**Title**

# Identification of Likely Alternative Supplementary Cementitious Materials in California: A Review of Supplies, Technical Performance in Concrete, Economic, and Climatic Considerations

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# Identification of Likely Alternative Supplementary Cementitious Materials in California: A Review of Supplies, Technical Performance in Concrete, Economic, and Climatic Considerations

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Partnered Pavement Research Center (PPRC) Project Numbers 4.84 (DRISI Task 3775):
Alternative Supplementary Cementitious Materials (SCMs) Sources

**PREPARED FOR:**

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16. ABSTRACT

This report is a comprehensive review of natural and human-made materials with the potential to reduce cement content in concrete by partially replacing portland cement or as additives. The review aims to reveal possible source materials as alternative supplementary cementitious materials (ASCMs) to coal-burned fly ash and ground granulated blast furnace slag as these SCMs supplies rapidly decline. Information required to estimate supplies of each ASCM was gathered, and ASCM candidates with enough abundance to support California's concrete paving sector were identified for further laboratory evaluation. In addition, the required chemical, thermal, and mechanical treatments of the source materials were gathered so the environmental and economic impacts of the processes could be considered. A review of scientific literature on the technical performance of the studied materials in cement paste, mortar, or concrete was also conducted when that information was available.

The reviewed feedstock material categories include biomass sources, construction and demolition wastes, natural pozzolans (volcanic and sedimentary materials), and post-consumer waste. As part of the biomass category, biopolymer-based nanomaterials were also included in the review for their promise to reduce cement content from added strength. The following information was included for each material considered in this report: feedstock description, the potential mechanism of performance in concrete, physical and chemical properties, feedstock supplies and processing method, technology readiness level (TRL), a summary of technical performance in cementitious systems based on the scientific literature, environmental impacts of the production phase, and cost considerations.

Based on the comprehensive information gathered, several materials present potential as ASCMs, fillers, and admixtures for the California paving industry. However, most materials identified are at TRL 3 or 4, requiring more research and development to move toward implementation. In addition, some of these ASCMs may not fully satisfy the current regulations for SCMs. For example, biomass ash from some sources may contain a high alkaline content and a greater than 6% unburnt carbon content. Furthermore, some natural pozzolans impose a high water demand and have slow strength gain. In addition, the reported performance in the literature for the biobased nanomaterials studied is conflicting and performance data in concrete is scarce. Finally, some reviewed materials were not selected for more advanced laboratory evaluation because a supplier was not found in California. These materials include municipal solid waste ash, wastewater treatment sludge, and seashell waste. In addition, ground glass, harvested coal-burnt fly ash, and fines from carpet recycling were not chosen for laboratory evaluation because they are being investigated in other Caltrans and non-Caltrans research contracts.

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# PROJECT OBJECTIVES

The goal of Caltrans Partnered Pavement Research Center Projects 4.84 and 4.85 is to perform a first-order assessment of the feasibility of alternative supplementary cementitious materials (ASCMs) to improve concrete properties, reduce environmental impacts and costs, and reduce waste stockpiles, if possible. In addition, the research will provide recommendations for further development of the most promising ASCMs produced using California rocks and minerals, biomass-based materials, waste, and coproducts of industrial and agricultural processes. This goal will be achieved through the completion of the following tasks:

- Task 1: Literature review
- Task 2: Identification of ASCM sources
- Task 3: Initial screening of ASCM sources
- Task 4: Laboratory and thermodynamic evaluation of ASCM sources
- Task 5: Environmental and economic assessments of ASCM sources and initial ranking based on supply curve
- Task 6: Elaboration of final report

This research project focuses on concrete for hardscapes, which includes but is not limited to pavements, street, and roadway features (e.g., curbs, gutters), railroad ties, and other flatwork applications. This report is the outcome of Task 1: Literature review and Task 2: Identification of ASCM sources.

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# LIST OF ABBREVIATIONS

| | |
|---|---|
| AASHTO | American Association of State Highway and Transportation Officials |
| AG | Agricultural |
| AP | Acidification potential |
| ASR | Alkali-silica reaction |
| ASCM | Alternative supplementary cementitious materials |
| BET | Brunauer-Emmett-Teller |
| BFA | Biomass fly ash |
| BFR | Brominated flame retardants |
| C&D | Construction and demolition |
| CAL FIRE | California Department of Forestry and Fire Protection |
| CalAPA | California Asphalt Pavement Association |
| CalCIMA | California Construction and Industrial Materials Association |
| CalRecycle | California Department of Resources Recycling and Recovery |
| Caltrans | California Department of Transportation |
| CARB | California Air Resource Board |
| CARE | Carpet America Recovery Effort |
| CCA | Crushed concrete aggregate |
| CE | Chloroacetic acid etherification |
| CED | Cumulative energy demand |
| CH | Calcium hydroxide |
| ChNC | Chitin nanocrystal |
| ChNF | Chitin nanofiber |
| CHNM | Chitin nanomaterial |
| CI | Crystallinity index |
| CMNF | Cellulose micro- and nanofibrils |
| CNC | Cellulose nanocrystal |
| CNCA | California Nevada Cement Association |
| CNF | Cellulose nanofibers |
| CNM | Cellulose nanomaterial |
| DE | Diatomaceous earth |
| EIA | Energy Information Administration |
| EMFAC | EMission FACtors |
| EP | Eutrophication potential |
| EPD | Environmental product declaration |
| FM | Forest management |
| GaBi | Ganzheitliche Bilanz |

| | |
|---|---|
| GCC | Ground calcium carbonate |
| GGBFS | Ground granulated blast furnace slag |
| GHG | Greenhouse gas |
| GWP | Global warming potential |
| HMA | Hot mix asphalt |
| HPC | High-performance concrete |
| HRM | Highly reactive metakaolin |
| HO | Homogenization |
| ILCD | International Reference Life Cycle Data System |
| LCA | Life cycle assessment |
| LCCA | Life cycle cost analysis |
| LCI | Life cycle inventory |
| LCIA | Life cycle impact assessment |
| LOI | Loss on ignition |
| LWSCC | Light weight self-compacting concrete |
| MK | Metakaolin |
| MPSP | Minimum product selling price |
| MSW | Municipal solid waste |
| MSWA | Municipal solid waste ash |
| NERC | North America Electricity Reliability Council |
| ODP | Ozone depletion potential |
| OPC | Ordinary portland cement |
| PCA | Portland Cement Association |
| PCC | Portland cement concrete |
| PCR | Product Category Rule |
| PFC | Perfluorinated compound |
| PG&E | Pacific Gas and Electric |
| PLC | Portland limestone cement |
| POCP | Photochemical oxidant formation potential |
| PPRC | Partnered Pavement Research Center |
| RBHG | Rice straw-based heat generating |
| RBP | Recycled brick powder |
| RCA | Recycled concrete aggregate |
| RCP | Recycled concrete powder |
| RHA | Rice hull ash |
| RSA | Rice straw ash |
| SCC | Self-consolidating concrete |
| SCM | Supplementary cementitious materials |

| | |
|---|---|
| SEM | Scanning electron microscope |
| SM | Sawmill |
| SO | Sonication |
| SSA | Sewage sludge ash |
| TA | Terrestrial acidification |
| TEA | Techno-economic analysis |
| TO | TEMPO oxidation |
| TRACI | Tool for Reduction and Assessment of Chemical and Other Environmental Impacts |
| TRL | Technology Readiness Level |
| UCPRC | University of California Pavement Research Center |
| UW | Urban wood |
| w/c | Water-to-cement ratio |
| WD | Water depletion |
| WECC | Western Electricity Coordinating Council |
| XRD | X-ray diffraction |
| USDA | US Department of Agriculture |
| USGS | US Geological Survey |

## SI* (MODERN METRIC) CONVERSION FACTORS

### APPROXIMATE CONVERSIONS TO SI UNITS

| Symbol | When You Know | Multiply By | To Find | Symbol |
|---|---|---|---|---|
| | | **LENGTH** | | |
| in. | inches | 25.40 | millimeters | mm |
| ft. | feet | 0.3048 | meters | m |
| yd. | yards | 0.9144 | meters | m |
| mi. | miles | 1.609 | kilometers | km |
| | | **AREA** | | |
| $in^2$ | square inches | 645.2 | square millimeters | $mm^2$ |
| $ft^2$ | square feet | 0.09290 | square meters | $m^2$ |
| $yd^2$ | square yards | 0.8361 | square meters | $m^2$ |
| ac. | acres | 0.4047 | hectares | ha |
| $mi^2$ | square miles | 2.590 | square kilometers | $km^2$ |
| | | **VOLUME** | | |
| fl. oz. | fluid ounces | 29.57 | milliliters | mL |
| gal. | gallons | 3.785 | liters | L |
| $ft^3$ | cubic feet | 0.02832 | cubic meters | $m^3$ |
| $yd^3$ | cubic yards | 0.7646 | cubic meters | $m^3$ |
| | | **MASS** | | |
| oz. | ounces | 28.35 | grams | g |
| lb. | pounds | 0.4536 | kilograms | kg |
| T | short tons (2000 pounds) | 0.9072 | metric tons | t |
| | | **TEMPERATURE (exact degrees)** | | |
| °F | Fahrenheit | (F-32)/1.8 | Celsius | °C |
| | | **FORCE and PRESSURE or STRESS** | | |
| lbf | pound-force | 4.448 | newtons | N |
| $lbf/in^2$ | pound-force per square inch | 6.895 | kilopascals | kPa |

### APPROXIMATE CONVERSIONS FROM SI UNITS

| Symbol | When You Know | Multiply By | To Find | Symbol |
|---|---|---|---|---|
| | | **LENGTH** | | |
| mm | millimeters | 0.03937 | inches | in. |
| m | meters | 3.281 | feet | ft. |
| m | meters | 1.094 | yards | yd. |
| km | kilometers | 0.6214 | miles | mi. |
| | | **AREA** | | |
| $mm^2$ | square millimeters | 0.001550 | square inches | $in^2$ |
| $m^2$ | square meters | 10.76 | square feet | $ft^2$ |
| $m^2$ | square meters | 1.196 | square yards | $yd^2$ |
| ha | hectares | 2.471 | acres | ac. |
| $km^2$ | square kilometers | 0.3861 | square miles | $mi^2$ |
| | | **VOLUME** | | |
| mL | milliliters | 0.03381 | fluid ounces | fl. oz. |
| L | liters | 0.2642 | gallons | gal. |
| $m^3$ | cubic meters | 35.31 | cubic feet | $ft^3$ |
| $m^3$ | cubic meters | 1.308 | cubic yards | $yd^3$ |
| | | **MASS** | | |
| g | grams | 0.03527 | ounces | oz. |
| kg | kilograms | 2.205 | pounds | lb. |
| t | metric tons | 1.102 | short tons (2000 pounds) | T |
| | | **TEMPERATURE (exact degrees)** | | |
| °C | Celsius | 1.8C + 32 | Fahrenheit | °F |
| | | **FORCE and PRESSURE or STRESS** | | |
| N | newtons | 0.2248 | pound-force | lbf |
| kPa | kilopascals | 0.1450 | pound-force per square inch | $lbf/in^2$ |

*SI is the abbreviation for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380.
(Revised March 2021)

# 1 INTRODUCTION

## 1.1 Environmental Impact of Cement Production

Cement is the glue that binds aggregates together to form concrete. The binder constituent of concrete is cement, most commonly referred to as ordinary portland cement (OPC). Cement is an essential building material for developing and maintaining the built environment that supports the growing global population, urbanization trends, infrastructure development, rebuilding, and economic growth. The global production of portland cement is projected to increase to 6.4 billion short tons (T) or 5.8 billion metric tons (t) by 2050 from 4.3 billion T (3.90 billion t) in 2020 *(1)*. However, meeting such immense global demands comes with noteworthy greenhouse gas (GHG) emissions equal to 7% to 8% of total global anthropogenic emissions *(2)*. The global cement industry must reduce emissions by 24% to avoid increases of 35.6°F (2°C) in global temperature by 2050, a goal proposed in the 2015 United Nations Climate Change Conference (COP21) agreement, known as the Paris Agreement *(2)*.

