Sources and Substitutes for Fly Ash in Concrete

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16. Abstract

Fly ash, a by-product of coal combustion, improves the workability, mechanical properties, durability, and sustainability of concretes when added as a supplement. Dwindling supplies of fly ash led Arizona DOT (ADOT) to investigate the use of alternative cementitious materials (ACMs) in concrete mixture designs. This study drew from a review of literature, a survey of state practice among state departments of transportation (DOTs), and the authors' own research and past experience. The report details currently available alternative SCMs in Arizona, possible test methods for fly ash alternatives, and testing considerations for alternative cementitious systems, including desired performance criteria. The survey revealed the most commonly used SCMs nationwide are silica fume, Class C fly ash, and slag cement. A third of survey respondents reported that supplies are consistent, reliable, and available throughout the state, with the top project selection factors of performance (68 percent of respondents) and availability (50 percent). Based on the study findings, the authors recommend (1) development of a roadmap for performance testing and life cycle assessment of fly ash alternatives for ADOT concretes, based on initial evaluation of candidate materials using computation platforms; (2) development of a ranking matrix of locally obtained candidates for the replacement of fly ash; a concept with metrics and a rating scale is presented; and (3) development of an implementation plan for using fly ash alternatives, stressing the need for additional considerations (market penetration and technical and financial barriers) and the importance of stakeholder partnerships.

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Acronyms, Abbreviations, and Symbols

ACM	alternative cementitious material
AAR	alkali-aggregate reactivity
AASHTO	American Association of State Highway and Transportation Officials
ADOT	Arizona Department of Transportation
AFm	alumina-ferric monosulfate (phases)
ARPA	Arizona Rock Products Association
ASR	alkali-silica reaction
ASTM	American Society for Testing and Materials
ASU	Arizona State University
BET	Brunauer-Emmett-Teller (method)
Caltrans	California Department of Transportation
CSH	calcium silicate hydrate
DOT	department of transportation
DTA	differential thermal analysis
GGBFS	ground granulated blast furnace slag
HVFA	high volume of fly ash
LC^3	limestone calcined clay cement
LCA	life cycle assessment
LFA	lagoon fly ash
LOI	loss on ignition (test)
OPC	ordinary portland cement
PSD	particle size distribution
R^3	rapid, relevant, and reliable (pozzolanic test method)
SCM	supplementary cementitious material
SRMG	Salt River Materials Group
TGA	thermogravimetric analysis (test method)

Introduction

Background

Supplementary cementitious materials (SCMs) are used in concrete to contribute to the cementitious system to help meet performance requirements. Adding SCMs also lowers the overall percentage of portland cement in the concrete mix. Fly ash, a by-product of the coal combustion process, is the preferred SCM for a majority of concretes used globally. In the United States, more than 60 percent of ready-mix concrete producers use fly ash as an SCM. Research shows that fly ash improves the workability, mechanical properties, durability, and sustainability of concretes. Fly ash also provides beneficial modifications to the concrete microstructure, such as improved pozzolanic activity, packing efficiency, macro pore reduction, and interface modification along the aggregate surfaces.

In recent years, many state departments of transportation (DOTs) have encountered tighter than anticipated supplies of concrete-quality fly ash that meet American Society for Testing and Materials (ASTM) or American Association of State Highway and Transportation Officials (AASHTO) specifications (satisfying, at a minimum, ASTM C 618 or AASHTO M 295 specifications). This supply issue is the result of a decline in coal-based power as energy generation has shifted toward natural gas and other sources.

In Arizona, the Salt River Project closed the Navajo Generating Station in 2019. Arizona Public Service is closing its Cholla Generating Station in 2025 and the Four Corners Generating Station by 2031. These closures will essentially eliminate most of the current sources of newly generated fly ash for concrete in the state. The Arizona Department of Transportation (ADOT) has a long history of using fly ash as a partial replacement for portland cement in highway concrete construction. Limited supplies of fly ash would require ADOT to use alternative materials in concrete mixture designs.

Project Objectives

To address the challenges with the market availability of fly ash for concrete mixes and reduce the agency's dependency on this material, ADOT initiated a research project to explore alternative materials that could serve as viable replacements to fly ash while improving the workability, mechanical properties, durability, and overall sustainability of concrete mixes. The goals of this project were to:

- Identify fly ash alternatives that can be used for highway construction in Arizona by conducting a comprehensive literature review, surveying state DOTs for best practices and lessons learned using fly ash alternatives, and drawing on the experience of the authors.
- Compile information from these sources and map the availability of cost-effective, abundant, and easily accessible fly ash alternatives in Arizona and neighboring states.
- Classify the identified materials based on their capability to reduce the amount of cement in concrete without compromising performance.
- Compile the properties of the potential fly ash substitutes (e.g., project type, geographic location, concrete strength, and durability) and their documented performance to allow materials to be chosen as viable alternatives on a project-by-project basis.

Recommendations

Based on the information gathered for this effort, the authors present three overarching recommendations.

1. Develop a Roadmap for Performance Testing and Life Cycle Assessment of Fly Ash Alternatives for ADOT Concretes.

To optimize materials based on their availability and potential use, standard specifications and performance criteria must be aligned with current and future infrastructure needs. To this end, the authors recommend development of a roadmap for performance testing of fly ash alternatives.

In this study, candidate materials were evaluated using computational platforms for integrating material properties into life cycle assessments (LCAs). It is recommended to collect and organize these data to develop a tool as needed so that quantitative computation of LCA parameters can be accomplished.

2. Develop a Ranking Matrix of Locally Obtained Candidates for the Replacement of Fly Ash.

This study presents a concept for determining the comparative strengths and weaknesses of candidate SCMs. The authors propose using a qualitative matrix of and assigning evaluation metrics on a one-to-four-point scale in the areas of:

a) Local availability.

b) Test results availability.

c) Early state and long-term performance metrics.

d) Local industry familiarity and ease of specifications.

e) Cost and additional facilities.

Total scores for different alternatives can be used to help rank alternatives.

3. Develop an Implementation Plan for Fly Ash Alternatives.

The roadmap and the ranking matrix recommended above can further inform the creation of an implementation plan. When designing an implementation plan, ADOT should also consider these metrics:

- Market penetration (acceptance and information generation based on local materials):
    - Two to three months for easy-to-implement materials.
    - Three to nine months of research.
    - Nine to 18 months of research and development.

- Technical and financial barriers:
    - Research in line with other industries that required changes to concrete formulation.
    - New equipment and processing facilities needed.
    - Information needed to be generated based on the novelty of the ideas.

For implementation, it is important to develop partnerships with business leaders in the area, including the Arizona Rock Products Association (ARPA), cement suppliers, sand aggregate suppliers, ready-mix producers, architect groups, and engineering firms. It is also possible to develop and conduct presentations and webinars to ADOT and local transportation and engineering communities to address the supplementary cementitious products.

Findings

Materials Selection and Evaluation

Appendix 1 reviews literature on the cementitious materials addressed in this report, including portland cement, fly ash, and alternatives to fly ash.

The qualitative ranking matrix of the alternative SCMs described in Recommendations is developed in detail in Appendix 2. As noted, it includes the following metrics: local availability, testing results, early and long-term performance metrics, local industry familiarity and ease of specifications, cost, and additional facilities.

The current alternative SCMs that are available in Arizona and sources for these materials (given in parentheses below) include:

- Reclaimed fly ash Class F (Salt River Materials Group (SRMG)).
- Natural pozzolan and reclaimed fly ash blends (SRMG).
- Copper slag (Minerals Research, Inc., formerly Minerals Research and Recovery Inc.)
- Mine tailings (Resolution Copper Project, Freeport-McMoRan).
- Natural pozzolans (Kirkland Mining Company).

Details are provided for each of these alternatives as available: contact information of stakeholders, site location and additional background information, overview of available SCMs and their properties, prior studies, and research citations.

Materials and Concrete Testing Methods and Considerations

Appendix 3 presents possible test methods for fly ash alternatives, including 10 tables detailing physical and chemical properties studied in Arizona and elsewhere:

- A table comparing cement substitution products studies by Arizona State University (ASU) in the past 10 years.
- Two tables showing the results of SRMG's testing.
- Eight tables listing additional properties of different fly ashes, bottom ashes, slags, pozzolans, and minerals.

Appendix 4 presents testing considerations for alternative cementitious systems. In the absence of field experience and long-term performance data, concrete produced using nontraditional binder technologies will need to meet the following criteria:

- Exhibit predictable and reproducible fresh and hardened properties as required for the intended application.
- Demonstrate sufficient uniformity in workability, setting time, and strength development.

- Maintain durability performance adequately over the range of environmental conditions (temperature and humidity) encountered in practice.
- Have an established relationship between different strength and stiffness properties (compressive, tensile, shear, flexure, and elastic modulus).
- Exhibit short- and long-term volume stability (e.g., thermal expansion, drying shrinkage, creep).

Testing of both the alternative cement and concrete produced using the alternative binder is required to obtain the necessary information to specify these materials for construction applications. Material properties and test methods for both binder and concrete are also presented in Appendix 4.

State of the Practice Survey

A survey distributed to all state DOTs received 35 responses: complete responses from 34 agencies and a partial response from an additional agency. All of the respondents reported using SCMs. Below is a summary of survey responses further detailed in Appendix 5.

Current Practices

The most commonly used SCMs reported by survey respondents were silica fume (26 respondents, or 76 percent), Class F fly ash (26 respondents, or 76 percent), Class C fly ash (23 respondents, or 68 percent), and slag cement (22 respondents, or 65 percent). In addition, notable allowances were made for natural pozzolans (12 respondents, or 35 percent), ground limestone (nine respondents, or 26 percent), and reclaimed fly ash (six respondents, or 18 percent). Two SCMs were less commonly used: bottom ash (two respondents, or 6 percent) and calcined clay (four respondents, or 12 percent).

Survey respondents use additional SCMs, including metakaolin; experimental admixtures (e.g., E5 Liquid Fly Ash); cements meeting ASTM C595 requirements; ground glass pozzolans meeting ASTM C1866; ground granulated blast furnace slag; and ultra fine fly ash.

Most participating agencies (28 respondents, or 85 percent) have used these products for decades. The longest duration of use was among agencies that used SCMs for 21 to 40 years (21 respondents, or 64 percent). Seven agencies (21 percent) have used SCMs for 11 to 20 years. The remaining three agencies (9 percent) have used SCMs for five to 10 years.

Agencies participating in the survey typically use SCMs on both highly traveled roads and in minor applications such as rest areas (26 respondents, or 76 percent). But some agencies limit SCM use to high-traffic roads only (five respondents, or 15 percent) or to minor roads only (three respondents, or 9 percent).

Supplementary Cementitious Material Availability and Selection

When assessing the supply of SCMs in their states—evaluating if these materials were consistently and reliably available throughout the state—survey participants were evenly divided in their responses. Eleven respondents (34 percent) reported that supplies are consistent, reliable, and available throughout the state. Ten respondents (31 percent) reported SCMs are not consistently available. The remaining 11 respondents (34 percent) noted occasional shortages or challenges with the SCM supply, particularly fly ash and slag cement.

Factors affecting SCM availability include product quality, power plant operations, and transportation costs. Respondents noted that the "SCM supply landscape is constantly evolving," with new sources, alternative materials, and innovative transportation solutions "emerging to address these challenges and ensure a more sustainable and reliable supply of SCMs in the future."

Selecting an SCM for a project is generally influenced by several factors:

- **Performance**. Meeting compressive strength and air content requirements is key to 23 respondents (68 percent) as are alkali-silica reaction (ASR) mitigation, permeability, and shrinkage.
- **Availability** (17 respondents, or 50 percent).
- **Mix design compatibility** (11 respondents, or 32 percent). Ideal features contribute to improving hardened concrete quality by mitigating ASR, reducing permeability, and enhancing long-term strength.
- **Testing qualifications**, including chemical and strength testing (10 respondents, or 29 percent).
- **Transportation cost** (eight respondents, or 24 percent).
- **Set time** (four respondents, or 12 percent).

Factors Influencing Implementation

Successful performance tests are critical to SCM selection to ensure the materials meet specified requirements beyond ASTM or AASHTO standards. Fresh concrete properties (12 respondents, or 35 percent); strength characteristics (14 respondents, or 41 percent); and durability (eight respondents, or 24 percent) are among those performance tests.

