanical performance. Chapter 6 closes the thesis with a sustainability assessment, the main conclusions, and recommendations for future work.

## Chapter 2: Literature Review

### 2.1 Environmental impact of ordinary Portland cement

Portland cement is the most widely used construction binder in the world, and its production is one of the most difficult industrial processes to decarbonize. Global output exceeds four billion tonnes per year and could approach six billion by 2050 [2, 22]. Most of the carbon emissions from cement come from two main sources that are hard to separate. The first is burning fossil fuels to reach the high sintering temperature of around 1,450°C. The second is breaking down limestone ( $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ ), which releases  $\text{CO}_2$  directly, regardless of the energy used. Together, these steps produce about 0.66-0.82 tonnes of  $\text{CO}_2$  per tonne of clinker produced [3]. As a result, cement is one of the largest industrial sources of greenhouse gases, accounting for about 5-7% of global emissions [4, 5]. The IEA (International Energy Agency) says this is one of the hardest sectors to decarbonize, since more than half of its emissions come from processes that electrification cannot fix [22]. Because of the Paris Agreement's 1.5–2°C target [7], there is a strong need for alternative binders [6]. Alkali-activated materials are a promising option, as they avoid clinker firing and can incorporate waste materials such as dredged sediments.

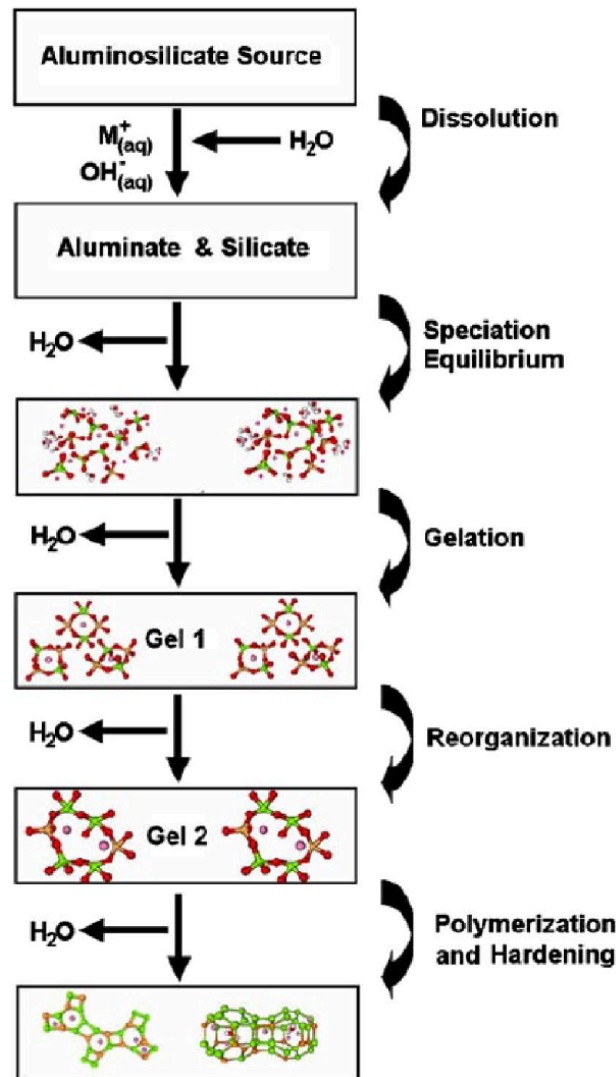
### 2.2 Alkali-activation fundamentals

Alkali-activated materials (AAMs) are inorganic binders produced by reacting an aluminosilicate precursor with a highly alkaline activating solution. No clinker sintering is involved, so the process-derived  $\text{CO}_2$  that makes cement so difficult to decarbonize is largely avoided. Reported reductions in global warming potential relative to OPC concrete typically fall within the 40–80% range, though the exact figure depends heavily on the precursor type and the activator's energy intensity [18, 23, 24]. Davidovits introduced the term geopolymer in the 1970s to describe low-calcium clay-based systems [8, 9]. Although many use geopolymer and AAM interchangeably, geopolymer is actually a subset of AAM. The AAM group also includes alkali-activated slag, hybrid OPC–geopolymer systems, and the sediment-based binders studied here. For a thorough overview, the RILEM State-of-the-Art Report by Provis and van Deventer [12] is still the main reference in the field.

#### 2.2.1 Reaction mechanisms

AAM formation proceeds through three overlapping stages. In dissolution, hydroxide ions attack the precursor surface, breaking Si–O–Si and Si–O–Al bonds and releasing silicate and aluminate monomers into solution. The rate is governed by  $\text{OH}^-$  concentration and temperature and, most critically, by the amorphous content of the precursor, since crystalline phases dissolve far more slowly [12, 25] — the central rationale for the thermal pre-treatment examined in Section 2.3.2. As speciation occurs, dissolved species come together to form short oligomeric units. At this point, sodium silicate in the activator adds more silica, increasing the Si/Al ratio and leading to denser cross-linking. Polycondensation then connects

these oligomers into a three-dimensional amorphous aluminosilicate gel that gradually hardens over time [8, 12].



**Figure 2.1** — The three overlapping stages of geopolymerisation: dissolution of the aluminosilicate precursor, speciation of dissolved monomers into oligomers, and polycondensation into a three-dimensional aluminosilicate gel (after the conceptual model of Duxson et al., 2007).

## 2.2.2 N-A-S-H and C-A-S-H gel products

The dominant gel type depends on calcium content. Low-calcium precursors such as metakaolin, class F fly ash, and most clay sediments produce sodium aluminosilicate hydrate (N-A-S-H) gel: a cross-linked, zeolite-like network with good chemical durability but slow ambient-temperature strength development [12]. Heat curing at 40–80°C is typically required to reach useful early strengths. When reactive calcium is present, whether from slag,  $Ca(OH)_2$ , OPC, or calcium-rich precursor fractions, calcium (alumino)silicate hydrate



(C-A-S-H) gel forms alongside or instead of [25, 26]. C-A-S-H develops strength faster and achieves higher ultimate values, though it is more susceptible to carbonation. In intermediate-calcium systems, both gels coexist, and their balance governs strength, porosity, and durability [26]. This duality matters for the blended sediment precursors used here, which fall within an intermediate calcium range, and forms the basis for including  $\text{Ca}(\text{OH})_2$  and OPC as experimental variables.

### **2.2.3 The binary $\text{NaOH} + \text{Na}_2\text{SiO}_3$ activator**

The vast majority of AAM research uses a binary activator:  $\text{NaOH}$  to supply alkalinity and sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) to provide dissolved silica and set the  $\text{SiO}_2/\text{Na}_2\text{O}$  molar ratio  $M_s$  [12, 27]. Commercial waterglass has an  $M_s$  of 2.0–3.3, which must be diluted with  $\text{NaOH}$  to roughly 1.0–2.0 for AAM use. Too low an  $M_s$  limits silica availability; too high an  $M_s$  increases viscosity and may suppress the full reaction. This binary system is the standard across AAM practice and the baseline in this study. Some studies have added sodium aluminate ( $\text{NaAlO}_2$ ) as a third component for high Si/Al precursors — discussed in Section 2.4.2.

## **2.3 Dredged sediments as AAM precursors**

Around one billion cubic meters of sediment are dredged annually from reservoirs, ports, and waterways worldwide [17]. Hydroelectric reservoirs are a particular case: fine particles build up there over decades, reducing storage capacity and eventually threatening dam safety. Much of Italy’s hydroelectric stock dates from the mid-twentieth century, so silting is now widespread, and the simplest disposal routes have been progressively restricted by regulation [19, 20] — leaving landfilling and containment, both of which carry real costs, as the main remaining options. Using dredged sediment as a binder precursor sidesteps that problem directly while also cutting reliance on clinker-based cement, a combination that fits squarely within circular economy thinking for the construction sector.

### **2.3.1 Chemical composition**

What makes a precursor suitable for AAM use comes down to its reactive  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  content. A combined share above roughly 70% by mass is the threshold usually cited [12, 28], though that figure only counts if the material is amorphous, since crystalline quartz barely dissolves under activation conditions. Dredged sediment usually contains 45 to 70%  $\text{SiO}_2$  and 10 to 25%  $\text{Al}_2\text{O}_3$ , along with smaller amounts of  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ , and  $\text{MgO}$  [17, 28]. Its composition is close enough to class F fly ash and calcined clay that comparing them makes sense. The biggest challenge is that the composition can vary. It depends on local geology, how the sediment was deposited, and human activity, and it may even change within a single reservoir. In practice, two factors matter most. If  $\text{CaO}$  is above about 10%, the gel chemistry shifts toward C-A-S-H, which affects how the material sets and its durability. Organic matter and volatile content also reduce the reactive fraction and must be considered in mix design, including  $\text{CO}_2$  released when calcite and dolomite break down in carbonate-rich samples.

### 2.3.2 Thermal pre-treatment and calcination

Raw sediment is, on the whole, a poor-reactivity precursor: its clay minerals — kaolinite, illite, smectite, and various mixed-layer forms — are crystalline and dissolve only slowly under alkaline conditions. Calcination is the standard fix, working through dehydroxylation: heat strips out structural OH groups, the clay lattice collapses, and what remains is a disordered, far more soluble amorphous phase. Kaolinite dehydroxylates between roughly 500°C and 750°C, yielding metakaolinite [17, 29]. Natural sediments are rarely pure kaolinite, though — they mix kaolinite, illite and chlorite alongside quartz and feldspar — and for that kind of mixed-clay assemblage the literature converges on 600–800°C as the practical sweet spot: hot enough to dehydroxylate the full clay fraction, but short of the ~900–1,000°C point where recrystallisation starts forming poorly reactive mullite and cristobalite instead [17, 29, 30]. Carbonate and iron hydroxide phases also decompose within this range, releasing CaO and Fe<sub>2</sub>O<sub>3</sub> in more reactive forms [30]. The 700°C target used in this study (Section 3.1.2) sits at the center of this optimum window.

Calcination does entail real energy costs, and several studies note that the reactivity gains do not always justify them — particularly where the sediment already contains a meaningful amorphous fraction, or where the activator is aggressive enough to mobilize sufficient Si and Al from the untreated material [17].

### 2.3.3 State of the art

Among the earliest Italian investigations, Ferone et al. [29] demonstrated that calcined hydroelectric reservoir sediments, activated with NaOH + Na<sub>2</sub>SiO<sub>3</sub>, produced functional geopolymer binders, identifying the calcination temperature and activator modulus as key variables. Molino et al. [20] confirmed feasibility at the Occhito reservoir and called for broader additive and variability studies. Messina et al. [31] took a different angle, blending calcined sediment with potabilization sludge to produce precast paving bricks. Mahfoud et al. [35] increased the amount of micronized sediment in fly ash geopolymers to 50% and observed strength improvements and a more refined pore structure. However, their later study [36] found that N-A-S-H systems are especially prone to carbonation. In a separate study, Brahim et al. [37] demonstrated that incorporating 50% sediment into alkali-activated compressed earth blocks is structurally viable. Most studies report 28-day compressive strengths ranging from 15 to 40 MPa when heat curing is used [17, 29]. Two consistent gaps stand out: nearly all studies use a single sediment source, making it impossible to separate precursor composition effects from mix-design effects; and systematic additive investigations are essentially absent. This thesis addresses both gaps directly.

## 2.4 Alkaline activator systems

### 2.4.1 Activator design for variable-reactivity precursors

Building on the binary activator fundamentals introduced in Section 2.2.3, the main design challenge is balancing activator concentration with workability. Using more NaOH

speeds up dissolution but reduces the time the mix stays workable. Raising  $M_s$  above about 2.0 thickens the solution and can prevent full gel formation [12, 27]. Sediment precursors make things harder because their reactive content is unpredictable, so the best  $M_s$  cannot be found from the bulk composition alone. This is why this study treats the activator proportions as part of the formulation range rather than fixing them to a single calculated value.

#### **2.4.2 Sodium aluminate as a supplementary component**

$\text{NaAlO}_2$  has been explored as a third activator component in systems where the precursor has a high Si/Al ratio and early aluminum availability is limiting [27]. It dissolves readily, releasing  $\text{Al}(\text{OH})_4^-$  ions that raise both pH and the dissolved Al concentration. Because aluminate is consumed faster than silicate in the early reaction, a transient Al-rich gel precursor forms and then re-equilibrates as silica becomes available [27]. This can accelerate early strength, which is useful for rapid precast demoulding, but the effect is dosage-sensitive: strength peaks at roughly 5–15%  $\text{NaAlO}_2$  by binder mass, and higher dosages disrupt cross-linking and reduce workability [27].  $\text{NaAlO}_2$  therefore remains a selective minority strategy.

#### **2.4.3 Molar ratio design**

Four ratios govern AAM performance: Si/Al (target 1.5–2.5 for N-A-S-H systems), Na/Al (0.8–1.2, to charge-balance tetrahedral Al), the activator modulus  $M_s$ , and the water-to-binder ratio [12, 27]. Industrial precursors can be fixed from XRF data with reasonable confidence. Natural sediments are less tractable: only the amorphous fraction reacts, and because XRF resolves bulk rather than reactive composition, the effective reactive Si/Al remains inaccessible by this route. Selective dissolution, calorimetry, and spectroscopic methods for quantifying the reactive fraction of waste-derived aluminosilicates have been reviewed, but none is yet routine for sediment precursors [33]. For this reason, the study treats the water-to-binder ratio as a clear variable and tests different formulations across a range rather than at a single design point.

### **2.5 Supplementary and modifying materials**

The experimental scheme is organized into three levels: the base binary activator (held constant), a supplementary activator ( $\text{NaAlO}_2$ , used in Series I–III only), and supplementary solid and liquid additives described below, together with two cross-cutting process variables (calcination state and water content). The additives span five functional categories, each introduced below with its intended role, from calcium-based additions through mineral correctors to the hydrophobic silicone resin.

#### **2.5.1 Calcium-based additives: $\text{Ca}(\text{OH})_2$ and OPC**

$\text{Ca}(\text{OH})_2$  at 2–8% by binder mass raises pH, promotes C-A-S-H gel, and accelerates early strength in low-calcium precursors [13, 26]. The mechanism is matrix densification, with C-A-S-H filling pores not occupied by N-A-S-H. If the dosage is too high, unreacted

$\text{Ca(OH)}_2$  can become vulnerable to carbonation-induced shrinkage and microcracking as portlandite turns into calcite, and it can also cause surface efflorescence. Ordinary Portland Cement (OPC) behaves differently. It brings in the  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$  phases, which hydrate during geopolymerisation to form C-S-H and portlandite [12, 32]. This process boosts early strength and workability, but it also leads to higher embodied carbon. In a strongly alkaline environment, the way OPC hydrates changes: portlandite is usually suppressed, and the C-S-H that forms contains more aluminum [32]. Whether the two reactions are synergistic in sediment-based systems remains unresolved.

### **2.5.2 Mineral modifiers: mullite and gypsum**

Mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) has a molar Si/Al ratio of 0.33 (2 Si atoms per 6 Al atoms per formula unit), making it among the most aluminum-rich silicate minerals stable under ambient conditions [48]. It can therefore shift the Si/Al ratio of a silica-dominant precursor toward the N-A-S-H gel formation window. The key caveat is that crystalline mullite is poorly soluble under activation conditions — it tends to act as an inert filler rather than a reactive aluminum source [48]. How much mullite actually contributes depends on its crystallinity and particle fineness. Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) plays a different role: in OPC systems it controls setting by moderating  $\text{C}_3\text{A}$  hydration, while in AAM and hybrid systems sulphate ions can react with Ca and Al to form ettringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$ ), a phase that may help fill pores [32, 34] — though gypsum has also been reported to retard setting in some AAM mixes. None of this has been studied specifically in a sediment-based system, which is exactly why it's included here on an exploratory basis.

### **2.5.3 Hydrophobic modifier: LUKOSIL M130**

LUKOSIL M130 is a methylsilicone (polydimethylsiloxane-based) resin used here to reduce water absorption, an important durability parameter in exposed construction elements. Le Chi et al. [38] are among the few authors to have applied it to a geopolymer system, using it as a surface impregnant on geopolymer foam and reporting a substantial reduction in water absorption alongside improved mechanical strength. Zhang et al. [39] used PDMS in fly ash–slag geopolymers and found that hydrophobicity improved significantly, with N-A-S-H gel responding more strongly than C-A-S-H. Adding silicone resins at 0.5–3% can reduce water absorption by forming a water-repellent layer on the pore surfaces [40]. Still, it is not clear how stable they are over time in the highly alkaline environment of AAMs. That is why this study incorporates the resin directly into the material rather than using it as a surface coating.

## **2.6 Performance benchmarks**

### **2.6.1 Mechanical performance**

Metakaolin- and calcined clay-based AAMs under heat curing typically reach 28-day compressive strengths of 20–60 MPa, whereas fly ash systems typically reach 20–80 MPa [12]. Sediment-based systems fall within the range of 15–40 MPa at 28 days, with higher

values associated with well-designed binary activators and elevated curing [17, 29]. Partial sediment incorporation alongside fly ash has matched or exceeded fly ash-only controls in several studies [35, 37]. Flexural strength typically runs at 15–25% of compressive strength, consistent with OPC mortar [12]. In this study, all specimens were cured at 60°C—within the heat-curing range reported in the literature.

### **2.6.2 Durability**

Water absorption in AAM mortars ranges from below 5% to above 20% by mass, depending heavily on mix design and curing; a widely cited practical threshold of below 10% is used for non-structural applications [41]. These differences trace back to the pore network itself: the porosity of metakaolin-based geopolymers evolves with activator composition and continues to coarsen as the material ages, which directly governs how readily water moves through the matrix [49]. Carbonation is a real concern for N-A-S-H-dominant systems, as CO<sub>2</sub> entering the material gradually lowers the alkalinity of the pore solution and can affect long-term integrity [36, 41, 51]. Efflorescence is another related risk to consider. In this case, soluble alkalis move to the surface and react with CO<sub>2</sub> in the air to form carbonate deposits. This is a known durability and appearance issue in sodium-activated systems, primarily due to loosely bound free Na<sup>+</sup> and an open pore network [51]. Against these vulnerabilities sit two well-documented strengths. Chloride penetration resistance is strong, dense-gel AAMs reaching permeabilities several times lower than equivalent OPC concrete [41], and sulfate resistance is similarly favorable, a consequence of the low or absent C<sub>3</sub>A content. Leachate pH from freshly cured specimens typically falls in the 11–12 range and declines further as residual activator is consumed [29, 34].

### **2.6.3 Sustainability and LCA trade-offs**

LCA comparisons consistently report 40–80% GWP reductions for low-calcium AAM systems relative to OPC, with sodium silicate manufacturing identified as the dominant contributor [18, 23, 24]. The main result depends on specific conditions; it does not hold in all cases. The et al. [42] used a hybrid LCA approach and found that high-strength metakaolin-based AAM can have an energy intensity equal to or higher than that of OPC concrete due to the use of a silicate activator. When fly ash is used instead of metakaolin and sodium silicate is reduced, the environmental benefits are more obvious. However, calcining the precursor increases energy use and reduces the advantage compared to systems that use raw or only lightly processed materials [17]. The sustainability case for sediment-based AAMs therefore rests on formulation choices — above all activator type and precursor pre-treatment — and is not secured merely by avoiding Portland cement. That principle directly shapes the mix design developed in Chapter 4, in which lower-silicate and lower-calcination pathways are structured alongside more conventional formulations.

## **2.7 Chapter summary**

Three conclusions from this review shaped the experimental program that follows.

First, many experts agree that we should move away from OPC. The emissions from clinker production stem from its chemical composition, not just from how kilns are run, so changing energy sources alone will not fix the issue. Alkali-activated materials are well-researched alternatives, but their advantages depend on the type of activator and how the starting material is handled. Life cycle assessment studies show this, although simple comparisons sometimes overlook these points.

Second, dredged sediment from reservoirs could be a useful chemical precursor. It has similar amounts of silica and alumina as fly ash, and in Italy, it is becoming a waste problem. Early studies from Italy indicate that it can produce workable binders, but research on this topic remains limited. Most studies draw on a single sediment source, making it difficult to tell whether the observed behavior reflects the raw material itself or the specifics of the mix design. Equally, very little is known about the influence of additives. Calcium-based additives such as  $\text{Ca}(\text{OH})_2$  and OPC are well understood in fly ash and slag systems, but less so in systems containing more variable and less reactive minerals found in reservoir sediments. Other additives, such as mineral correctors, water-repellent organosilicon modifiers, and sulfate additives, have also not been widely tested with these sediments. The contribution of this work is therefore to transfer these established additive strategies to a new and chemically less predictable substrate, and to ask whether the mechanisms documented for industrial precursors carry over to alkali-activated sediments.

Third, a few technical uncertainties carry straight into the experimental design. The reactive Si/Al ratio of a natural sediment cannot be read off bulk XRF data, so any molar-ratio target is an approximation rather than a precise figure. How additives such as gypsum and LUKOSIL M130 behave in a sediment-based system is essentially unknown. And calcination is not a guaranteed win: its energy cost can eat into the reactivity it buys, especially for sediments that already carry a meaningful amorphous fraction. These three points set the agenda for Chapters 3 and 4. Studying two distinct sediment groups side by side under identical conditions is what lets composition be separated from mix design. Varying eight compositional factors across 37 formulations builds the additive evidence the literature is missing. And designing the matrix to span calcined and uncalcined sediments, and both silicate-heavy and silicate-lean activators, means the sustainability trade-offs raised above can be weighed against the mechanical and durability results in Chapter 5 rather than assumed

## Chapter 3: Materials and Characterisation

### 3.1 Dredged sediment precursor materials

#### 3.1.1 Origin and geological context

The sediment samples used in this research come from two separate hydroelectric reservoir systems in the northern Italian Alps. The Alps are one of the most geologically diverse mountain chains in Europe, with crystalline basement rocks, carbonate sequences, and glacially reworked deposits all coexisting over short distances, and this variety shapes the chemical composition of the sediment that accumulates in downstream reservoirs.

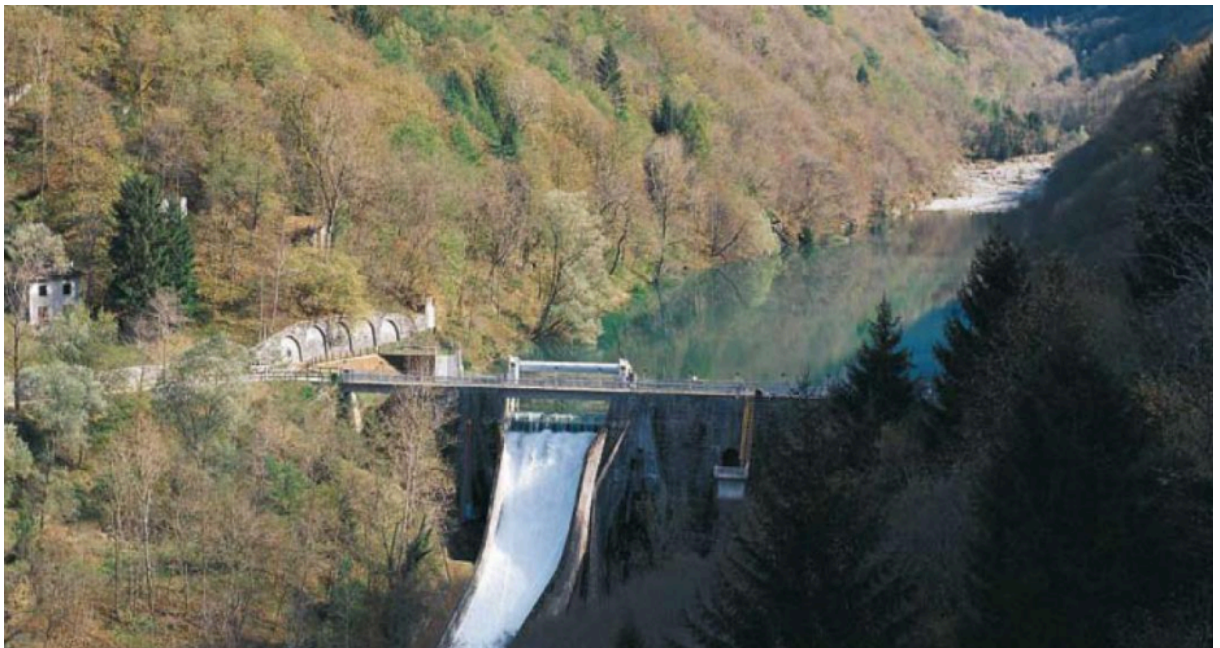
The first group includes fractions 1C, 2C, 3C, and 4C, all collected from the Perrères Dam in Valtournenche, Valle d'Aosta. The dam's catchment area is mainly made up of metamorphic and crystalline rocks such as gneisses, schists, micaschists, and granites, which are typical of the internal Western Alps. Each fraction was taken from a different spot or depth in the reservoir, which explains their different chemical makeups. Notably, fraction 4C has a high iron content ( $\text{Fe}_2\text{O}_3 = 9.39\%$ ), while fraction 3C has more calcium ( $\text{CaO} = 12.3\%$ ), likely due to local carbonate sources in the catchment. For the experiments, the four fractions were mixed in equal parts (25% each) to make a total sediment mass of 50 grams per mix (Group A). All samples arrived moist and were stored in sealed plastic containers at room temperature until they were used.