As part of this direction, the cement and concrete sector is beginning to face mandates to reduce emissions. For example, California passed the first US legislation on cement decarbonization. Senate Bill 596, signed by the California governor in September 2021, requires developing a comprehensive strategy for the cement industry to cut emissions by 40% by 2030 and achieve net-zero emissions by 2045 *(3)*. However, decarbonizing a hard-to-abate heavy industry such as the cement sector requires a multifaceted approach. This approach includes a combination of material optimization, energy efficiency improvements, innovative decarbonization technologies, and other strategies *(4)*.

California is the second leading cement-consuming state after Texas *(5)*. Cement production is an essential industry in California that contributed $35.6 million to state tax revenues in 2016, according to a Portland Cement Association (PCA) report *(6)*. Based on California's cement production (8.9 million t) and the global production of 3,700 million t in 2022 *(7)*, direct emissions from seven cement plants in California contributed 7.8 million t of $CO_2$-eq emissions in 2019 *(8)*.

## 1.2 Supplementary Cementitious Materials

One material optimization strategy is the more efficient use of OPC in concrete. In fact, according to the global Cement Technology Roadmap, reducing the clinker-to-OPC ratio can offer 2.9 billion T (2.6 billion t) $CO_2$-eq savings globally by 2050 *(9)*, equivalent to a 35% emissions reduction. However, for meaningful reductions in emissions, the clinker-to-cement ratio needs to drop further from around 0.75, achieved since 2012 *(10)*, to the 2050 target of under 0.6 *(9)*.

The implementation of portland limestone cement (PLC) as a means of reducing the global warming potential (GWP) of concrete is a recently completed step toward an industry goal of net-zero carbon emissions by 2045 *(11)*. The ready-mix concrete industry practices clinker reduction strategies by partially substituting OPC with supplementary cementitious materials (SCMs) in concrete. In addition to the environmental benefits of this practice, SCMs contribute to improving the hardened concrete properties through hydraulic or pozzolanic activity.

Pozzolans are materials with highly amorphous silica and alumina content. In the presence of water, the amorphous contents of SCMs react with the calcium hydroxide (CH) released from the hydration of portland cement to form additional calcium-silicate-hydrate (C-S-H) or calcium aluminate silicate hydrate (C-A-S-H) products. These extra products result in pore refinement and reduced permeability in concrete, which enhance concrete's mechanical properties at a later age. Reduced chloride permeability and improved resistance to alkali-silica reaction (ASR), sulfate attack, and freeze-thaw durability have also been reported for SCM-blended concrete *(12)*.

In addition, industrial byproducts lacking in pozzolanic reactivity may still perform as acceptable fillers for concrete, enhancing packing density and adding to the strength of concrete. Therefore, industrial byproduct filler materials are included in this review study. Laboratory evaluation is needed to determine if each potential material is a useful SCM or filler in concrete.

## 1.3 SCM Shortages

A major developing challenge is the shortage of supplies of the two most used SCMs, fly ash from coal-fired furnaces in energy plants and ground granulated blast furnace slag (GGBFS) generated in pig iron production. The reduced supply of GGBFS results from the decarbonization of the steel sector as the industry transitions from blast furnace-based oxygen furnaces to scrap-based electric arc furnaces. Similarly, restrictions on mercury and $CO_2$ emissions at coal-fired power plants have led to power plant closures or conversion of plant operations to natural gas. According to a US Energy Information Administration (EIA) projection, the kilowatt-hours of electrical energy generated by coal-fired power plants will drop 23% by 2050 compared to 2020 levels *(13)*. Thus, a parallel reduction in fly ash production would be expected. The EIA also predicts that the drop may be even larger, up to 49%, depending on policy regulations and the cost of other electricity generation alternatives. These shortages in domestic supplies of GGBFS and coal fly ash require concrete producers to find alternative SCMs (ASCMs) to reduce the clinker-to-OPC ratio. The PCA and California Nevada Cement Association (CNCA) roadmaps to carbon neutrality *(14,15)* acknowledge the challenge of meeting upcoming SCM demand as the supply of traditional SCMs declines. Consequently, the PCA roadmap includes “research into the use of alternative raw materials and SCMs” and the promotion of “markets and infrastructure for SCM recovery, distribution, and use” among the policy priorities for cement and concrete. Both priorities align with the goal of this research project.

To effectively reduce the carbon footprint of concrete produced in California, SCMs (human-made or naturally occurring) with regional abundance must be identified. Scientific literature, mineralogical, agricultural, and industry reports show that based on chemical composition and physical properties, numerous source materials can be processed and used as ASCMs to replace coal fly ash and GGBFS. However, there are obstacles hindering their implementation at an industrial scale. One challenge is the lack of a supply chain for new SCMs. For many ASCMs, the feedstock supplier, intermediary processor, testing, and distributing parties need to be developed and integrated to supply the concrete industry with a continuous supply of ASCMs with consistent quality.

Standardizing ASCMs is a slow process, especially from waste streams and industrial byproducts, given the variability in their composition and properties. Education and training are also required so concrete producers can overcome issues of higher water demand compared to fly ash and slow strength gain. In some cases, agency specifications may require modifications to allow for ASCM use. In addition, some ASCMs could be limited to one region or state by supply quantity or supply chain issues; thus, local education campaigns may be required for implementation. Another obstacle is the lack of awareness of available ASCMs and their potential to deliver acceptable performance in concrete.

The environmental impacts and costs of long-haul transportation may impose additional challenges to scale implementation, especially since most ASCMs (such as natural pozzolans) are available in certain geographical regions. Luckily for California, the western part of the country is rich in pyroclastic and sedimentary deposits of natural pozzolans, making them a viable ASCM for the region.

Finally, ASCMs may have difficulty competing with regard to environmental impacts compared to coal fly ash and GGBFS, as these are typically considered burden-free to concrete in most life cycle assessment (LCA) studies *(16)*. These materials are considered burden-free in typical LCA practice because they do not have economic value beyond recovery of the costs of their collection and transportation. Most natural ASCMs or byproducts will require some processing and treatment to increase reactivity and compatibility (e.g., milling, calcination, drying), which causes negative environmental impacts.

## 1.4 Project Scope

Due to the shortage of conventional SCMs (coal fly ash and GGBFS), the demand for new sources of SCMs has grown recently. Other opportunities for GWP reduction of concrete exist in mineral fillers with low or no pozzolanic reactivity as a replacement for portland cement or sand. Some of these materials offer opportunities for carbon sequestration and recycling of various waste streams in California. Furthermore, new advances in nanomaterials with high surface area and internal curing capabilities to promote the hydration of portland cement offer an alternative or additional approach to SCMs for reducing cement content in concrete.

Therefore, this project aims to identify ASCMs, fillers, and nanomaterials produced from California rocks and minerals, biomass, waste streams, and industrial byproducts with currently low recycling rates. Source materials from neighboring states will also be considered as a second priority.

The goals pursued by investigating these materials are the following: (1) identify alternative sources of SCMs other than fly ash and GGBFS to address the shortage of traditional SCMs, (2) reduce the GWP of concrete by partial replacement of portland cement with ASCMs/fillers or by reducing cement content with the use of nanomaterials, and (3) create recycling paths for large waste streams and industrial byproducts promoting a circular economy in California and preserving landfill space. For all identified ASCMs, concrete performance in terms of mechanical properties and durability must meet the required standard specifications for the application.

### 1.5 Report Layout

The following materials were scoped in this study and are reviewed in this report:

- Biomass-based materials group
  - Bioenergy plant fly ash and bottom ash, rice straw ash, biochar, cellulose, chitin nanomaterials, and seashell powder
- Natural pozzolans group
  - Volcanic (pumice, perlite, zeolite tuffs, scoria) and sedimentary deposits (diatomaceous earth, clay)
- Construction and demolition waste group
  - Recycled concrete aggregate (RCA) and crushed concrete aggregate (CCA) powder
  - Rock dust (asphalt baghouse fines and aggregate crushing fines)
  - Waste brick powder
- Post-consumer waste group
  - Municipal solid waste incinerator ash
  - Wastewater sludge ash
  - Carpet backing powder

For feedstock supply and availability, in addition to reviewing published information, information was gathered from suppliers and industry representatives. The findings for ASCM are summarized as follows:

- Product description
- Active mechanism
- Physical and chemical properties
- Feedstock description and supply
- Process description, NASA Technology Readiness Level (TRL) (1 to 9 scale, with 1 being the least advanced and 9 the most advanced), and potential suppliers
    - Process description
    - Technology readiness level
    - Potential suppliers
    - Current use of the product
    - Agents involved in production and distribution
- Performance based on literature
    - Impact on fresh properties
    - Impact on strength
    - Impact on durability
- Environmental considerations
    - Global warming potential (GWP)
    - Air pollution
    - Land use
    - Water consumption
    - Toxicity
- Cost considerations

## 1.6 Measurement Units

In this report, both English and metric units (in parentheses after the English units) are provided. A conversion table is provided on page xvi at the beginning of this report.

## 1.7 Literature Review Methodology

Potential ASCMs were identified based on a review of the scientific literature. Once a list of potential materials was compiled, information on supplies and processes was gathered for each material from various sources, including industry contacts and information available in the public domain and publications (reports, journal articles, conference papers, books, specifications). Based on the compiled information, the full production, further processing (washing, crushing, grinding), and treatment process were illustrated in a system diagram for each material. The system diagrams for the SCMs are presented in Appendix A of this report, which are anticipated to be used for performing life cycle assessment (LCA) and life cycle cost analysis (LCCA) for the SCMs in the later stages of this project. Next, a scientific literature review was performed to gather information on the performance of each material in cement paste, mortar, and concrete. The keywords used included the ASCM name, "fresh concrete properties," "fresh cement paste properties," "fresh mortar properties," "impact on strength," and "impact on durability."

Finally, a web search was conducted, and scholarly articles, technical reports, and databases were identified to locate the cost and environmental data published for the ASCMs reported in Section 1.5. The keywords primarily used for each SCM in the web search include "environmental impacts," "LCCA," "LCA," "cost of [name of ASCM]," "environmental product declaration (EPD)," "global warming potential (GWP)," and greenhouse gas emissions (GHG)." The order in which the information for each SCM was searched is the following:

For environmental impacts:

1. LCAs that have been performed
2. Published EPDs
3. Federal Commons Database: lcacommons.gov/lca-collaboration/
4. Proprietary databases[1]
    - SimaPro *(17)*

---

[1] Raw data are not shared from any proprietary databases in this report.