ASTM C618 and AASHTO M 295 are frequently considered foundational standards for SCM selection. But several survey respondents indicated that their states apply additional requirements and priorities in the selection process to meet other concerns such as environmental and infrastructure issues. For example, the California Department of Transportation uses AASHTO M 295, which establishes requirements for slag cement used in concrete, as a basic framework and supplements it with tests and acceptance criteria from state-specific Section 90.1-1.02 B (3).

Other respondents noted that their agencies may collaborate with contractors or material producers in SCM selection or may consider ASR mitigation requirements and other concerns.

The impact on construction activities or sequences when introducing new SCMs varied among survey respondents, with adjustments often made to ensure compliance with specifications and to achieve desired concrete properties and performance. Some respondents noted no modifications while others indicated potential changes in curing time and requirements, finishing techniques, mix properties and proportions, mixing sequence, workability and temperature sensitivity, and contractor decisions.

However, most respondents (21, or 66 percent) indicated that no special considerations impacted SCM implementation. Eleven respondents (34 percent) consider aggressive environments, restrictions on use, and processing and calcination before implementation.

Future Plans

In the next 10 years, survey respondents are most likely to use fly ash Class F (18 respondents, or 53 percent); slag cement (16 respondents, or 47 percent); fly ash Class C (15 respondents, or 44 percent); and microsilica (13 respondents, or 38 percent). Survey respondents' projected replacement levels in the next 10 years for pavement and bridge concretes varied significantly by SCM type, with most respondents anticipating replacement levels of specific SCMs in the 10 percent to 20 percent range or in the 20 percent to 30 percent range, depending on the different SCMs being used.

Methods

Comparison of Fly Ash Alternatives; Test Methods for Fly Ash Alternatives and Alternative Cementitious Systems

Appendix 1 is a review of literature on the materials and methods addressed in this report. Appendices 2, 3, and 4 of this report present and synthesize existing scholarship on this topic, drawing from the authors' extensive research and experience in this area of study:

- Appendix 2. Review and Comparison of Fly Ash Alternatives for Arizona.
- Appendix 3. Existing and Potential Methods for Testing Fly Ash Alternatives.
- Appendix 4. Testing Considerations for Alternative Cementitious Systems.

State of the Practice Survey

Researchers distributed a survey to all state DOTs to better understand current practices in selecting alternative materials to fly ash for highway construction. The survey collected detailed information about the materials that these agencies were considering, factors influencing their product decision-making processes, and strategies adopted to mitigate the impacts of fly ash shortages.

Respondents from 34 transportation agencies completed the survey; one additional agency representative provided a partial response. Results from the survey are summarized in the Findings section of this report. Detailed responses to individual survey questions are provided in Appendix 5 of the report.

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Note: For clarity, in-text references to testing standards throughout this report and its appendices are formatted as follows: *governing body* then *publication number* then *year*. For example: (ASTM A994 2016).

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Appendix 1

Literature Review

Portland Cement

The primary binding agent in concrete is the portland cement that sets and hardens by chemical reactions of its constituents with water; therefore, it is categorized as a hydraulic cement (American Concrete Institute 2018). Portland cement clinker, an intermediary material in the production of portland cement, is made by sintering a precise mixture of raw materials containing oxides of calcium, silicon, aluminum, and iron elements, and expressed in terms of the oxides (CaO, SiO_2, Al_2O_3, and Fe_2O_3, respectively) and partial amounts of impurities. These oxides are intermixed and go through the process of calcination in a kiln to produce the portland cement clinker. At this stage, the clinker is a hydraulic material that consists of two primary components of tri-calcium and di-calcium silicates ($3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$), the remainder consisting of aluminum- and iron-containing phases and other compounds (Jackson 2003).

Portland cement is produced by pulverizing clinker and mixing it with gypsum (calcium sulfate, or $CaSO_4$) to control setting. Types of cement are classified in different ways around the world.

United States

In the United States, most portland cements for commercial construction meet the requirements of ASTM C150 (ASTM C150 2018). ASTM C150 is a prescriptive specification with limits on both chemical and physical characteristics. Types of cement conforming to ASTM C150 are labeled as Type I through Type V, with some meeting multiple categories such as Type I/II, and some that include a secondary component as blended, such as an air-entraining component labeled with an “A” (for example: “Type IIA”). Interground and blended cements such as those with pozzolans (“P”) or slag (“S”) are also available and referred to similarly with such suffixes as Type IIP and Type IIS, respectively.

Canada

In Canada, portland cement is specified in A3001 (Canadian Standards Association 2018), a performance specification. Types of cement conforming to CSA A3001 are labeled as Type GU, Type MS, Type MH, Type HE, Type LH, or Type HS. An L is added after the two-letter code, as in GUL, to designate that a higher amount of limestone has been added into the cement.

Europe

In Europe, cement types are classified in EN 197 (European Committee for Standardization 2011) by composition for a total of 27 distinct common cements, seven sulfate-resisting cements, and three distinct low early strength blast-furnace cements, two sulfate resisting low early strength blast-furnace cements, and their constituents. Portland cements are labeled CEM I and blended cements are labeled CEM II, CEM III, CEM IV, or CEM V. Sulfate-resisting portland cements are labeled with an SR designation. In addition, cement is labeled with a strength class of 32.5, 42.5, or 52.5, which is the minimum 28-day strength of mortar, in MegaPascal (MPa), from standard testing. An example of a blended sulfate-resisting cement from EN 197 is CEM III/B-SR 32.5. The desired concrete performance and local availability of specific materials will guide the selection of the portland cement for a project. New cements such as Belite cements are also gaining popularity (Chatterjee 1996; Scrivener et al. 2018).

Supplementary Cementitious Materials

Use of supplementary cementitious materials (SCMs) is recognized as one of the most important sustainability aspects of the concrete industry's effort to address its carbon footprint (Damtoft et al. 2008a). SCMs are a category of inorganic powders with similar and compatible chemical and mineral characteristics to conventional portland cement and are referred to as mineral admixtures. They are added to the portland cement in a concrete mix or as a blended component, lowering the overall percentage of portland cement in the mix. SCMs are normally added to concrete on a weight basis and contribute to a percentage of the total cementitious system based on the overall performance requirements.

Although SCMs vary in their origin, physical properties, and chemistry, they all exhibit pozzolanic or cementitious properties. Figure 1 illustrates the relative positions of portland cement, fly ash, slag cement, silica fume, and metakaolin on a ternary diagram (CaO_2–SiO_2–Al_2O_3) (Panesar 2019).

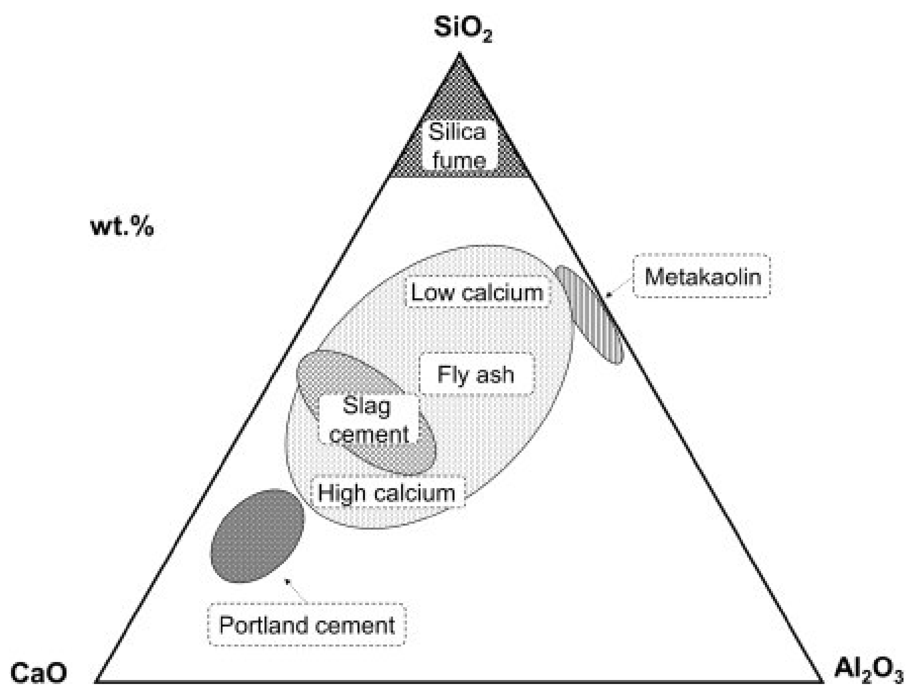

Figure 1. Ternary diagram of portland cement and supplementary cementing materials. (Source: Panesar 2019)

An SCM may serve several functions in the hydration process, such as reacting with the products of portland cement hydration via the pozzolanic reaction, providing a dense packing of the particles from a physical aspect, or providing hydration nucleation sites for chemical reactions that take place. Such improvements in the microstructure are due to the particle size and may alter chemical compositions and hydration reactions. Certain SCMs may also be partially cementitious, reacting directly with water. This partial replacement of portland cement with pozzolanic materials results in improved mechanical and durability properties compared with ordinary concrete formulations (American Coal Ash Association 2003; Mehta 2004; Malhotra et al. 2018).

A large array of SCMs with different chemical compositions is categorized based on their origin and include Classes F and C fly ash, silica fume, slag cement, metakaolin, calcined clay or shale, and natural pozzolans. Depending on the type and amount, SCMs serve several functions by improving the fresh and hardened concrete in terms of:

1. Rheology and workability by reducing the bleeding and segregation tendency.
2. Durability enhancements due to the reduction of permeability, pore size, additional hydration, matrix, and the interfacial transition zone packing.
3. Resistance to chemical attack such as sulfate attack and alkali-aggregate expansion. Reduction of heat generation, shrinkage potential and plastic shrinkage cracking, and resistance to thermal cracking.
4. Increase in early age and ultimate strength (Mobasher et al. 2024).

Blended cements have been used for decades to improve the mechanical properties and durability characteristics of concrete. The primary feature is the pozzolanic reactivity, which controls how much portlandite is consumed and converted to calcium silicate hydrate (CSH) (Bentz and Garboczi 1991). Over the past several decades, researchers have studied the effectiveness of blended cement materials in reducing the level of damage from sulfate attack (Tuthill 1936; Kalousek et al. 1972; Monteiro and Kurtis 2003a). Despite the wealth of studies conducted, the specific role of chemical composition of pozzolanic materials must be validated depending on the source, since there is a large variation in the origin and manufacturing process of pozzolans. Recent developments in the use of blended cements and procedures to use pozzolanic materials for alkali-silica reaction (ASR) and sulfate attack mitigation have accelerated the development of characterization tests. While the supplies are already running low, and expected to further reduce, new sources of SCMs will need to be optimized for use in concrete construction (Snellings and Scrivener 2016; Juenger et al. 2019).

SCM materials used are typically specified in terms of their specific ASTM designations that include Type I/II ordinary portland cement (OPC) conforming to ASTM C 150, fly ashes (Class F, and Class C), metakaolin, and natural pozzolans, all conforming to ASTM C618, slag conforming to ASTM C 989, limestone powder conforming to ASTM C 568, and microsilica (silica fume) conforming to ASTM C 1240. While these materials are significantly different in terms of their chemical and physical properties, their particle size can be used as a basis for comparison. The particle size distribution (PSD) curves of some of these materials are shown in Figure 2 (Arora et al. 2018). The median size in microns is shown in parentheses in this figure. The chemical compositions and physical characteristics of these materials are available in Mobasher et al. 2019.