Group B includes two samples, SUD and INVASO, both taken from the Poggia Dam in Cedegolo, Brescia, but from different areas of the reservoir. INVASO was collected at the upstream inlet, where the river slows down and fine sediment settles. SUD was taken from another part of the basin. SUD has a higher calcium content ( $\text{CaO}$ , 10.8%) than INVASO (7.19%), suggesting it comes from a sub-catchment with more carbonate-rich rocks. The two samples were mixed in equal parts to create Group B.





**Figure 3.1** — Aerial view of the Perrères Dam reservoir, Valtournenche (AO), Valle d'Aosta. The turquoise reservoir, concrete gravity dam wall (bottom right, height 24.36 m), and hydroelectric powerhouse (top left, 18 MW) are visible. The red-outlined area indicates dredged sediment accumulation — the precursor material collected for this study. (Source: CVA S.p.A., [www.cvaspa.it](http://www.cvaspa.it), 2021. All rights reserved CVA S.p.A.)



**Figure 3.2** — The Poggia Dam, Cedegolo, province of Brescia, Lombardy, showing the concrete dam wall and active spillway. Dredged sediments used in this study were collected from the upstream reservoir basin. (Source: Edison S.p.A., Dichiarazione Ambientale — Polo 3, 1° semestre 2012. Available at: [edison.it](http://edison.it). All rights reserved Edison S.p.A.)



### 3.1.2 Physical preparation and pre-treatment

All samples arrived moist and went through a standardised preparation sequence before any testing or mixing. The full sequence is shown in Table 3.1. Raw mixes use the 500 µm-sieved fraction directly, while the heated series go through a second 125 µm sieve before calcination.

*Table 3.1 — Physical preparation sequence for all dredged sediment samples*

| Stage                  | Operation                    | Equipment / Standard                                                                                        | Purpose                                                                 |
|------------------------|------------------------------|-------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------|
| 1                      | Oven drying                  | Open beakers, oven at 80°C; stored in sealed buckets                                                        | Remove free moisture without changing mineral structure                 |
| 2                      | Primary sieving at 500 µm    | Stainless steel sieve, ISO 3310-1                                                                           | Remove coarse sand and gravel; standardise particle size for raw mixes  |
| 3                      | Secondary sieving at 125 µm  | CDL sieve, 125 µm, ISO 3310-1                                                                               | Isolate fine clay-rich fraction before calcination (heated series only) |
| 4 — Heated series only | Thermal calcination at 700°C | Nabertherm muffle furnace, P16 CALCINATION-700: ramp ~120°C/h to 700°C, 1 h hold, cool ~300°C/h; ~9 h total | Dehydroxylate clay minerals; increase amorphous reactive content        |

*Particle size was controlled by sieving alone; no grinding or milling was applied at any stage, so the sediment grains were separated by size rather than fractured. For the raw series, samples were sieved at 500 µm only. For the heated series, samples were sieved at 500 µm, then 125 µm, and then calcined at 700°C.*

The initial drying took place at 80°C in open beakers. After drying, the powder was stored in sealed buckets. This drying temperature is well below the point at which clay minerals begin to lose hydroxyl groups, so it dries the sediment without altering its mineral composition. Once dry, all sediments were sieved at 500 µm to remove coarse inert materials, mainly quartz, feldspar, and mica, which do not dissolve much under alkaline conditions and do not contribute significantly to formation. Any coarse organic residues were also removed. For the heated series, a second 125 µm sieve was used before calcination. This step concentrates the clay-mineral fraction that calcination is meant to target and remove intermediate-sized particles, whose reactivity would not be significantly improved by calcination.

The sieved powder was placed in ceramic crucibles and heated in a Nabertherm muffle furnace (Nabertherm GmbH, Lilienthal, Germany) using the P16 CALCINATION-700 program. The process began at approximately 30 °C, and the temperature increased by 120 °C per hour until reaching 700 °C after six hours. The sample was held at 700 °C for 1 hour. The furnace then cooled at about 300 °C per hour back to 20 °C. The entire process, including heating, holding, and cooling, lasted about 9 hours.



**Figure 3.3** — Stacked test sieves (CDL, ISO 3310-1) used for particle separation; the 125  $\mu\text{m}$  sieve shown was applied to the heated series prior to calcination, following the 500  $\mu\text{m}$  primary sieving.

The 700°C target was chosen because it matches the thermal behavior of clay minerals. At this temperature, kaolinite and illite lose their structural hydroxyl groups and become a disordered amorphous phase, which reacts more easily to alkaline activation than the original crystalline minerals [25, 43]. When the temperature goes above about 800-900°C, mullite and cristobalite form through recrystallization. These new phases are thermally stable and do not react under the alkaline conditions used here [12]. The 700°C target therefore represents the practical optimum that maximizes reactivity without crossing into the recrystallization zone, consistent with the range identified in the literature for clay-rich sediments [17, 29].

Calcination was carried out in ambient air. For the iron-bearing fractions, particularly 4C ( $\text{Fe}_2\text{O}_3 = 9.39\%$ ) and 2C ( $\text{Fe}_2\text{O}_3 = 7.74\%$ ), calcination in air would be expected to oxidize any ferrous iron in the raw sediment toward the ferric state, although this was not measured directly. Note that XRF reports total iron as  $\text{Fe}_2\text{O}_3$  by convention, irrespective of the actual oxidation state, so the tabulated  $\text{Fe}_2\text{O}_3$  values reflect this reporting convention rather than a measured  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio. Under strongly alkaline activation conditions, ferric iron can form low-solubility iron hydroxide layers on dissolving particles, which may slow the early dissolution kinetics of these two fractions [12].

The principal instruments used for sediment characterisation and pre-treatment are shown in Figure 3.4.



*Figure 3.4 — Nabertherm muffle furnace loaded with ceramic crucibles containing sediment fractions prior to calcination at 700°C (programme P16 CALCINATION-700), Politecnico di Torino.*

### 3.1.3 X-ray fluorescence spectrometry (XRF) — elemental analysis

The chemical composition of all six sediment samples was determined by wavelength-dispersive X-ray fluorescence spectrometry (WD-XRF) using a Rigaku Supermini200 benchtop instrument (Rigaku Corporation, Tokyo, Japan), available at the Politecnico di Torino laboratory. The instrument uses a 200 W palladium X-ray tube and scans from fluorine to uranium using a sequential goniometer with interchangeable analyzing crystals. Each sample was prepared as a pressed powder pellet with a polyvinyl alcohol (PVA) binder at a ratio of 0.0600 and analyzed using the SQX fundamental parameters software, which calculates elemental concentrations from measured fluorescence intensities without requiring matrix-matched calibration standards [44]. Results are expressed as normalized oxide mass percentages. Table 3.2 presents the complete XRF results.

*Table 3.2 — XRF chemical composition of all sediment samples (mass%), Rigaku Supermini200, 12 November 2025, Politecnico di Torino*

| Oxide<br>(mass%)               | INVASO | SUD   | 1C    | 2C    | 3C    | 4C    |
|--------------------------------|--------|-------|-------|-------|-------|-------|
| SiO <sub>2</sub>               | 60.7   | 55.8  | 58.5  | 52.7  | 60.5  | 51.5  |
| Al <sub>2</sub> O <sub>3</sub> | 16.6   | 16.0  | 17.3  | 20.3  | 13.7  | 20.5  |
| Fe <sub>2</sub> O <sub>3</sub> | 4.77   | 5.36  | 5.08  | 7.74  | 5.46  | 9.39  |
| CaO                            | 7.19   | 10.8  | 6.81  | 6.76  | 12.3  | 5.45  |
| K <sub>2</sub> O               | 3.55   | 3.54  | 3.02  | 5.40  | 2.48  | 4.37  |
| Na <sub>2</sub> O              | 1.70   | 1.61  | 3.01  | 1.83  | 1.80  | 1.67  |
| MgO                            | 4.27   | 5.43  | 4.99  | 3.54  | 2.30  | 5.23  |
| TiO <sub>2</sub>               | 0.709  | 0.773 | 0.624 | 0.754 | 0.689 | 0.949 |

|                                                         |       |            |       |       |       |       |
|---------------------------------------------------------|-------|------------|-------|-------|-------|-------|
| SO <sub>3</sub>                                         | 0.067 | 0.087      | 0.054 | 0.322 | 0.192 | 0.371 |
| P <sub>2</sub> O <sub>5</sub>                           | 0.211 | 0.261      | 0.283 | 0.207 | 0.299 | 0.261 |
| MnO                                                     | 0.113 | 0.129      | 0.101 | 0.119 | 0.105 | 0.158 |
| Cr <sub>2</sub> O <sub>3</sub>                          | 0.041 | 0.032      | 0.037 | 0.034 | 0.025 | 0.073 |
| BaO                                                     | —     | —          | 0.094 | 0.095 | —     | —     |
| SiO <sub>2</sub> +Al <sub>2</sub> O <sub>3</sub><br>(%) | 77.3  | 71.8       | 75.8  | 73.0  | 74.2  | 72.0  |
| Molar Si/Al                                             | 3.10  | 2.95       | 2.87  | 2.19  | 3.71  | 2.13  |
| CaO class.                                              | Low   | Borderline | Low   | Low   | High  | Low   |

*Molar Si/Al =  $[m(\text{SiO}_2)/60.09] / [2 \cdot m(\text{Al}_2\text{O}_3)/101.96]$ . CaO classification: Low < 8%; Borderline 8–12%; High > 12%. '—' = below detection limit or not detected.*

All six samples contain sufficient silica and alumina to serve as geopolymer precursors. Their SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> values range from 71.8% in SUD to 77.3% in INVASO, both exceeding the commonly cited 70% minimum for reliable alkali activation [12, 28]. The molar Si/Al ratio is the key factor when designing geopolymers. The optimal value is around 1.5–2.5, corresponding to poly(sialate-siloxo) and poly(sialate-disiloxo) network types [27, 25]. Samples 2C (Si/Al = 2.19) and 4C (2.13) are already close to the lower end of this range. The others, 3C (3.71), INVASO (3.10), SUD (2.95), and 1C (2.87), are relatively silicon-rich and need supplementary aluminum to reach the target. This is the principal reason sodium aluminate (NaAlO<sub>2</sub>) was included as a third activator component in Series I–III, with its dosage adjusted for each sediment type as detailed in Section 3.3.2.

The CaO content separates samples into distinct gel-forming regimes. Fractions 1C (6.81%), 2C (6.76%), 4C (5.45%), and INVASO (7.19%) are low-calcium systems where N-A-S-H gel will predominate. Fraction 3C (12.3%) is a high-calcium precursor expected to also form C-A-S-H gel upon activation, analogous to alkali-activated slag behavior [26]. SUD (10.8%) sits on the borderline between the two regimes. Two additional observations from the data: 4C and 2C have notably elevated Fe<sub>2</sub>O<sub>3</sub> (9.39% and 7.74% respectively), which may slow dissolution kinetics by forming iron hydroxide surface layers under strongly alkaline conditions [12]; and elevated SO<sub>3</sub> in 2C (0.322%), 4C (0.371%), and 3C (0.192%) suggests sulphate-bearing mineral phases whose potential interaction with the activation chemistry is discussed in Chapter 5.



*Figure 3.5 — Rigaku Supermini200 wavelength-dispersive XRF spectrometer with the 10-position sample carousel, Politecnico di Torino.*

### 3.1.4 X-ray diffraction analysis (XRD) — mineralogical characterisation

While XRF shows which elements are present, it cannot distinguish among different mineral phases that contain those elements. Silica can exist as reactive amorphous glass, poorly reactive crystalline quartz, or feldspar — and these behave very differently during alkaline activation. Only the amorphous fraction dissolves readily under alkaline conditions; crystalline phases such as quartz and feldspar are largely inert [12, 25]. XRD was used to identify the crystalline mineral phases present in each sample and to qualitatively assess the relative balance between crystalline and reactive amorphous material.

XRD measurements were performed using a PANalytical X'PERT PRO diffractometer (PANalytical B.V., Almelo, Netherlands) equipped with a Cu X-ray tube operating at 40 kV and 40 mA, producing CuK $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Diffractograms were recorded over a  $2\theta$  range of  $5^\circ$  to  $70^\circ$  with a step size of approximately  $0.0016^\circ$  and a counting time of 21.42 seconds per step, using a PSD scanning mode with a  $3.35^\circ$  detector length. A fixed divergence slit ( $0.2177^\circ$ ) was used throughout. Measurements were performed at the Politecnico di Torino laboratory on 11 December 2025. Mineral phases were identified by matching peak positions against the ICDD PDF-4+ reference database.

*Table 3.3 — Crystalline phases identified by XRD in the six raw, 500  $\mu\text{m}$ -sieved sediment samples (PANalytical X'PERT PRO, CuK $\alpha$ , ICDD PDF-4+, 11 December 2025)*

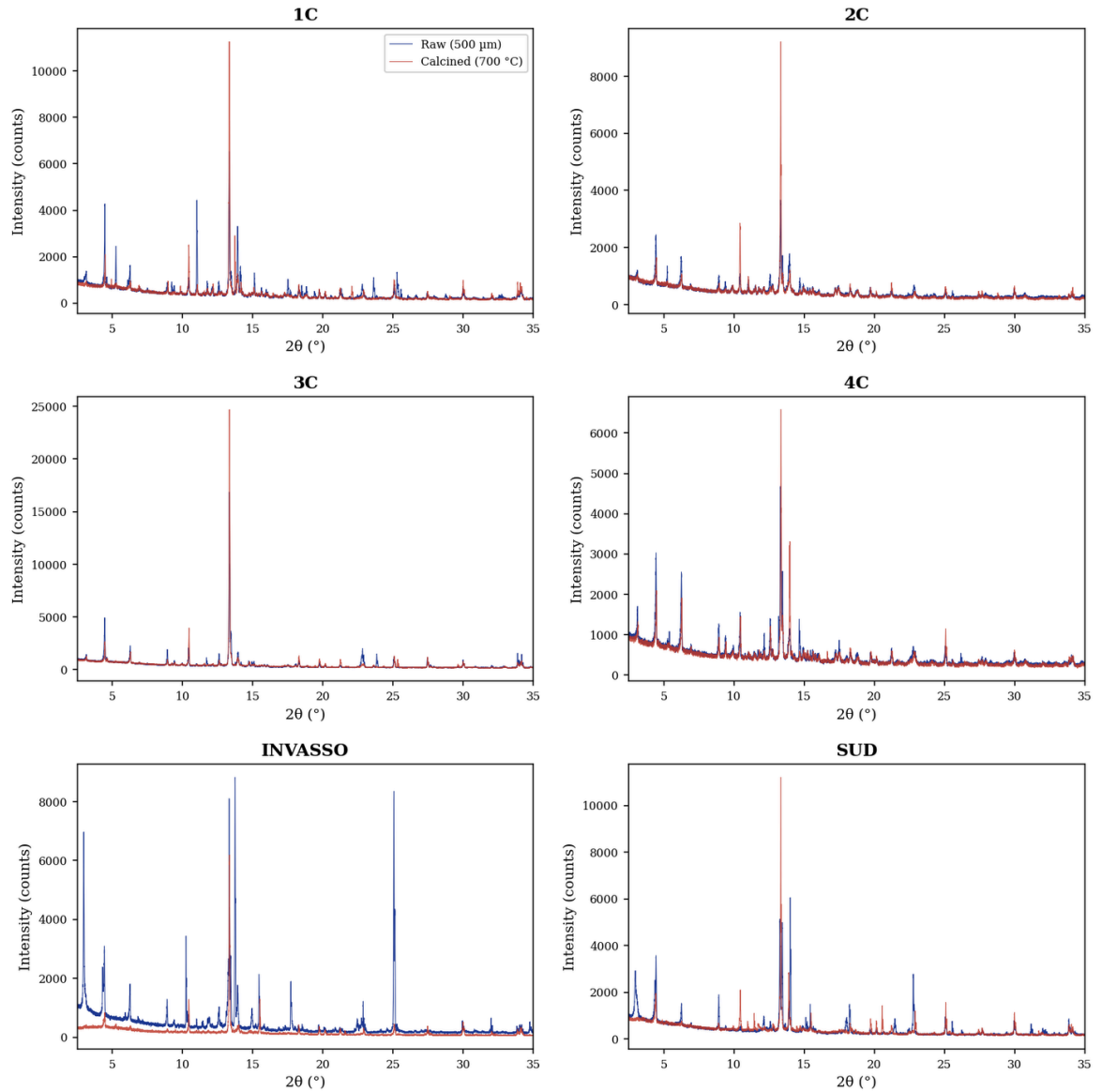
| Phase  | Formula          | Samples detected in | Role in alkaline activation                                                      |
|--------|------------------|---------------------|----------------------------------------------------------------------------------|
| Quartz | SiO <sub>2</sub> | All six             | Dominant crystalline phase; largely inert under alkaline activation; contributes |

|                                          |                                                                 |                                                 |  |                                                                                                                                                                                                            |
|------------------------------------------|-----------------------------------------------------------------|-------------------------------------------------|--|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                          |                                                                 |                                                 |  | SiO <sub>2</sub> to XRF totals without participating in gel formation                                                                                                                                      |
| Muscovite (illite-type mica)             | $\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$  | All six                                         |  | Primary Al-bearing clay; hosts the K <sub>2</sub> O and partial Al <sub>2</sub> O <sub>3</sub> detected by XRF; partial dehydroxylation at 700°C increases reactivity                                      |
| Albite (plagioclase feldspar)            | $\text{NaAlSi}_3\text{O}_8$                                     | All six                                         |  | Accounts for Na <sub>2</sub> O and part of Al <sub>2</sub> O <sub>3</sub> in XRF; poorly soluble under moderate NaOH; slowly releases Al under strongly alkaline conditions                                |
| Clinochlore / Chamosite (chlorite group) | $(\text{Mg,Fe,Al})_6(\text{Si,Al})_4\text{O}_{10}(\text{OH})_8$ | All six                                         |  | Fe/Mg-bearing phyllosilicate; accounts for part of MgO and Fe <sub>2</sub> O <sub>3</sub> ; dehydroxylates at 700°C, contributing to increased amorphous fraction                                          |
| Kaolinite                                | $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$                 | INVASO confirmed; expected in others (see note) |  | Key reactive clay; fully dehydroxylates at 550–700°C to metakaolinite (amorphous); most significant reactivity contribution of the heated series                                                           |
| Calcite                                  | $\text{CaCO}_3$                                                 | INVASO, SUD, 3C; minor in others                |  | Accounts for elevated CaO in 3C and SUD; decomposes above 800°C (outside the 700°C treatment window); dissolves under strongly alkaline conditions releasing Ca <sup>2+</sup> for C-A-S-H co-precipitation |
| Dolomite                                 | $\text{CaMg}(\text{CO}_3)_2$                                    | INVASO confirmed                                |  | Secondary carbonate; contributes to MgO and CaO in XRF; stable below 700°C; minor reactivity contribution                                                                                                  |

All six samples show similar mineral compositions, confirming a shared Alpine origin. XRF and XRD results are consistent: higher SiO<sub>2</sub> indicates quartz, while Al<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O suggest muscovite or illite clays, and MgO and Fe<sub>2</sub>O<sub>3</sub> point to minor chlorite-group minerals. Carbonate-bearing samples contain calcite and dolomite, explaining their higher CaO content. Overall, the reactive aluminosilicate phase is dominated by clay minerals rather than glassy phases, which explains why thermal activation is effective by transforming kaolinite into more reactive metakaolin. This is why thermal activation is useful: when kaolinite is heated to 700°C, it transforms into metakaolinite, thereby making the heated samples more reactive [25, 43].

Calcite is detected in INVASO, SUD, and 3C, consistent with the elevated CaO in those samples (7.19–12.3%); dolomite is additionally confirmed in INVASO, providing a supplementary source of both Ca<sup>2+</sup> and Mg<sup>2+</sup> for the activation chemistry. The XRD phase identification therefore corroborates the XRF elemental data and confirms that the reactive aluminosilicate pool in these materials consists primarily of clay minerals rather than glassy phases, making thermal activation a particularly relevant treatment for improving their geopolymeric potential [12, 25, 43].

It should be noted that the XRD analysis in this work was used for qualitative phase identification only. Quantitative phase analysis (for example, Rietveld refinement with an internal standard) was not performed, and the proportion of X-ray-amorphous material was therefore not quantified. This is acknowledged as a limitation: because only the amorphous and poorly crystalline fraction participates in alkali activation, the reactive-fraction arguments made throughout this work remain qualitative rather than numerically resolved. Nevertheless, the raw diffractograms (Figure 3.6) are dominated by sharp crystalline reflections superimposed on a relatively low, gently varying background, indicating that the untreated sediments are predominantly crystalline with only a limited amorphous content. This observation is itself consistent with the rationale for thermal treatment: comparison of the raw and calcined patterns shows a reduction in the intensity of several low-angle clay-mineral reflections after calcination at 700 °C, consistent with dehydroxylation and partial collapse of the clay lattice into a more reactive, disordered phase. Quantitative amorphous-content determination by Rietveld refinement is recommended for future characterisation of these materials



**Figure 3.6** — X-ray diffraction patterns of the six sediments in their raw (500  $\mu\text{m}$ , blue) and calcined (700  $^{\circ}\text{C}$ , red) states. Sharp reflections correspond to crystalline phases (predominantly quartz, micas/illite, feldspars and, in the calcium-rich samples, calcite). The reduction in several low-angle clay reflections after calcination is consistent with dehydroxylation of the clay fraction.

### 3.1.5 Laser granulometry — particle size distribution

Particle size was measured by laser diffraction granulometry for all six sediment samples, both in their raw form and after sieving at 500  $\mu\text{m}$ , at the Politecnico di Torino laboratory. This technique measures how laser light scatters at different angles and uses the resulting data to calculate a volume-weighted particle size distribution. For each sample, the volume-weighted mean diameter  $D[4,3]$  is reported. This parameter gives more weight to larger particles based on their volume, as defined in ISO 13320 [45]. Table 3.4 shows the percentile diameters ( $D_{10}$ ,  $D_{50}$ ,  $D_{90}$ ), the volume-weighted mean  $D[4,3]$ , and the distribution span for each sample.



Measurements were performed at the Politecnico di Torino laboratory using a Malvern Mastersizer 3000E laser diffraction analyzer (Malvern Panalytical Ltd., Malvern, UK) with an Aero S dry dispersion unit.

*Table 3.4 — Particle-size distribution for all six sediment samples*

| Sample | D10 (μm) | D50 (μm) | D90 (μm) | D[4,3] (μm) | Span | Category      |
|--------|----------|----------|----------|-------------|------|---------------|
| 2C     | 3.20     | 14.6     | 128      | 40.6        | 8.55 | Fine          |
| 4C     | 7.03     | 44.7     | 160      | 66.8        | 3.42 | Fine-medium   |
| 1C     | 27.0     | 153      | 421      | 193         | 2.58 | Medium        |
| 3C     | 51.6     | 149      | 482      | 271         | 2.89 | Medium-coarse |
| INVASO | 177      | 375      | 646      | 393         | 1.25 | Coarse        |
| SUD    | 188      | 387      | 665      | 407         | 1.23 | Coarse        |

*This table shows the particle-size distribution for all six sediment samples, both in their raw form and after sieving at 500 μm. It includes the percentile diameters (D10, D50, and D90), the volume-weighted mean diameter (D[4,3]), and the span, which is calculated as (D90 – D10)/D50. We calculated these values using laser-diffraction volume distributions measured with a Malvern Mastersizer 3000E, averaging five measurements for each sample. The span measures the width of the particle-size distribution. Lower span values indicate a narrower, more uniform distribution, which indicates better sorting.*

The D[4,3] values range from 40.6 μm in 2C to 407 μm in SUD, which is almost a tenfold difference. Smaller particles have more surface area for the alkaline activator per unit mass, so they dissolve faster and release more reactive aluminosilicate species early in gel formation [45, 46]. Table 3.4 and Figure 3.8 show more details about these distributions. Fraction 2C is the finest sample (D50 = 14.6 μm) and has the widest range, with a span of 8.55. This is about ten times wider than any other sample, so 2C contains many very fine, highly reactive particles along with some coarser grains. This broad, fine-skewed distribution makes 2C the most reactive part of the blend. Fraction 4C is also fine (D50 = 44.7 μm, span 3.42). In contrast, SUD and INVASO are both coarse and have narrow ranges (D50 = 387 and 375 μm; spans of 1.23 and 1.25). This matches the way they form in the inlet zone. As the water slows down, it sorts the material and leaves a layer of coarse particles behind. These two sediments have the lowest surface area and the most uniform, coarse particles, which means they also have the lowest surface reactivity. Fractions 1C and 3C fall in between (D50 = 153 and 149 μm; spans of 2.58 and 2.89). Calcination is most important for the coarser, more narrowly graded samples. In addition to removing water from the clay minerals, heating and cooling create microcracks that increase the accessible surface area [12]. This helps make up for the lower surface area of the coarse Group B sediments. Looking at the full distribution, not just the mean diameter, shows that the difference in reactivity between the fine, broadly graded Group A fractions and the coarse, uniformly graded Group B sediments comes from both the average size and the different spread of the two distributions.