    - Ganzheitliche Bilanz (GaBi) *(18)*

For cost:

1. LCCAs that have been performed
2. SCM consumer cost

# 2 BIOMASS-BASED MATERIALS

## 2.1 Fly Ash and Bottom Ash from Biomass Energy Plants

### 2.1.1 *Product Description*

Forest and other biomass feedstocks are used as renewable energy sources worldwide to replace fossil fuels with high greenhouse gas emissions *(19)*. Currently, biomass used for heat and electricity production is mainly from forestry and agricultural residues, dedicated energy crops, wood fuel/charcoal/chips/pellets, municipal solid waste, sewage sludge, and paper sludge, with wood biomass from forestry energy currently being the largest source of biomass *(19)*. Burning these biomass sources produces heat or energy, as well as fly ash and bottom ash, in various amounts depending on the feedstock and combustion conditions. Ash management is challenging for energy plants since large-scale biomass combustion generates significant amounts of ash. Biomass ash has physical and chemical properties that are different from coal fly ash, commonly used in concrete. Also, there is a lack of scientific knowledge on the long-term durability and performance of concrete made with wood biomass ashes *(20,21)*. Ash from biomass combustion has different physiochemical properties than coal fly ash and needs to be fully characterized and understood for use in concrete *(19)*. The physicochemical properties of the ashes produced from biomass combustion depend heavily on the feedstock type and the combustion method *(22)*.

The feedstock for California’s power plants may come from one or several of the following sources, according to the California Biomass Energy Alliance *(23)*:

- Sawmills: Bark, sawdust, and other low-grade byproducts of the sawmill manufacturing process (e.g., bark, chips, shavings).
- Forest management: Forest thinning, timber slash, and unmerchantable wood (small trees and branches).
- Urban wood: Used lumber, trim, shipping pallets, trees, branches, and other wood debris from construction and demolition.

- Agricultural products: Pruning waste, old trees, nut shells, fruit pits, hulls, and other waste. Agricultural waste is typically burned with one or several of the abovementioned products at biomass-combustion energy production plants.

Most biomass energy plants in California are typically fed with a combination of the above sources rather than a single source.

### 2.1.2 *Acting Mechanism in Concrete*

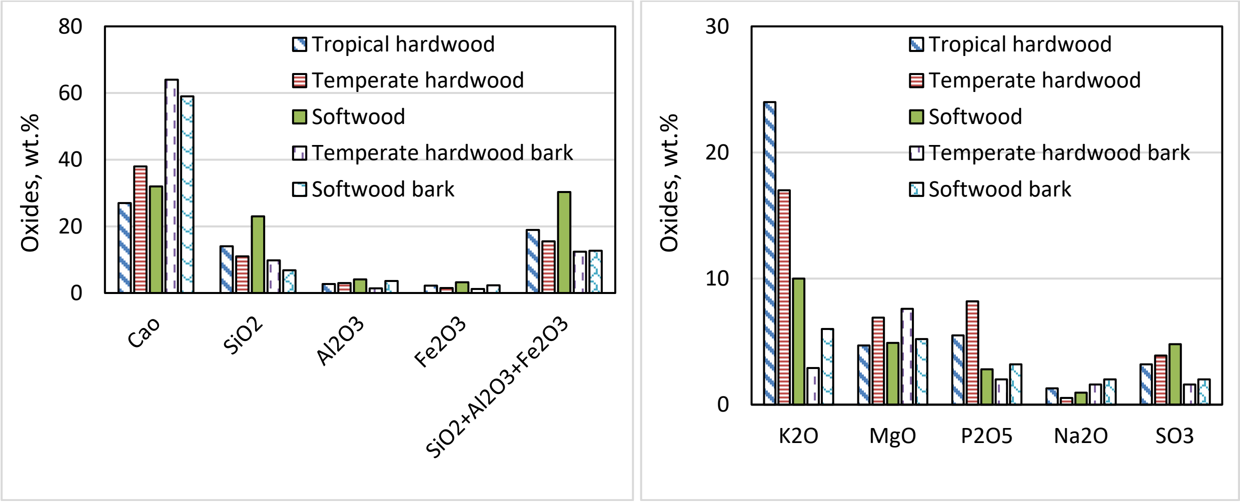
According to some studies, biomass-combustion ashes are rich in calcium, alumina, and silica and could produce $Ca(OH)_2$ and also deliver pozzolanic reactivity when used as a partial replacement for cement in concrete *(24)*. Both amorphous and crystalline phases were detected in wood fly ash and bottom ash. On average, amorphous content was about 72% (range of 46.6% to 94.2%) in fly ash and 66% (range of 53.8% to 73.3%) in the bottom ash *(25)*. The hydration of biomass ash resulted in products such as calcium aluminate hydration products ($3CaO.Al_2O_3.Ca(OH)_2.xH_2O$), C-S-H, $Ca(OH)_2$, and $CaCO_3$. The reactive aluminate phase of the ash consumed more $Ca(OH)_2$ by pozzolanic reaction and produced stratlingite (C2ASH8) *(26)*. Other studies have shown the potential of biomass ashes as alkali activators due to their high potassium content in alkali-activated concrete with the high content of coal fly ash or GGBFS and other precursors *(27)*.

### 2.1.3 *Chemical and Physical Properties*

The chemical composition of woody biomass ashes varies depending on the feedstock and combustion technology (fixed bed, pulverized fuel, or fluidized bed) *(26)*. The chemical composition of woody biomass is dominated by CaO, followed by moderate amounts of $SiO_2$ and lesser amounts of oxides of Mg, Al, K, and P *(28)*. The range of oxide contents for woody biomass was collected from the literature *(19)* and reported for tropical hardwood, temperate hardwood, softwood, temperate hardwood bark, and softwood bard.

The amount of CaO and the three oxides important for pozzolanic reactivity ($SiO_2$, $Fe_2O_3$, $Al_2O_3$) and the sum of the three oxides are shown in Figure 2.1(a). The mean values of some other oxides also important to the performance of concrete are shown in Figure 2.1(b). Figure 2.1(a) shows that the sum of the three oxides essential for pozzolanic reactivity is less than 30% for most ashes, which is significantly below the 70% threshold prescribed in ASTM C618 for pozzolanic reactivity *(29)*. However, a moderate amount of these oxides is present in softwood, about 30%. A minimum of 18% CaO is required for Class C fly ash, which is met by all wood types. Figure 2.1(b) shows that softwood, temperate hardwood, and softwood bark have lower amounts of alkalis than the other species.

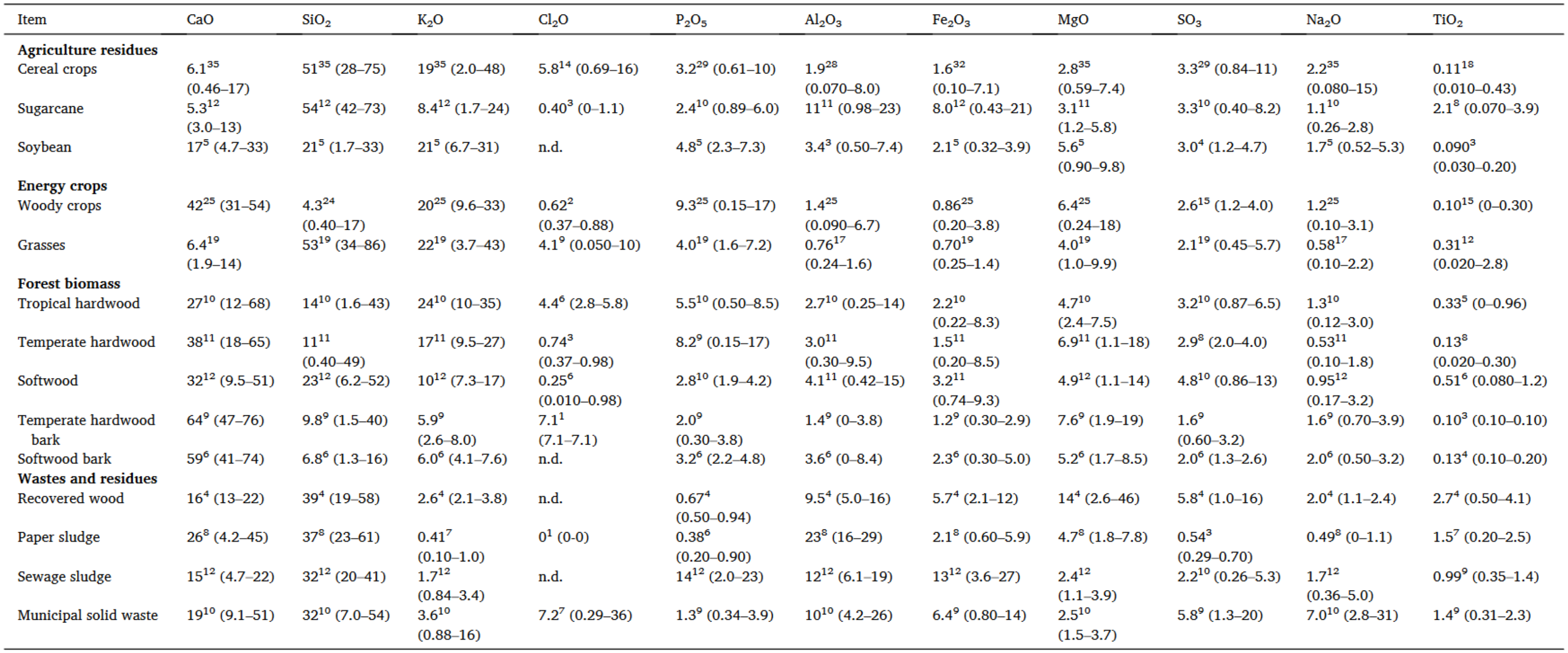
In contrast, hardwood has a high concentration of $K_2O$, followed by softwood and then temperate hardwood and softwood bark. High contents of water-soluble alkalis of potassium and sodium in a cementitious system could react with the amorphous silica content of aggregate and result in the formation of harmful alkali-silica gel inside the concrete, known as an alkali-silica reaction (ASR). The ASR gel could result in physical damage to concrete upon expansion and lead to failure. The amount of $SO_3$ is the lowest in temperate hardwood and softwood bark. Temperate hardwood and softwood have a higher $SO_3$ content than the allowable threshold for SCMs for concrete use of 4%, shown in Figure 2.1(b). The full report of the mean oxides is provided in Figure 2.2.



(a) (b)

Source: Zhai, Burke, and Stewart (2021) *(19)*.