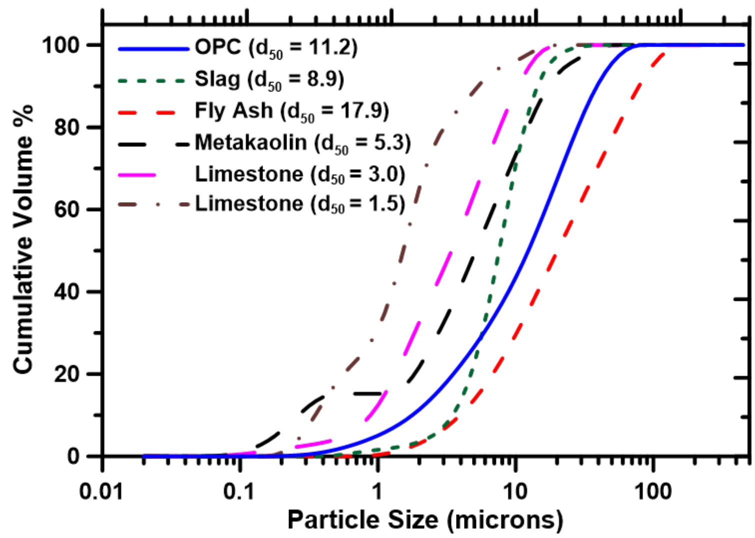

Figure 2. Particle size distribution curves for cement, fly ash, slag, metakaolin and limestone powders. (Source: Arora et al. 2018)

Some of the more common SCMs include fly ash, silica fume, slag, and metakaolin, which provide significant economic and environmental benefits (Damtoft et al. 2008b), as further described in this literature review.

Silica Fume (Microsilica)

Silica fume is a very fine amorphous silica that is produced in an electric arc furnace as a by-product of the elemental silicon or silicon alloy manufacturing (Malhotra et al. 1987). Due to the nature of processing of silica, the particulate size of silica fume is an order of magnitude smaller than that of OPC, which helps with the densification of the cement paste matrix. The extremely high surface area serves to provide an abundant number of nucleation sites for cement hydration, thereby enhancing the rates of reaction during the early stages of hydration (Cheng-yi and Feldman 1985). Silica fume is usually added in a concrete mix at an addition rate of 5 percent to 15 percent by mass of cement (Silica Fume Association 2005) and requires the use of a high-range water-reducing admixture to improve its workability and ensure dispersion.

Due to its fine particle size and challenges in handling and mixing, it is used in different forms of microsilica powder, condensed silica fume, or slurry form. Dry densified is the one more commonly used forms due to its condensed nature, safety aspects, and ease of handling. Research has shown that silica fume particles tend to agglomerate, resulting in extremely low workability (Boddy et al. 2000; Mitchell et al. 1998; Bonen and Diamond 1992), and therefore it is important to develop mixing methods to reduce the agglomerations for a workable concrete mixture. Silica fume is pozzolanic and enhances the mechanical properties of the matrix due to pore size and interface transition zone refinement as a result of formation of secondary hydration products (Yajun and Cahyadi 2003; Mazloom et al. 2004; Poon et al. 2006; Rao 2003; Igarashi et al. 2005)

The high reactivity of silica fume is due to its small particle size and large amounts of reactive silica, which results in faster property development than other SCMs. This is apparent from the strength activity indices of cementitious systems containing silica fume or fly ash (Neithalath et al. 2009). While the very small particle sizes increase the reactivity in the system, the uniform dispersion of mixtures containing such fine particles is challenging. Therefore, a high dosage of superplasticizer is needed with high silica fume applications. The agglomeration of these particles sometimes causes a reduction in mechanical properties or durability due to ASR reactions caused by the agglomeration of condensed silica grains.

Fly Ash

Description and Production

Fly ash is the finely divided residue that is collected as a by-product of the burning of coal at a steam-generating power plant. Pulverized fuel ash is a less common term for fly ash. The chemical nature of fly ash comes from the properties of the coal that is burned at the power plant. Due to their spherical shape, fly ash particles are known to improve the workability of concrete and packing density of the mixture, thus improving the permeability. Fly ash is primarily glassy (amorphous) spherical particles that react via the pozzolanic reaction only, or have both pozzolanic and cementitious properties.

Pulverized coal ignites as it is blown into the combustion chamber, generating heat and a molten mineral residue. Cooling of the flue gas causes the molten inorganic mineral residues to harden and form bottom ash and the airborne particles suspended in the flue gas are captured using electrostatic separators and collected in the bag house as fly ash. Particulate emission control devices, such as electrostatic precipitators or filter fabric bag-houses, remove the fly ash (American Coal Ash Association 2003; Malhotra and Mehta 2005). In addition to the economic and environmental benefits of using fly ash in concrete, there is a technical advantage in increasing strength and improving mechanical properties. Using fly ash reduces greenhouse gases, decreases life cycle costs, and increases concrete's durability. During the 1990s, about 100 million tons of fly ash were produced each year, of which only 20 percent was used in engineering applications such as blended cements, road-base stabilization, and the rest was landfilled. The availability is reduced today due to many power plants switching from coal to natural gas.

Classification

Fly ash may be siliceous or calcareous in nature. While both have pozzolanic properties, higher calcium levels indicate potentials for hydraulic properties. Siliceous fly ash is a fine powder of mostly spherical particles that consist of reactive silicon dioxide (SiO_2) and aluminum oxide (Al_2O_3). The remainder contains iron oxide (Fe_2O_3) and other compounds. The proportion of reactive calcium oxide (CaO) is normally less than 10 percent by mass. In the United States, fly ash is classified depending on the amount of calcium it contains as high-calcium (Class C) or low-calcium (Class F) and its chemical composition in accordance with ASTM C618. The Class C fly ashes typically have some cementitious nature, owing to the presence of high levels of calcium in the glass. In Canada, Class C fly ashes are further divided into Class CI, for intermediate calcium content, and Class CH, for high calcium content (Kosmatka 2016). Fly ash is often used at a level of 15 percent to 30 percent of the total cementitious content of a concrete mix. Class C ash is referred to as high-calcium because it contains as much as

20 percent CaO, a key factor in mitigating sulfate attack and ASR. Class C ashes from sub-bituminous coals consist of calcium alumino-sulfate glass, such as quartz (SiO_2) and free lime (CaO). Changes in the sources of coal used in power generation affect the quality of fly ash by-products (Monteiro and Kurtis 2003b).

Use with Portland Cement

The reaction of calcium silicate phases (C_3S and C_2S) in the portland cement generates calcium silicate hydrate (CSH) gel and the extra calcium is released in the form of the calcium hydroxide. As a pozzolanic material, fly ash reacts with the released calcium hydroxide to form its CSH hydration product. This reaction takes longer to accomplish than the hydration of portland cement because of the need for calcium hydroxide, the production of which is dependent on cement hydration. The additional CSH production ultimately improves concrete properties due to the enhanced pore refinement (Richardson 1999). It is also well-documented that fly ash lowers the heat of hydration, enhances the amount of hydration products (CSH gel), and thus improves the mechanical properties and durability of concrete (Nochaiya et al. 2010). The combination of fly ash with certain cement replacement materials, such as silica fume and metakaolin, has been shown to accelerate property development at early ages (Vance et al. 2013). One of the disadvantages is the reaction of fly ash (in general Class F) in cement-based systems being a slow process, thus affecting the setting times, slowing early age reaction kinetics, and reducing early age strengths. Also, the variability of fly ash sources introduces uncertainty in the setting time, which affects the operation schedule.

In general, the replacement levels of cement by Class F fly ash in concrete range from 10 percent to 30 percent by mass, while Class C fly ash can be used in higher proportions. The use of high volumes of fly ash in cementitious systems and the use of geo-polymeric systems (where OPC is not used at all and fly ash is the sole cementing medium, aided by high concentration of alkali hydroxides and silicates) are also becoming common (Garcia-Lodeiro et al. 2011).

Benefits and Advantages

Early promotion of the use of fly ash can be attributed to the significant amount of research conducted in the 1980s and 1990s. Planet ecology, concrete durability, and various obstacles to the use of such by-products were discussed (Aïtcin 1998). Many studies have addressed the effects of curing on compressive strength, porosity, and permeability of plain and fly ash/cement concrete, and have shown that fly ash concrete displayed strength comparable to plain cement concrete. High temperature curing decreased the porosity of fly ash concrete as compared with low and standard temperature curing.

Mehta related the advantages of using mineral by-products to the future development of infrastructure and construction in the world (Malhotra and Mehta 2005; Mehta 1998; Mehta 2004). Neville and Aïtcin (1998) reported on high performance concrete containing fly ash, ground granulated blast furnace slag, and silica fume. The dosage of fly ash in high volume of fly ash, or HVFA, concrete can exceed 50 percent (Malhotra and Mehta 2005) and may change the chemistry and reactivity of the cementitious phase in concrete. Larger amounts of fly ash—of the order of 25 percent to 35 percent—could be used depending on the application as well as its proportioning. Other studies and reviews have been conducted to address the chemical (including trace elements), mineralogical, loss on ignition (LOI) test and physical properties of low and high calcium fly ashes as well as the properties of fresh and hardened concrete containing fly ash, with special emphasis on the reaction rates in either hot or cold weather conditions (Ravina 1998). The LOI tests determine the unburnt carbon content of fly ash as it affects the influence of carbon content on air-entraining admixture demand.

Class C ashes are much more variable in chemistry and less efficient at mitigating ASR than Class F ashes, and performing ASTM C1567 testing is required for switching the source from a Class F to a Class C ash—or switching to a different Class C ash—to determine the minimum dosage needed. In designing for ASR resistance, decreasing the portland cement content reduces the potential for ASR to limit the alkali loading to ≤ 3.5 lb/cubic-yard. ASTM C1567 testing is recommended to determine if reduced dosages are acceptable or if other local Class C ashes or tertiary blends can be used.

Figure 3 shows a micrograph from a scanning electron microscope detailing the small and characteristically round fly ash particles (Arora et al. 2019).

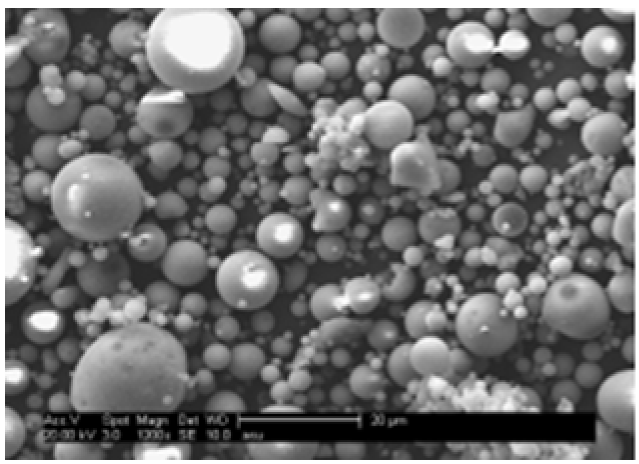

Figure 3. Scanning electron microscope image for typical class F fly ash. (Source: Arora et al. 2019)

Figure 4 shows the X-ray diffraction pattern of Class F fly ash, which illustrates the generally amorphous nature of fly ash containing quartz and mullite as the few crystalline phases present (Arora et al. 2019).

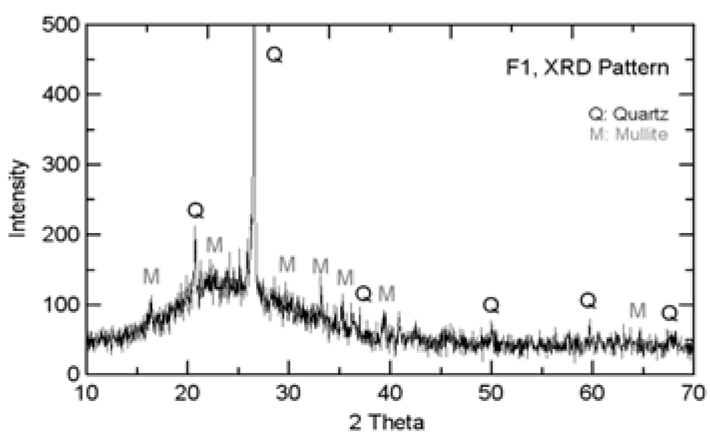

Figure 4. X-ray diffraction pattern for typical class F fly ash. (Source: Arora et al. 2019)

Availability

To address the risks from improper disposal and discharge of coal ash, new environmental guidelines for coal ash disposal were put in place. However, the reduction in the use of coal in the energy sector has resulted in the highest rate of decline in the generation of coal combustion products such that availability of new fly ash sources have become limited. With the conversion of power generation plants to natural gas in recent years, the supplies of conventional SCMs—such as freshly produced coal combustion fly ash or blast furnace slags—are diminishing (Scrivener et al. 2016). Another option in beneficiation of reclaimed and low-quality fly ashes may provide large volumes of SCMs (McCarthy et al. 2017).