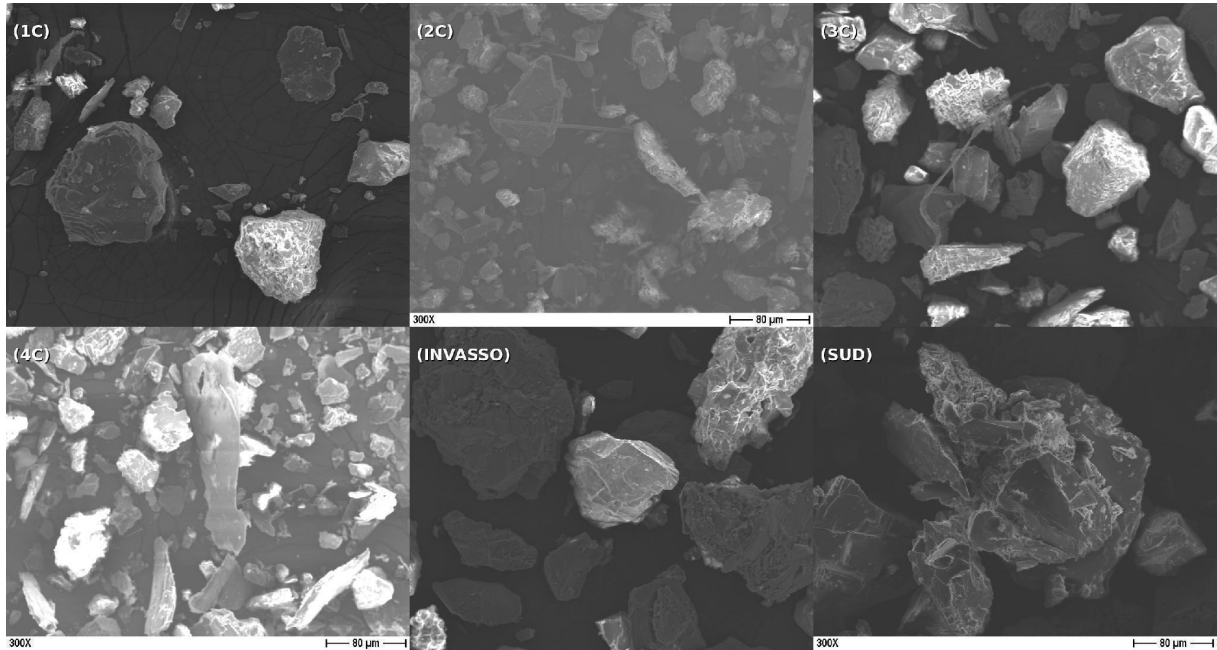
*Figure 3.7 — Malvern Mastersizer 3000E laser diffraction analyser with Aero S dry dispersion unit, Politecnico di Torino.*

### **3.1.6 Scanning electron microscopy — grain morphology**

Scanning electron microscopy was performed on the raw, 500  $\mu\text{m}$ -sieved sediment powders to characterize grain morphology and surface texture. Figure 3.8 presents representative images of all six samples at nominally equivalent magnification, and these confirm a substantial variation in particle size and morphology between fractions, consistent with the  $D[4,3]$  values in Table 3.4. The fine, densely packed angular grains of fractions 2C and 4C match their low  $D[4,3]$  values (40.6 and 66.8  $\mu\text{m}$ ); 1C and 3C, by contrast, form coarser and more heterogeneous assemblages of rounded to sub-angular particles. Group B sediments (INVASO and SUD) are very different from the others. Their grains are large and blocky, with clear surface features that fit their inlet-zone depositional origin, and they have high  $D[4,3]$  values (393 and 407  $\mu\text{m}$ ). This size difference also affects how they react. The fine, angular 2C and 4C grains have much more surface area for the activator to reach, so they are likely to dissolve the fastest and release reactive species first. On the other hand, the coarse, blocky Group B grains have less surface area and are expected to react more slowly if left untreated.

Across every sample, planar cleavage surfaces and stepped morphologies characteristic of the mica-group minerals (muscovite/illite) appear alongside more rounded quartz grains, in agreement with the XRD phase identification in Section 3.1.4. The angular-to-subangular shapes, with sharp edges and well-preserved crystal faces, indicate limited fluvial transport prior to deposition. Prolonged transport in river systems abrades grains through repeated collision, rounding their edges and smoothing their surfaces; the angularity observed here instead reflects short-distance transport from the Alpine catchment and rapid settling within the reservoir basin, with too little mechanical reworking to round the grain edges. From an activation standpoint, the angular, cleavage-dominated surfaces of the mica- and illite-type particles expose reactive edge sites that are more readily attacked by hydroxide ions than basal planar surfaces, whereas the rounded quartz grains contribute little to dissolution; this layered, sharp-edged morphology is shown at higher magnification in

Figure 3.9. The coarse, low-surface-area Group B grains ( $D[4,3] \approx 393\text{--}407\ \mu\text{m}$ ) are correspondingly expected to be the slowest to dissolve, reinforcing the rationale for calcining these sediments to enhance their reactivity.



**Figure 3.8** — SEM images of the six raw, 500  $\mu\text{m}$ -sieved sediment samples. Top row (Group A, Perrères Dam): (1C), (2C), (3C). Bottom row: (4C, Group A) and Group B sediments from Poggia Dam: (INVASSO), (SUD). All images acquired at  $\times 300$  magnification in secondary electron (SE) mode; scale bar = 80  $\mu\text{m}$ .

## 3.2 Supplementary and modifying materials

Six categories of supplementary material were incorporated into selected mixes, each with a distinct role in the binder system, as set out below; Table 3.5 collates the dosages across all experimental series.

### 3.2.1 Calcium hydroxide ( $\text{Ca}(\text{OH})_2$ )

Calcium hydroxide (portlandite,  $\text{Ca}(\text{OH})_2$ , molar mass 74.09 g/mol, reagent grade) was used in Series II and III mixes at dosages ranging from 22 g to 26 g per batch. It serves two simultaneous roles: as a supplementary alkalinity source, releasing  $\text{OH}^-$  ions that support precursor dissolution without introducing additional sodium; and as a calcium source that promotes C-A-S-H gel formation alongside the primary N-A-S-H network, thereby accelerating early strength development [26, 47]. The dosage was adjusted for each sediment type based on the molar ratio calculations in Section 3.3.2.

### 3.2.2 Mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ )

Commercial mullite powder ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , white powder,  $-325$  mesh, 0–45  $\mu\text{m}$ , Jiangsu) was used in Series VI mixes at dosages ranging from 5 g to 10.5 g per batch. At

roughly 72%  $\text{Al}_2\text{O}_3$  and 28%  $\text{SiO}_2$  by mass (molar  $\text{Si}/\text{Al} = 0.33$ , or 2 Si atoms per 6 Al atoms per formula unit), mullite ranks among the most aluminum-rich silicate minerals that remain stable at ambient conditions [48]. That is precisely why it is here: pushing the composite binder's bulk  $\text{Si}/\text{Al}$  ratio toward the optimal N-A-S-H window matters most for the more silica-rich sediments (3C at  $\text{Si}/\text{Al} = 3.71$ , INVASO at 3.10). One caveat is worth stating plainly — crystalline mullite barely dissolves under moderate alkaline activation, so its role here is compositional correction, not direct reactive participation [48].

### 3.2.3 Ordinary Portland cement (Type 3B)

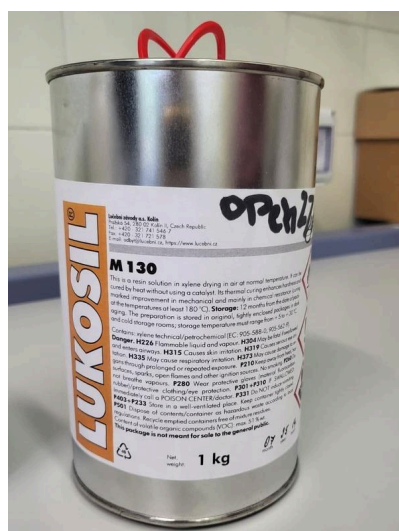
OPC type 3B was used in Series V, VII, and IX mixes at dosages ranging from 13 g to 22.5 g per batch. The cement was used as received. Type 3B in the Italian classification is a Portland composite cement blended with blast-furnace slag within the limits set by EN 197-1. Its inclusion leverages the rapid hydration of alite and belite clinker phases to supplement early-age strength through C-S-H gel formation, and the calcium released further contributes to C-A-S-H co-precipitation alongside the geopolymer network [32].

### 3.2.4 Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )

Gypsum (calcium sulfate dihydrate,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , molar mass 172.17 g/mol) was added to Series VIII mixes at 1.0 g per batch (Mixes 29–30) and 2.5 g per batch (Mixes 36–37). In conventional cement, gypsum controls setting by moderating  $\text{C}_3\text{A}$  hydration. In AAM systems, sulfate ions can interact with aluminum and calcium species in the gel-forming system, thereby modifying reaction kinetics [34]. Its inclusion here is exploratory, motivated by the fact that fractions 2C, 3C, and 4C already contain endogenous sulfate ( $\text{SO}_3$  up to 0.371%), allowing investigation of whether additional sulfate promotes or retards geopolymerisation.

### 3.2.5 LUKOSIL M130 silicone resin

LUKOSIL M130 (Lučební závody a.s. Kolín, Czech Republic) is a methylsilicone resin dissolved in xylene, used as a hydrophobic modifier in Series IV, VII, VIII, and IX mixes at dosages of 3, 3.75, 5, 7, 10, and 15 g per batch. The product contains approximately 50% non-volatile silicone resin and approximately 50% xylene (per the supplier's SDS). The Si–O–Si backbone with methyl ( $-\text{CH}_3$ ) groups attached to silicon makes the material strongly water-repellent. The motivation for its inclusion is to reduce water absorption, limit alkali ion transport through the pore network, and mitigate efflorescence, a common problem in alkali-activated materials [38, 39]. Organosilicon surface modifiers have shown particular promise here: Lv et al. [52] reported that incorporating polydimethylsiloxane into a sodium geopolymer densified the pore structure, reduced water absorption and alkali leaching, and markedly suppressed efflorescence — a direct precedent for the methylsilicone resin examined in this study. M130 was added directly to the fresh paste as a liquid during mixing, without dilution.



**Figure 3.9** — LUKOSIL M130 methylsilicone resin (Lučební závody a.s., Kolín, Czech Republic), 1 kg metal tin, as used in this study. The product is a resin solution in xylene (VOC max. 51 wt%), used without dilution at dosages of 3–15 g per batch.

### 3.2.6 Standard sand

Standard silica sand, supplied in 1350 g plastic bags labeled 'standard sand', was used as the granular filler in all mixes at dosages ranging from 23 g to 50 g per batch. The sand was used as received. Standard sands used in Italian construction materials laboratories typically conform to EN 196-1 (CEN standard sand), a well-graded natural silica sand with a maximum particle size of 2 mm and SiO<sub>2</sub> content above 98%. It is chemically inert under the alkaline conditions used in these experiments and contributes to the mortar's mechanical skeleton without participating in the binder chemistry.

**Table 3.5** — Supplementary material dosages across all experimental series

| Series                   | Mixes          | Ca(OH) <sub>2</sub><br>(g) | Mullite<br>(g) | OPC 3B<br>(g) | Gypsum<br>(g) | M130<br>(g)    | Sand<br>(g) |
|--------------------------|----------------|----------------------------|----------------|---------------|---------------|----------------|-------------|
| I — Reference            | 1, 2           | —                          | —              | —             | —             | —              | 50          |
| II — Ca(OH) <sub>2</sub> | 3–6            | 22–26                      | —              | —             | —             | —              | 50          |
| III — Heated             | 7–10           | 26 (7,8);<br>— (9,10)      | —              | —             | —             | —              | 50          |
| IV — M130                | 11–16, 19–20   | —                          | —              | —             | —             | 3–15           | 50          |
| V — Cement 3B            | 17, 18, 21, 22 | —                          | —              | 13–17         | —             | —              | 33–37       |
| VI — Mullite             | 23–26, 31–32   | —                          | 5–10.5         | —             | —             | —              | 40–45       |
| VII<br>Cement+M130       | 27, 28         | —                          | —              | 15            | —             | 5              | 30          |
| VIII — Gypsum            | 29, 30, 36, 37 | —                          | —              | —             | 1–2.5         | .75<br>(36,37) | 40–45       |
| IX<br>Cement+M130        | 33, 34, 35     | —                          | —              | 13–22.5       | —             | 7–10           | 30          |

*Dosages are per batch. '—' = not used in this series. M130 = LUKOSIL M130 silicone resin. OPC 3B = Ordinary Portland Cement type 3B. Series VIII mixes 36–37 combine gypsum (2.5 g) and M130 (3.75 g).*

### 3.3 Alkaline activator system

#### 3.3.1 Components: $\text{NaAlO}_2$ , $\text{NaOH}$ , and $\text{Na}_2\text{SiO}_3$

The alkaline activator in this study is a three-component system comprising sodium aluminate ( $\text{NaAlO}_2$ ), sodium hydroxide ( $\text{NaOH}$ ), and sodium silicate ( $\text{Na}_2\text{SiO}_3$ ). The composition varies by series, as detailed in Table 3.6, the definitive reference for all activator dosages.

Series I–III (Mixes 1–10) use a three-component activator including  $\text{NaAlO}_2$ . This is specific to those series and serves a dual purpose: supplying additional reactive aluminum to the activating solution and increasing its overall alkalinity. As discussed in Section 2.4.2, adding  $\text{NaAlO}_2$  to a sodium silicate solution raises dissolved Al availability, promotes earlier gel network percolation, and can accelerate early strength — particularly useful for high-Si/Al precursors such as 3C (Si/Al = 3.71) and INVASO (3.10) [27].

Series IV–IX (Mixes 11–37) do not use  $\text{NaAlO}_2$ . Most mixes in this series use 1.5 g of  $\text{NaOH}$ , as shown in Table 3.6. The exception is Mixes 31 and 32 (Series VI, mullite), which use 7 g and 9 g of  $\text{NaOH}$ , respectively; the higher  $\text{NaOH}$  dosage in these mixes reflects the compositional adjustment required when mullite is the principal additive, as confirmed in Table 3.6. For all Series IV–IX mixes,  $\text{Na}_2\text{SiO}_3$  is fixed at 30.6 g.

Sodium aluminate ( $\text{NaAlO}_2$ , molar mass 81.97 g/mol, anhydrous powder) dissolves in alkaline solution to release the tetrahedral aluminate anion  $[\text{Al}(\text{OH})_4]^-$ , directly enriching the reactive aluminate pool. Dosages in Series I–III range from 5.0 g (for 4C) to 5.5 g (for 2C), the fractions closest to Si/Al = 2.0, up to 13.5 g (for 3C, highest Si/Al at 3.71), as calculated in Section 3.3.2. Sodium hydroxide ( $\text{NaOH}$ ,  $\geq 98\%$  purity, pellet form) is the primary source of  $\text{OH}^-$  ions for initiating precursor surface dissolution. Sodium silicate solution ( $\text{Na}_2\text{SiO}_3$ , nominal  $\text{Na}_2\text{O}$  8–9 wt%,  $\text{SiO}_2$  25–29 wt%, balance water) provides both soluble silica for gel network formation and additional alkalinity. The nominal oxide composition corresponds to a silicate modulus  $M_{\square} = \text{SiO}_2/\text{Na}_2\text{O}$  of approximately 3.3 (mass-ratio basis  $\approx 3.1$ ), placing the as-supplied waterglass at the upper end of the commercial range noted in Section 2.2.3; in the binary Series IV–IX mixes, the addition of 1.5 g  $\text{NaOH}$  to 30.6 g of this solution lowers the effective modulus of the combined activator below this figure.

#### 3.3.2 Molar ratio calculations

The activator formulation for each precursor in Series I–III was designed using molar ratio calculations for the full binder system—sediment together with all activator components and  $\text{Ca}(\text{OH})_2$ . Three target ratios governed the design: Si/Al  $\approx 2.0$ , which controls network cross-linking; Na/Si  $\approx 1.0$ , which secures adequate charge-balancing without the excess free sodium that drives efflorescence; and a working Si/Ca of approximately 1.1 (Table 3.6). The Si/Al  $\approx 2.0$  and Na/Si  $\approx 1.0$  targets follow established geopolymer design practice and correspond to the poly(sialate-siloxo) network type widely identified as optimal for N-A-S-H

systems [25, 27]. No comparable consensus target exists for blended sediment–Ca(OH)<sub>2</sub> systems, so the Si/Ca ratio was fixed at an internal reference value of 1.1 — high enough to retain sufficient silica for network formation while still supplying calcium for C-A-S-H co-precipitation — adopted to hold the activator designs mutually consistent across precursors rather than imported from any published source.

For each batch (50 g), we combined the sediment’s XRF oxide composition with the amounts of each activator component and Ca(OH)<sub>2</sub> to calculate the molar quantities. We used the standard molar masses: SiO<sub>2</sub> = 60.09 g/mol, Al<sub>2</sub>O<sub>3</sub> = 101.96 g/mol, NaOH = 40.00 g/mol, Na<sub>2</sub>SiO<sub>3</sub> = 122.06 g/mol, NaAlO<sub>2</sub> = 81.97 g/mol, and Ca(OH)<sub>2</sub> = 74.09 g/mol. We then adjusted the NaAlO<sub>2</sub> and Ca(OH)<sub>2</sub> dosages until all three corrected ratios were as close as possible to their targets.

**Table 3.6** — *Molar ratio calculations: corrected values for the full binder system (sediment + activator + Ca(OH)<sub>2</sub>)*

| Precursor | NaOH<br>_base<br>(g) | NaOH_a<br>dd (g) | Na <sub>2</sub> SiO <sub>3</sub><br>(g) | NaAlO <sub>2</sub><br>(g) | Ca(OH) <sub>2</sub><br>(g) | Si/Al<br>correcte<br>d | Na/Si<br>correcte<br>d | Si/Ca<br>correcte<br>d |
|-----------|----------------------|------------------|-----------------------------------------|---------------------------|----------------------------|------------------------|------------------------|------------------------|
| 2C        | 1.22                 | 6.0              | 30.6                                    | 5.5                       | 27.0                       | 1.996                  | 0.993                  | 1.130                  |
| 4C        | 1.22                 | 6.0              | 30.6                                    | 5.0                       | 27.0                       | 1.989                  | 1.000                  | 1.166                  |
| 3C        | 1.22                 | 8.5              | 30.6                                    | 13.5                      | 22.0                       | 1.993                  | 0.992                  | 1.182                  |
| 1C        | 1.22                 | 9.0              | 30.6                                    | 9.7                       | 28.0                       | 2.006                  | 0.999                  | 1.194                  |
| SUD       | 1.22                 | 9.0              | 30.6                                    | 10.0                      | 21.0                       | 1.997                  | 1.002                  | 1.199                  |
| INVASO    | 1.22                 | 10.0             | 30.6                                    | 11.0                      | 31.0                       | 2.013                  | 0.999                  | 1.128                  |

*NaOH\_base* = constant base dose in all Series I–III mixes. *NaOH\_add* = additional NaOH adjusted per precursor. Corrected ratios account for ionic contributions from all components including Ca(OH)<sub>2</sub>. Target: Si/Al ≈ 2.0, Na/Si ≈ 1.0, Si/Ca ≈ 1.12.

The corrected Si/Al ratios reach the target of approximately 2.0 (±0.02) for all six precursor systems, despite intrinsic Si/Al ratios ranging from 2.13 (4C) to 3.71 (3C). Na/Si ratios stay near 1.0, and Si/Ca values are around 1.12. Because these values are similar across different precursors, it suggests that the initial network-forming conditions are alike. This makes it possible to compare results in Chapter 5, where the main variable is composition rather than activator chemistry.

## Chapter 4: Mix Design and Experimental Programme

### 4.1 Mix design

The experimental program was structured around two groups of dredged sediment precursors, Group A (fractions 1C, 2C, 3C, and 4C blended in equal proportions from Perrères Dam, Valle d'Aosta) and Group B (SUD and INVASO blended 50:50 from Poggia Dam, Brescia), as characterized in Chapter 3. Nine experimental series (I–IX) were defined, each targeting one or two compositional variables identified as likely to influence the mechanical and durability performance of alkali-activated mortars based on low-reactivity clay-bearing precursors [24, 28]. The variables under test span calcium hydroxide addition, thermal pre-treatment via calcination at 700°C, LUKOSIL M130 methylsilicone resin as a hydrophobic modifier, Ordinary Portland Cement type 3B as a hybrid binder component, mullite as an aluminosilicate corrector, and gypsum as a sulfate source [19, 34]. Series VII and IX go a step further, combining OPC 3B with the silicone resin to check whether the two modifiers together do something different from either alone — using the OPC-only formulations (Series V) and resin-only formulations (Series IV) as the reference point for that comparison.

In total, 37 mortar formulations were prepared and tested. The baseline activator for Series IV–IX is a binary NaOH + Na<sub>2</sub>SiO<sub>3</sub> system (NaOH 1.5 g, Na<sub>2</sub>SiO<sub>3</sub> 30.6 g per batch); Series I–III use the three-component NaOH + Na<sub>2</sub>SiO<sub>3</sub> + NaAlO<sub>2</sub> system, with dosages calculated by molar ratio for each precursor group, as given in Table 3.6. The three-component, molar-ratio-targeted design of Series I–III was the program's original activator strategy, formulated to bring every precursor to a common Si/Al  $\approx$  2.0 condition (Section 3.3.2). The binary activator was adopted as the baseline for the larger additive program (Series IV–IX) on two grounds: it imposes a lower demand for silicates and alkali, in keeping with the low-carbon rationale of the binder, and it casts more reproducibly. To determine how much of each chemical to use, we started with the XRF oxide composition of each sediment (50 g at a time) and added the amounts of all activator components plus Ca(OH)<sub>2</sub>. We used standard molar masses: SiO<sub>2</sub> = 60.09 g/mol, Al<sub>2</sub>O<sub>3</sub> = 101.96 g/mol, NaOH = 40.00 g/mol, Na<sub>2</sub>SiO<sub>3</sub> = 122.06 g/mol, NaAlO<sub>2</sub> = 81.97 g/mol, and Ca(OH)<sub>2</sub> = 74.09 g/mol. Then, we adjusted the amounts of NaAlO<sub>2</sub> and Ca(OH)<sub>2</sub> until the calculated ratios matched their targets as closely as possible.

After these adjustments, all six sediment types reached the target Si/Al ratio of about 2.0 ( $\pm$ 0.02), even though their original Si/Al ratios ranged from 2.13 (for 4C) to 3.71 (for 3C). The Na/Si ratios were all close to 1.0, and the Si/Ca values were around the 1.12 target. By bringing all these ratios into alignment, we ensured that every sediment sample started with similar chemical conditions. This was important for the study in Chapter 5 because it allowed us to compare how different sediments performed based on their composition, without the results being affected by differences in the chemicals we added.