**Figure 2.1: Mean percent weight of select oxides in woody biomass ash from the literature: (a) oxides essential for pozzolanic reactivity, and (b) other oxides important in terms of durability issues in concrete.**



| Item | CaO | $SiO_2$ | $K_2O$ | $Cl_2O$ | $P_2O_5$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | $SO_3$ | $Na_2O$ | $TiO_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Agriculture residues** | | | | | | | | | | | |
| Cereal crops | $6.1^{35}$ (0.46–17) | $51^{35}$ (28–75) | $19^{35}$ (2.0–48) | $5.8^{14}$ (0.69–16) | $3.2^{29}$ (0.61–10) | $1.9^{28}$ (0.070–8.0) | $1.6^{32}$ (0.10–7.1) | $2.8^{35}$ (0.59–7.4) | $3.3^{29}$ (0.84–11) | $2.2^{35}$ (0.080–15) | $0.11^{18}$ (0.010–0.43) |
| Sugarcane | $5.3^{12}$ (3.0–13) | $54^{12}$ (42–73) | $8.4^{12}$ (1.7–24) | $0.40^{3}$ (0–1.1) | $2.4^{10}$ (0.89–6.0) | $11^{11}$ (0.98–23) | $8.0^{12}$ (0.43–21) | $3.1^{11}$ (1.2–5.8) | $3.3^{10}$ (0.40–8.2) | $1.1^{10}$ (0.26–2.8) | $2.1^{8}$ (0.070–3.9) |
| Soybean | $17^{5}$ (4.7–33) | $21^{5}$ (1.7–33) | $21^{5}$ (6.7–31) | n.d. | $4.8^{5}$ (2.3–7.3) | $3.4^{3}$ (0.50–7.4) | $2.1^{5}$ (0.32–3.9) | $5.6^{5}$ (0.90–9.8) | $3.0^{4}$ (1.2–4.7) | $1.7^{5}$ (0.52–5.3) | $0.090^{3}$ (0.030–0.20) |
| **Energy crops** | | | | | | | | | | | |
| Woody crops | $42^{25}$ (31–54) | $4.3^{24}$ (0.40–17) | $20^{25}$ (9.6–33) | $0.62^{2}$ (0.37–0.88) | $9.3^{25}$ (0.15–17) | $1.4^{25}$ (0.090–6.7) | $0.86^{25}$ (0.20–3.8) | $6.4^{25}$ (0.24–18) | $2.6^{15}$ (1.2–4.0) | $1.2^{25}$ (0.10–3.1) | $0.10^{15}$ (0–0.30) |
| Grasses | $6.4^{19}$ (1.9–14) | $53^{19}$ (34–86) | $22^{19}$ (3.7–43) | $4.1^{9}$ (0.050–10) | $4.0^{19}$ (1.6–7.2) | $0.76^{17}$ (0.24–1.6) | $0.70^{19}$ (0.25–1.4) | $4.0^{19}$ (1.0–9.9) | $2.1^{19}$ (0.45–5.7) | $0.58^{17}$ (0.10–2.2) | $0.31^{12}$ (0.020–2.8) |
| **Forest biomass** | | | | | | | | | | | |
| Tropical hardwood | $27^{10}$ (12–68) | $14^{10}$ (1.6–43) | $24^{10}$ (10–35) | $4.4^{6}$ (2.8–5.8) | $5.5^{10}$ (0.50–8.5) | $2.7^{10}$ (0.25–14) | $2.2^{10}$ (0.22–8.3) | $4.7^{10}$ (2.4–7.5) | $3.2^{10}$ (0.87–6.5) | $1.3^{10}$ (0.12–3.0) | $0.33^{5}$ (0–0.96) |
| Temperate hardwood | $38^{11}$ (18–65) | $11^{11}$ (0.40–49) | $17^{11}$ (9.5–27) | $0.74^{3}$ (0.37–0.98) | $8.2^{9}$ (0.15–17) | $3.0^{11}$ (0.30–9.5) | $1.5^{11}$ (0.20–8.5) | $6.9^{11}$ (1.1–18) | $2.9^{8}$ (2.0–4.0) | $0.53^{11}$ (0.10–1.8) | $0.13^{8}$ (0.020–0.30) |
| Softwood | $32^{12}$ (9.5–51) | $23^{12}$ (6.2–52) | $10^{12}$ (7.3–17) | $0.25^{6}$ (0.010–0.98) | $2.8^{10}$ (1.9–4.2) | $4.1^{11}$ (0.42–15) | $3.2^{11}$ (0.74–9.3) | $4.9^{12}$ (1.1–14) | $4.8^{10}$ (0.86–13) | $0.95^{12}$ (0.17–3.2) | $0.51^{6}$ (0.080–1.2) |
| Temperate hardwood bark | $64^{9}$ (47–76) | $9.8^{9}$ (1.5–40) | $5.9^{9}$ (2.6–8.0) | $7.1^{1}$ (7.1–7.1) | $2.0^{9}$ (0.30–3.8) | $1.4^{9}$ (0–3.8) | $1.2^{9}$ (0.30–2.9) | $7.6^{9}$ (1.9–19) | $1.6^{9}$ (0.60–3.2) | $1.6^{9}$ (0.70–3.9) | $0.10^{3}$ (0.10–0.10) |
| Softwood bark | $59^{6}$ (41–74) | $6.8^{6}$ (1.3–16) | $6.0^{6}$ (4.1–7.6) | n.d. | $3.2^{6}$ (2.2–4.8) | $3.6^{6}$ (0–8.4) | $2.3^{6}$ (0.30–5.0) | $5.2^{6}$ (1.7–8.5) | $2.0^{6}$ (1.3–2.6) | $2.0^{6}$ (0.50–3.2) | $0.13^{4}$ (0.10–0.20) |
| **Wastes and residues** | | | | | | | | | | | |
| Recovered wood | $16^{4}$ (13–22) | $39^{4}$ (19–58) | $2.6^{4}$ (2.1–3.8) | n.d. | $0.67^{4}$ (0.50–0.94) | $9.5^{4}$ (5.0–16) | $5.7^{4}$ (2.1–12) | $14^{4}$ (2.6–46) | $5.8^{4}$ (1.0–16) | $2.0^{4}$ (1.1–2.4) | $2.7^{4}$ (0.50–4.1) |
| Paper sludge | $26^{8}$ (4.2–45) | $37^{8}$ (23–61) | $0.41^{7}$ (0.10–1.0) | $0^{1}$ (0-0) | $0.38^{6}$ (0.20–0.90) | $23^{8}$ (16–29) | $2.1^{8}$ (0.60–5.9) | $4.7^{8}$ (1.8–7.8) | $0.54^{3}$ (0.29–0.70) | $0.49^{8}$ (0–1.1) | $1.5^{7}$ (0.20–2.5) |
| Sewage sludge | $15^{12}$ (4.7–22) | $32^{12}$ (20–41) | $1.7^{12}$ (0.84–3.4) | n.d. | $14^{12}$ (2.0–23) | $12^{12}$ (6.1–19) | $13^{12}$ (3.6–27) | $2.4^{12}$ (1.1–3.9) | $2.2^{10}$ (0.26–5.3) | $1.7^{12}$ (0.36–5.0) | $0.99^{9}$ (0.35–1.4) |
| Municipal solid waste | $19^{10}$ (9.1–51) | $32^{10}$ (7.0–54) | $3.6^{10}$ (0.88–16) | $7.2^{7}$ (0.29–36) | $1.3^{9}$ (0.34–3.9) | $10^{10}$ (4.2–26) | $6.4^{9}$ (0.80–14) | $2.5^{10}$ (1.5–3.7) | $5.8^{9}$ (1.3–20) | $7.0^{10}$ (2.8–31) | $1.4^{9}$ (0.31–2.3) |

Source: Zhai, Burke, and Stewart (2021) *(19)*.

**Figure 2.2: Mean and ranges for the percent weight of select oxides in woody and agricultural biomass ash from the literature.**

The higher amount of alkalis and higher pH than coal fly ash is a characteristic of biomass ash. In fact, in some studies biomass ash was used as an alkali activator *(30)*. The high alkali content of biomass ashes is a concern because if these alkalies are available for participation in ASR in concrete, they could be harmful to concrete. However, a study in 2015 showed that despite the more than double available alkalies in co-fired biomass and coal ashes, they reduced ASR expansion by a comparable amount or much higher than Class C coal fly ash *(31)*. The ASR mitigation potential of biomass ashes needs to be investigated more.

Another characteristic of biomass ashes concerning its use in concrete is unburnt carbon content, which is not pozzolanic. The amount of unburnt carbon depends on biomass type, load, combustion, and operating conditions *(22)*. Regarding the combustion method, research has shown that the fluidized bed is more efficient than the grate furnace method in reducing unburnt carbon. In addition, unburnt carbon was more concentrated in the coarser grain size fraction in the grate furnace combustion *(22)*. Loss on ignition higher than the 6% requirement in ASTM C618 for coal fly ash has been reported for wood ash *(32)*. The high unburnt carbon has been shown to cause unstable air entrainment, which is required for freeze-thaw durability of concrete used in cold climate regions *(30)* and increases the water demand.

In terms of physical properties, the shape of the wood fly ash particles is highly irregular and highly porous *(33,34)*. Wood ash particles are more irregular, less rounded, and have a rougher surface texture than coal fly ash particles *(25,35,36)*. The average amount of wood fly ash smaller than 75 µm and 45 µm was reported as 50% and 31%, respectively *(32)*. In another study, the mean particle size of biomass fly ash varied between 10 and 500 µm depending on the source *(34,37,38)*. Mechanical size reduction of wood ashes may be required as certain particle fineness is required for the reactivity of SCMs. According to ASTM C618, the maximum amount larger than 45 µm should not exceed 34%. Overall, wood ashes are much lighter than portland cement. The specific gravities ranged from 2.4 to 2.48 for biomass fly ash and 1.70 for bottom ash. Low moisture content is desired in high-calcium ashes to avoid hardening. The moisture content limit is 3% for SCMs, according to ASTM C618. The moisture content of biomass ashes highly depends on handling, transport, and storage. For example, water is usually added to avoid dust clouds during transportation. For this reason, varied moisture contents were found in the literature. For example, 15% was reported for biomass fly ash and 22% for bottom ash in one study *(39)*, while another study *(25)* reported only 1.81% for moisture content in the studied wood ash.

### 2.1.4 *Feedstock Description and Supply*

The total estimated biomass resource potential of California is around 47 million T (42.63 million t) bone dry annually *(40)*. The feedstock consists of wood and other vegetal materials from the sources listed earlier (sawmills, forest management, agricultural, and urban wood). The 23 solid-fuel biomass electric generating plants in California reused around 7.3 T of the 47 million T (6.6 t of 42.63 million t) of biomass resource potential annually *(23)*. The feedstock is relatively well distributed across Northern California, with a higher concentration in forest areas north of the state and Sierra Nevada and agricultural lands in the Central Valley. The geographic distribution of biomass energy plants is shown in Figure 2.3.

### 2.1.5 *Process Description, Technology Readiness Level, and Potential Suppliers*

Figure 2.3 shows the geographical distribution of California’s 25 biomass-combustion energy production plants. According to the California Energy Commission, these plants produced 5680 GWh (5,680,000 MWh) in 2020, representing approximately 2.8 % of the electricity production in California that year and about 2.3% of the state’s renewable energy *(40)*.