Slag Cement

Slag cement, also called ground granulated blast furnace slag (GGBFS), is a hydraulic and pozzolanic material that is produced by rapid quenching, granulating, and grinding of the molten slag that is a by-product of steel production in a blast furnace. Although some use the terms slag and slag cement interchangeably, it should be noted that slag is the material that is the by-product of steel production, and it is only by rapid quenching that it becomes reactive in cementitious systems.

Air-cooled slag is nonreactive and may be used as aggregate. Slag cement fume is usually added in a concrete mix at a level of 30 percent to 50 percent of the total cementitious content of a concrete mix, but higher levels can be used. Slag cement may be used in concrete to improve compressive strength, reduce permeability, improve sulfate resistance, improve resistance to ASR, and reduce thermal stress in mass concrete (American Concrete Institute 2017; Slag Cement Association, n.d.).

ASTM C989 covers different grades of finely ground granulated blast-furnace slag for use as a cementitious material. The slag is used both for blending with portland cement to meet ASTM C595 and as a separate ingredient in concrete and mortar mixtures. The material may also be useful in a variety of grouts and mortars.

Metakaolin

Metakaolin is a calcined clay that is produced by low-temperature calcination of high purity kaolin clay. It is a white powder that is often used as a substitute for silica fume when light-colored concrete is required. It is added in a concrete mix at a rate of 5 percent to 20 percent by mass of cement to improve the durability of the concrete through reducing permeability and increasing compressive strength. Concrete with metakaolin will almost always require the use of a high-range water-reducing admixture to improve its workability and ensure the dispersion of the powder.

Commercially available since the mid-1990s, metakaolin ($Al_2Si_2O_7$) has been used as a high-reactivity pozzolan for high performance concrete applications. Metakaolin is a thermally activated alumino-silicate material that is manufactured primarily by calcination of kaolin clay in a temperature range of 1300 to 1560 °F (700 to 850 °C) (Sabir et al. 1996). It typically contains 50 percent to 55 percent SiO_2 and 40 percent to 45 percent Al_2O_3 and is considered as a high reactivity natural pozzolan (Poon et al. 2001).

Metakaolin improves the workability and constructability and positively affects the time and energy in finishing and pumping of concrete, provided that proper superplasticizers are used. Brooks et al. (2000) reported a 30 percent reduction of slump when using 15 percent metakaolin in concrete followed by a 20 percent reduction of setting times. The mechanical and durability properties of concrete with metakaolin have shown excellent properties for 15 percent replacement of the portland cement by metakaolin. Use of metakaolin significantly improved the durability performance and sulfate resistance of concrete (Al-Akhras 2006).

Metakaolin is superior to many other pozzolanic materials due to its high reactivity with calcium hydroxide, and thus a high rate of strength gain due to accelerated cement hydration (Sabir et al. 1996; Khatib and Wild 1996a). The presence of both silica and alumina in metakaolin decreases the calcium/silica (C/S) ratio of the produced CSH gel as compared to that produced from cement hydration (Zibara et al. 2008). The calcium hydroxide (CH) consumption in the mixture was dependent on the level of metakaolin replacement according to Khatib and Wild (1996b). After one year of curing, CH content was reported as much as 50 percent lower in paste with 15 percent metakaolin as compared to pasres with no cement replacement material present. Higher CH consumption is an indication of higher proportion of CSH gel in concrete, implying improved microstructure. It was also reported that the average pore diameter of paste (w/b=0.3) decreased by 66 percent (0.0122 micron) when 20 percent metakaolin was incorporated, as compared to those with no metakaolin, after 28 days of curing.

Limestone

The use of limestone as a partial cement replacement material has increased in recent years. Portland limestone cements are used in several countries, including the United States. ASTM C595 has defined a Type IL cement that can include up to 15 percent limestone powder as a partial cement replacement material (Tennis et al. 2011).

The use of limestone powder is becoming an attractive cement replacement material based on its ability to reduce the carbon footprint of the blended cement system through the bypassing of the flow of limestone through the kiln and either co-grinding it with the clinker or blending it with the portland cement after separate grinding. Once fine limestone particles are specified and used in the micron range, particle packing and enhancements in packing density are obtained. The small size of particles also contributes to a high number of nucleation sites for the initiation of hydration reactions in the presence of aluminate-rich materials. Limestone powder can chemically interact with the aluminate phases in cement to form a carboaluminate phase (Puerta-Falla et al. 2016; Arora et al. 2016a; Arora et al. 2016b; Das et al. 2015; Vance et al. 2013; Vance et al. 2015; Kumar et al. 2013). Studies have shown that fine limestone, in the presence of metakaolin or fly ash, enhances the amount of CSH gel formed as early as 28 days and has a beneficial impact in strength development (Vance et al. 2013). This provided the rationale for using fine limestone in ultra-high performance concrete mixtures in combination with other SCMs, which in turn improves the sustainability of concrete.

Natural Pozzolans

During the past several decades, the use of natural pozzolans and minerals in concrete has increased in popularity. In addition to economic considerations, this may be attributed to the current awareness of the environmental aspects of cement manufacture and fly ash disposal. Locally sourced natural pozzolans have also entered the market in Arizona and California.

Limestone Calcined Clay Cements

Limestone calcined clay cements (LC^3s) are promising new types of cements with lower CO_2 emissions and consisting of a ternary binder system made of portland cement clinker, limestone, and calcined clay. Many widely known and well-studied SCMs discussed in this literature review are not within the scope of large-scale cement manufacture. Since limestone and clays are the most abundant natural materials in the world, wider use of calcined clays can meet the growing demand for cement alternative materials. The production of calcined clays involves similar equipment to OPC and an approximately similar cost of investment. Lower energy is consumed in calcination at lower temperatures of clay (750 to 850°C) than that of clinker (1,450°C) (Scrivener et al. 2018). In addition, compared with OPC production in CO_2 emissions, the LC^3 usually emits around 30 percent less CO_2 (Scrivener et al. 2018).

Due to the limestone present, the reactive calcined clay generates an additional amount of AFm (alumina-ferric monosulfate) phases (i.e., monocarboaluminate and hemicarboaluminate), resulting in a complementary reaction between calcined clay and limestone. As a highly reactive pozzolan, calcined clay can improve its microstructure and pore structure at an early stage (Tironi et al. 2013).

Dhandapani et al. (2018) studied the mechanical strength and durability performance of concretes with LC^3. Results showed that when compared with OPC, LC^3 binder showed comparable mechanical strength development, better chloride resistance, lower gas permeability and capillary water absorption, and early enhancement of durability parameters. Although there are few applications and research about solidification/stabilization of contaminated soil by using the LC^3, LC^3 is likely to be a good binder to immobilize contaminants because its lower permeability would allow less leaching of contaminants.

Harvested Fly Ash

Many of the harvested ashes are recovered from landfills that were specially dedicated to their storage. The primary processing after removal of any cover layer is to dry the ash to meet the maximum 3.0 percent moisture limit as specified in ASTM C618. The next step is to process the ash to break up agglomerated particles and separate the +45 micrometer (+Number 325 mesh) residue. Microscopic examination of the ashes showed mostly spherical particles but with some agglomerated particles. (Hooton and Thomas 2021)

There are a range of challenges of harvested fly ashes, as studied from those processed from a plant in Pennsylvania (Hooton and Thomas 2021; Kaladharan et al. 2019). These include:

1. High moisture content.
2. High unburned carbon (LOI) content.

3. Presence of free lime (calcium oxide or calcium hydroxide).
4. Excess alkalis or sulfur (for Class C ashes).
5. Contaminants salts, soil, and organic materials.
6. Heterogeneity in fly ash properties within a landfill.
7. Reduction in fly ash reactivity due to agglomeration and partial reaction as a result of long-term exposure to moisture.

Beneficiation processes to address the efficiency of harvested fly ash are addressed in the Recommendations section of this report.

Appendix 2

Review and Comparison of Fly Ash Alternatives for Arizona

This section presents an evaluation and qualitative comparison matrix for fly ash alternative material selection based on availability and potential for utilization in Arizona.

Standard specifications and performance criteria must be aligned with current and future infrastructure needs. Candidate materials were evaluated using computational platforms for integrating material properties into life cycle assessments (LCAs). Collecting and organizing these data to develop a tool as needed would allow quantitative computation of LCA parameters.

Data were compiled from available reports and the project survey. Investigation of new supplementary cementitious materials (SCMs) has already been advanced by several states such as California and Minnesota. They explored alternative SCMs with potential environmental and performance benefits.

Fly Ash Alternatives Considered

The primary materials identified through the survey were Classes F and C fly ashes, silica fume, and slag as the major cement replacement materials, followed by natural pozzolans, ground limestone, reclaimed fly ash, calcined clay, and bottom ash. A limited number of survey respondents reported the use of ground glass and metakaolin used as SCMs. These materials are further described below:

- Ground granulated blast-furnace slag (GGBS): A by-product of the steel industry with similar properties to slag cement but potentially lower embodied carbon footprint.
- Calcined clays: Offering pozzolanic activity and potential for local sourcing, reducing transportation emissions.
- Limestone pozzolans: Utilizing waste limestone for sustainable SCM production. Limestone pozzolans offer a new opening in this arena.
- Industrial waste materials: Researching the feasibility of using industrial by-products like glass cullet or recycled concrete in concrete mixes.

The current alternative SCMs for fly ash available in Arizona include the following sources:

- Reclaimed fly ashes (Class F, from Salt River Materials Group (SRMG)).
- Blends of natural pozzolans and reclaimed fly ash (from SRMG).
- Copper slag (Minerals Research and Recovery Inc., www.umint.com/minerals-research-inc-mri).
- Mine tailings (Resolution copper mine and Freeport McMoran).
- Natural pozzolans (e.g., Kirkland mine pozzolan, kirklandmining.com/about-pozzolan.html)

While natural pozzolan, reclaimed fly ash, and fly ash-natural pozzolan blends satisfy relevant ASTM specifications, several other materials need further processing to satisfy the requirements. There are specific means of developing concrete mixture proportions for specific ADOT applications using these materials to ensure they meet the performance-related specifications of either ASTM C595 or ASTM C1157. Moving away from prescriptive to performance-based specifications would allow ADOT to design sustainable, low carbon concrete mixtures with many of the local/regional materials available in Arizona.

Evaluating Locally Obtained Replacement Candidates

Table 1 shows a qualitative matrix of strengths and weaknesses of the selected candidates and documents the available knowledge of design with cement byproduct systems in their utilization in the transportation industry. Evaluation metrics are defined in terms of cost, access, processing, transportation, existing infrastructure, local support in the concrete industry, cement and aggregate suppliers, local resources, and overall properties. The following metrics were chosen to address in the qualitative assessment process:

a) Local availability.

b) Test results availability.

c) Early state and long-term performance metrics.

d) Local industry familiarity and ease of specifications.

e) Cost and additional facilities.

Table 1. Comparison of candidate supplementary cementitious materials

SCM Type	(a) Local material distribution availability	(b) Test results availability	(c) Early state and long-term performance metrics	(d) Local industry familiarity, ease of specifications	(e) Cost/ additional handling facilities
Reclaimed fly ash	++++	+++	++	++++	++
Natural pozzolan and reclaimed fly ash blends	+++	+++	++	++++	++
Copper slag	++	+++	+++	++	+
Mine tailings	++	++	+	+	+
Natural pozzolans	+++	++	++	++	++

Additional dimensions may be considered in this evaluation matrix for the development of an implementation plan. These are presented here, each with a scale of 1 (easiest) to 3 (most difficult) for implementation:

A. Market penetration acceptance and information generation based on the local materials:
    1. Easy to implement (two to three months).
    2. Three to nine months of research.
    3. Nine to 18 months of research and development.
B. Technical and financial barriers to the implementation:
    1. Research in-line with other industries that required changes to concrete formulation.
    2. New equipment and processing facilities needed.
    3. Information needed to be generated based on the novelty of the ideas.

For implementation, it is important to develop partnerships with business leaders in the area, including Arizona Rock Products Association (ARPA), cement suppliers, sand aggregate suppliers, ready-mix producers, architect groups, and engineering firms. It is also possible to develop and conduct presentations and webinars to the Arizona Department of Transportation (ADOT) and the local transportation and engineering community to address the supplementary cementitious products.