**Table 4.1a** — *Mix identity, sediment group and series assignment*

| <b>Mix</b> | <b>Sediment (50 g unless noted)</b>      | <b>State</b> | <b>Series</b>            |
|------------|------------------------------------------|--------------|--------------------------|
| 1          | 1C + 2C + 3C + 4C, 25% each              | Raw          | I — Reference            |
| 2          | SUD + INVASO, 50% each                   | Raw          | I — Reference            |
| 3          | 1C + 2C + 3C + 4C, 25% each              | Raw          | II — Ca(OH) <sub>2</sub> |
| 4          | SUD + INVASO, 50% each                   | Raw          | II — Ca(OH) <sub>2</sub> |
| 5          | 1C + 2C + 3C + 4C, 25% each              | Raw          | II — Ca(OH) <sub>2</sub> |
| 6          | SUD + INVASO, 50% each                   | Raw          | II — Ca(OH) <sub>2</sub> |
| 7          | 1C + 2C + 3C + 4C, 25% each, heated      | Heated       | III — Heated             |
| 8          | SUD + INVASO, 50% each, heated           | Heated       | III — Heated             |
| 9          | 1C + 2C + 3C + 4C, 25% each, heated      | Heated       | III — Heated             |
| 10         | SUD + INVASO, 50% each, heated           | Heated       | III — Heated             |
| 11         | 1C + 2C + 3C + 4C, 25% each, heated      | Heated       | IV — M130                |
| 12         | SUD + INVASO, 50% each, heated           | Heated       | IV — M130                |
| 13         | 1C + 2C + 3C + 4C, 25% each              | Raw          | IV — M130                |
| 14         | SUD + INVASO, 50% each                   | Raw          | IV — M130                |
| 15         | 1C + 2C + 3C + 4C, 25% each              | Raw          | IV — M130                |
| 16         | 1C + 2C + 3C + 4C, 25% each              | Raw          | IV — M130                |
| 17         | 1C + 2C + 3C + 4C, 25% each              | Raw          | V — Cement 3B            |
| 18         | 1C + 2C + 3C + 4C, 25% each              | Raw          | V — Cement 3B            |
| 19         | SUD + INVASO, 50% each                   | Raw          | IV — M130                |
| 20         | SUD + INVASO, 50% each                   | Raw          | IV — M130                |
| 21         | SUD + INVASO, 50% each                   | Raw          | V — Cement 3B            |
| 22         | SUD + INVASO, 50% each                   | Raw          | V — Cement 3B            |
| 23         | 1C + 2C + 3C + 4C, 25% each              | Raw          | VI — Mullite             |
| 24         | 1C + 2C + 3C + 4C, 25% each              | Raw          | VI — Mullite             |
| 25         | SUD + INVASO, 50% each                   | Raw          | VI — Mullite             |
| 26         | SUD + INVASO, 50% each                   | Raw          | VI — Mullite             |
| 27         | 1C + 2C + 3C + 4C, 25% each              | Raw          | VII — Cem + M130         |
| 28         | SUD + INVASO, 50% each                   | Raw          | VII — Cem + M130         |
| 29         | 1C + 2C + 3C + 4C, 25% each              | Raw          | VIII — Gypsum            |
| 30         | SUD + INVASO, 50% each                   | Raw          | VIII — Gypsum            |
| 31         | 1C + 2C + 3C + 4C, 25% each              | Raw          | VI — Mullite             |
| 32         | SUD + INVASO, 50% each                   | Raw          | VI — Mullite             |
| 33         | 1C + 3C + 4C, 12.5 g each (37.5 g total) | Raw          | IX — Cem + M130 v2       |
| 34         | 1C + 2C + 3C + 4C, 25% each              | Raw          | IX — Cem + M130 v2       |
| 35         | SUD + INVASO, 50% each                   | Raw          | IX — Cem + M130 v2       |
| 36         | 1C + 2C + 3C + 4C, 25% each              | Raw          | VIII — Gypsum            |

| Mix | Sediment (50 g unless noted) | State | Series        |
|-----|------------------------------|-------|---------------|
| 37  | SUD + INVASO, 50% each       | Raw   | VIII — Gypsum |

*Heated = 500  $\mu\text{m}$   $\rightarrow$  125  $\mu\text{m}$  sieve  $\rightarrow$  700°C calcination (~9 h, Nabertherm). Raw = 500  $\mu\text{m}$  sieve only. Mix 33: 1C + 3C + 4C only, 37.5 g total sediment.*

**Table 4.1b** — Activator and additive dosages for all 37 mixes

| Mix | NaAlO <sub>2</sub><br>(g) | NaOH<br>(g) | Na <sub>2</sub> SiO <sub>3</sub> (g) | Ca(OH) <sub>2</sub><br>(g) | Additives (g)        | Extra<br>water<br>(mL) | Sand (g) |
|-----|---------------------------|-------------|--------------------------------------|----------------------------|----------------------|------------------------|----------|
| 1   | 8.5                       | 7.5         | 30.6                                 | —                          | —                    | 10                     | 50       |
| 2   | 10.5                      | 9.5         | 30.6                                 | —                          | —                    | 10                     | 50       |
| 3   | 8.5                       | 7.5         | 30.6                                 | 26                         | —                    | 20                     | 50       |
| 4   | 10.5                      | 9.5         | 30.6                                 | 26                         | —                    | 20                     | 50       |
| 5   | 10.0                      | 3.0         | 40.0                                 | 22                         | —                    | 40                     | 50       |
| 6   | 13.0                      | 3.0         | 40.0                                 | 26                         | —                    | 40                     | 50       |
| 7   | 8.5                       | 7.5         | 30.6                                 | 26                         | —                    | 20                     | 50       |
| 8   | 10.5                      | 9.5         | 30.6                                 | 26                         | —                    | 20                     | 50       |
| 9   | 8.5                       | 7.5         | 30.6                                 | —                          | —                    | 20                     | 50       |
| 10  | 10.5                      | 9.5         | 30.6                                 | —                          | —                    | 20                     | 50       |
| 11  | —                         | 1.5         | 30.6                                 | —                          | LUKOSIL M130: 3      | —                      | 50       |
| 12  | —                         | 1.5         | 30.6                                 | —                          | LUKOSIL M130: 3      | 5                      | 50       |
| 13  | —                         | 1.5         | 30.6                                 | —                          | LUKOSIL M130: 3      | —                      | 50       |
| 14  | —                         | 1.5         | 30.6                                 | —                          | LUKOSIL M130: 3      | 5                      | 50       |
| 15  | —                         | 1.5         | 30.6                                 | —                          | LUKOSIL M130: 10     | —                      | 50       |
| 16  | —                         | 1.5         | 30.6                                 | —                          | LUKOSIL M130: 15     | —                      | 50       |
| 17  | —                         | 1.5         | 30.6                                 | —                          | OPC 3B: 13           | 2                      | 37       |
| 18  | —                         | 1.5         | 30.6                                 | —                          | OPC 3B: 17           | 4                      | 33       |
| 19  | —                         | 1.5         | 30.6                                 | —                          | LUKOSIL M130: 10     | —                      | 50       |
| 20  | —                         | 1.5         | 30.6                                 | —                          | LUKOSIL M130: 15     | —                      | 50       |
| 21  | —                         | 1.5         | 30.6                                 | —                          | OPC 3B: 13           | —                      | 37       |
| 22  | —                         | 1.5         | 30.6                                 | —                          | OPC 3B: 17           | —                      | 33       |
| 23  | —                         | 1.5         | 30.6                                 | —                          | Mullite: 5           | —                      | 45       |
| 24  | —                         | 1.5         | 30.6                                 | —                          | Mullite: 10          | 4                      | 40       |
| 25  | —                         | 1.5         | 30.6                                 | —                          | Mullite: 5           | 4                      | 45       |
| 26  | —                         | 1.5         | 30.6                                 | —                          | Mullite: 10          | —                      | 40       |
| 27  | —                         | 1.5         | 30.6                                 | —                          | OPC 3B: 15 + M130: 5 | —                      | 30       |
| 28  | —                         | 1.5         | 30.6                                 | —                          | OPC 3B: 15 + M130: 5 | —                      | 30       |
| 29  | —                         | 1.5         | 30.6                                 | —                          | Gypsum: 1            | —                      | 40       |
| 30  | —                         | 1.5         | 30.6                                 | —                          | Gypsum: 1            | —                      | 40       |

| Mix | NaAlO <sub>2</sub><br>(g) | NaOH<br>(g) | Na <sub>2</sub> SiO <sub>3</sub> (g) | Ca(OH) <sub>2</sub><br>(g) | Additives (g)            | Extra<br>water<br>(mL) | Sand (g) |
|-----|---------------------------|-------------|--------------------------------------|----------------------------|--------------------------|------------------------|----------|
| 31  | —                         | 7.0         | 30.6                                 | —                          | Mullite: 8.25            | —                      | 40       |
| 32  | —                         | 9.0         | 30.6                                 | —                          | Mullite: 10.5            | —                      | 40       |
| 33  | —                         | 1.5         | 30.6                                 | —                          | OPC 3B: 22.5 + M130: 10  | —                      | 30       |
| 34  | —                         | 1.5         | 30.6                                 | —                          | OPC 3B: 13 + M130: 7     | —                      | 30       |
| 35  | —                         | 1.5         | 30.6                                 | —                          | OPC 3B: 13 + M130: 7     | —                      | 30       |
| 36  | —                         | 1.5         | 30.6                                 | —                          | Gypsum: 2.5 + M130: 3.75 | —                      | 45       |
| 37  | —                         | 1.5         | 30.6                                 | —                          | Gypsum: 2.5 + M130: 3.75 | —                      | 45       |

'—' = component not used. NaOH = total dose per batch. For Series I–III (Mixes 1–10), NaAlO<sub>2</sub> and NaOH values are per-precursor from Table 3.6 (Chapter 3). M130 = LUKOSIL M130 silicone resin. OPC 3B = Ordinary Portland Cement type 3B. Extra water = volume of water added during mixing to reach a workable consistency, over and above the water already present in the sodium silicate solution; '—' indicates no additional water was required.

## 4.2 Preparation procedure

Each mortar batch was prepared following a consistent three-stage procedure: activator solution preparation, mixing and casting, and oven curing.

### 4.2.1 Activator solution preparation

The alkaline activator was prepared before each mixing session. For the binary system (Series IV–IX), sodium silicate solution (Na<sub>2</sub>SiO<sub>3</sub>, 30.6 g) was weighed into a plastic beaker, and NaOH pellets (1.5 g) were added. For the three-component system (Series I–III), only the NaOH was dissolved into the Na<sub>2</sub>SiO<sub>3</sub> solution at this stage; the weighed NaAlO<sub>2</sub> powder was not added to the activator solution. Like Ca(OH)<sub>2</sub>, NaAlO<sub>2</sub> is supplied as a dry powder and was introduced directly into the mixing bowl alongside the sediment during the mixing stage (Section 4.2.2), rather than pre-dissolved in the activator.



*Figure 4.1 — Preparation of the alkaline activator on a VELP Scientifica ARE 5 magnetic stirrer (stirring only, no applied heat), with the sodium silicate–NaOH solution in a plastic beaker.*

#### **4.2.2 Mixing and casting**

Each batch was mixed mechanically using an IKA EUROSTAR 60 control overhead stirrer (IKA-Werke GmbH, Staufen, Germany) fitted with a mixing shaft at the Politecnico di Torino. The sediment powder was slowly added to the activator solution in the mixing bowl. This helped wet the particle surfaces evenly and avoid dry clumps. When  $\text{Ca}(\text{OH})_2$  or  $\text{NaAlO}_2$  was used, it was first blended with the sediment before the activator was introduced. Mixing continued for about two to three minutes until a homogeneous paste formed. The pre-weighed sand was then incorporated and mixed for an additional one to two minutes. Liquid additives (LUKOSIL M130) were added undiluted at this stage. Solid additives (mullite, gypsum, and OPC 3B) were weighed in advance and added to the sand. If the mixture was still not workable, a measured amount of additional water was added until the mixture reached a uniform consistency. Table 4.1b shows the amount of water added to each affected mix.



**Figure 4.2** — IKA EUROSTAR 60 control overhead stirrer (IKA-Werke GmbH, Staufen, Germany) used for mechanical mixing of the mortar batches.



**Figure 4.3** — Fresh mortar cast into the prismatic moulds (specimen "MIX 28" shown), compacted by hand and labelled before oven curing.

The fresh mortar was cast immediately into prismatic plexiglass molds of nominal dimensions  $20 \times 20 \times 80 \text{ mm}^3$  after mixing; measured specimen lengths ranged from approximately 73 to 80 mm<sup>3</sup> owing to normal casting and demoulding tolerances, and each specimen was measured individually before testing. Mold interiors were treated beforehand with a lubricating release oil. Mold interiors were lightly oiled beforehand. The paste was

compacted by hand pressing and tapping to eliminate visible voids. Specimens were labelled on the mold side panel before transfer to the oven.

#### 4.2.3 Oven curing at 60°C

All specimens were cured in a Memmert convection oven at 60 °C for 14 days. Elevated curing was necessary to drive the geopolymerisation reaction: at ambient temperature, alkali activation of clay-bearing sediment precursors proceeds slowly and may not reach adequate gel maturity in a comparable period [21]. At 60 °C, dissolution of aluminosilicate species, polycondensation of dissolved monomers, and gel-network densification all accelerate, without the dehydration cracking or evaporation-related microstructural damage that higher temperatures can cause [12, 21]. We chose a 14-day period to make sure the reaction was complete and that the specimens were fully hardened and dry before testing. This method made sure all formulations started from the same point. In low-calcium alkali-activated systems cured at 60 °C, most of the strength develops within the first 7 to 14 days because the higher temperature speeds up dissolution and polycondensation [12, 21]. So, the 14-day results show mature strength rather than early-age strength. It is important to note that strength was never measured over time, and 28-day values reported in other studies often reflect different curing methods. So, comparisons with those values are only approximate. After 14 days, the specimens were removed from their molds and weighed before testing.



*Figure 4.4 — Memmert convection oven (right) used for curing at 60 °C, alongside the laboratory cabinet (left); the display shows the 60 °C set-point.*

### 4.3 Testing methods

All specimens followed the same testing program in order. For each formulation, we cast and tested two prismatic specimens. Flexural testing of each prism produced two half-specimen fragments, and each fragment was then tested in compression. We report

compressive strength as the average of up to four tests per formulation, and flexural strength as the average of up to two tests per formulation. Chapter 5 lists the exact number of valid results for each mix and notes any specimens that were excluded because they broke down during immersion or were otherwise compromised. We set up the process so that each step would not influence the next. First, we measured the dimensions and initial mass. Then we immersed the samples in water, monitored the pH, dried them again, and finally conducted the mechanical tests.

#### **4.3.1 Testing sequence**

After the specimens were removed from their molds, each one was tested in this order:

(1) Measuring size and initial mass. Length, width, and height were measured with a vernier caliper to 0.1 mm, and mass was recorded on a lab balance to 0.01 g.

(2) Water immersion. Specimens were placed in distilled water at room temperature for 24 hours. Any specimens that broke apart, cracked badly, or collapsed were marked as failed and not used for further testing.

(3) pH monitoring. The pH of the water was measured at four different times (see Section 4.3.3).

(4) Post-immersion drying. Specimens that remained intact were dried on the surface, weighed to determine their wet mass, and then placed in an oven at 60°C for about a week until their mass no longer changed.

(5) Flexural strength. The dried specimens were tested using three-point bending (see Section 4.3.4), which produced two half-specimens.

(6) Compressive strength. Each half-specimen was then tested in compression immediately (see Section 4.3.5), yielding two results per specimen, which were averaged.

#### **4.3.2 Water immersion and absorption measurement**

Each specimen was completely submerged in about 500 mL of filtered water at 20°C for 24 hours, ensuring that all surfaces were in contact with the water. Using the same amount of water for each sample allows for direct comparison of pH values across different mixes. In this context, leachate pH shows how much alkali each mix releases compared to the others, not the exact amount leached. The filtered water started with a pH of about 7.2 before the samples were added. This starting point matters when looking at the lowest early leachate readings, since some are close to it.

Water absorption by mass (WA, %) was calculated as:

$$\text{WA (\%)} = [(m_{\text{wet}} - m_{\text{dry}}) / m_{\text{dry}}] \times 100$$

where  $m_{\text{dry}}$  is the pre-immersion dry mass and  $m_{\text{wet}}$  the mass after immersion and surface drying with absorbent paper. The post-drying mass  $m_{\text{dry}}$  post was also recorded to identify any irreversible mass loss during the cycle.



**Figure 4.5** — Specimens MIX37-1 (top) and MIX37-2 (bottom) after the 24-hour water immersion. MIX37-1 remained largely intact, whereas MIX37-2 fractured and partially disintegrated during immersion. A leachate-pH reading was still obtained for this mix (Table 5.4), but the damaged specimens were not taken forward to mechanical testing.

#### 4.3.3 pH measurement of immersion water

The pH of the immersion water was monitored throughout the 24-hour period to characterize the alkalinity of the leachate released by each formulation. Leachate pH reflects the concentration of free  $\text{OH}^-$  ions at the specimen surface — a proxy for unreacted alkali not incorporated into the gel network during curing [41]. A lower leachate pH indicates better alkali retention within the binder matrix and a reduced risk of efflorescence in service [41].

Measurements were made using an Eutech Instruments CyberScan pH 510 meter. Before each session, the electrode was calibrated using the three-buffer method: pH 4 (pink), pH 7 (yellow), and pH 10 (blue) buffer solutions, applied in sequence with thorough rinsing between solutions. pH readings were recorded at four time points as shown in Table 4.2.





**Figure 4.6** — Measurement of immersion-water pH using a Eutech Instruments CyberScan pH 510 meter; with the electrode in the beaker containing a submerged specimen.

**Table 4.2** — pH measurement schedule during 24-hour water immersion

| No. | Time from start | Purpose                                             |
|-----|-----------------|-----------------------------------------------------|
| 1   | t = 30 min      | Initial leaching — capture early rapid ion release  |
| 2   | t = 60 min      | Short-term stabilisation check                      |
| 3   | t = 120 min     | Continued early leaching trend                      |
| 4   | t = 24 h        | Long-term equilibrium — maximum leachate alkalinity |

*Readings at t = 30 min, 60 min, 120 min and 24 h from moment of submersion. Electrode rinsed between specimens.*

The 30-minute reading shows the first release of surface alkali [35], while the 24-hour reading reflects a steady leachate concentration. Chapter 5 reports all four values.

#### 4.3.4 Flexural strength — three-point bending

We measured flexural strength using three-point bending, following EN 1015-11 [50], with a Zwick/Roell universal testing machine (50 kN load cell, built in 2014) at Politecnico di Torino. Each prismatic specimen ( $20 \times 20 \times 80 \text{ mm}^3$ ) was set on two rollers and loaded in the middle until it broke. We calculated flexural strength  $f_f$  (MPa) as:

$$f_f = (1.5 \times F_f \times L) / (b \times d^2)$$

Here,  $F_f$  is the highest load before failure (N),  $L$  is the distance between supports (mm),  $b$  is the width (mm), and  $d$  is the depth in the loading direction (mm). If we tested more than one specimen per mix, we averaged the results.

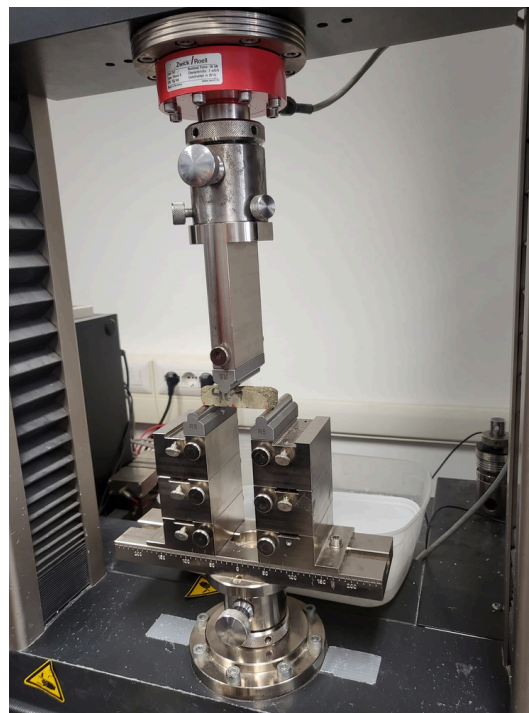
#### 4.3.5 Compressive strength — standard and protocol

We measured compressive strength in accordance with EN 1015-11 [50]. After each flexural test, we placed the two broken halves of the specimen into the compression machine and loaded each half until it broke. We calculated compressive strength ( $f_c$ , in MPa) using this formula:

$$f_c = F_c / A$$

Here,  $F_c$  is the highest force recorded during compression, and  $A$  is the area of the half-specimen that was loaded (in mm<sup>2</sup>). For each specimen, the two readings were averaged. One thing to note about the specimens: they were smaller than the EN 1015-11 standard,  $20 \times 20 \times 80$  mm<sup>3</sup> rather than the specified  $40 \times 40 \times 160$  mm<sup>3</sup>. The calculation steps followed the standard exactly — the reduced size simply allowed us to test a wider range of formulations in the same effort. Because a smaller cross-section tends to inflate apparent strength, the absolute values reported here shouldn't be read against standard-prism literature directly.

All comparisons are made between samples cast with the same geometry. Another difference is that we applied compression to the irregular half-prism fragments left from the flexural test, not to purpose-cast cubes. We measured the loaded area of each fragment individually to account for the uneven fracture surface. However, the variable contact area and shape of these fragments add extra variation beyond the size effect. This is a limitation of the mechanical data, which is discussed again in Section 6.2.2. Table 4.3 shows the protocol for both mechanical tests.



**Figure 4.7** — Three-point bending test of a prismatic specimen on the Zwick/Roell universal testing machine (50 kN load cell), Politecnico di Torino.



**Figure 4.8** — Compressive strength test: a half-specimen (labelled) is crushed between the platens of the RMU compression jig on the Zwick/Roell machine (50 kN load cell), Politecnico di Torino.

**Table 4.3** — Mechanical testing protocol

| Test                           | Standard        | Equipment                                 | Key output                       |
|--------------------------------|-----------------|-------------------------------------------|----------------------------------|
| Flexural — three-point bending | EN 1015-11 [50] | Universal testing machine                 | Flexural strength $f_f$ (MPa)    |
| Compressive                    | EN 1015-11 [50] | Universal testing machine (half-specimen) | Compressive strength $f_c$ (MPa) |

*Tests performed at Politecnico di Torino. EN 1015-11: Methods of test for mortar for masonry — Part 11: Determination of flexural and compressive strength of hardened mortar.*

## Chapter 5: Results and Discussion

Results are reported throughout by series and by sediment group (Group A: Perrères Dam fractions 1C, 2C, 3C, and 4C blended 25% each; Group B: Poglia Dam samples SUD and INVASO blended 50:50), so that both the effect of the compositional variables and the influence of the sediment source can be assessed. Three specimens are excluded from the analyses that follow. MIX9-1 broke apart during the 24-hour water immersion, so it is not included in later evaluations. Mix 32 broke during oven curing and is not included. Mix 23-1 was made too thin and is not used for mechanical testing, but its water immersion data are still included. The mixed names are listed in Table 4.1a.

### 5.1 Water immersion and pH response

After 14 days of oven curing, all hardened specimens were placed in water for 24 hours. Two things were measured: the change in mass from before to after immersion, and the pH of the water four times (30 minutes, 60 minutes, 120 minutes, and 24 hours). Since not every specimen had a recorded pre-immersion mass, water absorption as a percentage could only be calculated for some mixes. For the others, apparent density was estimated from their dimensions as an extra physical description. The results are shown in Tables 5.1-5.4.

#### 5.1.1 Water absorption results by series

Apparent density was calculated from the measured mass and the specimen volume ( $V = h \times w \times l$ , where  $h$ ,  $w$ , and  $l$  are the three orthogonal dimensions measured with a vernier caliper to the nearest 0.1 mm). Water absorption follows the convention defined in Section 4.3.2:  $WA (\%) = (m_{wet} - m_{dry}) / m_{dry} \times 100$ , so that a negative value denotes a net loss of mass during immersion — leaching of soluble material exceeding water uptake. Table 5.1 shows results for each specimen when the pre-immersion mass was available. Table 5.2 summarizes the averages for each mix. Table 5.3 lists specimens where only the post-immersion mass was recorded, so density is only approximate.