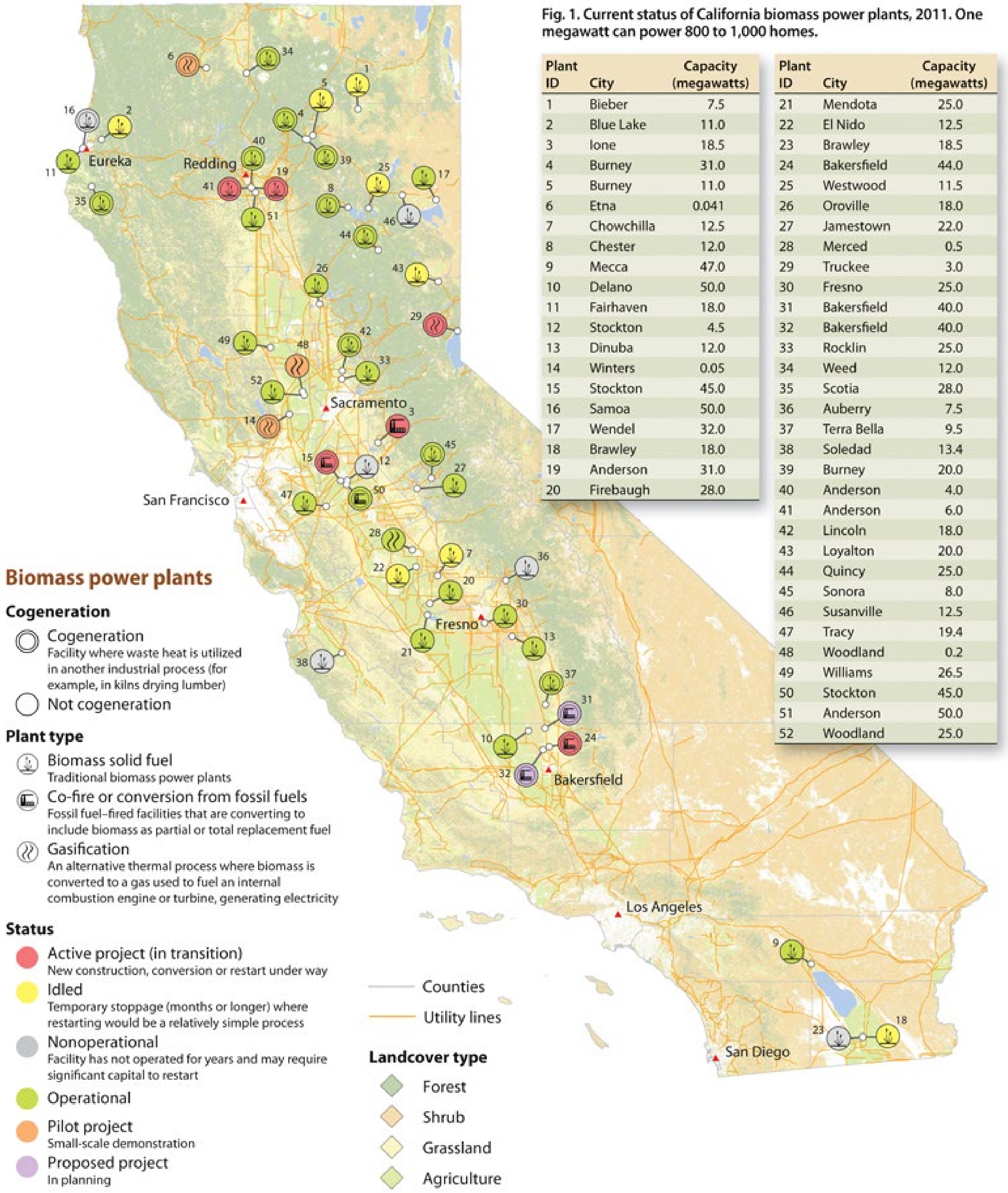


Fig. 1. Current status of California biomass power plants, 2011. One megawatt can power 800 to 1,000 homes.

| Plant ID | City | Capacity (megawatts) |
|---|---|---|
| 1 | Bieber | 7.5 |
| 2 | Blue Lake | 11.0 |
| 3 | Ione | 18.5 |
| 4 | Burney | 31.0 |
| 5 | Burney | 11.0 |
| 6 | Etna | 0.041 |
| 7 | Chowchilla | 12.5 |
| 8 | Chester | 12.0 |
| 9 | Mecca | 47.0 |
| 10 | Delano | 50.0 |
| 11 | Fairhaven | 18.0 |
| 12 | Stockton | 4.5 |
| 13 | Dinuba | 12.0 |
| 14 | Winters | 0.05 |
| 15 | Stockton | 45.0 |
| 16 | Samoa | 50.0 |
| 17 | Wendel | 32.0 |
| 18 | Brawley | 18.0 |
| 19 | Anderson | 31.0 |
| 20 | Firebaugh | 28.0 |
| 21 | Mendota | 25.0 |
| 22 | El Nido | 12.5 |
| 23 | Brawley | 18.5 |
| 24 | Bakersfield | 44.0 |
| 25 | Westwood | 11.5 |
| 26 | Oroville | 18.0 |
| 27 | Jamestown | 22.0 |
| 28 | Merced | 0.5 |
| 29 | Truckee | 3.0 |
| 30 | Fresno | 25.0 |
| 31 | Bakersfield | 40.0 |
| 32 | Bakersfield | 40.0 |
| 33 | Rocklin | 25.0 |
| 34 | Weed | 12.0 |
| 35 | Scotia | 28.0 |
| 36 | Auberry | 7.5 |
| 37 | Terra Bella | 9.5 |
| 38 | Soledad | 13.4 |
| 39 | Burney | 20.0 |
| 40 | Anderson | 4.0 |
| 41 | Anderson | 6.0 |
| 42 | Lincoln | 18.0 |
| 43 | Loyalton | 20.0 |
| 44 | Quincy | 25.0 |
| 45 | Sonora | 8.0 |
| 46 | Susanville | 12.5 |
| 47 | Tracy | 19.4 |
| 48 | Woodland | 0.2 |
| 49 | Williams | 26.5 |
| 50 | Stockton | 45.0 |
| 51 | Anderson | 50.0 |
| 52 | Woodland | 25.0 |

Source: Charnley and Long (2014) *(41)*.

**Figure 2.3: Biomass-combustion energy production plants in California based on 2011 data.**

**Process Description**

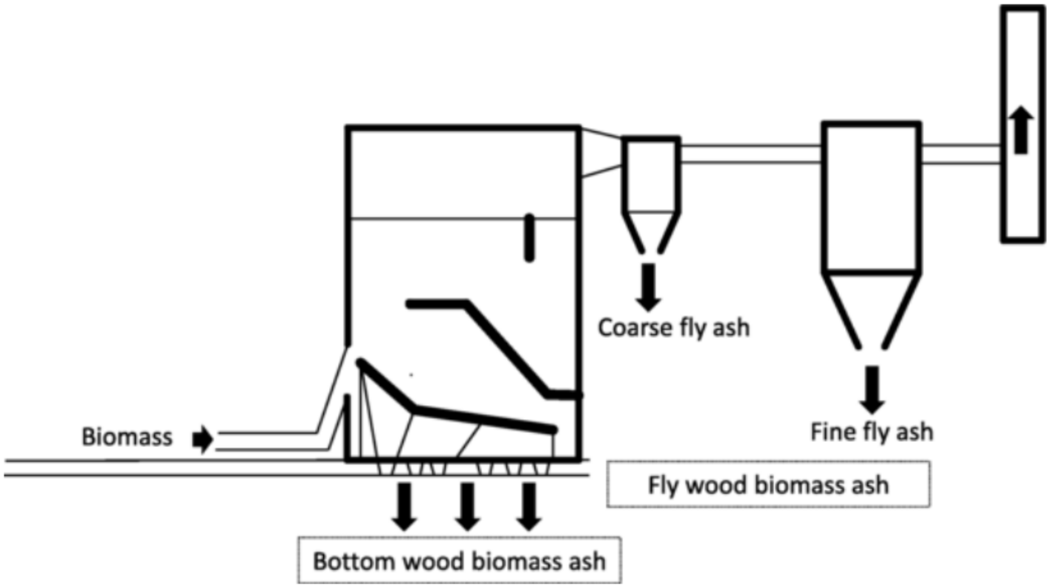
A graphical summary of the feedstock characteristics and various steps in processing the woody feedstock for energy generation at sawmills is shown in Figure A.1. A biomass-combustion energy production plant comprises a boiler, where combustion occurs, and a steam turbine that generates the electrical energy.

The properties of the ashes are related, among other factors, to the combustion process. Several relevant factors associated with the combustion process are the following:

- Type of boiler: Several types are currently used in California, including circulating fluidized beds, fixed grates, and traveling grates.
- Combustion temperature: Based on research about rice hull and straw combustion ashes, the combustion temperature is a critical variable for the ash properties, with combustion temperatures required for optimum electricity production (around 1832°F [1,000°C]) being higher than combustion temperatures needed for optimum ash performance as an SCM at around 1112°F (600°C) *(42)*.
- Exhaust control injections: Several products are injected into the combustion chamber or the exhaust stream to control NOx and $SO_2$ emissions (e.g., ammonia and limestone for NOx and $SO_2$ control, respectively).

Two types of ashes are produced at the plants, bed (bottom) ashes and fly ashes. The first type is collected by gravity at the bottom of the combustion chamber, while the second type is collected from the exhausts by the particulate control system (multiclones and electrostatic precipitators). A schematic diagram of ash generation at a typical biomass energy plant is shown in Figure 2.4.

The biomass-combustion bottom ashes require grinding to achieve fineness comparable to portland cement, fly ash, or similar SCMs. Feedstock leaching (e.g., in water) to remove undesirable alkalis may also be required.



Source: Štirmer and Carević (2022) *(43)*.

**Figure 2.4: Woody biomass ash generation at a biomass energy plant.**

## Technology Readiness Level

Some laboratory studies have shown that ashes from biomass-combustion energy production plants can be successfully used as a mineral admixture for concrete. However, more research is required as the full impact of biomass ashes on various properties of concrete is not well characterized, and the mechanism driving the behaviors is not fully understood. Once the required performance data are generated, standards and specifications must be developed to regulate the properties and quality of biomass ashes for concrete use. Therefore, biomass-combustion ashes used in concrete are at Level 3 on the NASA TRL scale, "proof-of-concept demonstrated, analytically and/or experimentally."

## Potential Suppliers

Based on initial consultation with Sierra Pacific Industries, a ratio of 0.12 T (0.10 t) of ash per MWh of electric energy production was estimated. This ratio has been applied to the gross production in California to estimate the amount of ash produced by each facility. Using this preliminary approach, it is estimated that around 400,000 T (362,873 t) of biomass-combustion ashes are produced yearly in California. Another method to estimate the amount of ash produced is based on the average ash weight fraction of woody biomass reported to be in the 6% to 10% range *(44)*. At this ash fraction, based on the 7.3 million T (6.62 million t) of biomass used in California in one year, the estimated amount of ash would be 438,000 T (397,000 t), which agrees well with the amount estimated above. The estimated 400,000 T (362,000 t) of ash covers a large portion of California's fly ash usage, estimated to be around 500,000 to 600,000 T (453,000 to 553,000 t) per year *(45)*.

**Current Use of Product**

The most common beneficial use of biomass ashes is as a soil conditioner, as these ashes have nutrient elements for plant growth, such as Ca, K, P, and Mg. Other uses are as soil stabilizers in roadbed construction. However, other than these applications, ashes are not recovered and reused in a specific application such as construction materials *(19)*.

**Agents Involved in Production and Distribution**

Most of the biomass-combustion energy production plants in California are associated with the California Biomass Energy Alliance *(23)*, whose goal is to "promote biomass energy as a means to reach the environmental and economic goals of California." Information regarding biomass energy production in California, including biomass-combustion plants, can be found on the website of the California Energy Commission *(40)*.

**Product Consideration in Caltrans Specifications**

California Department of Transportation (Caltrans) specifications currently do not include wood biomass ash as an accepted SCM for concrete.

### 2.1.6 *Performance in Concrete Based on the Literature*

**Impact on Fresh Properties**

A water demand of 118% higher than 100% portland cement paste was reported for wood fly ash-cement paste *(25)*. This higher water demand with the addition of biomass fly ash was a common finding in several other studies *(33,37,46)*. Another study showed that the mortar consistency decreases with an increase in biomass percentage in the mix *(37)*. This outcome was attributed to water absorption of the ashes (high carbon content) and the less rounded shape and rougher surface of the particles. For concrete, the workability and unit weight did not change much when 25% of wood fly ash was added to concrete in the study (*25*). However, other studies reported a decrease in the workability of concrete with the addition of waste biomass fly ash at a constant water-cement ratio *(37,46)*. The setting time of concrete was reported to remain unaffected by biomass fly ash at replacement levels lower than 30% *(33)*. Effects on set time were found to be comparable to coal fly ash *(33,36)*. Any delay in the set times is attributed to the dilution of the portland cement as a portion of the cement is replaced by the wood ash *(32)*.