Details of various aspects of the SCM materials shown in Table 1, as initiated and developed by the investigator team and others at Arizona State University (ASU), follow.

Reclaimed Fly Ash—Ongoing ASU Collaboration with SRMG

Contact: Salt River Materials Group, srmaterials.com

The Coronado landfill in St. Johns, Arizona, covers 210 acres and holds around 10 million metric tons of fly ash. Some treatment processes might be required before harvested fly ashes can be used as a concrete pozzolan that satisfies ASTM C618/AASHTO M295 specifications. These include:

1. Drying to reduce the moisture content.
2. Sieving to separate soil and large agglomerates.
3. Grinding to enhance the reactivity (especially when comingled with bottom ash).
4. Thermal processing to reduce the carbon content.

However, the difficult-to-address challenges in fly ash harvesting stem from the heterogeneity and variability in the material properties of landfilled fly ash due to:

1. Changes in operating conditions of the power plant over time (e.g., coal type, emission control, etc.).
2. Exposure conditions, such as rainfall that causes physical and chemical variability.

3. Presence of excess alkalis, sulfates, and chlorides in preferential locations, such as the top and bottom of the landfill.

Several fly ash suppliers, including SRMG, are well equipped to carry out such processing if needed to increase the potential supply of fly ash in ash-deficient regions. To this end, SRMG has started marketing harvested fly ash from the Coronado power plant. One type is harvested fly ash without additives, with chemical and physical characteristics of a batch as shown in Table 2. A second type, created when the sulfate content is high in the harvested fly ash as discussed above, involves blending with a high calcium (Class C) fly ash in predetermined amounts.

SRMG fly ash has been certified for use by ADOT in its products. SRMG sources confirm that this fly ash has been supplied to ADOT and is a reliable product with abundant supply for the foreseeable future.

Table 2. Physical and chemical analysis of SRMG fly ash harvested from the Coronado power plant

Analysis Type	Parameter	Value	Min/Max
Chemical Composition	SiO_2	59.11%	-
Chemical Composition	Al_2O_3	22.94%	-
Chemical Composition	Fe_2O_3	6.68%	-
Chemical Composition	$SiO_2 + Al_2O_3 + Fe_2O_3$	88.73%	50.00 min.
Chemical Composition	CaO	2.75%	18.00 max.
Chemical Composition	MgO	1.13%	-
Chemical Composition	SO_3	0.33%	5.00 max.
Chemical Composition	Moisture content	0.08%	3.00 max.
Chemical Composition	Loss on ignition	0.58%	6.00 max.
Chemical Composition	Na_2O	1.55%	-
Chemical Composition	K_2O	1.19%	-
Chemical Composition	Total alkalis	2.33%	-
Chemical Composition	Available alkalis	0.70%	-
Physical Analysis	Fineness, % retained on #325 sieve	23.00	34.00 max.
Physical Analysis	Fineness, variation, points from average	1.05	5.00 max.

Analysis Type	Parameter	Value	Min/Max
Physical Analysis	Density, g/cm3	2.12	-
Physical Analysis	Density, variation from average, %	0.07	5.00 max.
Physical Analysis	Strength activity index with portland cement at 7 days, % of cement control	79.24	-
Physical Analysis	Strength activity index with portland cement at 28 days, % of cement control	83.38	75.00 min.
Physical Analysis	Water requirement, % of cement control	97.52	105.00 max.
Physical Analysis	Soundness, autoclave expansion or contraction, %	- 0.03	0.80 max.

Natural Pozzolans

Contacts: Kirkland Mine Products, kirklandmining.com; Eco Material Technologies, ecomaterial.com

ASU Research and Initial Evaluation (2014-2015)

ASU researchers conducted a comprehensive analysis of the Kirkland Mine high-quality natural pozzolans as a partial cement replacement material in concretes for structural applications. Studies on hydration (isothermal calorimetry, thermal analysis), compressive strength, pore characteristics, and chosen durability characteristics were carried out for the aluminosilicate material from Kirkland Mine, along with Class F fly ash and metakaolin. The powder used in this study was ground by Hazen Research to obtain a median particle size of 60 µm for the coarse powder. It was further ground to a median particle size of 10 µm for the fine powder.

The study provided guidelines on the commercialization and applicability of this material as a high quality natural pozzolan for use as an alternative to commonly available Class F fly ash, metakaolin, and other SCM applications.

Additional research citations and details:

- Mobasher and Neithalath 2016.
- Mobasher et al. 2017.

Current Commercialization

The main components of Kirkland Mining Company deposits consist of 89.73 percent silica and alumina oxides. The natural material, when used in conjunction with portland cement, contributes to the properties of the hardened concrete through pozzolanic activity. The deposit is an outcropping, thermally formed from a volcanic ash, and consists of a lightweight, porous rock that is predominantly white in color and amorphous in nature.

There are several new products in the processing stage. Scaled trials are being conducted on a blended product: interground natural pozzolans combined with Class F bottom ash. The aim is to attain Class F properties while reducing the water demand. Eco Material is currently harvesting over 1 million tons of bottom ash per year and is developing methods to increase this capacity.

New lines of blended natural pozzolana are also being developed using large-scale tests of Pozzoslag products. Pozzoslag is a 50 percent replacement natural pozzolan that also uses perlite ore as beneficiating material (Eco Material Technologies 2022). This facility will be the first on-scale green cement facility in the United States, with 300,000 tons per year capacity.

Copper Slag—ASU Initial Research, 1993-1997

Contact: Minerals Research and Recovery, www.umint.com/minerals-research-inc-mri

This work represented ASU's initial evaluation of copper slag as a pozzolan in Arizona.

Additional research citations and details:

- Tixier et al. 1997.
- Ariño and Mobasher 1999.
- Mobasher and Devaguptapu 1993.
- Mobasher et al. 1996.
- Ariño et al. 1996.

Mine Tailings

Contacts: Freeport-McMoran, fcx.com/sustainability/tailings-americas; Rio Tinto Resolution www.riotinto.com/en/sustainability/environment/tailings

There are several copper and gold mines in Arizona, and the state has produced an estimated 17.5 billion tons of copper tailings since the late 19th century, with researchers estimating that the copper industry will add 200 million tons annually. This vast quantity can support the construction market in Arizona and beyond for decades to come.

It may be possible to use copper mine tailings as a partial substitute for cement in concrete construction, per Ghazi et al. 2022, as follows:

The particles range in sizes appropriate for immediate use for these applications to sizes usable with minimal grinding. Approximately 80 percent of copper mine tailings are composed of silicate, calcite, and clay; these compounds are also present in the structure of raw materials used to manufacture cement. Typical composition of a copper mine tailing is 24.6 percent SiO_2, 6.85 percent Al_2O_3, 42.65 percent Fe_2O_3, 17.2 percent CaO, 2.37 percent MgO, 0.64 percent K_2O, 0.61 percent Na_2O, 1.21 percent SO_3, 1.62 percent CuO, 0.39 percent BaO, 0.12 percent Cl, and 0.72 percent MnO.

In addition to the high concentration of Fe_2O_3, SiO_2, CaO, and Al_2O_3, heavy metals are also found in the copper mine tailings. Therefore, their leaching potential from concretes also needs investigation to ensure that any deleterious metals are safely encapsulated.

The high silicate content of the tailings can be beneficially utilized, along with external substitution of alumina or calcium source as needed to synthesize networked silicate structures with enhanced properties. Past studies on copper mine tailings as a replacement for cement in concrete have shown satisfactory mechanical and durability properties for concretes up to 30 MPa (4,500 psi) in strength.

Appendix 3

Existing and Potential Methods for Testing Fly Ash Alternatives

This appendix, which draws from Hooton and Thomas (2021), describes existing and potentially new test methods for evaluation of fly ash alternatives.

In addition to the recently developed test methods for fly ash characterization, the following research is an indication of the currently available test methods.

Pozzolanic Test Method

A rapid, relevant, and reliable (R^3) pozzolanic test method and modified R^3 are being used (Avet et al. 2016) and an ASTM standard is being developed. The R^3 test correlates pozzolanic activity with total heat released by the reaction of calcined waste clay, portlandite, and limestone pastes mixed with alkali-sulfates. Samples are hydrated for six days at 20°C. Further details of test results on pozzolanic metakaolin reactions appear in Weise et al. (2024).

Quantitative Characterization and Comparison with Fly Ash

Chemical and physical properties would be used to quantitatively characterize different materials. As materials such as reclaimed fly ashes and natural pozzolans are selected, this information can help in categorization, classification, and materials approval. Applications in need of additional testing include copper slag, ground glass, and calcined clays.

Additional background on the physical and chemical characteristics of utility solid wastes appears in Summers et al. (1983). Trace elements in coal are addressed in Valkovic (1985).

Individual compilation of various physicochemical properties of such materials listed can be compared with fly ash. A listing of such materials is shown in the following tables, which draw from X-ray analysis of oxide data and ASTM C618-type physical and chemical data.

- Table 3 compares cement substitution products studies by ASU in the past 10 years.
- Table 4 and Table 5 show the results of SRMG testing.
- Table 5 through Table 12 show additional properties of different fly ashes, bottom ashes, slags, pozzolans, and minerals.

Table 3. Comparison of various cement substitution products used by ASU in the past decade

Binder components	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	LOI	Specific surface area: Blaine (m^2/kg)*	Specific surface area: BET (m^2/kg)*
OPC (Type I/II as per ASTM C150)	19.60%	4.09%	3.39%	63.21%	3.37%	3.17%	2.54%	412	1,318
Slag (S)	39.41%	8.49%	0.37%	35.53%	12.05%	2.83%	1.31%	395	1,282
Fly ash (F)	58.40%	23.80%	4.19%	7.32%	1.11%	3.04%	2.13%	366	3,021
Metakaolin (K)	51.70%	43.20%	0.50%	-	-	-	0.16%	-	14,915
Micro silica (M)	> 90.0%	-	-	< 1.0%	-	-	-	-	18,253
Limestone (L), 1.5 µm, avg. particle size	1.5 µm	1.5 µm	1.5 µm	1.5 µm	1.5 µm	1.5 µm	1.5 µm	-	7,518
Limestone (L), 3 µm, avg. particle size	3.0 µm	3.0 µm	3.0 µm	3.0 µm	3.0 µm	3.0 µm	3.0 µm	925	1,860

**Note:* Specific surface areas determined through Blaine's fineness and the Brunauer-Emmett-Teller (BET) methods are different. BET is a direct and more appropriate method since it does not make any assumptions on particle shapes. The BET method measures a monolayer of N_2 molecules covering the surface area, while in Blaine's method, the flowing air might not "see" all parts of the surface being measured. However, the ease of use and economy of Blaine's apparatus makes it a preferred surface area measurement method for many cementitious materials. The difference between the surface areas measured by the two methods is more prominent for materials such as fly ash because BET is also able to interrogate the small pores in the particles. The BET-specific surface areas of the source materials reported here are in line with generally reported values for such materials.

Table 4. SRMG chemical analysis of Class F ash from Cholla Generating Station

SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	SiO_2+ Al_2O_3+ Fe_2O_3 (%)	CaO (%)	MgO (%)	SO_3 (%)	Moisture Content (%)	LOI (%)	Na_2O (%)	K_2O (%)	Total Alkalis (%)	Avail-able Alkalis
59.11	22.94	6.68	88.73	2.75	1.13	0.33	0.08	0.58	1.55	1.19	2.33	0.70

Referenced test specifications are ASTM C311, ASTM C114, AASHTO T105, and ASTM D4326.