*Table 5.1 — Per-specimen apparent density and water absorption for mixes with both pre- and post-immersion mass recorded.  $WA = (m_{wet} - m_{dry}) / m_{dry} \times 100$ ; negative  $WA$  indicates net mass loss during immersion.*

| Mix   | Spec. | $m_{dry}$ (g) | $m_{wet}$ (g) | V (cm <sup>3</sup> ) | $\rho$ (g/cm <sup>3</sup> ) | WA (%) |
|-------|-------|---------------|---------------|----------------------|-----------------------------|--------|
| MIX7  | 1     | 47.80         | 45.60         | 29.06                | 1.645                       | −4.60  |
| MIX7  | 3     | 49.85         | 47.60         | 30.36                | 1.642                       | −4.51  |
| MIX8  | 2     | 57.55         | 51.70         | 34.83                | 1.652                       | −10.17 |
| MIX8  | 3     | 42.20         | 39.70         | 23.18                | 1.820                       | −5.92  |
| MIX11 | 1     | 72.80         | 71.00         | 36.98                | 1.969                       | −2.47  |
| MIX11 | 2     | 39.96         | 38.50         | 19.85                | 2.014                       | −3.65  |
| MIX12 | 1     | 70.75         | 67.90         | 38.23                | 1.851                       | −4.03  |
| MIX12 | 2     | 41.13         | 38.80         | 22.26                | 1.847                       | −5.66  |

| Mix   | Spec. | m <sub>dry</sub> (g) | m <sub>wet</sub> (g) | V (cm <sup>3</sup> ) | ρ (g/cm <sup>3</sup> ) | WA (%) |
|-------|-------|----------------------|----------------------|----------------------|------------------------|--------|
| MIX17 | 1     | 68.10                | 66.90                | 35.44                | 1.922                  | −1.76  |
| MIX17 | 2     | 41.00                | 39.90                | 21.10                | 1.943                  | −2.68  |
| MIX18 | 1     | 42.60                | 41.65                | 23.07                | 1.847                  | −2.23  |
| MIX18 | 2     | 66.70                | 65.43                | 34.65                | 1.925                  | −1.90  |
| MIX21 | 1     | 40.90                | 40.70                | 21.02                | 1.946                  | −0.49  |
| MIX21 | 2     | 67.90                | 67.60                | 34.49                | 1.968                  | −0.44  |
| MIX22 | 1     | 66.65                | 66.30                | 35.01                | 1.904                  | −0.53  |
| MIX22 | 2     | 43.80                | 43.10                | 22.94                | 1.909                  | −1.60  |
| MIX23 | 1     | 34.40                | 32.60                | 18.49                | 1.860                  | −5.23  |
| MIX23 | 2     | 75.90                | 73.30                | 38.63                | 1.965                  | −3.43  |
| MIX24 | 1     | 43.40                | 41.90                | 21.21                | 2.046                  | −3.46  |
| MIX24 | 2     | 64.80                | 63.20                | 32.06                | 2.021                  | −2.47  |
| MIX27 | 1     | 37.90                | 37.80                | 20.06                | 1.889                  | −0.26  |
| MIX27 | 2     | 69.60                | 69.30                | 36.24                | 1.920                  | −0.43  |
| MIX28 | 1     | 35.02                | 34.80                | 18.46                | 1.898                  | −0.63  |
| MIX28 | 2     | 69.40                | 69.10                | 37.01                | 1.875                  | −0.43  |
| MIX29 | 1     | 36.00                | 34.01                | 17.72                | 2.032                  | −5.53  |
| MIX29 | 2     | 62.34                | 59.90                | 31.21                | 1.997                  | −3.91  |
| MIX31 | 1     | 66.87                | 60.78                | 34.05                | 1.964                  | −9.11  |
| MIX31 | 2     | 43.78                | 39.37                | 22.61                | 1.936                  | −10.07 |
| MIX33 | 2     | 44.58                | 43.95                | 26.00                | 1.715                  | −1.41  |
| MIX34 | 1     | 70.51                | 69.79                | 39.94                | 1.765                  | −1.02  |
| MIX34 | 2     | 34.74                | 34.12                | 19.55                | 1.777                  | −1.78  |
| MIX35 | 1     | 45.75                | 44.76                | 25.01                | 1.830                  | −2.16  |
| MIX35 | 2     | 62.97                | 61.76                | 35.14                | 1.792                  | −1.92  |
| MIX36 | 1     | 69.74                | 67.88                | 36.94                | 1.888                  | −2.67  |
| MIX36 | 2     | 37.32                | 35.86                | 21.18                | 1.762                  | −3.91  |

*Dimensions measured by vernier calliper (±0.05 mm). Negative WA values reflect a net mass loss: soluble alkali and loosely bound surface material leached into the immersion water at a rate exceeding water uptake into the pore network. The MIX33-1 reading was discarded as a transcription error (recorded post-immersion mass exceeded the dry mass).*

**Table 5.2** — Per-mix average apparent density and water absorption (mixes with ≥ 1 valid specimen).  $\bar{\rho}$  = mean apparent density;  $\bar{WA}$  = mean water absorption;  $\sigma$  = spread across specimens. With only two specimens per mix,  $\sigma$  is the half-range and indicates scatter rather than a statistically inferential standard deviation.

| Mix   | n | $\bar{\rho}$ (g/cm <sup>3</sup> ) | $\sigma_{\rho}$ | $\bar{WA}$ (%) | $\sigma_{WA}$ | Series                |
|-------|---|-----------------------------------|-----------------|----------------|---------------|-----------------------|
| MIX7  | 2 | 1.643                             | 0.002           | −4.55          | 0.04          | III — Heated          |
| MIX8  | 2 | 1.736                             | 0.084           | −8.04          | 2.12          | III — Heated          |
| MIX11 | 2 | 1.991                             | 0.022           | −3.06          | 0.59          | IV — M130 3 g, heated |

| Mix   | n | $\bar{\rho}$ (g/cm <sup>3</sup> ) | $\sigma_{\rho}$ | W $\bar{A}$ (%) | $\sigma_{WA}$ | Series                   |
|-------|---|-----------------------------------|-----------------|-----------------|---------------|--------------------------|
| MIX12 | 2 | 1.849                             | 0.002           | -4.85           | 0.81          | IV — M130 3 g, heated    |
| MIX17 | 2 | 1.933                             | 0.011           | -2.22           | 0.46          | V — Cement 3B 13 g       |
| MIX18 | 2 | 1.886                             | 0.039           | -2.06           | 0.17          | V — Cement 3B 17 g       |
| MIX21 | 2 | 1.957                             | 0.011           | -0.46           | 0.02          | V — Cement 3B 13 g       |
| MIX22 | 2 | 1.906                             | 0.003           | -1.06           | 0.54          | V — Cement 3B 17 g       |
| MIX23 | 2 | 1.913                             | 0.052           | -4.33           | 0.90          | VI — Mullite 5 g         |
| MIX24 | 2 | 2.034                             | 0.012           | -2.96           | 0.49          | VI — Mullite 10 g        |
| MIX27 | 2 | 1.905                             | 0.015           | -0.34           | 0.08          | VII — Cem 15 + M130 5    |
| MIX28 | 2 | 1.886                             | 0.011           | -0.53           | 0.10          | VII — Cem 15 + M130 5    |
| MIX29 | 2 | 2.014                             | 0.017           | -4.72           | 0.81          | VIII — Gypsum 1 g        |
| MIX31 | 2 | 1.950                             | 0.014           | -9.59           | 0.48          | VI — Mullite 8.25 g      |
| MIX33 | 1 | 1.715                             | 0.000           | -1.41           | 0.00          | IX — Cem 22.5 + M130 10  |
| MIX34 | 2 | 1.771                             | 0.006           | -1.40           | 0.38          | IX — Cem 13 + M130 7     |
| MIX35 | 2 | 1.811                             | 0.019           | -2.04           | 0.12          | IX — Cem 13 + M130 7     |
| MIX36 | 2 | 1.825                             | 0.063           | -3.29           | 0.62          | VIII — Gypsum 2.5 + M130 |

All mean WA values are negative, indicating net mass loss during immersion — see Section 5.1.3 for interpretation. MIX33 retains only one valid specimen after exclusion of the MIX33-1 outlier.

**Table 5.3** — Approximate density for specimens where only the post-immersion mass was recorded ( $m_{wet}$  used as the mass proxy; density is therefore a slight underestimate). WA cannot be calculated for these specimens.

| Mix   | Spec. | $m_{wet}$ (g) | V (cm <sup>3</sup> ) | $\rho_{approx}$ (g/cm <sup>3</sup> ) | Series                   |
|-------|-------|---------------|----------------------|--------------------------------------|--------------------------|
| MIX3  | 2     | 56.60         | 29.74                | 1.903                                | II — Ca(OH) <sub>2</sub> |
| MIX4  | 2     | 56.70         | 32.04                | 1.770                                | II — Ca(OH) <sub>2</sub> |
| MIX13 | 1     | 64.56         | 34.69                | 1.861                                | IV — M130 3 g, raw       |
| MIX13 | 2     | 37.00         | 20.68                | 1.789                                | IV — M130 3 g, raw       |
| MIX15 | 1     | 46.56         | 26.35                | 1.767                                | IV — M130 10 g, raw      |
| MIX15 | 2     | 59.20         | 34.09                | 1.737                                | IV — M130 10 g, raw      |
| MIX16 | 1     | 52.70         | 31.78                | 1.658                                | IV — M130 15 g, raw      |
| MIX16 | 2     | 57.80         | 32.81                | 1.762                                | IV — M130 15 g, raw      |

All tested specimens showed a negative water absorption value, meaning the post-immersion surface-dried mass was always lower than the pre-immersion dry mass. This consistent negative absorption is unusual and should be interpreted carefully. Several factors could cause this result, such as incomplete drying before immersion, differences in how operators surface-dried the samples, loss of loose surface material during handling, or leaching of soluble substances into the immersion water.

Two of these can be at least partly bounded. The pre-immersion mass was recorded only after oven curing at 60 °C for 14 days, and after the mass had stabilized (Section 4.2.3),

so gross saturation of the baseline is unlikely, although the absence of a final constant-mass check at a higher drying temperature means a small residual-moisture contribution cannot be entirely excluded. Leaching, for its part, is demonstrably occurring: the immersion water becomes strongly alkaline within hours (Section 5.1.3), which can only result from the release of soluble unreacted alkalis from the specimen. The quantity involved, however, is modest. Taking a representative 24 h leachate pH of approximately 11.7 for MIX15 gives a free hydroxide concentration of about  $5 \times 10^{-3} \text{ mol L}^{-1}$ , corresponding — if charge-balanced by sodium — to only of order 10–40 mg of leached alkali per specimen across a plausible immersion volume.

This is one to two orders of magnitude smaller than the gravimetric mass change itself (for MIX15, a loss of about 0.9 g, or 1.9 % of the dry mass). Leaching therefore accounts for only a fraction of the recorded negative absorption; the remainder lies within the combined uncertainty of surface-drying, fines loss and residual moisture, which for a change of one to two percent is at the resolution limit of the gravimetric method as applied here. The honest reading of these data is thus twofold: alkali release from the hardened binder is real and is independently evidenced by the leachate pH, but the magnitude of the negative water absorption should be treated as a qualitative indicator of net surface mass loss rather than as a quantitative leaching measurement. Consistent with a leaching contribution, the largest mass losses tend to occur in the most heavily dosed mixes — the Series III heated mixes (MIX8, mean  $-8.0 \%$ ) and the elevated-NaOH MIX31 ( $-9.6 \%$ ), which also return among the highest 24 h leachate pH values — but the limited number of specimens per mix means this association is indicative rather than statistically established, and a dedicated test with controlled immersion volume, a water blank and a defined constant-mass drying endpoint would be required to quantify the leached fraction directly (Section 6.3.3).

Density tracked the underlying chemistry in a way that makes physical sense. The Series III heated specimens had the lowest values (MIX7:  $1.643 \text{ g/cm}^3$ ; MIX8:  $1.736 \text{ g/cm}^3$ ), which is consistent with their porous microstructure and high additional water content (20 g per batch). At the other end, MIX29 ( $2.015 \text{ g/cm}^3$ ), MIX24 ( $2.034 \text{ g/cm}^3$ ), and MIX11 ( $1.991 \text{ g/cm}^3$ ) recorded the highest densities. A Group A/Group B gap shows up consistently within shared series — MIX11 ( $1.991 \text{ g/cm}^3$ ) against MIX12 ( $1.849 \text{ g/cm}^3$ ) in Series IV, for instance — and traces back to the coarser, less reactive Group B sediments (SUD:  $D[4,3] = 407 \text{ }\mu\text{m}$ ; INVASO:  $D[4,3] = 393 \text{ }\mu\text{m}$ ) compared with Group A, whose  $D[4,3]$  values range from  $40.6 \text{ }\mu\text{m}$  (2C) to  $271 \text{ }\mu\text{m}$  (3C), the finer 2C and 4C fractions in particular giving far more surface area; the coarser grains simply pack into a less dense gel matrix under the same curing conditions.

The magnitude of mass loss during immersion also varied meaningfully. Series III specimens showed the largest losses (MIX8 mean WA =  $-8.0\%$ ), reflecting high residual alkali from the large  $\text{NaAlO}_2$  and NaOH doses of the three-component activator together with the relatively poor gel maturity of the Group B heated series. MIX31 also showed a large loss (mean WA =  $58 -9.6\%$ ), consistent with its elevated NaOH dose of 7 g (against the standard 1.5 g of the binary series). The smallest losses were recorded for the OPC- and

OPC–silicone-resin combinations of Series VII (MIX27, MIX28) and the Series V Group B mixes (MIX21, MIX22), all between  $-0.3\%$  and  $-1.1\%$ , suggesting that those additive systems promoted more complete alkali consumption during geopolymerisation and left less soluble sodium available for leaching.

### 5.1.2 pH of immersion water by series

The pH of the immersion water was measured at four time points ( $t = 30$  min, 60 min, 120 min, and 24 h) for 31 of the 37 mixes. All measurements were made with a calibrated Eutech Instruments CyberScan pH 510 meter following the three-buffer protocol described in Section 4.3.3. The complete dataset is presented in Table 5.4.

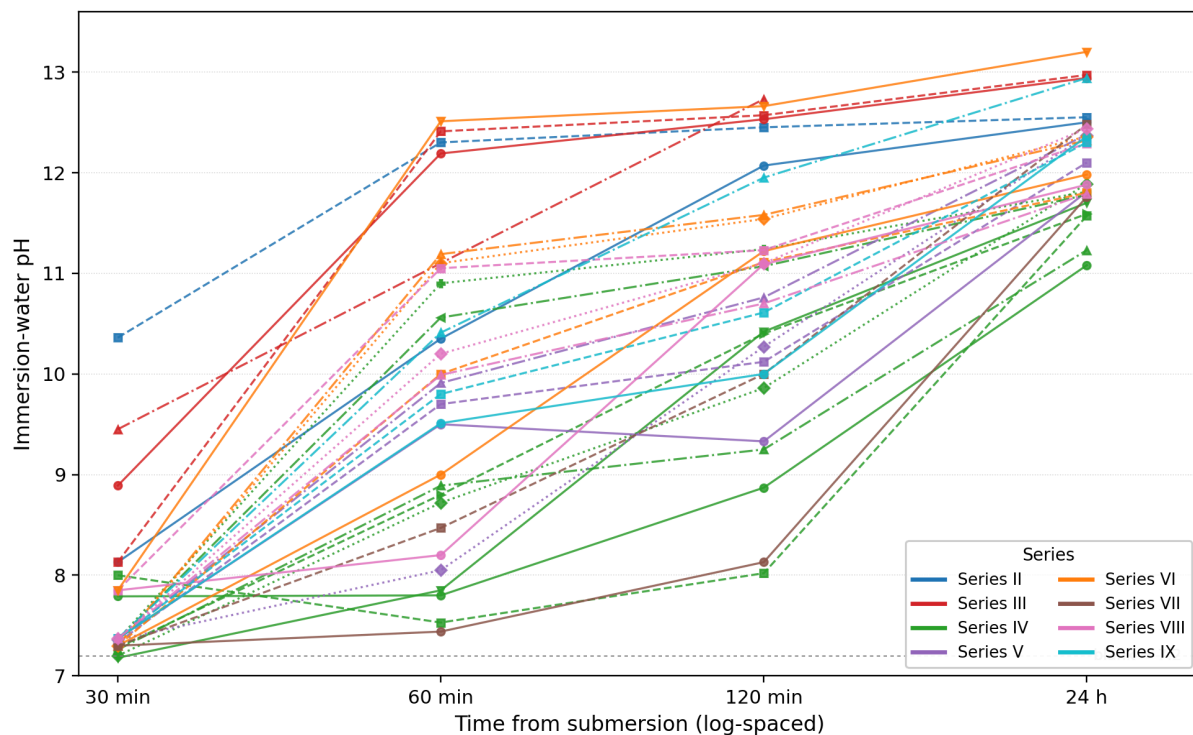
**Table 5.4** — Immersion-water pH at four time points during the 24-hour water immersion test. A lower final (24 h) pH indicates better alkali retention within the binder matrix.

| Mix   | Series | Group | pH 30 min | pH 60 min | pH 120 min | pH 24 h |
|-------|--------|-------|-----------|-----------|------------|---------|
| MIX3  | II     | A     | 8.13      | 10.35     | 12.07      | 12.50   |
| MIX4  | II     | B     | 10.36     | 12.30     | 12.45      | 12.55   |
| MIX7  | III    | A     | 8.89      | 12.19     | 12.53      | 12.94   |
| MIX8  | III    | B     | 8.13      | 12.41     | 12.57      | 12.97   |
| MIX9  | III    | A     | 9.45      | 11.10     | 12.73      | —       |
| MIX11 | IV     | A     | 7.79      | 7.80      | 8.87       | 11.08   |
| MIX12 | IV     | B     | 8.00      | 7.53      | 8.02       | 11.57   |
| MIX13 | IV     | A     | 7.26      | 8.89      | 9.25       | 11.23   |
| MIX14 | IV     | B     | 7.20      | 8.72      | 9.86       | 11.89   |
| MIX15 | IV     | A     | 7.18      | 7.85      | 10.42      | 11.70   |
| MIX16 | IV     | A     | 7.28      | 8.80      | 10.40      | 11.59   |
| MIX17 | V      | A     | 7.37      | 9.50      | 9.33       | 11.81   |
| MIX18 | V      | A     | 7.33      | 9.70      | 10.12      | 12.10   |
| MIX19 | IV     | B     | 7.36      | 10.56     | 11.07      | 11.78   |
| MIX20 | IV     | B     | 7.36      | 10.90     | 11.24      | 11.81   |
| MIX21 | V      | B     | 7.36      | 9.91      | 10.76      | 12.38   |
| MIX22 | V      | B     | 7.36      | 8.05      | 10.27      | 12.37   |
| MIX23 | VI     | A     | 7.30      | 9.00      | 11.22      | 11.98   |
| MIX24 | VI     | A     | 7.30      | 10.00     | 11.11      | 11.80   |
| MIX25 | VI     | B     | 7.30      | 11.19     | 11.58      | 12.32   |
| MIX26 | VI     | B     | 7.30      | 11.10     | 11.54      | 12.36   |
| MIX27 | VII    | A     | 7.30      | 7.44      | 8.13       | 11.76   |
| MIX28 | VII    | B     | 7.30      | 8.47      | 10.00      | 12.48   |
| MIX29 | VIII   | A     | 7.85      | 8.20      | 11.09      | 11.88   |
| MIX30 | VIII   | B     | 7.85      | 11.05     | 11.23      | 12.29   |



| Mix   | Series | Group | pH 30 min | pH 60 min | pH 120 min | pH 24 h |
|-------|--------|-------|-----------|-----------|------------|---------|
| MIX31 | VI     | A     | 7.85      | 12.51     | 12.66      | 13.20   |
| MIX33 | IX     | A     | 7.37      | 9.51      | 10.00      | 12.36   |
| MIX34 | IX     | A     | 7.37      | 9.80      | 10.61      | 12.30   |
| MIX35 | IX     | B     | 7.37      | 10.41     | 11.95      | 12.94   |
| MIX36 | VIII   | A     | 7.37      | 9.99      | 10.70      | 11.79   |
| MIX37 | VIII   | B     | 7.37      | 10.20     | 11.10      | 12.44   |

*MIX9-1 disintegrated before the 24 h reading could be taken. — = measurement not obtained. Mix 32 excluded (failed during curing). MIX31 used an elevated NaOH dose (7 g) compared with the standard Series VI dose (1.5 g), which accounts for its anomalously high pH. Series labels abbreviated to the roman numeral; full additive detail is given in Table 4.1b.*



**Figure 5.1** — Evolution of immersion-water pH over the 24-hour immersion test for all 31 mixes, measured at four time points ( $t = 30 \text{ min}$ ,  $60 \text{ min}$ ,  $120 \text{ min}$ , and  $24 \text{ h}$ )

### 5.1.3 Effect of key variables on absorption and pH

The 24-hour leachate pH ranged from 11.08 (MIX11) to 13.20 (MIX31) across all tested mixes — a difference of more than two pH units that reflects genuine differences in the degree of alkali incorporation into the gel network during the 14-day curing period. In practical terms, a lower final pH indicates better alkali fixation, a lower risk of efflorescence in service, and a lower long-term environmental impact [41].

Leachate pH tracked the activator system more closely than almost everything else. The three-component  $\text{NaOH} + \text{Na}_2\text{SiO}_3 + \text{NaAlO}_2$  activator used in Series I–III, dosed at elevated levels (NaOH up to 9.5 g per batch,  $\text{NaAlO}_2$  up to 13.5 g), pushed every one of those

mixes to a final pH of 12.5–13.0. Even here, the first 30-minute readings were well below that (8.1–9.5), indicating a rapid early burst of ion release followed by gradual equilibration as the remaining activator dissolved into the water. Series IV to IX, which used the binary NaOH- $\text{Na}_2\text{SiO}_3$  activator with the usual low NaOH dose of 1.5 g, showed a different pattern. The initial pH readings were lower, ranging from 7.2 to 8.0 at 30 minutes, and the 24-hour values were also lower, ranging from 11.0 to 12.5. This result fits with the idea that less free alkali remains in the pore solution. One mix, MIX31, was different: it used a higher dose of 7 g NaOH with 8.25 g mullite and reached a 24-hour pH of 13.20, the highest in the program. This shows that the NaOH dose, rather than the mullite, increases the alkalinity of the leachate in this series. The standard Series VI mixes (MIX23, MIX24, MIX25, MIX26) with 1.5 g NaOH stayed between 11.80 and 12.36, similar to the rest of the binary-activator series.

LUKOSIL M130 (Series IV) had a noticeable but secondary effect on leachate pH. The heated Group A specimen with 3 g M130 (MIX11) had the lowest 24-hour pH in the program at 11.08, compared to 11.23 for the similar raw Group A specimen (MIX13). Increasing the M130 dose to 10 g (MIX15) or 15 g (MIX16) did not lower the 24-hour pH further (11.70 and 11.59). These results suggest that M130 does not chemically bind alkali. Instead, it makes the matrix denser and slows down ion movement through the surface.

Group B (SUD and INVASO) always had higher 24-hour pH values than Group A in each matched series: 12.38 (MIX21) compared to 11.81 (MIX17) in Series V; 12.48 (MIX28) compared to 11.76 (MIX27) in Series VII; and 12.94 (MIX35) compared to 12.30 (MIX34) in Series IX. This trend fits what is already known about the two sediments. Group B is less reactive and has larger particles, so more unreacted activator stays in the pore solution after curing.

The way pH changed over time also depended on the activator. In Series IV-IX, most samples showed a two-stage pattern. For the first 30 to 60 minutes, the pH remained flat or increased slowly as diffusion spread outward from the specimen's interior. Between 60 and 120 minutes, the pH increased more rapidly once the surface pores were reached. After that, the pH either leveled off or increased slowly over 24 hours as the system reached equilibrium. Series I-III behaved quite differently — pH shot up within the first 30 minutes and stabilized almost immediately, a sign of just how much freely soluble activator sat right at the specimen surface in those heavily dosed formulations.

#### **5.1.4 Best-performing formulations — water absorption and pH**

When durability performance is evaluated against the two immersion-derived criteria together — a small net mass loss during immersion and a low 24-hour leachate pH, both of which indicate good alkali fixation within the binder matrix — a consistent group of formulations stands out. For leachate pH, MIX11 (11.08), MIX13 (11.23), and MIX16 (11.59) performed best. All three are from the LUKOSIL M130 series (Series IV). The silicone-resin modification seems to be the most effective way to limit alkali release, likely by reducing the cured matrix's permeability instead of chemically binding sodium. absorption, the smallest mass losses were recorded for the OPC and OPC-silicone-resin mixes of Series V and VII (MIX21, MIX22, MIX27, MIX28, all between -0.3% and -1.1%), indicating that

the calcium-bearing additives promoted more complete consumption of the activator during curing.

The two criteria do not point to a single dominant mix, but they converge on the M130 and OPC additive families as the most favorable for durability. MIX11 is the strongest individual performer for leachate pH and also exhibits a moderate mass loss (−3.06%), but its dependence on the calcination step is a drawback, as discussed in Sections 5.2.4 and 5.4.2. Among the raw-sediment formulations, MIX16 (M130 15 g, pH 11.59, WA −2.67%) and MIX13 (M130 3 g, pH 11.23) offer the best combination of low leachate alkalinity and modest mass loss without any thermal pre-treatment, and they are therefore the most attractive candidates from the standpoint of the binder's overall durability and environmental profile. These conclusions are revisited alongside the mechanical results in Section 5.4.3, where the best formulations across all criteria are identified.

## 5.2 Mechanical performance

Mechanical tests were performed on specimens that remained undamaged after 24 hours of water immersion. The procedure, outlined in Section 4.3, began with flexural strength testing using three-point bending (EN 1015-11), followed by compressive strength testing of the two half-specimen fragments. These tests were conducted using a Zwick/Roell universal testing machine with a 50 kN load cell. Compressive strength results were obtained for 21 of 37 mixes, and flexural strength results for 16 of 37 mixes. Series I (Mixes 1, 2) and Series III (Mixes 7–10) were not taken to mechanical testing within the timeframe of this study and are therefore absent from this section.