## Impact on Strength

Overall, biomass ashes are expected to result in lower strength and slower strength development in concrete when compared to coal fly ash as they generally have a lower amount of reactive aluminosilicate content to participate in pozzolanic reactions. One study showed that the initial (3 to 14 days) compressive strength and split tensile strength were much lower in concrete containing 25% wood fly ash. However, beyond 28 days, those strength properties were comparable to the control concrete with no wood fly ash *(25)*. Wood ashes at 30% cement replacement resulted in about 20% lower 56-day compressive and flexural strength than cement alone and cement with coal fly ash at the same replacement level *(33)*. On the other hand, wood ash at 10% cement replacement resulted in a 12% compressive strength increase versus cement alone after one year *(47)*. These results indicate that adding biomass ash usually results in a slower strength gain in concrete, and strength decreases as the amount of biomass ash increases *(33,34,37,46,48)*. Another study similarly showed that compressive strength decreased with increased ash content *(47)*.

## Impact on Durability

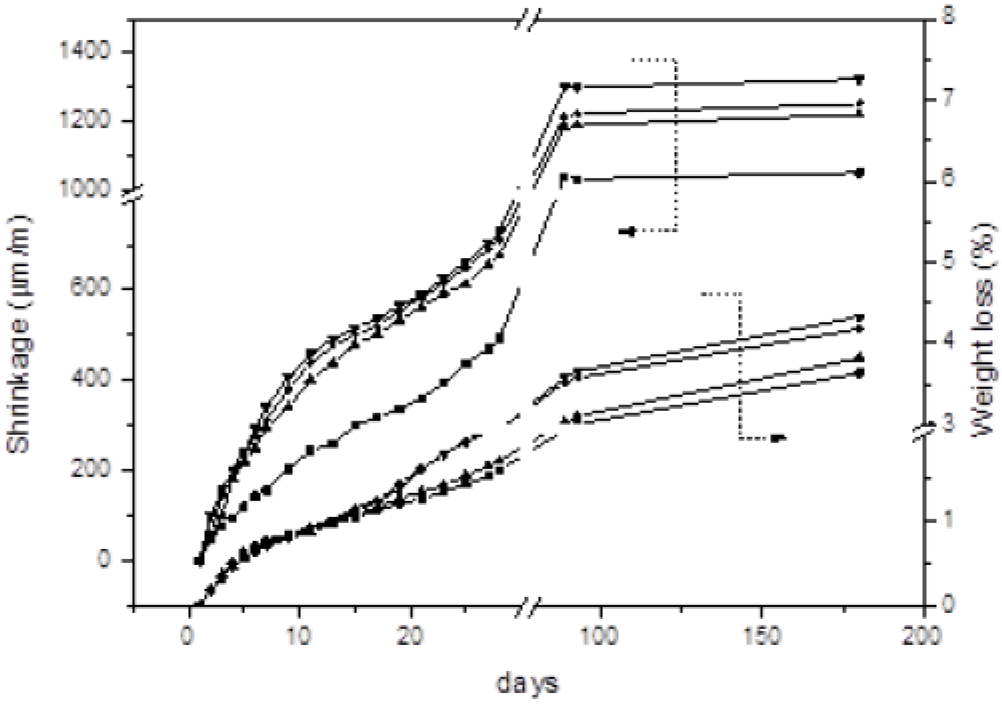
The high available alkali content in the pore solution from the binder phase, aggregate, or environment could react with available amorphous silica from aggregate sources and result in ASR gel, which is expansive in volume and could lead to serious damage in concrete. SCMs low in calcium oxide, such as Class F coal fly ash, are successful as ASR mitigators *(49)*. In one study, the tested biomass ashes reduced ASR expansion to 0.1% in 6 months. Biomass ashes were more effective in mitigating ASR expansion in concrete than Class C fly ash. However, the biomass ashes were from co-fired plants that burned 10% to 20% switchgrass mixed with 80% to 90% coal *(48)*. Whether biomass ashes can effectively mitigate ASR expansion has not been studied and needs more research.

Another durability issue in concrete occurs in high-sulfate exposure environments, leading to sulfate penetration into the concrete. The sulfate can react with certain hydrate phases, develop expansive ettringite, and damage the concrete. Sulfate attack could also develop internally in concrete from sulfate-rich aggregate or the cementitious phases. Not many studies have investigated the impact of biomass ash on the sulfate attack resistance of concrete. However, one study showed improved sulfate resistance with 10% cement replacement with wood biomass ash in mortars *(50)*.

The electrical resistivity of the cementitious material is used as a simple, nondestructive method to evaluate its durability. The concept is that higher electrical resistivity indicates a more refined and less interconnected pore network, and the pore solution then conveys less electrical charge. Overall, cementitious systems with more refined pore systems are more resistant to the penetration of harmful ions (such as sulfates and chlorides) carried by water into the concrete; thus, the concrete with a higher electrical resistivity is considered more durable. One study investigated the impact of biomass ash on the electrical resistivity of mortar. In that study, using biomass bottom ash in mortar did not have a significant effect on the electrical resistivity, but it increased the chloride diffusion compared to plain mortar *(47)*. Another study showed wood ash with nearly 53 wt% silica oxide, 13% alumina, and nearly 6% iron oxide resulted in better performance in terms of electrical resistivity than the control after 28 days *(50)*. Conversely, another study showed that wood fly ash concrete had lower chloride permeability than the control OPC concrete *(30)*.

Durability to damage from freeze-thaw cycling in concrete is achieved by entraining a sufficient amount of well-distributed small air voids into concrete. As discussed earlier, a relatively higher loss on ignition of wood biomass ash could interfere with the air-entraining agent functionality and reduce the amount of entrained air *(21)*. A study showed that biomass fly ash at a 15% replacement rate of OPC in concrete increased freeze-thaw durability. However, the source of the biomass ash was not provided in the study. Based on the reported chemical composition in the study, the biomass fly ash used had a high silica of 68.53% *(51)*.

Another durability issue in concrete is its potential to crack due to excessive drying shrinkage. Many SCMs, especially those with high fineness and unburnt carbon, can lead to a less workable concrete mixture. This issue should be mitigated using water-reducing admixtures and not adding more water. A higher water-to-cement ratio concrete is well known to result in more drying shrinkage and other durability issues. A study showed forest biomass ash adversely affected the drying shrinkage of mortar, shown in Figure 2.5. According to the study, all mortar mixes had the same water amount *(52)*. More studies are needed to fully understand how wood biomass ashes affect the drying shrinkage behavior of cementitious systems.



*Note:* ■ 0% ▲ 10% ● 20% ▼ 30%

Source: Candamano et al. (2014) *(52)*.

**Figure 2.5: Shrinkage and weight loss of mortar containing 0 wt%, 10 wt%, 20 wt%, and 30 wt% forest biomass ash.**

A summary of the impact of biomass ash on various properties of cement-based systems based on a literature review is shown in Table 2.1.

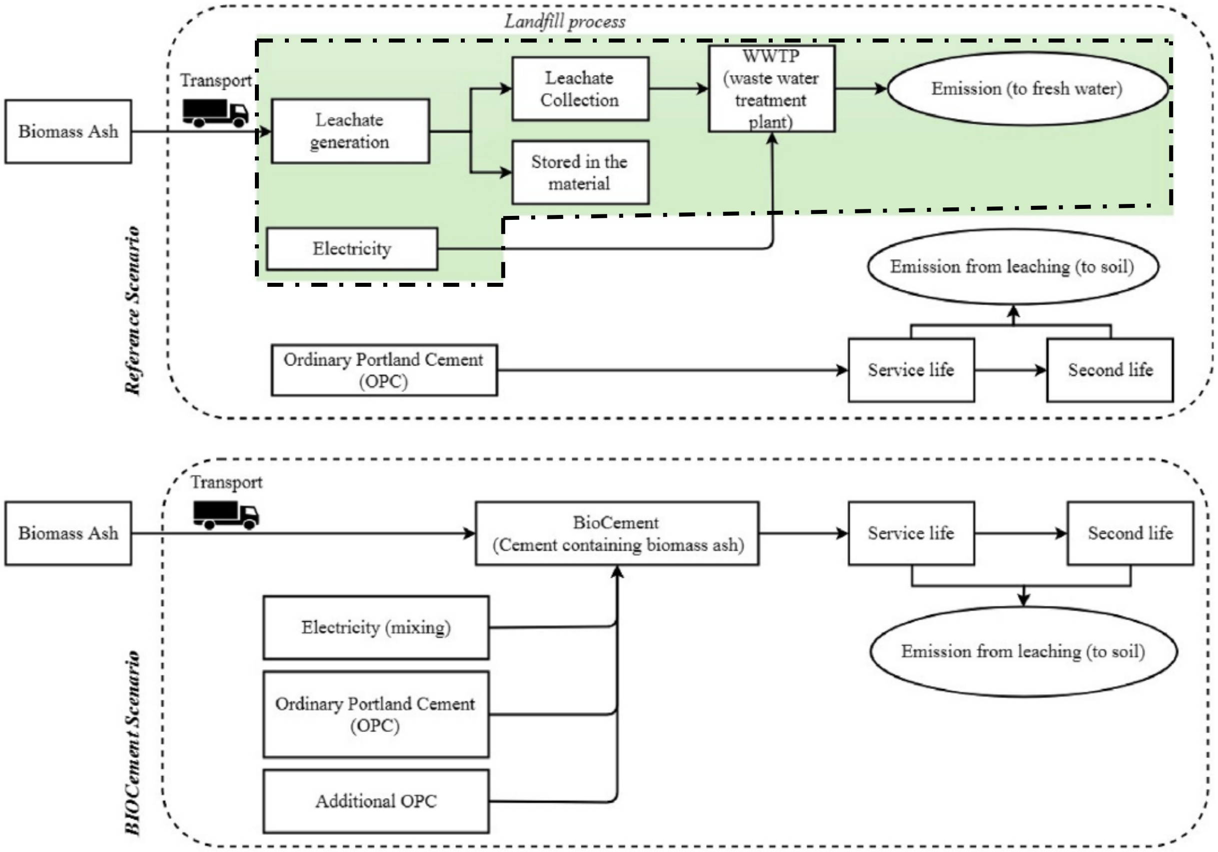
**Table 2.1: Summary of the Effect of Biomass Ash on the Properties of Cement-Based Materials**

| Property of Concrete | Comparison to 100% OPC Concrete |
|---|---|
| Water demand | Increase or no change |
| Early strength | Decrease |
| Late strength | No change at low replacement rates |
| Pozzolanic reactivity | Low to moderate |
| Setting time | No change or slight delay from the dilution of cement |
| Drying shrinkage | Needs more research |
| Alkali-silica reaction | Needs more research |
| Sulfate attack resistance | Needs more research |
| Freeze-thaw durability | Increase |

### 2.1.7 *Environmental Considerations*

Biomass-combustion ashes can be regarded as a waste product of energy generation because they have no economic value beyond the cost of their processing and transportation. As a waste product, the environmental burdens associated with the ashes' production can be attributed to energy generation. To assess the environmental impacts of biomass ashes as a concrete mineral admixture, all the required treatments (e.g., grinding) to make the ashes suitable as an SCM must be considered.