Table 5. Eight SRMG tests of reclaimed fly ashes

Test No.	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	Total SAF (%)	CaO (%)	MgO (%)	SO_3 (%)	LOI (%)	Total Alkalis (%)
1	50.82	20.66	5.44	76.92	10.73	2.59	0.90	2.07	2.28
2	56.92	21.05	5.11	83.08	7.46	2.08	0.65	1.71	2.27
3	53.46	20.57	5.29	79.32	8.84	2.26	1.18	2.21	2.16
4	52.60	20.56	5.51	78.67	9.31	2.21	0.8	2.66	2.01
5	54.26	20.32	5.18	79.76	8.76	2.28	0.65	1.65	2.23
6	53.24	20.39	5.33	78.96	9.39	2.40	0.70	1.75	2.15
7	53.57	20.63	5.42	79.62	8.98	2.24	0.64	1.99	2.09
8	54.05	20.59	5.25	79.89	8.75	2.27	0.71	1.62	2.22

Table 6. Properties of raw harvest fly ashes (McCarthy et al. 2018)

Property	Portland Cement	Lagoon Fly Ash (LFA1)	Lagoon Fly Ash (LFA2)	Stockpile Fly Ash (SFA1)
Fineness 45 µm sieve retention (%)	364*	48.2	44.0	33.8
LOI (%)	1.40	6.40	10.3	15.1
Particle Density (kg/m^3)	3,140	2,120	1,970	1,980
Particle Size Distribution: d_{10} (µm)	-	6.20	4.60	2.60
Particle Size Distribution: D_{50} (µm)	-	46.1	40.6	21.9
Particle Size Distribution: d_{90} (µm)	-	133.6	139.0	95.7
Oxide: SiO_2 (%)	21.5	48.3	46.9	49.8
Oxide: Al_2O_3 (%)	5.40	27.2	28.7	23.9
Oxide: Fe_2O_3 (%)	2.60	6.20	5.10	5.70
Oxide: CaO (%)	64.2	2.90	1.80	2.40
Oxide: MgO (%)	2.6	1.6	1.7	1.2
Oxide: TiO_2 (%)	0.3	1.5	1.4	1.4
Oxide: K_2O (%)	0.7	1.2	1.5	2.1
Oxide: Na_2O (%)	0.3	1.4	0.8	0.5
Oxide: P_2O_5 (%)	0.1	0.6	0.4	0.8
Oxide: C1 (%)	0.0	2.1	1.0	0.0
Oxide: SO_3 (%)	2.8	0.5	0.5	0.6
Mineral: Quartz (%)	-	10.8	4.6	3.8
Mineral: Mullite (%)	-	16.6	18.0	8.0
Mineral: Noncrystalline** (%)	-	65.3	66.8	72.7

**Note: Specific surface area m^2/kg (Blaine Method).*

***Note: By difference.*

Table 7. Properties of processed ashes (McCarthy et al. 2018)

Sample	Fineness 45 um Sieve Retention (%)	LOI (%)	Particle Density (kg/m^3)
LFA1 Reference*	26.8	6.1	2,120
LFA1 63 µm sieved	12.0	3.2	2,210
LFA1 Air Classified	6.1	5.8	2,120
LFA1 Ground	8.1	5.3	2,310
LFA2 Reference	33.4	9.7	2,010
LFA2 63 µm sieved	8.7	5.1	2,130
LFA2 Air Classified	8.1	7.6	2,020
LFA2 Ground	6.3	10.8	2,170
SFA1 Reference	23.8	14.2	2,060
SFA1 63 µm sieved	10.2	10.7	2,160
SFA1 Air Classified	12.9	13.1	2,100
SFA1 Ground	0.6	14.1	2,230

**Note: Recovered material screened at 600 µm.*

Table 8. Physical characteristics of fly ash and bottom ash from coal combustion (Tishmack and Burns 2004)

Property	Fly Ash	Bottom Ash
Particle size range (mm)	10^{-4}–10^{-1}	10^{-1}–10^{1}
Mean particle diameter (µm)	20–80	500–700
Saturated hydraulic conductivity (cm/s)	10^{-6}–10^{-4}	10^{-3}–10^{-1}
Specific gravity	1.59–3.1	2.17–2.78
Dry bulk density	1.0–1.6	0.74–1.6

Table 9. ASU chemical and physical analysis of slag

SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	SO_3 (%)	Na_2O (%)	K_2O (%)	LOI (%)	Specific gravity	Specific surface area (m^2/kg)
36.0	10.5	0.67	39.8	7.93	2.10	0.27	0.80	3.01	2.90	487

Table 10. Composition of a typical natural pozzolan

SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	Na_2O (%)	SO_3 (%)	Moisture Content (%)	LOI (%)
41.9	18.84	10.54	1.25	0.06	.084	1.40

Table 11. ASU analysis of mine tailings: chemical and physical properties

SiO_2 (%)	Al_2O_3 (%)	SO_3 (%)	Fe_2O_3 (%)	Sn (%)	Mn (%)	Ti (%)	Sb (%)	P (%)	Specific gravity	Blaine's Fineness (cm^2/g)
64.2	19.95	1.94	8.26	1.35	0.81	0.48	2.49	0.15	2.76	898

Table 12. Composition and physical properties of minerals

Filler	Composition	Density (g cm^{-3})	Mohs hardness	Shape
Calcium carbonate	$CaCO_3$	2.7	3	sphere
Talc	$Mg_3(Si_4O_{10})(OH)_2$	2.8	1	plate
Kaolin	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$	2.6	2.5–3.0	plate
Wollastonite	$CaSiO_3$	2.9	4.5	needle
Mica	$KM(AlSi_3O_{10})(OH)_2$	2.8	2.0–2.5	plate
Barite	$BaSO_4$	4.5	3.5	plate

Appendix 4

Testing Considerations for Alternative Cementitious Systems

The standard specifications and research grade test methods provided in the References section of this report address empirical indirect methods as well as fundamental material properties to arrive at a combination of prescriptive and quasi-performance-based specifications.

Some of the alternative cementitious systems require specific handling and processing techniques to arrive at properties that are fundamentally different from conventional concrete mixtures, and care should be taken in the adoption of such systems. Several specifications may not be applicable for these new binder technologies (ACI ITG-10.1R-18).

Hooton (2015) documented the main properties that need to be demonstrated in the development of standards and specifications for concrete produced using nontraditional binder technologies in the absence of field experience and long-term performance data. These properties are summarized below:

- Exhibit predictable and reproducible fresh and hardened properties as required for the intended application.
- Demonstrate sufficient uniformity in workability, setting time, and strength development.
- Maintain durability performance adequately over the range of environmental conditions (temperature and humidity) encountered in practice.
- Have an established relationship between different strength and stiffness properties (compressive, tensile, shear, flexure, and elastic modulus).
- Exhibit short- and long-term volume stability (e.g., thermal expansion, drying shrinkage, creep).

Testing of both the alternative cement and concrete produced using the alternative binder is required to obtain the necessary information to specify these materials for construction applications. The following sections provide a summary of the material properties and test methods for both the binder and the concrete.

Testing Alternative Cements

Table 13 summarizes the material properties and test methods to understand the properties of alternative cements.

Table 13. Material properties and test methods for alternative cements (adapted from ACI ITG-10.1R-18)

Property	Description and Purpose of the Test	Test Methods, Standards, and Other Considerations
Chemical Composition	Used to identify desired and deleterious components	Loss on ignition. X-ray fluorescence (XRF) . X-ray diffraction. Thermogravimetric analysis/differential thermal analysis (TGA/DTA).
Porosity and surface area measurement	Identify the pore structure, permeability parameters, and measurement	Mercury Intrusion Porosimetry BET surface area measurement
Particle Size	Particle size impacts uniformity and performance; smaller particles react more quickly due to higher specific surface area.	Laser-based particle size analyzers, air permeability, and Blaine surface area based on ASTM C204.
Density	Density is an essential parameter for mix design.	ASTM C188: Standard test method for density of hydraulic cement. Pycnometry
Strength	Most commonly specified property	ASTM C109/109M: For many alternative cements, water-to-binder ratio correlation to the strength or flow measurements may not be applicable.

Property	Description and Purpose of the Test	Test Methods, Standards, and Other Considerations
Volume Stability	Volume stability addresses the volume or length change due to thermal and hygral effects, i.e., thermal expansion, creep, and shrinkage characteristics.	• ASTM C151/151M: autoclave expansion test; may not be suitable for geopolymers or alkali-activated materials. • ASTM C157/C157M and ASTM C596: drying shrinkage tests; issues related to the selection of appropriate duration and type of curing prior to initiating drying. Other aspects such as chemical shrinkage need to be considered. • ASTM C1038/C1038M: potentially suitable to evaluate volume stability of binders with high sulfate content; may need to extend test duration beyond 14 days. Sulfate penetration test may be done using analytical instruments and correlated with the aluminate or magnesium phases.
Setting Time and Rheology	Setting time depends on binder composition and mixture formulation; impacts a variety of constructability aspects such as workability and finishing.	ASTM C191: Vicat needle test; determining appropriate mixing cycle and consistency for sample may be an issue if mixture rheology is vastly different from portland cement-based mixtures. Standard rheology tests in terms of plastic viscosity and yield strength may be useful.
Heat of Hydration	Temperature development during the binder hardening process impacts the rate of strength development.	ASTM C1702 and C1897: Isothermal and adiabatic calorimetry heat of hydration test method is a more suitable test for alternative cements. Could be done in conjunction with DTA/TGA tests.

Property	Description and Purpose of the Test	Test Methods, Standards, and Other Considerations
Admixture Compatibility	Interaction between admixtures and the binder impacts a range of fresh and hardened concrete properties. It is important to understand the hydration kinetics of mixtures that incorporate one or more chemical admixtures.	ASTM C1679: Isothermal calorimetry test can be used to study the hydration kinetics of binders when combined with different admixtures.

Testing Alternative Cement Concrete

Table 14 summarizes the concrete characteristics and test methods to understand the properties of concrete produced using alternative cements. It should be noted that all the test methods discussed in

Table 14 were developed for use with conventional portland cement concrete mixtures. In many cases, specific mixing procedures are also specified in the standards, and these may not be applicable to all concretes featuring alternative cements. Curing regimens may also be vastly different, depending on the nature of the alternative cement being used. Specimen preparation procedures, curing practices, and other testing protocols specific to alternative cements need to be established through a collaborative effort between organizations developing the standards and the alternative cementitious materials (ACMs) industry. While most of the test methods identified in

Table 14 are expected to be generally applicable, targeted modifications will be required to the standards in the future to accommodate considerations for alternative cements.

Table 14. Material properties and test methods for alternative cement concrete (adapted from ACI ITG-10.1R-18)

Concrete Characteristics	Test Methods, Standards, and Other Considerations
Compressive Strength, Rate of Strength Development	ASTM C39/C39M: compressive strength of cylindrical concrete specimens; the standard refers to ASTM C31/31M and ASTM C192/192M for specimen preparation. These may not apply to concretes produced using alternative cements.
Stiffness (Elastic Modulus, Poisson's Ratio)	ASTM C469/C469M: Elastic modulus of concrete in compression; specimen preparation approach may not be applicable.
Ductility (Toughness)	ASTM C1550: Flexural toughness of fiber-reinforced concrete using centrally loaded round panel. Since this test method does not specify mixing or curing conditions, it is applicable for alternative cement concrete.
Tensile Strength	• ASTM C78/C78M: Flexural strength using simple beam with third point loading. • ASTM C293/C293M: Flexural strength using simple beam with center-point loading. • ASTM C496/C496M: Splitting tensile strength of cylindrical concrete specimens. • All test methods are restricted to moist-cured concrete; may not be directly applicable to all alternative cementitious systems.

Concrete Characteristics	Test Methods, Standards, and Other Considerations
Temperature Effects (Fire Resistance, Thermal Expansion)	• ASTM E119: Used to measure fire resistance of concrete. • AASHTO T336: Used to determine coefficient of thermal expansion.
Shrinkage and Creep	• ASTM C157: Free shrinkage test; test method allows for alternative mixing and curing regimes. • ASTM C1581/C1581M: Restrained shrinkage test; may not be directly applicable to alternative cement concrete. • ASTM C512: Creep of concrete under compression.
Bond	• Standard bond strength test methods for concrete do not exist. ACI408R documents considerations; however, test methods are not cited. • ASTM A944: Used to measure bond of reinforcing steel with concrete using beam end specimens. The test method may be applicable to alternative cement concrete; however, it is to be noted that this test procedure tests the reinforcing steel and not the concrete. • Other bond test methods such as the slant shear test method (ASTM C882) and the pull-off test (ASTM C1583) may be used to evaluate concrete bond strengths, but as with other tests, these were not developed for alternative cement concrete.
Resistance to Freeze-Thaw Cycling	• ASTM C666/C666M: Used to evaluate impact of freezing and thawing cycling on concrete by measuring the loss in relative dynamic elastic modulus. • ASTM C672/C672M: Can be used to assess the scaling potential of concrete when exposed to deicing salts. Since surface finishing can have a significant impact on scaling test results, this test procedure may require some modifications to be applicable to alternative cement concrete. • Both test methods discussed above are subject to sample preparation and curing limitations.