A small number of half-specimens reached the 40 kN ceiling of the testing machine load cell without failing. Where this occurred, the affected half-specimen is reported as exceeding the corresponding stress at 40 kN rather than as a measured strength, and it is excluded from the averaged value for that mix. This affected one half-specimen pair each in MIX22, MIX24 and MIX27, all with cross-sectional areas of approximately 390–425 mm<sup>2</sup> (equivalent to a stress limit of about 94–102 MPa). These results confirm an exceptionally high load-bearing capacity for those particular fragments but cannot be used as quantitative strength values; the reported mean for each of those mixes therefore rests solely on the failing half-specimens.

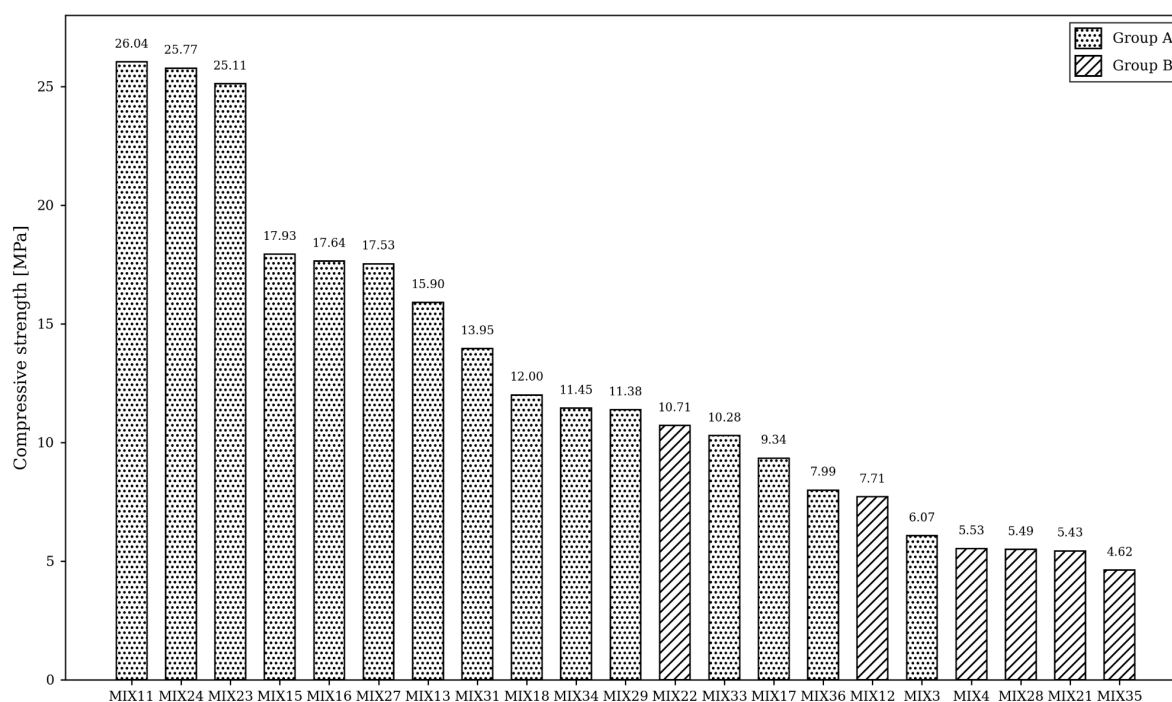
### 5.2.1 Compressive strength results by series

**Table 5.5** — Compressive strength results for each mix, ranked by the average value.  $\sigma_c$  is the mean compressive strength of the half specimens that failed.  $n$  is the number of half-specimens averaged. S1 and S2 are the two specimen sub-series, with two prisms per mix, each split into two halves. “> limit” means a half-specimen reached the 40 kN maximum of the load cell without failing and is not included in the average.

| Rank | Mix   | $\sigma_c$ (MPa) | S1 (MPa) | S2 (MPa) | $n$ | Group | Series                |
|------|-------|------------------|----------|----------|-----|-------|-----------------------|
| 1    | MIX11 | 26.04            | 25.42    | 26.67    | 4   | A     | IV — M130 3 g, heated |

| Rank | Mix   | $\bar{\sigma}_c$ (MPa) | S1 (MPa) | S2 (MPa) | n | Group | Series                   |
|------|-------|------------------------|----------|----------|---|-------|--------------------------|
| 2    | MIX24 | 25.77                  | > limit  | 25.77    | 2 | A     | VI — Mullite 10 g        |
| 3    | MIX23 | 25.11                  | —        | 25.11    | 2 | A     | VI — Mullite 5 g         |
| 4    | MIX15 | 17.93                  | 16.61    | 19.25    | 4 | A     | IV — M130 10 g, raw      |
| 5    | MIX16 | 17.64                  | 15.64    | 19.65    | 4 | A     | IV — M130 15 g, raw      |
| 6    | MIX27 | 17.53                  | > limit  | 17.53    | 2 | A     | VII — Cem 15 + M130 5    |
| 7    | MIX13 | 15.90                  | 19.35    | 12.44    | 4 | A     | IV — M130 3 g, raw       |
| 8    | MIX31 | 13.95                  | 17.48    | 10.41    | 4 | A     | VI — Mullite 8.25 g      |
| 9    | MIX18 | 12.00                  | 13.72    | 10.27    | 4 | A     | V — Cement 3B 17 g       |
| 10   | MIX34 | 11.45                  | 13.10    | 9.80     | 4 | A     | IX — Cem 13 + M130 7     |
| 11   | MIX29 | 11.38                  | 7.60     | 15.17    | 4 | A     | VIII — Gypsum 1 g        |
| 12   | MIX22 | 10.71                  | 10.71    | > limit  | 2 | B     | V — Cement 3B 17 g       |
| 13   | MIX33 | 10.28                  | 11.77    | 8.80     | 4 | A     | IX — Cem 22.5 + M130 10  |
| 14   | MIX17 | 9.34                   | 8.89     | 9.79     | 4 | A     | V — Cement 3B 13 g       |
| 15   | MIX36 | 7.99                   | 10.62    | 5.37     | 4 | A     | VIII — Gypsum 2.5 + M130 |
| 16   | MIX12 | 7.71                   | 8.53     | 6.88     | 4 | B     | IV — M130 3 g, heated    |
| 17   | MIX3  | 6.07                   | 3.97     | 8.17     | 4 | A     | II — Ca(OH) <sub>2</sub> |
| 18   | MIX4  | 5.53                   | 1.88     | 9.19     | 4 | B     | II — Ca(OH) <sub>2</sub> |
| 19   | MIX28 | 5.49                   | 4.10     | 6.89     | 4 | B     | VII — Cem 15 + M130 5    |
| 20   | MIX21 | 5.43                   | —        | 5.43     | 2 | B     | V — Cement 3B 13 g       |
| 21   | MIX35 | 4.62                   | 4.40     | 5.06     | 3 | B     | IX — Cem 13 + M130 7     |

*Ranking based on the mean over failing half-specimens. For mixes with a half-specimen at the load-cell limit, only the failing half-specimen values contribute to S1/S2 and to the mean.*



**Figure 5.2** — Compressive strength results for all mechanically tested mixes, ranked by mean value over the failing half-specimens (Group A and Group B).

MIX11 achieved the highest compressive strength in the program, averaging 26.04 MPa across four half-specimens, with consistent results between samples (S1 mean: 25.42 MPa; S2 mean: 26.67 MPa). The mixture consisted of heated Group A sediment, 3 grams of LUKOSIL M130, and the binary activator at the standard dosage. Three primary factors likely account for the observed results. First, heating the sediment increased its reactive amorphous content. Second, the binary activator required less water, resulting in a denser paste. Third, the M130 resin reduced porosity by coating the pore surfaces with a water-repellent layer. This layer prevented water ingress during immersion and maintained gel integrity prior to mechanical testing. It is important to read this value in context, however. MIX11 required calcination of the precursor at 700 °C, an energy-intensive step that runs counter to the low-carbon rationale of the binder (Section 5.4.1), and its flexural specimens were lost, so its performance cannot be assessed on the second mechanical axis. For these reasons, MIX11 is treated here as the upper bound on compressive strength achievable in this program rather than as the best overall formulation.

The Series VI mullite mixes, MIX24 and MIX23 from Group A, had strengths of 25.77 MPa and 25.11 MPa in the half-specimen failure tests, just below MIX11. For both mixes, the thicker S1 (MIX24) or half specimen exceeded the load cell's capacity, so the actual average strength is likely higher but could not be measured. Adding 5 to 10 grams of mullite per batch primarily served as a fine, inert filler that reduced porosity and improved particle packing. While this addition lowers the overall Si/Al ratio of the composite binder toward the N-A-S-H range (Section 2.2.2), its low solubility indicates a change in bulk composition rather than a reactive adjustment (Section 5.2.3).

The effect was stronger at 10 g (MIX24 > MIX23), consistent with greater matrix densification at the higher solid dosage. As with MIX11, these high values come with a caveat — the load-cell-limited fragments mean the figures rest on a reduced number of failing half-specimens — and they should be interpreted alongside, not above, the formulations with complete, fully-failing datasets.

Of the mixes with four half-specimens that failed cleanly, MIX15 (raw Group A, 10 g M130) had the highest strength at 17.93 MPa, with MIX16 (raw Group A, 15 g M130) just behind at 17.64 MPa. In Series IV, pre-treatment made a clear difference. MIX11 (heated, 3 g M130) reached 26.04 MPa, while MIX13 (raw, 3 g M130) only reached 15.90 MPa. This shows that using a more reactive, calcined precursor increased strength by more than 10 MPa. The amount of M130 also affects strength, but only up to a certain point. Raising M130 from 3 g (MIX13, 15.90 MPa) to 10 g (MIX15, 17.93 MPa) in raw sediment improved strength, but increasing it further to 15 g (MIX16, 17.64 MPa) made little difference. This suggests the benefit levels off at around 10 g.

The OPC–silicone resin mixes of Series IX prepared with Group A sediment displayed moderate strength: MIX34 (13 g cement + 7 g M130) reached 11.45 MPa, and MIX33 (22.5 g cement + 10 g M130) reached 10.28 MPa. The corresponding formulation based on Group B sediment, MIX35, attained only 4.62 MPa, once again underscoring the critical role of the precursor's reactivity. The mullite mix prepared with an elevated NaOH concentration (MIX31) reached 13.95 MPa. Among the gypsum-containing formulations, MIX29 (Group A, gypsum addition) measured 11.38 MPa, while the gypsum + M130 combination (MIX36) gave 7.99 MPa. Finally, MIX27—the Series VII Group A cement-and-M130 blend—recorded 17.53 MPa on the half-specimen that failed, a value comparable to those of MIX15 and MIX16.

Compressive strength was lowest in the  $\text{Ca(OH)}_2$  series (Series II, Mixes 3 and 4), with 6.07 MPa for Group A and 5.53 MPa for Group B. These are the lowest values among any mechanically tested mixes, even though portlandite is expected to promote C-A-S-H gel co-precipitation. The likely reason is the high water content in these mixes (20 g of extra water per batch; Table 4.1b), which led to a high water-to-binder ratio and a more porous matrix. The scatter within these mixes is also the highest in the program (MIX3 S1/S2: 3.97–8.17 MPa; MIX4: 1.88–9.19 MPa), suggesting incomplete and uneven gel development rather than a dense, uniform binder network.

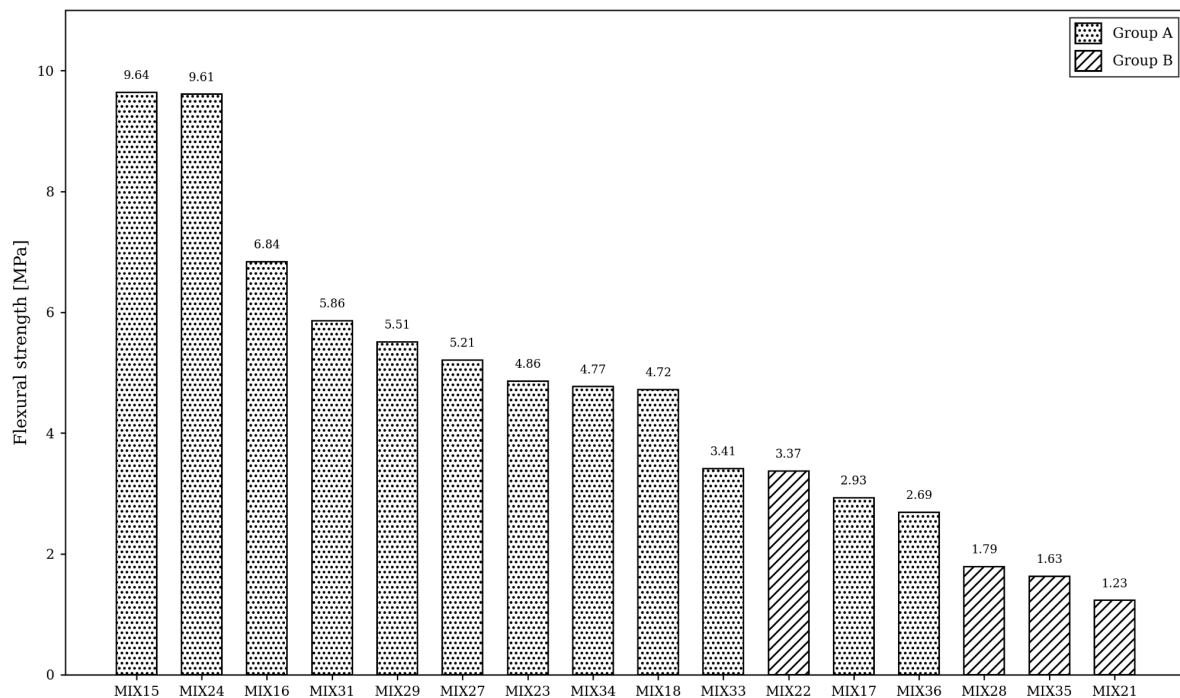
### 5.2.2 Flexural strength results by series

**Table 5.6** — Flexural strength results by mix, ranked by mean.  $\bar{\sigma}_f$  = mean flexural strength (three-point bending, EN 1015-11);  $n$  = number of specimens;  $\sigma_f/\sigma_c$  = flexural-to-compressive ratio where both are available.

| Rank | Mix   | $\bar{\sigma}_f$ (MPa) | Specimen values | $n$ | $\sigma_f/\sigma_c$ | Group | Series              |
|------|-------|------------------------|-----------------|-----|---------------------|-------|---------------------|
| 1    | MIX15 | 9.64                   | 11.74 / 7.54    | 2   | 0.538               | A     | IV — M130 10 g, raw |
| 2    | MIX24 | 9.61                   | 10.03 / 9.19    | 2   | 0.373               | A     | VI — Mullite 10 g   |
| 3    | MIX16 | 6.84                   | 7.22 / 6.46     | 2   | 0.388               | A     | IV — M130 15 g, raw |

| Rank | Mix   | $\bar{\sigma}_f$ (MPa) | Specimen values | n | $\sigma_f/\sigma_c$ | Group | Series                   |
|------|-------|------------------------|-----------------|---|---------------------|-------|--------------------------|
| 4    | MIX31 | 5.86                   | 7.29 / 4.42     | 2 | 0.420               | A     | VI — Mullite 8.25 g      |
| 5    | MIX29 | 5.51                   | 4.39 / 6.63     | 2 | 0.484               | A     | VIII — Gypsum 1 g        |
| 6    | MIX27 | 5.21                   | 5.31 / 5.12     | 2 | 0.297               | A     | VII — Cem 15 + M130 5    |
| 7    | MIX23 | 4.86                   | 4.28 / 5.43     | 2 | 0.194               | A     | VI — Mullite 5 g         |
| 8    | MIX34 | 4.77                   | 4.70 / 4.83     | 2 | 0.417               | A     | IX — Cem 13 + M130 7     |
| 9    | MIX18 | 4.72                   | 4.24 / 5.20     | 2 | 0.393               | A     | V — Cement 3B 17 g       |
| 10   | MIX33 | 3.41                   | 2.87 / 3.95     | 2 | 0.332               | A     | IX — Cem 22.5 + M130 10  |
| 11   | MIX22 | 3.37                   | 2.58 / 4.15     | 2 | 0.315               | B     | V — Cement 3B 17 g       |
| 12   | MIX17 | 2.93                   | 2.93            | 1 | 0.314               | A     | V — Cement 3B 13 g       |
| 13   | MIX36 | 2.69                   | 3.20 / 2.17     | 2 | 0.337               | A     | VIII — Gypsum 2.5 + M130 |
| 14   | MIX28 | 1.79                   | 1.79            | 1 | 0.326               | B     | VII — Cem 15 + M130 5    |
| 15   | MIX35 | 1.63                   | 1.69 / 1.57     | 2 | 0.353               | B     | IX — Cem 13 + M130 7     |
| 16   | MIX21 | 1.23                   | 1.23            | 1 | 0.227               | B     | V — Cement 3B 13 g       |

$\sigma_f/\sigma_c$  uses the mean compressive strength from Table 5.5. For MIX22, MIX24 and MIX27 the compressive mean reflects only the failing half-specimens, so their ratios are based on a conservative (lower-bound) compressive value and should be read with that in mind.



**Figure 5.3** — Flexural strength results for all mechanically tested mixes, ranked by mean value (Group A and Group B).

MIX15 had the highest mean flexural strength in the program at 9.64 MPa, just ahead of MIX24 at 9.61 MPa. The results are nearly identical, but each mix achieved this strength in a different way: MIX15 used Series IV (10 g LUKOSIL M130, raw Group A), while

MIX24 used Series VI (10 g mullite, Group A). This shows that both pore-surface hydrophobization and reactive Si/Al correction can each produce a strong matrix. MIX31 (5.86 MPa) and MIX29 (5.51 MPa) were next, performing better than the Series IX and Series V Group A mixes.

In every series where reduced groups were tested, the initiating Group B consistently had lower peripheral strength. For example, MIX17 (Group A, cement 13 g) reached 2.93 MPa, while MIX21 (Group B) only reached 1.23 MPa. MIX18 and MIX22 had 4.72 and 3.36 MPa, MIX27 and MIX28 had 5.21 and 1.79 MPa, and MIX34 and MIX35 had 4.77 and 1.63 MPa, respectively. This consistent difference, regardless of which additive was used, shows that sediment reactivity, not the additive, is the primary factor limiting flexural performance.

The flexural-to-compressive ratios ( $\sigma_f/\sigma_c$ ) ranged from about 0.16 to 0.54 across the mixes with both measurements. These ratios are generally consistent with, and in some instances exceed, the 0.15–0.25 range commonly reported for ordinary Portland cement (OPC) mortars [12]. MIX15 ( $\sigma_f/\sigma_c = 0.54$ ) is especially noteworthy, as its flexural strength is disproportionately high compared to its compressive strength. This observation indicates an improved resistance to crack propagation, a property frequently associated with more continuous, low-porosity gel networks. However, it is not clear from the current data whether the LUKOSIL M130 phase plays an active role, for example, by absorbing energy at the crack tip. Since there were only two flexural specimens, the high ratio might also be due to differences between samples. The observation is therefore reported as notable but tentative, pending the fracture-surface analysis recommended in Section 5.3. The low ratios returned for MIX24 and MIX27 (0.16 and 0.09) are artifacts of the load-cell limitation: their compressive means are lower bounds based solely on the failing half-specimens, so the ratios understate the true value and should not be read as evidence of brittleness.

### **5.2.3 Effect of key variables on mechanical performance**

The dominant variables can only be interpreted in relation to the dataset's resolution. Since there are only two to four half-specimens per mix, the results show considerable variation within each mix (MIX13 ranges from 12.4 to 19.4 MPa; MIX29 from 7.6 to 15.2 MPa). Because of this, differences between mixes smaller than about 2-3 MPa are not considered significant. All the effects discussed below are larger than this variation. Rankings that differ by less than a few MPa are included for completeness, but they are not considered meaningful. Based on these results, three compositional factors mainly influence compressive strength: thermal pre-treatment of the sediment, the amount of LUKOSIL M130, and the addition of mullite. Thermal pre-treatment (Series III/IV) has the strongest effect. For example, MIX11 (heated Group A, 3 g M130) compared to MIX13 (raw Group A, 3 g M130) shows a difference of 10.1 MPa under otherwise identical conditions, which is much greater than the variation. The reason is clear: heating at 700 °C removes water from kaolinite and partially disordered illite, creating a metakaolinite-like phase. This phase has a reactive, amorphous structure that dissolves quickly in the alkaline 65 activator, which helps form a denser gel network [17, 25, 43]. As explained in Section 5.4, this improvement must be balanced against the energy cost of the heating step.



The amount of LUKOSIL M130 added does not increase compressive strength in a straight line for raw Group A sediment. Raising the dose from 3 g (MIX13, 15.90 MPa) to 10 g (MIX15, 17.93 MPa) yields a clear improvement, but increasing it further to 15 g (MIX16, 17.64 MPa) provides no additional benefit. This leveling off suggests that the pore surfaces accessible to the silicone resin are fully covered at about 10 g per batch. Any extra M130 after that likely stays as unreacted liquid and does not help make the matrix denser [38, 39].

The Series VI mullite mixes, MIX24 and MIX23 (both in Group A), ranked just below MIX11 in strength for the half-specimens tested to failure, with values of 25.77 MPa and 25.11 MPa, respectively. In both cases, either the thicker S1 (MIX24) or one half-specimen exceeded the load-cell capacity, so the actual average strength is likely higher but cannot be measured. Adding 5 to 10 grams of mullite per batch primarily served as a fine, inert filler, reducing effective porosity and improving particle packing. Although this addition lowers the bulk Si/Al ratio of the composite binder toward the N-A-S-H window (Section 2.2.2), mullite's low solubility means this is a change in overall composition rather than a reactive adjustment (Section 5.2.3). The strengths for the 5 g and 10 g doses were statistically the same, with only a 0.66 MPa difference, which falls within the normal variation for the mix. Doubling the mullite did not yield a noticeable improvement, suggesting that mullite primarily improves particle packing rather than through a chemical reaction. Like with MIX11, these higher strength values need to be interpreted carefully. Since the load-cell-limited fragments reduced the number of half-specimens that actually failed, these results should be considered alongside those from formulations with complete datasets, rather than placed above them. OPC 3B (Series V) performed better than the  $\text{Ca}(\text{OH})_2$  baseline but was still not as strong as the M130 and mullite series for Group A. This is partly because Series V used less sand (23–37 g compared to 50 g in Series IV), which changes the aggregate-to-binder ratio and makes it harder to compare the series directly. In Series V, using 17 g of cement consistently yielded higher strengths than using 13 g in both groups (Group A: 12.00 MPa vs. 9.34 MPa), as expected because more clinker phases support greater secondary C–S–H hydration [32]. Series IX's combined cement–M130 system landed in between for Group A (MIX34 11.45 MPa, MIX33 10.28 MPa), carrying the same heavy Group B penalty seen elsewhere (MIX35 4.62 MPa).

#### **5.2.4 Best-performing formulations — compressive and flexural strength**

When comparing compressive and flexural strength, three formulations stand out, each achieving a strong matrix in a different way. MIX11 (heated Group A, 3 g M130) has the highest compressive strength at 26.04 MPa. However, its flexural specimens are missing, and it relies on precursor calcination, so it is best seen as the upper limit for compressive strength rather than the best overall option. MIX24 (Group A, 10 g mullite) stands out in the compositional-correction approach. It has the highest flexural strength (9.61 MPa) and is also among the top in compressive strength. The load-cell limit on its strongest half-specimens means its actual average compressive strength could be even higher.

MIX15 (raw Group A, 10 g M130) is the most balanced. It has the highest flexural strength (9.64 MPa), is the strongest among mixes with a full set of failing compressive

half-specimens (17.93 MPa), and has the highest flexural-to-compressive ratio in the program (0.54). Since a binder with low embodied energy is needed, MIX15 is the best choice of the three. It provides balanced compressive and flexural strength, using raw, uncalcined sediment, only the binary activator, and a moderate amount of M130. This avoids the extra energy use required by the thermal pre-treatment that MIX11 depends on. MIX15 also has the most complete and consistent dataset among the top performers. MIX16 (raw Group A, 15 g M130) matches MIX15 in compressive strength (17.64 vs. 17.93 MPa, which is within the expected variation), but is much lower in flexural strength (6.84 vs. 9.64 MPa). This difference in flexural strength is significant and shows that increasing M130 beyond about 10 g per batch does not improve mechanical performance. MIX15, MIX11, and MIX24 are examined further in the microstructural observations of Section 5.3 and the integrated assessment in Section 5.4.3, where durability is also considered.