One study performed LCA of the reuse of biomass fly ash as an SCM in the mortar as an alternative to the scenario of landfilling the ash *(53)*. The study's goal was to compare the potential impacts associated with the current waste management of fly ash from biomass combustion with its potential reuse as an SCM in cement formulations as an alternative management strategy. Two scenarios were studied, and a comparative analysis was performed. Figure 2.6 represents the two scenarios that were considered in that study. The first scenario included the use of portland cement as the binder material and transporting of the biomass ash to the landfill (reference scenario, inside box with dashed line), while the second scenario considered the use of BioCement, where the biomass fly ash was used as an SCM with a reduced amount of portland cement. The functional unit of the study was set to be 1 metric ton of binder material. The dashed line indicates the boundary conditions for the LCA model.



Source: Tosti et al. (2020) *(53)*.

**Figure 2.6: Flow chart showing the system boundaries for the two scenarios.**

A total of 13 impact categories recommended by the European Commission in the *International Reference Life Cycle Data System (ILCD) Handbook* were calculated in the study for the two scenarios *(54)*. The study concluded that using biomass ash as an SCM is preferable over landfilling for all the nontoxic categories. The study also found that where the replacement was 20% and 40% by weight of the concrete, GWP ($CO_2$-eq) reduction was between 11% and 26% with the use of biomass as an SCM compared to biomass being landfilled. In addition, human toxicity and ecotoxicity midpoint impacts were found to be lower for the biomass ash-blended cement scenario.

Another study investigated the suitability of wood biomass fly ash (BFA) to be used as an SCM with ordinary portland cement *(55)*. The study evaluated the effects of portland cement replacement by high levels of BFA on the environment. The functional unit of the study was 1 metric ton of final blended mortar defined by 0%, 10%, 20%, 30%, 40%, 50%, 60%, and 70% weight of BFA. A total of 15 impact categories were studied using the IMPACT 2002+ methodology (v3.15, Simapro 8.5). The data for the raw materials production, processing, transport emissions, and energy production were acquired from the ecoinvent database (v3.5) *(55)*.

The impact categories used in the study were the following: aquatic acidification, aquatic ecotoxicity, aquatic eutrophication, carcinogens, global warming, ionizing radiation, land occupation, mineral extraction, non-carcinogens, nonrenewable energy, ozone layer depletion, photochemical oxidation, respiratory inorganics, respiratory organics, terrestrial acidification/nitrification, and terrestrial ecotoxicity. The environmental midpoint impact categories were used to determine the endpoint impact categories, which included human health, ecosystem quality, climate change, and resources *(55)*. The study concluded that approximately 25% potential savings could be achieved in primary energy consumption and carbon dioxide emissions when portland cement was partially replaced with 30% BFA replacing portland cement. At this replacement level, the mechanical properties of the BFA concrete were maintained at acceptable levels. The overall environmental benefits can reach 50% if higher amounts of BFA are used, but the loss in mechanical properties would limit the application *(55)*.

### 2.1.8 *Cost Considerations*

Biomass ashes have some reuse applications, but these applications are of low or zero value. Based on conversations with biomass plants as part of this literature review, most ashes are disposed of in landfills or transported to farms as soil amendments. Therefore, the current use of biomass-combustion ashes provides either minimal economic benefits or imposes expenses on plants as they arrange to transport ashes to farms. However, any treatments required to render the ashes usable as SCM (e.g., grinding of bottom ash, drying) will be added costs.

## 2.2 Rice Straw Ash

Much scientific research has been devoted to rice hull ash (RHA) use in concrete, as hulls are collected and available off-site at the mill as part of the grain processing and used as a fuel source for various processes *(56)*. However, there has been much less focus on ash from rice straw, and the high-value utilization of rice straw biomass still needs development *(56)*. Therefore, because RHA has a rich history of research as SCM in concrete and it is already an accepted ASCM in Caltrans specifications for minor concrete, this report focuses on rice straw ash (RSA) as an ASCM for concrete; its technical, economic, and environmental benefits; and its pitfalls *(57)*.

### 2.2.1 *Product Description*

The United States is among the top 15 rice producers in the world. Rice straw is a residual byproduct of rice cultivation after harvest. Straw can be collected and processed into other useful products, burned and left on the field to decompose, or burned in open fields. However, open-field burning of a straw causes air pollution and is banned in California, and leaving straw on the field drives methane emissions *(58)*. Therefore, developing economic and socially acceptable reuse applications for straw is advantageous.

Ash can be derived from the combustion of rice straw as part of energy generation, including bioethanol, biogas, bio-oil, and direct burning *(56)*. However, there are challenges with using straw as feedstock for these operations. For instance, for bioethanol production, the lignin content of straw must first be removed by chemical methods to enable fermentable sugars by biocatalysts *(56)*. Straw as a replacement for coal or oil as fuel in energy generation also faces some challenges as certain elements (potassium, chloride, sodium) present in rice straws could lead to slagging, agglomeration, and fouling in furnaces and other thermal conversion facilities *(59)*. Further feedstock treatment may be required, such as rinsing, washing, and soaking to leach the harmful elements and then drying for burning. As a result, RSA is not currently available at scale in California as rice straw is not used as feedstock in biomass-combustion energy production plants.

### 2.2.2 *Acting Mechanism in Concrete*

The primary mechanism of RSA in concrete is expected to be pozzolanic reactions from the high amorphous silica content (similar to RHA). Rice straw ash could meet the requirements of ASTM C618 in terms of oxide content for Class N and Class F pozzolans. It is important that rice straw is burned below the silica crystallization temperature as crystalline silica, such as tridymite or cristobalite, does not react with portlandite *(60)*. However, much of the research on pozzolanic benefits from rice-based ashes is on RHA and only a few studies used RSA as a pozzolan in concrete. Therefore, more research is needed to fully understand how RSA reacts in the cementitious system, especially considering the high alkali metal content of unleached straw.

### 2.2.3 *Chemical and Physical Properties*

The rice straw is composed of lignin, cellulose, hemicellulose, and ash, which is the primary silica component of the waste. Table 2.2 shows the quantitative composition of rice straw by weight percentage, which is similar to many common natural fibers *(61)*.

**Table 2.2: Composition of Rice Straw**

| Constituent | Rice Straw (%) |
|---|---|
| **Cellulose** | 32.0–38.6 |
| **Hemicellulose** | 19.7–35.7 |
| **Lignin** | 13.5–22.3 |
| **Ash** | 10–17 |

Source: Mirmohamadsadeghi and Karimi (2020) *(62)*.

Chemical composition is shown for an example RSA in Table 2.3. The table shows that RSA is high in silica content (62% to 82%). However, RSA silica content is less than RHA by about 10% *(60)*. RSA is also relatively high in alkali metals, such as potassium (11.87% in Table 2.3), compared to RHA. This high alkali metal content, if available for reaction with amorphous silica in the aggregate, may lead to durability issues, specifically ASR in concrete, but it has not been determined experimentally to date. In addition, if not leached from straw fuels, the same elements have been shown to cause glass buildup in various parts of the combustion system at biomass power plants *(59)*.

**Table 2.3: Oxide Content of Rice Straw Ash**

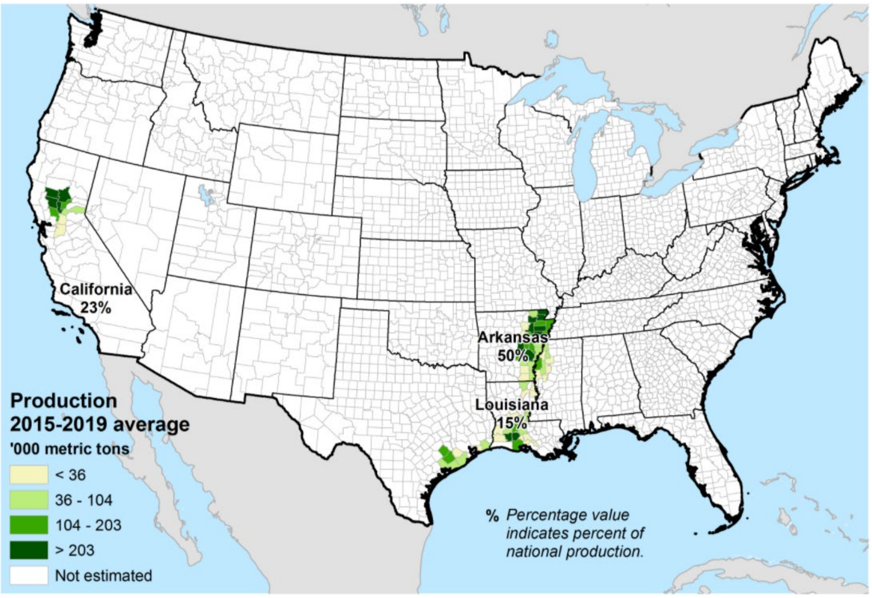
| Oxide | Percent Weight (%) |
|---|---|
| $SiO_2$ | 67.78 |
| $Al_2O_3$ | 1.54 |
| CaO | 1.11 |
| MgO | 1.11 |
| $Na_2O$ | 1.48 |
| $K_2O$ | 11.87 |

Source: AboDalam et al. (2022) *(63)*.

In one study, RSA was produced in uncontrolled burning conditions and sieved through a 0.09 mm sieve. The resulting RSA had a mean particle size of 3.3 µm with a specific surface area of 1.846 $m^2/g$ and a specific gravity of 2.25 *(64)*. The same specific surface area and specific gravity were obtained for RSA produced in another study that produced RSA in a controlled temperature incinerator *(1)*. However, a larger particle size distribution with a median of 44 to 62 µm was obtained in the latter study.

### 2.2.4 *Feedstock Description and Supply*

California produces approximately 23% of all the rice produced in the United States, with a potential availability of 400,000 T (362,873 t) of rice straw and rice hull ash annually. Figure 2.7 shows the average rice production in the United States between 2015 and 2019. In 2021 alone, California produced about 2,016,000 T (1,828,884 t) of rice *(65)*. Most of the rice grown in California is grown in the Sacramento Valley, shown in Figure 2.7. It is estimated that 2.20 to 3.30 lb. (1 to 1.5 kg) of straw is produced for every 2.20 lb. (1 kg) of paddy rice cultivated, which is a maximum grain-to-straw ratio of 1:1.5 *(66)*. Thus, based on the rice production in California, an estimated 2,000,000 T (1,814,369 t) of rice straw is generated.



Source: US Department of Agriculture *(67)*.

**Figure 2.7: Geographical distribution of rice production across the United States.**

### 2.2.5 *Process Description, Technology Readiness Level, and Potential Suppliers*

**Process Description**

Treatments for transforming rice straw into ash after cultivation are pre-combustion, combustion, and post-combustion *(68)*. Typical pre-combustion pretreatments include drying straws and leaching, while post-combustion treatments are primarily cooling and grinding. One study established that drying rice straws before combustion could minimize remnant carbon present in the straw *(69)*. Another study showed that water or acid leaching is crucial to reducing the potassium content in the straw, which could otherwise inhibit the combustion process or reactivity of the ash *(42)*. Decreases in metallic alkalis were obtained using water, acid, and alkali as leaching agents, although varying efficiencies were observed *(69)*. Leaching treatments may be useful for generating coproducts such as fertilizer. Figure A.2 summarizes the treatment processes for producing RSA from rice straw.

Key combustion parameters that influence the reactivity of RSA include combustion type (controlled or uncontrolled), time, technology, and temperature. Maximum reactivity and amorphousness of RSA are achieved under low combustion temperatures between 932°F and

1292°F (500°C to 700°C) to avoid the crystallization of amorphous silica that occurs beyond this temperature range *(70)*. A temperature lower than this range will result in high remnant carbon content, while a temperature higher than this produces crystalline silica and thus necessitates grinding to increase reactivity *(71)*. Typical combustion times are over 12 hours for the combustion temperature range of 572°F to 932°F (300°C to 500°C), 12 to 24 hours for 932°F to 1292°F (500°C to 700°C), and less than one hour for temperatures from 1292°F (700°C) and above.