Concrete Characteristics	Test Methods, Standards, and Other Considerations
Resistance to Sulfate Attack	Predicting sulfate resistance based on chemical composition (per ASTM C150/C150M) or using immersion tests in sodium sulfate (ASTM C1012/C1012M) may not be applicable to alternative cementitious systems. Additional research is needed to understand behavior of different types of alternative cementitious systems in surface environments.
Resistance to Acids	Standard test methods are not available.
Resistance to Alkali-Aggregate Reaction (AAR)	• ASTM C1260: Mortar bar method, test method for alkali reactivity of aggregates. • ASTM C1293: Concrete prism test, length change concrete due to alkali silica reaction. • ASTM C1567: Modified version of ASTM C1260 to evaluate effect of fly ash on AAR. • All the test methods indicated above are empirical, and the results of the test may not have a direct correlation with AAR resistance. • ASTM C1293 could be a meaningful test for alternative cement concrete with the following exceptions: (a) Formulation may need to be adjusted to provide appropriate workability, and (b) additional sodium hydroxide may need to be added to increase alkali loading to promote activation of certain alternative cements rather than compensating for the alkali leaching over the duration of the test.
Permeability and Fluid Transport Properties	ASTM C1556: Bulk chloride diffusion test may be more appropriate for alternative cement concrete when compared to ASTM C1202, which provides an electrical indication of concrete's ability to resist chloride ion penetration. Interpretation of test data may be challenging due to the influence of pore solution chemistry.

Guidelines for Practical Concrete Mixture Design

According to ACI (ACI ITG-10R-18), to use concretes containing alternative cements safely and effectively, it is important to understand the key differences in their material properties and concrete behavior when exposed to different environmental conditions. This section provides some practical guidelines and considerations for using concretes prepared using alternative cements.

Table 15 summarizes the considerations related to concrete mixture design.

Table 15. Concrete mixture design considerations (adapted from ACI ITG-10R-18)

Item	Issues to Consider
Strength	• Factors influencing strength. For some alternative cements, strength may not be directly related to the water-to-binder ratio. It is important to understand the approaches used to control strength and achieve desired target strength, and the impact of water-to-binder ratio on strength development. • Impact of chemical admixtures on the rate of strength development.
Workability	• Impact of water-reducing admixtures on concrete workability. • Compatibility issues between chemical admixtures and alternative cements. • Impact of accelerators and retarders. • Need for high-range water reducers. • Approaches to extend duration of placement and finishing through the use of admixtures or other means without negatively impacting rate of strength gain and other key properties.
Aggregates	• Quality of cement paste and aggregate bond. • Impact of aggregate type on strength and permeability. • AAR susceptibility when used with alternative cements. • Impact of aggregate shape and gradation on workability.
Admixtures	• Applicability of admixtures for use with alternative cements. • Incompatibility issues related to admixture combinations.
Permeability	• Impact of water-to-binder ratio on permeability. • Factors that impact permeability of cement paste.
Freeze-Thaw Resistance	• Field testing to establish freeze-thaw resistance. • Need for air entrainment (depending on binder system utilized). • Air entraining admixtures that can and cannot be used in conjunction with the alternative cement being considered.
Material Availability	Need for specialized materials to produce concrete mix and local material availability.

Concrete Pavement Construction Considerations

Table 16 summarizes key considerations related to concrete pavement construction using ACMs.

Table 16. Concrete pavement construction considerations (adapted from ACI ITG-10.R-18)

Item	Issues to Consider
Safety	Need for safety equipment to protect workers from situations such as excess heat from materials during setting and highly reactive chemicals such as highly concentrated alkalis used in alkali-activated cements and geopolymers.
Material Handling, Mixing, and Transportation	• Need for specialized equipment and procedures to transport, store, and handle materials. • Need for specialized mixing equipment and/or mixing procedures. • Understanding of batch size restrictions per mix.
Workability, Placement, and Consolidation	• Suitability of mixture for slipform paving. • Mix segregation issues during placement and vibration. • Need for specialized admixtures to improve workability. • Ease of implementing adjustments in the field to address workability and consolidation issues. • Edge slump issues.
Finishing and Curing	• Length of finishing window. • Special considerations related to surface texture. • Type and duration of curing procedure.
Joint Sawing	• Joint sawing window after placement. • Special considerations for joint sawing.
Opening to Traffic	• Effect of ambient temperature and weather conditions on concrete strength development.

Concrete Pavement Design Considerations

Pavement design using concretes featuring alternative cementitious systems represents a significant challenge. Concrete pavement design procedures require several material properties (e.g., elastic modulus, modulus of rupture, Poisson's ratio) that serve as input parameters. There are no standardized test procedures available today that are focused on measuring these material properties for concrete made with alternative cementitious systems. Another challenge is the lack of long-term performance data for different types of materials.

With the limited data available, it is difficult to develop reliable performance prediction models that can be calibrated to different types of materials for use in conjunction with pavement design procedures. Due to the unknowns associated with performance, durability, and the general lack of experience in using these materials for pavement applications, concretes using ACMs may be more suitable for low-risk applications.

As the ACM industry matures, standards and specifications specific to these materials will emerge. With the availability of more field performance data, the use of concretes featuring nonportland cement-based systems is expected to increase in the future (ACI ITG-10R-18).

Appendix 5

Details of State of the Practice Survey

A survey of state departments of transportation (DOTs) gathered information about practices for selecting and implementing supplementary cementitious materials (SCMs). Respondents from 34 transportation agencies completed the survey; one additional agency representative provided a partial response. Survey participants' responses are summarized below for each survey question.

Summary of Survey Results

1. What SCMs does your state DOT currently allow? For those not in the list, please specify.

The most commonly allowed SCMs reported by survey respondents are silica fume, Class C and Class F fly ash, and slag cement. Natural pozzolans, ground limestone, and reclaimed fly ash are allowed to a lesser extent, and bottom ash and calcined clay are less commonly allowed. The reluctance to use bottom ash is likely due to its low reactivity; use of calcined clay is expected to increase in the future.

Other SCMs reportedly used by survey participants are:

- Metakaolin and cements meeting ASTM C595 requirements.
- Experimental admixtures under brand names such as E5-Liquid Fly Ash (from Specification Products in Noblesville, Indiana). These products may confuse specifiers since some admixtures may be colloidal silica based. Indiana DOT uses such a material as a pozzolan for mitigating damage from salt and calcium oxychloride formation, but not to mitigate alkali-silica reaction (ASR). Research into potential use for ASR mitigation is ongoing.
- Ground glass pozzolans meeting ASTM C1866 (at least four states).
- Class N natural pozzolans, ground granulated blast furnace slag, and ultra fine fly ash.

Table 17 summarizes survey responses.

Table 17. Use of SCMs

SCM	Responses	Percent (%)
Bottom ash	2	6
Calcined clay	4	12
Fly ash, Class C	23	68
Fly ash, Class F	26	76
Ground limestone	9	26
Natural pozzolans	12	35
Reclaimed fly ash	6	18
Silica fume	26	76

SCM	Responses	Percent (%)
Slag cement	22	65
Other	8	24

2. How long have SCMs been used by your state DOT?

All of the respondents reported using SCMs, and most participating agencies have used these products for decades. Most respondents (21, or 64 percent) indicated their agencies have used SCMs for the past 21 to 40 years. Additionally, seven agencies (21 percent) have used SCMs for the past 11 to 20 years, and three agencies (9 percent) have used SCMs for the past five to 10 years. Table 18 summarizes survey responses.

Table 18. Duration of SCM use

Number of Years	Responses	Percent (%)
5 to 10 years	3	9
11 to 20 years	7	21
21 to 40 years	21	64
Not using SCMs	0	0
Other	2	6

3. Is the supply of SCMs consistent, reliable, and available throughout the state?

Eleven respondents (approximately 34 percent) reported that SCMs are consistently, reliably, and readily available. Conversely, 10 respondents (31 percent) reported that SCMs are not consistently available. Another 11 respondents (34 percent) chose to comment on SCM supply and availability. Several of these respondents mentioned occasional shortages or challenges in the SCM supply, or potential concerns regarding the future supply, particularly for materials like fly ash and slag cement. Factors affecting SCM availability include variations in coal power generation, production issues, and transportation costs. One respondent mentioned plans for a supplier to close in the future, which may affect the SCM supply. Table 19 summarizes survey responses.

Table 19. Market availability of SCMs

SCM Supply	Responses	Percent (%)
Consistent, reliable, and available	11	34
Not consistent, reliable, and available	10	31
Other	11	34

Below are additional comments from survey participants, including factors that may affect supply such as product quality, power plant operations, and transportation costs:

- Fly ashes have fallen out of favor due to percent within limits specifications that impact payment if the air content is too variable. Slag cement generally has good availability despite occasional challenges. One agency has been approached by two companies about importing foreign slag cement.

- Slag cement, silica fume, and fly ash are currently available, but fly ash supply is declining. For instance, Heidelberg added grinding capacity for slag cement in a new facility that completed construction in June 2024. The consistency, reliability, and availability of specific categories include:

Class F Fly Ash

- Fly ash quality may vary depending on the coal source and power plant operations. Some states, such as California, have strict specifications for fly ash used in their concrete, ensuring consistent performance. A relatively stable supply due to the availability of nearby power plants and imports from surrounding states helps the consistency.
- Supply can be impacted by fluctuations in coal power generation and competition from other industries like concrete block production.
- While fly ash is generally available, transportation costs can increase for remote areas.

Natural Pozzolans

- The supply of natural pozzolans is consistent. Several are currently available to the California Department of Transportation (Caltrans) within the state and from Nevada.
- Natural pozzolans are generally available throughout the state, but transportation costs can increase for remote areas.

Slag Cement

Slag cement is a manufactured product with consistent quality controlled by the producer. The supply is generally reliable and available in major urban centers, but disruptions can occur due to production or infrastructure issues. Transportation costs may be higher in rural areas.

Silica Fume

The highly consistent quality of silica fume is attributed to its controlled manufacturing process. The supply is reliable, but demand can sometimes outpace production, leading to temporary shortages. Silica fume is primarily available from a limited number of producers, potentially increasing transportation costs for distant locations.

Overall

- California has a moderate SCM supply compared to other regions. Fly ash is the most readily available and widely used SCM, but its supply can be impacted by external factors. Slag cement and silica fume offer consistent quality and reliable supply, but their availability might be limited in certain areas.
- The SCM supply landscape is constantly evolving. New sources, alternative materials, and innovative transportation solutions are emerging to address these challenges and ensure a more sustainable and reliable supply of SCMs in the future.

- While there is a consistent supply for a majority of SCMs, producers are allowed to change from one approved source to another when there are short-term supply issues, as long as the alternative source is an approved mix design.
- While the industry has warned about the potential supply sources, concerns with both slag and fly ash availability has never been an actual issue.
- In Maine, the supply of slag cement has been very reliable, but the agency's supplier is planning to close at the end of 2024. Supply may become more variable in the future.

4. Is the use of alternative SCMs on, a) highly traveled/loaded roadways, b) minor areas like rest areas, or c) all applications?

Twenty-six respondents (approximately 76 percent) use alternative SCMs in all roadway applications, from highly traveled roads to minor areas such as rest areas, regardless of traffic volume or usage intensity. In contrast, five respondents (15 percent) use SCMs on highly traveled roads, and three respondents (9 percent) limit use to minor roads.

Some respondents, including Connecticut DOT, use a performance-based specification approach, allowing producers to decide whether to use SCMs to meet specifications. Other respondents indicated a selective use of specific SCMs, such as silica fume, fly ash, and slag, across all applications. Additionally, not all SCMs are allowed as replacement of those already listed on the approved product lists.

Table 20 summarizes survey responses.