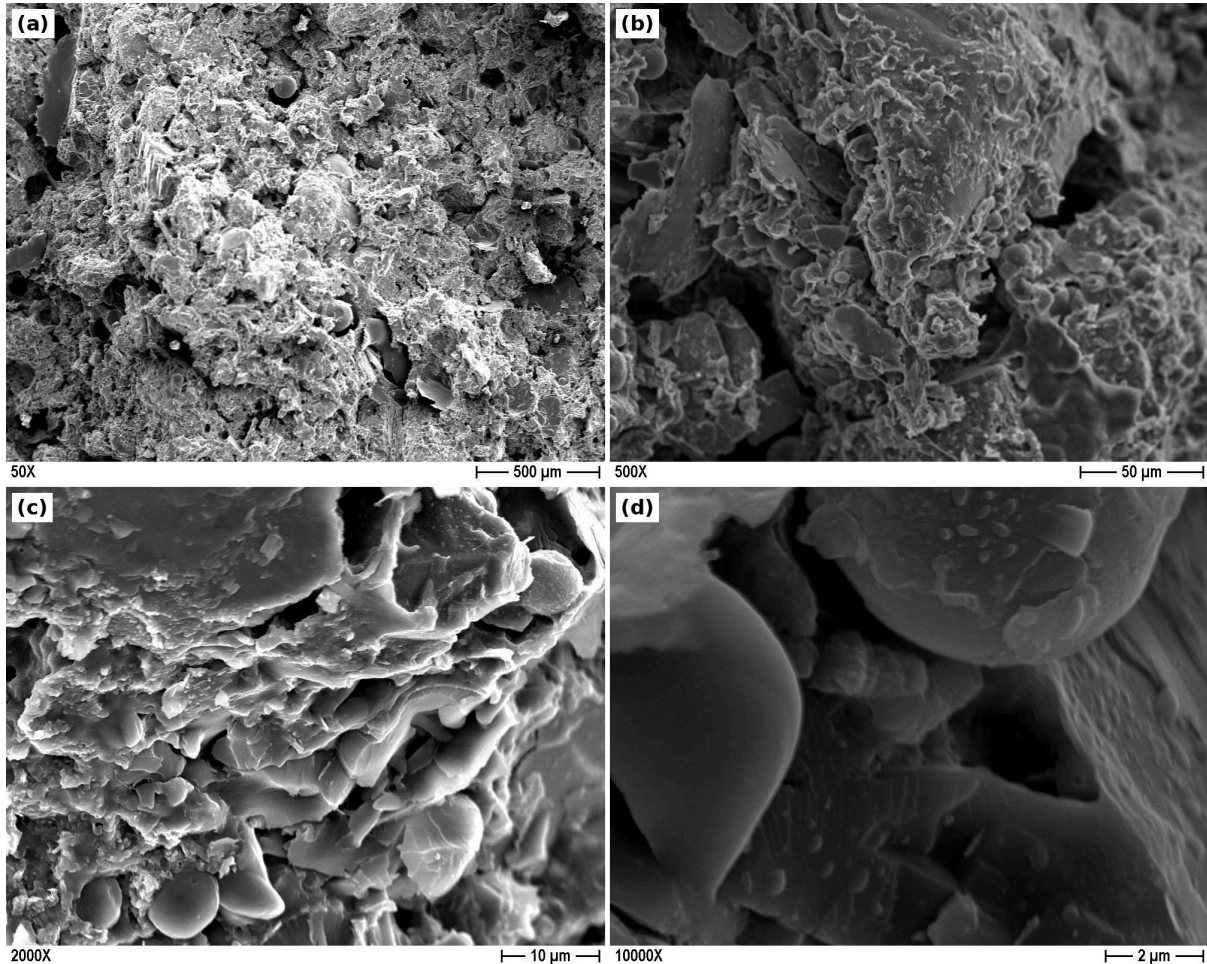
### 5.3 Microstructural observations

On the basis of the mechanical and durability results in Sections 5.1 and 5.2, three formulations have been selected for scanning electron microscopy (SEM) of the hardened specimens. MIX15 (Series IV, raw Group A + M130 10 g) is the primary candidate: it is the best-balanced formulation in the programme, leading on flexural strength (9.64 MPa), strong on compressive strength (17.93 MPa from a complete, fully-failing dataset), and notable for its high flexural-to-compressive ratio (0.54), all achieved on raw, uncalcined sediment. MIX11 (Series IV, heated Group A + M130 3 g) is included as the upper bound on compressive strength (26.04 MPa) and the lowest leachate pH (11.08), so that the microstructural effect of the calcination step can be examined directly. MIX24 (Series VI, Group A + mullite 10 g) is included as the representative of the alternative, mullite-based densification route, joint-highest on flexural strength (9.61 MPa) and among the highest on compressive strength. These three span two distinct mechanistic pathways — reactive surface densification via M130 and Si/Al correction via mullite — across both the raw and heated precursor states. The three specimens were imaged using secondary-electron (SE) mode after the 24-hour immersion test and final drying. There was not enough time to perform EDS analysis, which would have given the chemical composition. As a result, the following descriptions focus only on the shape and texture of the surfaces, and this limitation is reflected in their writing (Section 6.3.1).

#### 5.3.1 SEM images and gel morphology

Figure 5.4 presents the fracture surface of MIX15 at four different magnifications. At  $\times 50$  (a), the surface appears compact, with a few scattered rounded holes a few hundred micrometers wide. These holes are probably air pockets trapped during hand compaction (Section 6.2.2), and a few sand grains are also visible. At  $\times 500$  (b), the binder forms a continuous mass around flat, layered particles. These are leftover mica and illite grains, which are the same clay minerals identified by XRD in the raw sediment (Section 3.1.4). Because this sediment was not calcined, only part of the crystalline material dissolved, while the rest stayed in the gel. Looking closer, more details become visible. At  $\times 2,000$  (c), there

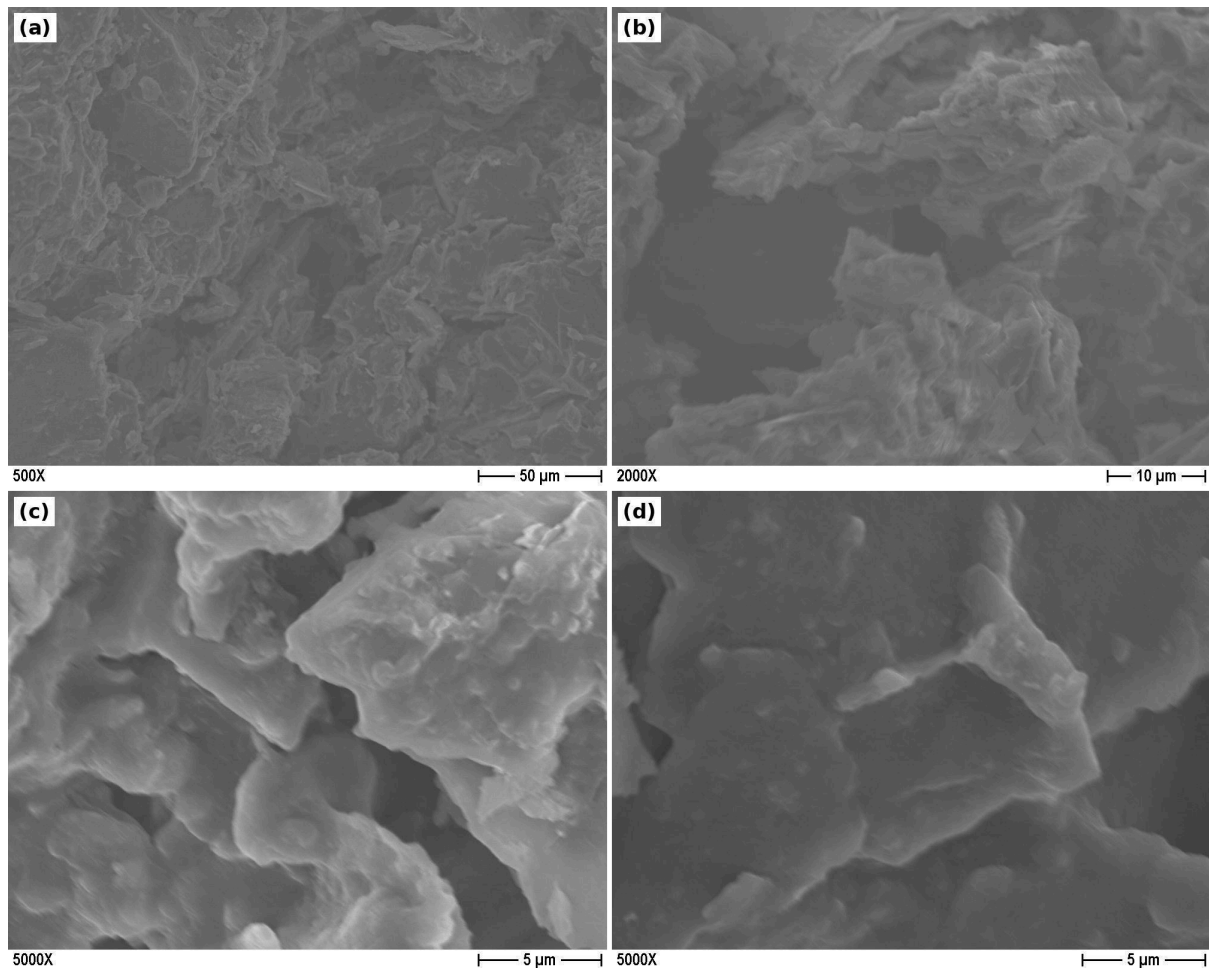
are small rounded globules, about one to ten micrometers wide, inside the matrix. At  $\times 10,000$  (d), their surfaces are covered with tiny droplets much smaller than a micrometer, and the nearby broken edges appear smooth rather than sharp. This soft, coated appearance is what we would expect if the LUKOSIL M130 resin, added at 10 grams in this mix, had spread as a thin film over the inner surfaces. Still, shape alone does not prove this, as explained below.



**Figure 5.4** — These secondary-electron SEM images show the MIX15 fracture surface (raw Group A sediment with 10 g LUKOSIL M130) after a 24-hour immersion test. The images include: (a) an overview at  $\times 50$ ; (b) the binder matrix with platy phyllosilicate relicts at  $\times 500$ ; (c) rounded globular domains in the matrix at  $\times 2,000$ ; and (d) droplet-decorated faces and softened fracture edges at  $\times 10,000$ . The scale bars are shown on each panel.

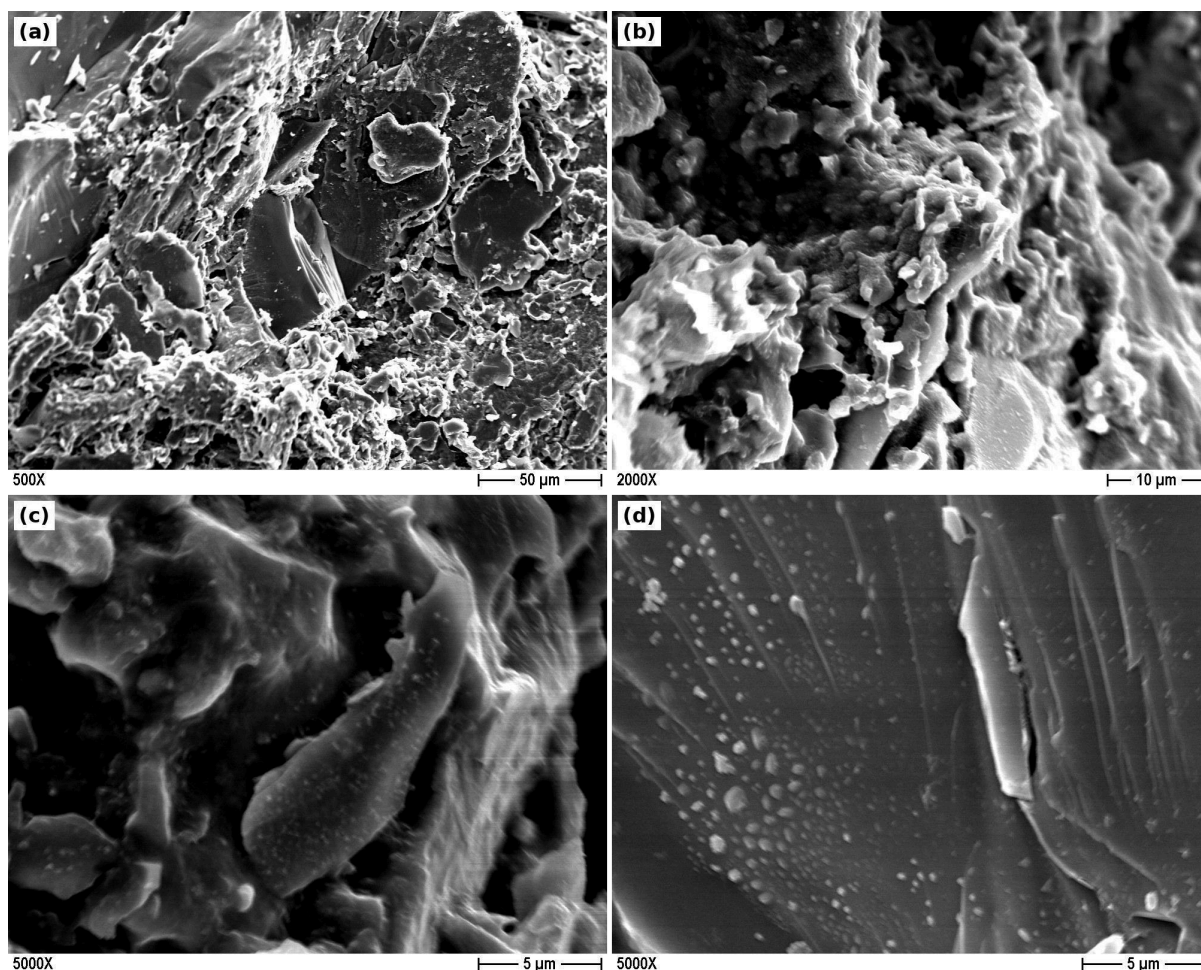
MIX11 was made from calcined sediment, and its texture stands out (Figure 5.5). At  $\times 500$  (a), the fracture surface looks flat and even, not rough and broken like the raw-sediment mixes. At  $\times 2,000$  (b), the matrix seems merged, with the original particle outlines blending into the gel. At  $\times 5,000$  (c, d), it appears as dense, blocky lumps with rounded edges and very little visible porosity. This aligns with what we expect when calcination increases the reactive, amorphous content of the sediment: more of the solid dissolves and reforms into a gel, leaving fewer original grain shapes. This compact look matches MIX11's two best results: the highest compressive strength in the program (26.04 MPa) and the lowest 24-hour

leachate pH (11.08). These results together suggest that most of the alkali was absorbed into the gel instead of remaining free (Section 5.1.3).



**Figure 5.5** —Secondary-electron SEM images show the MIX11 fracture surface (calcined Group A sediment with 3 g LUKOSIL M130). Image (a) displays a flat, low-relief surface at  $\times 500$  magnification. Image (b) shows a coalesced binder matrix at  $\times 2,000$ . Images (c) and (d) reveal a dense, blocky gel with little visible porosity at  $\times 5,000$ . The scale bars are shown on each panel.

MIX24 contains mullite and is positioned between the other two samples (see Figure 5.6). At 500x magnification, the fracture surface looks rough and uneven, with large flat grains set in a textured matrix. At 2,000x, the gel is filled with fine particles, most of which are just a few micrometers or smaller. This texture is unique to MIX24 and matches the fine fraction of the  $-325$  mesh mullite powder ( $0\text{--}45\text{ }\mu\text{m}$ ) mixed into the binder. At 5,000x, you can see angular plates embedded in the gel and a smooth cleavage face dotted with tiny deposits.



**Figure 5.6** — Secondary-electron SEM images show the MIX24 fracture surface (raw Group A sediment with 10 g mullite): (a) a heterogeneous fracture surface with a large platy grain at  $\times 500$ ; (b) a matrix containing fine particles that match the dispersed mullite filler at  $\times 2,000$ ; (c) angular plates interlocked with gel at  $\times 5,000$ ; (d) a cleavage face covered with sub-micrometer deposits at  $\times 5,000$ . The scale bars are shown on each panel.

This applies to all three specimens. Since the specimens were imaged after being immersed and dried again, some of these deposits are likely soluble material that left the pore solution and re-formed on the surface as it dried. This matches the alkali release measured in the leachate (Section 5.1.3).

### 5.3.2 Correlation with mechanical and durability results

If we rank the three surfaces by how compact they appear, MIX11 comes first, followed by MIX24 and then MIX15. This matches their average compressive strengths (26.04, 25.77, and 17.93 MPa), though the middle value is a lower bound due to the load-cell limit. We should not read too much into this, since there were only two specimens per mix and the SE images are of broken surfaces, so this is a qualitative comparison rather than a measurement. Still, the trend is reasonable, and each mix shows the features expected from its recipe. The calcined mix probably contains more gel, the mullite mix has a matrix filled with fine filler, and the mix with the most resin has film-like surfaces.

The MIX15 images also connect to its unusually high flexural-to-compressive ratio, as discussed in Section 5.4.4. There are no fibers, bridging phases, or other surface features that would prevent crack propagation, so the images do not show any special toughening mechanism. Instead, they support the simpler explanation from that section: a compact, low-defect matrix and a small number of flexural specimens. The durability results are consistent, too. MIX11's dense, low-porosity surface matches its low leachate pH, while MIX15's soft, film-covered surfaces match the low leachate alkalinity seen in the LUKOSIL M130 mixes (Section 5.1.4).

## **5.4 Integrated discussion**

### **5.4.1 Most influential compositional variables**

The experimental program explored eight categories of compositional variables across 37 formulations and two sediment groups. Of these, three emerge as clearly dominant in governing compressive strength: thermal pre-treatment of sediment, addition of LUKOSIL M130, and addition of mullite. All three act on the same fundamental parameter — the density and connectivity of the aluminosilicate gel network — through different mechanisms. Thermal pre-treatment acts upstream, increasing the reactive pool available to the activator. M130 acts on the cured pore structure, reducing permeability and preserving gel integrity during water exposure. Mullite acts physically as a fine inert filler that improves particle packing and reduces porosity rather than chemically correcting the reactive Si/Al ratio.

The thermal pre-treatment result deserves particular comment because the highest compressive value in the program (MIX11, 26.04 MPa) depended on it. Calcination at 700 °C is energy-intensive, and the central rationale of this work is to valorize a waste precursor into a low-carbon binder. A strength gain obtained at the cost of a high-temperature firing step, therefore, has to be judged against the embodied energy it adds and against the alternative routes — M130 and mullite — that achieve strong performance on raw sediment without it. On that basis, the raw-sediment formulations are the more promising direction for the binder system as a whole, even though they do not achieve the highest single compressive strength. This consideration is taken up again in Section 5.4.3.

The  $\text{Ca(OH)}_2$  addition (Series II) did not produce the strength enhancement that its theoretical role as a C-A-S-H promoter might suggest, most plausibly because the high water content of those mixes diluted the activator and increased porosity. Future formulations targeting  $\text{Ca(OH)}_2$  as a performance variable should fix the water content independently of the portlandite dose. The OPC 3B addition (Series V) yielded intermediate results that are difficult to disentangle from the concurrent reduction in sand content; a dedicated series with a fixed aggregate content would be needed to isolate the cement contribution. Gypsum addition (Series VIII) and the combined gypsum + M130 formulations were taken to mechanical testing in this revised programme (MIX29: 11.38 MPa; MIX36: 7.99 MPa) and gave moderate Group A strengths, but their leachate pH (MIX29 = 11.88, MIX36 = 11.79) is

not notably different from the comparable M130-only mixes, suggesting that gypsum's primary role in this system is kinetic (setting modification) rather than structural.

#### **5.4.2 Effect of thermal pre-treatment — calcined vs raw sediment series**

The clearest single result of the experimental program is the effect of thermal pre-treatment on compressive strength. Series IV allows for a direct comparison because both heated and raw Group A samples were prepared with the same M130 dose (3 g) under identical conditions. MIX11 (heated) reached 26.04 MPa, while MIX13 (raw) reached 15.90 MPa. This is a difference of 10.1 MPa, or about 64%. Group B showed a similar pattern, with MIX12 (heated) reaching 7.71 MPa. Heating at 700 °C removes water from kaolinite and other disordered clay minerals, thereby creating a metakaolinite-like phase. This phase is reactive and mostly amorphous, so it dissolves easily in the alkaline activator and helps form a denser, more continuous gel network [17, 25, 43]. This is consistent with the lower leachate pH of MIX11 (11.08, the lowest in the program), indicating that more of the available alkali was consumed during gel formation rather than remaining free to leach.

The strength advantage of the calcined series is therefore real and substantial, but it has to be read against the central objective of this work — to valorize a waste sediment into a low-carbon binder. Calcination is an energy-intensive step, and a strength gain obtained at the cost of a high-temperature firing stage erodes the environmental advantage that motivates the use of sediment in the first place. The main result of the raw-sediment tests is that firing is unnecessary. Both the M130 and mullite methods work well with raw Group A sediment. For example, MIX15 (raw, 10 g M130) reached 17.93 MPa in compression and 9.64 MPa in flexure, and MIX24 (raw, 10 g mullite) showed similar results. Neither mix required thermal pre-treatment. These raw-sediment mixes appear to be a better choice for the binder system, even though the highest compressive strength is still achieved with the calcined MIX11.

In all tests, Group A sediment from Perrères Dam was stronger and more durable than Group B from Poggia Dam. This is mainly because of differences in precursor reactivity, which calcination is designed to improve. The sediments differ in several ways. Group A has much finer fractions ( $D[4,3]$  ranges from about 41  $\mu\text{m}$  for 2C to 271  $\mu\text{m}$  for 3C), while Group B fractions are larger (393–407  $\mu\text{m}$  for the INVASO and SUD fractions). This means Group A has more surface area for dissolution. Also, Group A contains more kaolinite and disordered clay minerals, while Group B is coarser and has more quartz. Third, Group A fractions 2C and 4C ( $\text{Al}_2\text{O}_3$  about 20.3–20.5%) provide more reactive alumina than SUD (16.0%) and INVASO (16.6%). The higher bulk Si/Al ratios in SUD and INVASO are less suitable for N-A-S-H formation unless adjusted. The practical implication is that, for the less reactive Poggia Dam sediments to approach the performance of the Perrères Dam material, either mechanical activation (milling to reduce  $D[4,3]$ ), thermal pre-treatment, or a more aggressive compositional correction (higher mullite or  $\text{NaAlO}_2$  dose) would be required — all technically feasible directions for future work.

### 5.4.3 Best-performing formulations across all criteria

Sections 5.1.4 and 5.2.4 separately identified the best formulations for durability (water absorption and leachate pH) and for mechanical performance (compressive and flexural strength). Pulling those together and weighing them against the low-embodied-energy requirement, MIX15 emerges as the strongest overall formulation in the program. This mix has the highest flexural strength (9.64 MPa), the best compressive strength among those tested (17.93 MPa), and the highest flexural-to-compressive ratio (0.54), indicating a dense, low-defect matrix. It also does well in durability tests, with a leachate pH of 11.70 and a mass loss of  $-1.92\%$ . These results were achieved using raw, uncalcined Group A sediment, a binary activator, and 10 grams of LUKOSIL M130. The mix performs well across all criteria without the extra energy needed for thermal pre-treatment, making it the most promising option for the thesis goal.

MIX11 records the highest single compressive value (26.04 MPa) and the lowest leachate pH (11.08), and is the strongest illustration of what calcination can achieve; but it depends on the 700 °C firing step, and its flexural data were lost, so it is best regarded as the compressive-strength ceiling of the program rather than the best all-round formulation. MIX24 (mullite 10 g) is the leading representative of the alternative densification route, joint-highest on flexural strength (9.61 MPa) and among the highest on compressive strength, although the load-cell limitation on its strongest half-specimens means its true compressive mean is a lower bound. These three formulations — MIX15, MIX11 and MIX24 — are the selected candidates for the SEM analysis described in Section 5.3, chosen to span the raw-resin, heated-resin and mullite-correction pathways.

### 5.4.4 Benchmarking against published literature values

The compressive strengths achieved by the best-performing formulations fall within the middle-to-upper range of 15–40 MPa reported for heat-cured, sediment-based AAMs in the literature [17, 29]. Any closer comparison must be made with caution. As noted in Section 4.3.5, the specimens used here had a reduced  $20 \times 20 \times 80 \text{ mm}^3$  geometry rather than the standard  $40 \times 40 \times 160 \text{ mm}^3$  prism, and the half-prism fragments were tested in compression on irregular fracture surfaces; both factors raise apparent strength by an amount that was not quantified in this study. The values below are therefore offered as order-of-magnitude context only, not as strict comparisons. On that basis, MIX11's 26.04 MPa falls in the same broad band as the 18–22 MPa reported by Ferone et al. [21] for calcined hydroelectric reservoir sediments activated with  $\text{NaOH} + \text{Na}_2\text{SiO}_3$  at 70 °C and the 24–28 MPa reported by Messina et al. [31] for calcined sediment–potabilization-sludge blends cured at 80 °C; the geometry difference precludes any claim that one value is genuinely higher than another. The mullite-densified MIX24 and MIX23 at approximately 25 MPa lie in a similar range to Mahfoud et al.'s [35] data for fly-ash–sediment geopolymers, although that system used fly ash as a co-precursor rather than sediment alone.