Table 20. Use of SCMs across roadway applications

Type of Application	Responses	Percent (%)
Highly traveled roads	5	15
Minor roads	3	9
All applications	26	76

5. Which of the following alternative SCMs do you think will be MOST utilized in the next 10 years in your state? Select all those applicable along with the maximum replacement cement levels for pavement and bridge concretes (A = 0%–10%, B = 10%–20%, C = 20%–30%, D = other).

Many respondents specified numerical values or percentage ranges that didn't directly correspond to the given options. To ensure a comprehensive analysis of all responses, relevant information provided in the comments was categorized by identifying numerical values or percentage ranges mentioned in the comments and aligning them with the classification provided in the survey question.

SCM selection and use are based on factors such as material availability, performance requirements, and project specifications. According to survey results, use of fly ash, Class C and Class F, is projected across multiple replacement ranges, most notably in the 20 percent to 30 percent and 30 percent to 40 percent ranges for both pavement and bridge applications. Slag cement is expected to be used across a broad range of replacement levels due to its acceptability, versatility, and widespread use. Calcined clay, ground limestone, and reclaimed fly ash will primarily be used in the 10 percent to 20 percent replacement range, and microsilica in the 0 percent to 10 percent range.

Below are the highest rates of application of SCMs for both pavement and bridge concretes:

- 0 percent to 10 percent range: microsilica.
- 10 percent to 20 percent range: fly ash, Class F; ground limestone; reclaimed fly ash; and calcined clay.
- 20 percent to 30 percent range: fly ash, Class C and Class F; and natural pozzolans.
- 30 percent to 40 percent range: fly ash, Class C and Class F; and slag cement.

Note: The data reported for microsilica in the 40+ percent range is suspect and unreasonable.

Table 21 and Table 22 present respondents' projections for using various SCMs over the next 10 years, categorized by the maximum replacement cement levels for pavement and bridge concretes.

Table 21. Maximum replacement cement levels for pavement and bridge concrete, 10-year projection

SCM	0%-10%	10%-20%	20%-30%	30%-40%	40+%
Calcined clay	1	4	2	–	–
Fly ash, Class C	–	2	5	4	–
Fly ash, Class F	1	6	5	10	2
Ground limestone	2	6	1	–	–
Microsilica	7	1	–	–	2
Natural pozzolans	2	1	4	–	1
Reclaimed fly ash	1	6	3	1	–
Slag cement	–	2	3	5	2
Other	1	2	–	–	1

Table 22. Use projections of various SCMs over the next 10 years

SCM	Responses	Percent (%)
Bottom ash	3	9
Calcined clay	8	24
Fly ash, Class C	15	44
Fly ash, Class F	18	53
Ground limestone	10	29
Microsilica	13	38
Natural pozzolans	10	29
Reclaimed fly ash	11	32
Slag cement	16	47
Other	5	15

6. What are the major criteria evaluated for the selection of these SCMs? Select all that apply.

The key criteria influencing the selection of a specific SCM for a project are:

- **Performance.** Twenty-three respondents (68 percent) emphasized the need to meet performance requirements such as compressive strength and air content. Other performance factors that influence SCM choice include ASR mitigation, permeability, and shrinkage.
- **Availability.** Seventeen respondents (50 percent) highlighted SCM availability to ensure a consistent and reliable supply that meets construction demands. Long-term SCM availability is crucial for ensuring concrete performance over time. Availability of Class C fly ash and slag plays a significant role in decision-making. SCM availability is also a major concern affecting future specification requirements. Concrete suppliers prioritize SCM sources based on proximity and transportation cost, with options like port use or long trucking routes.
- **Mix design compatibility.** Eleven respondents (32 percent) mentioned mix design compatibility as a consideration, highlighting the need for SCMs to seamlessly integrate into concrete mixes without compromising workability or setting characteristics. Ideal features include the ability to contribute to improving hardened concrete quality by mitigating ASR, reducing permeability, and enhancing long-term strength. Contractors adjust SCM selection based on mix compatibility, particularly regarding water demand and setting characteristics.
- **Testing qualifications.** Ten respondents (29 percent) underscored the importance of rigorous testing, including chemical and strength testing, to ensure SCMs conform to specified standards and performance requirements. ASR issues have historically influenced SCM use to prevent aggregate failure. SCMs are avoided if they negatively impact concrete performance.

- **Transportation cost.** Eight respondents (24 percent) noted transportation cost as a factor in optimizing supply chain logistics. Respondents reported that contractors tend to choose the source closest to their facility to minimize transportation expenses.
- **Set time.** Four respondents (12 percent) indicated that set time was a factor in SCM selection.

Other considerations reported by survey respondents included environmental considerations, ASR mitigation, future specification concerns, and long-term availability.

Table 23 presents survey results.

Table 23. Criteria for selecting a specific SCM

Criterion	Responses	Percent (%)
Availability	17	50
Mix design compatibility	11	32
Performance	23	68
Set time	4	12
Testing qualifications	10	29
Transportation cost	8	24
Other	5	15

7. Is the SCM selection purely based on the ASTM 618 and/or AASHTO M 295 standard, or are there performance tests specific to your state? If so, please check all that apply and specify additional items.

Performance Tests

Respondents highlighted the importance of performance tests, such as those for fresh concrete properties (12 respondents, or 35 percent) and strength characteristics (14 respondents, or 41 percent), in material selection to ensure SCMs meet specified performance requirements beyond basic standards. Specific respondent comments are provided below:

- **Durability tests**: Surface resistivity test (AASHTO T 358).
- **Fresh concrete properties**:
    - Air content, slump, and temperature.
    - Tested for performance to specifications.
- **Strength characteristics**:
    - Tested for performance to specifications.
    - Trial batch data to prove design strength.
    - 28-day strength requirement.

Table 24 summarizes survey responses.

Table 24. SCM test selection

Criterion	Responses	Percent (%)
Durability tests	8	24
Fresh concrete properties	12	35
Strength characteristics	14	41
Other	9	26

Standards and Specifications

While ASTM C618 and AASHTO M 295 serve as foundational standards for SCM selection, several states also have specific requirements and priorities to refine the selection process, including standards for fly ash, slag cement, natural pozzolans, metakaolin, and silica fume. Various combination test methods were provided, including:

- ASTM C989 Grade 100 minimum, ASTM C595, and ASTM C1240.
- Fly ash ASTM C 618, ASTM C 1697, and GGBFS-ASTM C 989 Grade 100 or Grade 120.
- ASTM C1567 or M 295/M 302/M 307.
- AASHTO standards for fly ash, microsilica, and slag cement. Ground glass specifications met by comparing test mixes with 10 percent and 20 percent replacement for ordinary portland cement (OPC) with a 100 percent OPC control mix. Such specifications (711-15) were written before ASTM C1866 was established; there are plans to update this specification to be in line with ASTM guidelines.
- ASTM C618 and loss on ignition (LOI) test less than 5.

Some states combine national standards with state-specific requirements to optimize results for infrastructure and environmental priorities. For example, California uses AASHTO M 295, which establishes requirements for slag cement used in concrete, as a basic framework and supplements it with tests and acceptance criteria from state-specific Section 90.1-1.02 B (3):

- **Fly ash**: Complying with AASHTO M 295, Class F, and either of the following:
  - Available alkali as Na_2O +0.658 K_2O must not exceed 1.5 percent when tested under ASTM C311.
  - Total alkali as Na_2O +0.658 K_2O must not exceed 5 percent when tested under AASHTO T 105.
- **Ultra fine fly ash**: Complying with AASHTO M 295, Class F, and chemical and physical requirements meeting Section 90.1-1.02 B (3) #2.
- **Raw or calcined natural pozzolans**: Complying with AASHTO M 295, Class N (except for a maximum LOI of 10 percent), and either of the following:
  - Available alkali as Na_2O +0.658 K_2O must not exceed 1.5 percent under ASTM C311.
  - Total alkali as Na_2O +0.658 K_2O must not exceed 5 percent under AASHTO T 105.

- **Metakaolin:** Complying with AASHTO M 295, Class N, and chemical and physical characteristics in Section 90.1-1.02 B (3) #4.
- **Ground granulated blast furnace slag (GGBFS)**: Complying with AASHTO M 302, Grade 100 or 120.
- **Silica fume**: Complying with AASHTO M 307, with a minimum reduction in mortar expansion of 80 percent when using the cement from the proposed mix design.

Additional Criteria

Some respondents indicated that SCM selection may involve collaboration with contractors or producers, allowing them to determine SCMs based on mix design needs and performance specifications. Other respondents noted a need to meet ASR mitigation requirements and a lack of support from industry in better addressing the specifications.

8. Does the construction activity/sequence change with the introduction of these new materials (e.g., curing requirements, mixing sequence change)? If so, please explain.

Respondents reported varied effects of introducing new SCMs to construction activities, with adjustments often made to ensure compliance with specifications and to achieve desired concrete properties and performance.

The Minnesota DOT respondent reported that the agency has not modified any mixing or placement specifications related to specific SCMs. Based on the research conducted in 2022 at its MnROAD pavement test track, using some of the newer SCMs in concrete may require variations in mix proportions to achieve uniformity in concrete. However, the respondent noted that "[v]ery limited data is available for sharing at this point."

The California respondent reported the following potential changes:

Curing requirements:

- Fly ash typically requires extended curing periods compared to portland cement concrete because its pozzolanic activity, while contributing to long-term strength, occurs more slowly. Caltrans often specifies longer moist curing periods or alternative methods like fog curing for fly ash concrete to ensure proper hydration and strength development.
- Slag cement generally shows faster or similar early strength gain than portland cement, sometimes allowing for shorter initial curing periods. However, long-term strength development might be slower, prompting extended moist curing or alternative methods like steam curing for specific applications.

Finishing techniques: SCMs can impact finishing techniques such as troweling, requiring adjustments in timing or technique to achieve the desired surface finish.

Mixing sequence: Specific mixing sequences may be required based on SCM properties and their interaction with other mix components.

Workability and temperature sensitivity: Some SCMs like fly ash can affect the workability of the concrete mix and may be more sensitive to temperature fluctuations during mixing and placement. Additional water reducers or adjustments in mixture proportions and temperature control may be necessary, especially in extreme weather conditions and to maintain desired workability for placement and finishing.

Below are additional comments from respondents:

Contractor decision:

- In some cases, changes in construction activity and sequence are left to the discretion of the contractor, as standard specifications may not provide specific guidance.
- Changes in construction activity and sequence may provide implementation flexibility.
- Despite potential changes, contractors are typically able to meet strength requirements even with partial SCM replacements.

Curing time and requirements:

- New SCMs may have higher water demands and require specific admixture sequencing during batching, impacting plastic and early shrinkage cracking.
- Silica fume concrete requires seven days of curing instead of the standard four days of moist curing.
- Sawcut times have to be monitored, especially with weather changes.
- Activities are often controlled by maturity.

Mix properties and proportions:

- Design properties may change, affecting both fresh and hardened properties, along with project requirements.
- SCMs may not be used in high early strength mixes or concrete for patchwork due to specific project requirements.

Mixing sequence:

- Specific mixing sequences may be required based on the properties of the SCM and its interaction with other components.
- New SCMs may have higher water demands and require specific admixture sequencing during batching, impacting plastic and early shrinkage cracking.
- Liquid fly ash (E5-LFA) requires a proper batching sequence.

9. For a particular SCM alternative, are there special considerations beyond the items mentioned above that impact their implementation?

Most respondents (21, or 66 percent) indicated that no special considerations impacted SCM implementation. Eleven respondents (34 percent) reported the following considerations before implementation:

- **Aggressive environments**: Certain applications, such as those in high chloride or sulfate environments or in mass concrete, drilled shaft, and precast/prestressed concrete, require special considerations for SCM implementation due to the unique challenges posed by these conditions.
- **Restrictions on use**: Some respondents mentioned restrictions on the use of specific SCMs, such as ground glass, which is limited to situations where there are no concerns regarding alkali-aggregate reactivity (AAR). While ground glass can reduce AAR, it may not completely mitigate the reaction, necessitating careful consideration of its application.
- **Processing and calcination**: Special considerations are required for the processing and calcination of natural clay to obtain optimal pozzolanic reactivity, indicating that the manufacturing process of certain SCMs influences their implementation.

Table 25 presents survey responses.

Table 25. Special considerations when implementing SCMs

Implementation Considerations	Responses	Percent (%)
Special considerations	11	34
No special considerations	21	66