The flexural strengths recorded here (up to 9.64 MPa for MIX15) are high relative to most sediment-AAM studies, which rarely report flexural data at all. A flexural strength of 9.64 MPa against a compressive strength of 17.93 MPa corresponds to a ratio of



approximately 0.54, well above the 0.15–0.25 rule of thumb commonly cited for geopolymer mortars [12]; the expected flexural strength on that rule would be only about 2.7–4.5 MPa. A denser, more defect-free matrix is the most plausible explanation, though, with only two flexural specimens ( $n = 2$ ), a favorable specimen pair cannot be excluded. The observation, therefore, stands as a result to be checked against the SEM fracture surfaces (Section 5.3) rather than as evidence of a toughening mechanism, which in mortars would normally require fiber reinforcement.

The leachate pH values for the Series IV–IX mixes (11.0–12.5 at 24 hours) are consistent with values reported by Ferone et al. [29] and Lirer et al. [28] for comparable systems, where a 24-hour leachate pH of 11.5–12.5 was taken as indicative of satisfactory alkali fixation. The lower pH achieved by MIX11 (11.08) is notable and comparable to the best-performing mixes in the LUKOSIL M130 study of Le Chi et al. [38], suggesting that the hydrophobic surface modification is effective not only in reducing water uptake but also in limiting ion transport out of the matrix under immersion conditions.

# Chapter 6: Sustainability Assessment and Conclusions

## 6.1 Sustainability assessment

The fifth research objective of this thesis was to assess the sustainability implications of the proposed binder systems in terms of CO<sub>2</sub> reduction potential, valorization of dredged sediment, and alignment with circular economy principles. The assessment is necessarily indicative rather than a full life-cycle analysis, which falls outside the scope of a laboratory-scale study (Section 1.5); it relies on the measured mix compositions from this work, combined with published embodied-carbon coefficients for the constituent materials.

### 6.1.1 CO<sub>2</sub> reduction potential compared to OPC

The principal environmental argument for alkali-activated materials is the avoidance of clinker. As established in Chapter 1, ordinary Portland cement production releases approximately 0.66–0.82 tonnes of CO<sub>2</sub> per tonne of clinker, of which more than half is process-derived — the unavoidable result of the calcination of limestone ( $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ ) — and therefore cannot be eliminated by fuel-switching or efficiency gains alone [3, 4]. Because the binders developed in this work contain almost no clinker, this process-derived emission is avoided entirely; the system's carbon footprint instead arises from the alkaline activator and any supplementary materials. Published life-cycle assessments of alkali-activated systems report CO<sub>2</sub> reductions of 40–80% relative to OPC, but with an important qualification that recurs throughout the literature: the magnitude of the saving is critically dependent on the dosage of the alkaline activator, and excessive activator use can erode or even reverse the benefit [4, 18,42].

To place the binders of this work within that range, an indicative cradle-to-gate calculation was carried out for the best-balanced formulation, MIX15, using its measured composition (50 g blended Group A sediment, 1.5 g NaOH, 30.6 g Na<sub>2</sub>SiO<sub>3</sub> solution, 10 g LUKOSIL M130 silicone resin) and published embodied-carbon coefficients. The coefficients adopted are 1.514 kg CO<sub>2</sub>/kg for commercial sodium silicate solution, 0.68 kg CO<sub>2</sub>/kg for sodium hydroxide from the chlor-alkali process, approximately 5 kg CO<sub>2</sub>/kg for the silicone resin, and a nominal 0.004 kg CO<sub>2</sub>/kg for the dredged sediment to account for transport and drying only, since the sediment is a waste material requiring no manufacture [18,24]. A reference OPC binder of equal mass was assigned a coefficient of 0.83 kg CO<sub>2</sub>/kg [4]. The results are summarised in Table 6.1.

*Table 6.1 — Indicative cradle-to-gate CO<sub>2</sub> footprint of the MIX15 binder system compared with an equal mass of OPC, using published embodied-carbon coefficients. The sand fraction is common to both systems and is excluded. Figures are per 92.1 g binder-system batch; the percentage change is relative to OPC.*

| Constituent      | Mass (g) | Coeff. (kg CO <sub>2</sub> /kg) | CO <sub>2</sub> (g) | Share |
|------------------|----------|---------------------------------|---------------------|-------|
| Dredged sediment | 50.0     | 0.004                           | 0.20                | 0%    |

| Constituent                               | Mass (g) | Coeff. (kg CO <sub>2</sub> /kg) | CO <sub>2</sub> (g) | Share |
|-------------------------------------------|----------|---------------------------------|---------------------|-------|
| NaOH                                      | 1.5      | 0.68                            | 1.02                | 1%    |
| Na <sub>2</sub> SiO <sub>3</sub> solution | 30.6     | 1.514                           | 46.33               | 47%   |
| LUKOSIL M130                              | 10.0     | ~5.0                            | 50.00               | 51%   |
| <b>MIX15 total</b>                        | 92.1     | —                               | 97.55               | 100%  |
| <b>OPC (equal mass)</b>                   | 92.1     | 0.83                            | 76.44               | —     |

*Coefficients from published LCA literature; the silicone-resin value is a conservative estimate for an energy-intensive material. The calculation is cradle-to-gate and excludes curing energy, which is discussed separately below.*

There are two main findings, with the second being more significant. First, the current version of MIX15 is not carbon-favorable by mass. Each batch produces 97.6 g of CO<sub>2</sub>, which is slightly more than the 76.4 g produced by the same amount of OPC. This higher footprint is mostly due to two ingredients: silicone resin, responsible for 51% of the emissions, and sodium silicate, which accounts for 47%. The sediment, which is the waste being reused, contributes very little. The second, more important, finding is that removing the silicone resin completely changes the results. A binder made only from sediment and activator (50 g sediment, 1.5 g NaOH, 30.6 g Na<sub>2</sub>SiO<sub>3</sub>) produces 47.6 g CO<sub>2</sub> per 82.1 g batch, or about 0.58 kg CO<sub>2</sub> per kg. This is a 30% reduction compared to OPC. In this resin-free mix, sodium silicate alone is responsible for 97% of the remaining emissions.

A final caveat concerns the basis of comparison, and it is the most important qualification of the figures above. The per-mass comparison used so far is the weakest possible basis, because a binder is used to deliver strength, not mass; the appropriate functional unit is carbon per unit of delivered strength. On that basis, the resin-free advantage narrows and may reverse: taking the resin-free binder at 0.58 kg CO<sub>2</sub>/kg and its raw-sediment compressive strength of approximately 18 MPa gives roughly 0.032 kg CO<sub>2</sub> per kg per MPa, against approximately 0.024 kg CO<sub>2</sub> per kg per MPa for OPC at a representative mortar strength of 35 MPa (0.83 kg CO<sub>2</sub>/kg ÷ 35 MPa). In other words, the ~30 % per-mass saving is offset by OPC's higher strength once normalized, and the two systems become broadly comparable per unit of load capacity — a sobering result that the per-mass figure conceals (these normalized values are illustrative, and sensitive to the strength assumed for OPC and to the non-standard specimen geometry of this study).

Curing energy is another important factor that is often overlooked. In this study, each sample was cured at 60 °C for 14 days, but earlier cradle-to-gate calculations did not include this step. For context, heating a mortar batch to 60 °C once uses about 0.01 kWh per kilogram, which equals about 0.003 kg CO<sub>2</sub> per kilogram with a typical grid factor. In a laboratory oven, most of the energy is used to maintain a steady temperature for 14 days, which can consume much more energy than the initial heating. In contrast, an efficient industrial tunnel kiln would use much less energy for each unit of material. The main point is to be cautious. The binders created in this study avoid the clinker emissions that make OPC difficult to decarbonize. Using a resin-free, optimized formula also reduces CO<sub>2</sub> per unit of mass. Still, when we account for strength normalization and the energy needed for curing, the overall benefit is less significant. To reach the highest savings found in other studies, it is

important to optimize both the activator system and the curing process, not just the use of sediment.

### **6.1.2 Valorization of dredged sediment as industrial waste**

Beyond avoiding clinker, the second sustainability dimension of this work is the valorization of a problematic waste stream. As set out in Chapter 1, the accumulation of sediment behind hydroelectric dams is a continual operational and environmental challenge: reservoir capacity is progressively lost, periodic dredging is mandatory, and the dredged material must then be managed under increasingly strict disposal regulations that carry real and rising costs.

This thesis demonstrates that the same material can serve as the primary ingredient in a construction binder. In all 37 mixes tested, dredged sediment accounted for most of the solids content, with 50 grams per batch. The best mixes reached compressive strengths of up to 26 MPa when calcined and 18 MPa when raw, and flexural strengths close to 10 MPa. These results are consistent with the literature on non-structural and semi-structural precast products, so these uses are realistic. However, this depends on long-term durability, curing under normal conditions, and full-scale testing, which are not covered in this study (see Section 6.3). When sediment is treated as a resource rather than waste, both its economic and environmental impacts change. Instead of paying to dispose of it, sediment can be used as a valuable material. This means less ends up in landfills or storage, and there is less need for transport and treatment. This is the main point of the dual-benefit argument in this thesis: a single material stream can help address both the carbon impact of cement and the problem of disposing of dredged material.

There are two important limitations to this claim. First, the positive results were observed only for sediments from two specific hydroelectric basins in northern Italy (the Perrères and Poglia dams). The clear difference in performance between the two groups studied—Group A consistently outperformed the coarser, less reactive Group B—shows that the effectiveness of the sediment depends on its source. Not all sediments will perform as well without extra processing.

Second, the sediment required physical preparation, such as drying and sieving. For the highest strengths, thermal pretreatment was also required. These steps require additional energy and incur costs, so they should be considered in a full valorization assessment. Although these factors do not alter the main result, they indicate that valorization should be assessed on a case-by-case basis rather than assumed to apply to all dredged sediment.

### **6.1.3 Circular economy alignment and potential applications**

The valorization pathway demonstrated here aligns directly with circular economy principles. In place of the linear take–make–dispose model that characterizes both conventional cement (extract limestone, fire clinker, use, demolish) and conventional sediment management (dredge, transport, landfill), the approach of this thesis closes a loop: a waste output from one industrial process — hydroelectric power generation — becomes the raw material input for another, the manufacture of construction binders.

How this material can be used depends on its performance and curing method. Because all samples were heat-cured, these results are most relevant to precast and prefabricated products made in factories, where high-temperature curing is standard, and the sediment feedstock remains the same. Under these conditions, the material's strength makes it a good fit for non-structural and semi-structural products such as paving blocks, curbs, partitions, masonry units, backfill, stabilization blocks, and other items that require a compressive strength of 15–26 MPa and perform well in immersion tests. The hydrophobic, low-permeability properties that LUKOSIL M130 brings to the best mixes could be especially useful for moisture-exposed products. Moving into primary structural or in-situ applications would require, at the very least, validation under ambient curing plus the long-term durability testing set out in Section 6.3.

## **6.2 Conclusions**

### **6.2.1 Summary of key findings by objective**

This thesis is organized around five research objectives, each with key findings described below.

Objective 1: Characterization of the sediment precursors. Both sediment groups were fully analyzed in raw and calcined states using XRF, XRD, and laser granulometry. The tests revealed a key finding: the two sources behave very differently. Group A (Perrères Dam) is finer, with D[4,3] values ranging from about 41 to 271  $\mu\text{m}$ , and contains more reactive alumina and clay minerals. Group B (Poglia Dam) is much coarser, with D[4,3] values ranging from 393 to 407  $\mu\text{m}$ , and has more quartz and less alumina. This main difference shaped how we interpreted the later results and explains the performance differences between the groups.

Objective 2: design and production of 37 formulations. We made 37 different alkali-activated mortar mixes, grouped into 9 experimental series based on 8 main variables: binder composition, calcium-based additives, mineral modifiers, silicone-resin modifier, activator components and dosage, sediment pre-treatment, sediment group, and water content. The standard mix used NaOH and  $\text{Na}_2\text{SiO}_3$  as the activator, with sodium aluminate and other supplementary materials added to certain groups. By changing these factors one at a time, we could see how each variable affected performance.

Objective 3: Durability behavior. We put all hardened samples in water for 24 hours. During this period, we measured how much water they absorbed and checked the water's pH to track alkaline leaching. Each sample lost some mass, which matched the expected loss of soluble alkali. After 24 hours, the water pH ranged from 11.08 to 13.20. The LUKOSIL M130 series (MIX11) had the lowest pH at 11.08, showing the best alkali fixation in our tests. Group A sediments always had a lower leachate pH than Group B sediments.

Objective 4: Mechanical performance. Compressive strength was measured for 21 mixes, and flexural strength for 16. The highest compressive strength came from calcined MIX11 (26.04 MPa), while the highest flexural strength was from raw MIX15 (9.64 MPa).

Three main factors influenced compressive strength. First, heating the sediment before use increased strength by 10 MPa in Series IV. Second, adding more than 10 grams of LUKOSIL M130 per batch did not lead to much improvement. Third, adding mullite helped adjust the Si/Al ratio closer to the N-A-S-H optimum. Considering these factors and the energy needed for calcination, MIX15 was the best overall. It had the highest flexural strength and strong compressive strength when using raw, uncalcined sediment, thereby avoiding the extra energy required to achieve the higher compressive strength of MIX11. SEM images of the fracture surfaces for the three main mixes (see Section 5.3) supported these findings. Calcined MIX11 showed the densest and most merged gel, while MIX15 had a compact, low-defect matrix with a film-like surface coating.

Objective 5: Sustainability implications. The sustainability assessment (Section 6.1) showed that these binders avoid the clinker emissions that make OPC hard to decarbonize. Using a resin-free, dosage-optimized sediment binder can cut CO<sub>2</sub> emissions by 30% compared to OPC. The study also found that most of the system's carbon footprint comes from the sodium silicate activator and, when used, the silicone resin. To reduce carbon emissions, both should be used less. Beyond carbon, the research showed that dredged sediment can be used as a binder feedstock and fits well with circular economy principles. Precast products are the most suitable for immediate application.

### **6.2.2 Research contributions and limitations**

The principal contribution of this thesis is the systematic demonstration that dredged sediment from northern Italian hydroelectric reservoirs can serve as the dominant precursor for alkali-activated mortars of useful strength, and the identification of which compositional variables govern that performance. Three more specific contributions stand out. The first is reach: with 37 formulations across eight variable categories and two sediment sources, the program maps the design space in a structured way — isolating the individual effects of thermal pre-treatment, silicone-resin modification, mineral correction, and calcium addition — rather than reporting a single optimized mix in isolation. The second key point is the direct comparison of two sediment sources with different reactivity. This shows that both the source of the sediment and the particle size are the main factors affecting performance. These findings have practical implications for anyone trying to generalize sediment valorization. The third point is the sustainability assessment. Instead of using a broad 40–80% reduction range, this study provides a detailed, composition-specific analysis. It highlights activator and resin dosage as the main factors influencing carbon impact. This approach gives practitioners a clearer and more useful understanding than a simple headline figure.

The limitations of this study come directly from its laboratory scale and specific scope and should be stated clearly. Since the specimens were small and cured only at 60 °C, the results primarily apply to heat-cured precast applications and cannot be extended to ambient-cured or in situ applications without further testing. There are three main mechanical constraints. First, the specimens had a non-standard 20 × 20 × 75 mm<sup>3</sup> shape and were compression-tested on irregular half-prism fragments left over from flexural tests. Both factors increase the apparent strength by an unknown amount, making it unreliable to

compare these results with the standard-prism literature. Therefore, the reported strengths should be seen as relative values between mixes cast in the same way. Second, only two prisms were cast per mix, giving two flexural and up to four compressive results. This means there is considerable variation within each mix, so the spread of results should be seen as a sign of variability rather than a statistically meaningful standard deviation. Differences between mixes that are smaller than this variation are not considered real. Third, compaction was performed by hand, an uncontrolled source of porosity variation that likely explains the wide variation observed in some mixes. Fresh-state workability was not measured. The characterization was qualitative in three ways. XRD identified the mineral phases present, but it did not quantify the amorphous fraction via Rietveld refinement. The mass lost during calcination was not recorded. In Section 5.3, the SEM analysis looked only at broken surfaces of three mixes after immersion, using secondary-electron imaging. It did not include EDS or polished-section analysis, which are needed to identify gel phases or measure porosity.

Since sediment was taken from only two basins, the results should not be applied to sediments from very different sources without further validation. Three specimens were lost due to handling or curing failures, and some compressive half-specimens reached the testing machine's load limit without failing. As a result, some high strengths (especially MIX24, whose strongest fragments were not tested) are reported as lower bounds based on a single failing half-specimen. The sustainability assessment is a basic cradle-to-gate calculation, not a full life-cycle analysis, and does not include curing energy or end-of-life factors. While none of these points undermine the main findings, each limits how broadly the results can be applied, and each leads directly to the future work discussed below.

## **6.3 Recommendations for future research**

The results of this thesis open several clear directions for further investigation. Four are identified as priorities, in approximate order of immediacy.

### **6.3.1 Compositional and microstructural analysis**

The SE imaging in Section 5.3 was qualitative and examined only the fracture surfaces of the three best mixes. The next step should be a more detailed, quantitative analysis. EDS analysis comes first, since it provides the chemical composition at each point. This could answer questions that shape alone cannot, such as whether the smooth, film-like surfaces on MIX15 are actually silicone resin or just soluble material that reformed during immersion and drying. It could also show whether the binding gel is sodium-based (N-A-S-H), calcium-based (C-A-S-H), or a mix of both. This last point is central to the discussion of the  $\text{Ca}(\text{OH})_2$ , OPC, and calcined series in Chapter 5. Another important step would be backscattered-electron imaging of polished, cut surfaces, along with image analysis, to measure porosity and pore size. Porosity was used throughout Chapter 5 to explain differences in strength and water absorption, such as the weak, high-water  $\text{Ca}(\text{OH})_2$  mixes compared to the dense mullite and calcined mixes, but it was never measured directly. Using polished-section image analysis or mercury intrusion porosimetry would provide solid, measured data to support these arguments.

We should imagine more than just the three best mixes. Including a wider range from the whole program—especially the coarse, less reactive Group B samples with their Group A counterparts, as well as matched pairs of raw and calcined, and LUKOSIL M130 and no-LUKOSIL M130 samples—will help us see reactivity differences in the microstructure more clearly. This would be better than only inferring them from strength, density, and pH, as done in this thesis. It is also important to image specimens that have not gone through the 24-hour immersion, so we can tell which deposits formed during immersion and which were part of the original, as-cured gel. Taking these steps would expand the current small, three-sample survey into a more complete microstructural picture of why the mixes behave differently.

### **6.3.2 Long-term durability testing**

Durability in this work was assessed only by a 24-hour water immersion test. A proper read on service durability would require longer, more varied exposure testing: immersion extended over weeks and months to track progressive leaching and strength evolution; wet-dry and freeze-thaw cycling for outdoor relevance; carbonation testing; and — given the residual alkalinity observed in the leachate — efflorescence assessment. Pinning down the long-term stability of the gel network and how well the hydrophobic effect of LUKOSIL M130 persists would be essential before any structural or load-bearing use could even be entertained. Ambient-temperature curing warrants parallel investigation, since the restriction to 60 °C curing is one of the main factors limiting how far the present results extend.

### **6.3.3 Leaching and ecotoxicological assessment**

Dredged reservoir sediments can contain heavy metals and other contaminants accumulated from their catchments, and the immersion tests in this work showed that soluble species do leach from the hardened binder. Proper environmental clearance would require standardized leaching tests — such as the EN 12457 batch leaching protocol — to quantify the release of any regulated element from the hardened mortar, along with ecotoxicological screening of the leachate. It is a necessary step in the valorization pathway and cannot be inferred from the mechanical and pH data collected here.

### **6.3.4 Scale-up to pilot production**

Moving from laboratory specimens to practical use ultimately requires pilot-scale investigation. As a useful step before full-scale-up, the leading formulation (MIX15) could be made into standard  $40 \times 40 \times 160 \text{ mm}^3$  prisms and tested in accordance with EN 1015-11. This would provide a geometric-based strength value that can be compared directly with the literature and help calibrate the strengths reported here for the non-standard 20 mm half-prisms. A pilot study would also allow direct measurement of curing energy and processing burdens, which were identified as significant in the sustainability assessment but were not included in its cradle-to-gate scope. This would complete the environmental accounting needed to confirm the net benefit. Along with the durability and leaching work



discussed above, scaling up is the logical endpoint of the valorization pathway outlined in this thesis.

In closing, this thesis has shown that a waste material with no current value — sediment dredged from hydroelectric reservoirs — can be transformed into a functional construction binder through alkali-activation, simultaneously addressing the disposal burden of the sediment and the carbon burden of conventional cement. The performance achieved, the design variables identified, and the clear-eyed accounting of both the opportunities and the limits define a foundation on which the recommended future work can build toward a genuinely sustainable, circular use of this overlooked resource.

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## Appendix A

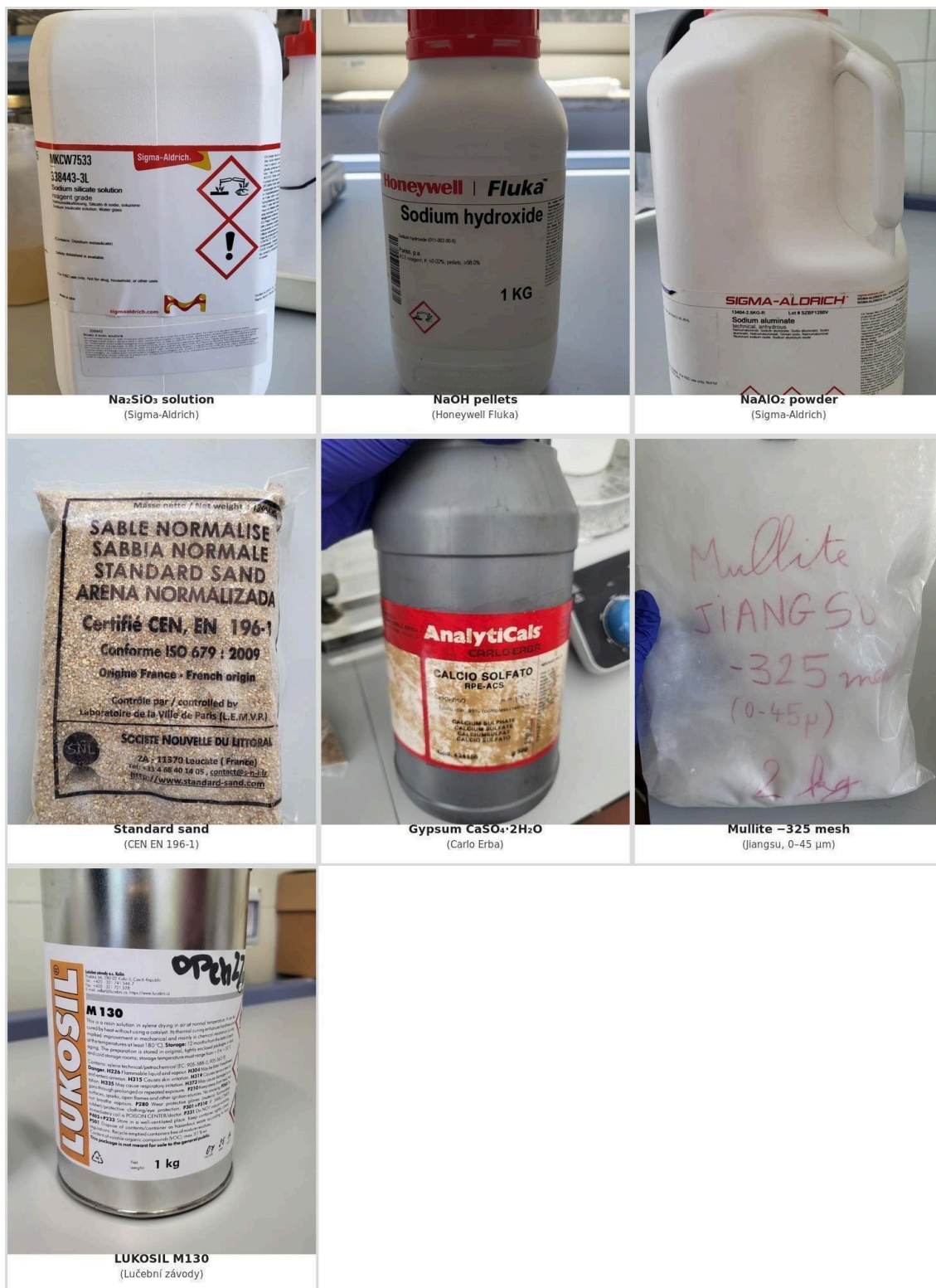


Figure A.1 — Photographs of the reagent containers used in the experimental programme.