Grinding as a post-combustion treatment also influences the reactivity of ash. Different levels of grinding resulting in different ash fineness have been shown to impact the pozzolanic properties of RSA. However, no significant crystalline mineralogy or chemical composition variations occur when grinding time increases *(72)*. The cooling process also influences ash reactivity. One study noted that slow cooling reduces quantities of silanol groups in combusted straw and subsequently weakens pozzolanic reactivity, while rapid cooling results in an increased network of reactive surfaces, which enhances reactivity *(71)*. Thus, pre-combustion, combustion and post-combustion treatments must be controlled and optimized to maximize the desired pozzolanic characteristic of RSA as an SCM.

In only one study was a pre-combustion treatment applied to rice straw, and other produced resources, including steam and potassium-rich fertilizer, were considered *(73)*. Results showed that water leaching reduced potassium from the straw more than acid leaching. However, using acid improved the removal of most other soluble elements, including Mg, Cu, Na, Fe, Ca, and Zn. It was also shown that changes in concentrations of these soluble elements were minimal and unlikely to influence ash reactivity.

## Technology Readiness Level

While significant progress has been made toward using RHA in concrete on an industrial scale, such as adopting state department of transportation specifications, RSA has only been tested at a laboratory scale as an SCM to produce mortar and concrete with varied treatment conditions. Based on these studies, there appears to be limited knowledge of the effects of different straw treatments on the ash reactivity and reclamation of leachates such as potassium as fertilizer.

Furthermore, the combustion condition is critical for the cogeneration of energy and straw ash. The combustion temperature for generating electricity from rice-based feedstock is about 1832°F (1000°C), while the optimum temperature for the desired ash property as an SCM is around 1,112°F (600°C). Thus, developing strategies or technologies to cogenerate electricity and ash while burning straw is essential. Based on the NASA Technology Readiness Level (TRL), using RSA as a mineral admixture in portland cement concrete (PCC) is at Level 3, "proof-of-concept demonstrated, analytically and/or experimentally."

### Potential Suppliers

According to a study, California produced 2,052,568 T (1,862,058 t) of rice in 2021, indicating the generation of approximately 2,000,000 T (1,814,369 t) of rice straw using a 1:1 grain-to-straw ratio *(65)*. Most of the rice grown in California is in the Sacramento Valley. Based on a 10% ash content assumption, 200,000 T (181,436 t) of RSA could be available in California. However, due to pretreatment requirements to avoid damage to combustion systems, straw is not currently used as direct fuel, and RSA is therefore not available at the industry scale from energy plants.

### Current Use of Product

Figure 2.8 shows some current and potential uses of rice straw in California. As shown in the figure, some of the current uses of the product include cattle feed, animal bedding, fertilizer offsetting, and wallboard production. CalPlant produces Eureka MDF, a medium-density fiberboard from rice straw. About 280,000 T (254,011 t) of post-harvest rice straw are recovered and converted to fiberboard *(74)*. The exact quantities of rice straw used as cattle feed, animal bedding, and wattles will be determined from this research via site visits. Currently, Wadham Energy, a rice hull-to-energy plant in California, uses rice hulls to generate electric energy *(75)*. Ashes produced from the combustion process are usually used as soil improvement for agricultural purposes or sold to the steelmaking industry. There may also be a potential to burn rice straw for electricity generation, provided metallic impurities are removed before the combustion process.

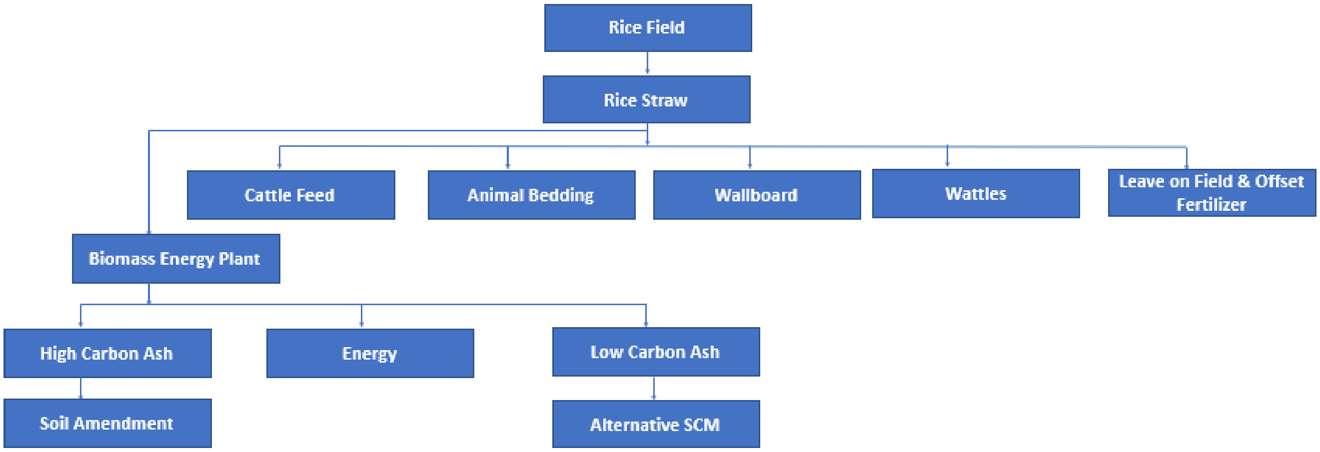


**Figure 2.8: Current use of rice straw (dashed line box) and potential future use of rice straw (solid line box).**

## Agents Involved in Production and Distribution

Agents involved in the production and distribution of rice straw ash and the generation of electricity from rice-based waste include rice farmers, rice balers, concrete suppliers, energy plants, and potassium fertilizer companies. These agents were interviewed to understand business as usual in their operations and their perception of using rice straws for the coproducts (ash, fertilizer, electricity).

## Product Consideration in Caltrans Specifications

Caltrans specifications do not include provisions for rice straw ash. However, Caltrans specifications allow RHA to comply with AASHTO M 321 with a usage of 5% to 15% as an SCM in minor concrete *(76)*.

### 2.2.6 *Performance in Concrete Based on the Literature*

## Impact on Fresh Properties

Rice straw ash has been tested in concrete and mortar mixes only in a few studies and appears to reduce the workability of the system in general. For example, it was shown that the workability of lightweight self-compacting concrete (LWSCC) decreased as the percentage of RSA increased since RSA particles have a higher surface area than OPC particles *(77)*. In another study, the effect of rice straw ash on the behavior of high-performance concrete (HPC) was studied. The compressive, tension, and flexural strength of the four different concrete mixes (RSA0, RSA5, RSA10, and RSA15) based on the percent replacement were investigated. The findings showed that RSA reduced the workability of concrete, while concrete with 10% RSA replacement had the greatest 28-day compressive strength *(78)*. RSA was shown to increasingly delay the initial and final setting times of the cement paste with increased replacement rates *(1)*. Table 2.4 presents a summary of the literature between 2009 and 2021 that studied the production of RSA and its use in different concrete or mortar mixes.

**Table 2.4: Summary of Method and Properties Investigated in Selected Literature**

| Reference | Treatments | Replacement Level | Properties |
|---|---|---|---|
| Eldin et al. (2013) *(78)* | Pre-combustion: Unstated | HPC: RSA (5%, 10%, and 15%) | Workability, compressive strength, tensile strength, flexural strength. |
| | Combustion: Unstated | | |
| | Post-combustion: Unstated | | |
| Pandey and Kumar (2020) *(64)* | Pre-combustion: None | Concrete pavement: RSA (5%-30%), MS (2.5%-10%), RSA (5%, 10%) + MS (5%, 7.5%) | Compressive strength, tensile strength, flexural strength, air entrainment, saturated water absorption, chloride ion penetration, acidic exposure |
| | Combustion: Open-air burning | | |
| | Post-combustion: Sieving | | |
| Agwa et al. (2020) *(77)* | Pre-combustion: None | LWSCC: RSA (5%, 10%, and 20%) | Workability, compressive strength, tensile strength, flexural strength |
| | Combustion: 700°C furnace | | |
| | Post-combustion: Cooling, grinding, and sieving | | |
| Hidalgo et al. (2021) *(79)* | Pre-combustion: None | Mortar: RSA (15% and 30%) | Compressive strength, flexural strength |
| | Combustion: 500°C using a self-made burner (outdoor) | | |
| | Post-combustion: Grinding, sieving | | |
| Cunningham et al. (2021) *(42)* | Pre-combustion: Milling, leaching | Mortar: RSA (15%) | Compressive strength |
| | Combustion: Torrefaction, controlled burning | | |
| | Post-combustion: Unstated | | |

## Impact on Strength and Durability

Mechanical properties (compressive, tensile, and flexural strength) and durability performance of the concrete and mortar from the literature are presented in Table 2.5. Conflicting results were obtained for flexural and tensile strength, indicating differences in the water-to-cement ratio and fine-to-coarse aggregate ratio. One study found that RSA can replace OPC up to 10% in concrete without reducing the compressive strength of the control mix *(64)*. Another study found that the flexural strength for mortar mix with 15% and 30% RSA replacement was lower than for the control after 28 days *(78)*. In another study, a 5% RSA blended with 7.5% microsilica produced the maximum improvement in compressive strength over the OPC control *(64)*.

**Table 2.5: Summary of Concrete/Mortar Performance Based on the Literature**

| Properties | Performance Compared to 100% OPC in Concrete | Reference |
|---|---|---|
| Workability | Decrease | Damatty et al. (2009) and Agwa et al. (2020) *(77,80)* |
| Compressive strength | Increase | Pandey et al. (2020), Agwa et al. (2020), Eldin, et al. (2013), Munshi et al., (2019), and Hidalgo et al. (2021) *(64,77,78,79,81)* |
| Flexural strength | Increase | Pandey et al. (2020) and Eldin, et al. (2013) *(64,78)* |
| | Decrease | Agwa et al. (2020) and Hidalgo et al. (2021) *(77,79)* |
| Tensile strength | Increase | Pandey et al. (2020) and Agwa et al. (2020) *(64,77)* |
| | Decrease | Eldin et al. (2013) *(78)* |
| Carbonation | Decrease | Pandey et al. (2020) *(64)* |
| Chloride permeability | Decrease | Pandey et al. (2020) *(64)* |
| Water absorption | Decrease | Pandey et al. (2020) *(64)* |

### 2.2.7 *Environmental Considerations*

#### Global Warming Potential

Rice straw ash-blended concrete is expected to have lower GHG emissions than 100% OPC concrete due to reduced OPC use while improving some properties of concrete. However, the environmental impact varies depending on the pretreatment methods, combustion method and conditions, and post-combustion treatments. Furthermore, processes such as leaching and milling may be additional contributors to the environmental impacts. In one study, it was shown that chemical leaching drives the net GHG emissions in rice-based ash/energy generation. Still, it may be possible to minimize the emissions if the leaching solution is recycled and recovered as fertilizer *(73)*.

Different studies have assessed the environmental impact of generating heat or electricity from rice straws *(82–85)*. However, these studies did not consider leaching as a pretreatment method for effective combustion and did not consider ash as a valuable material. One study assessed the impacts of four rice straw utilization methods: (1) direct combustion for electricity, (2) biochemical conversion to bioethanol and biogas, (3) thermochemical conversion to bio-dimethyl ether, and (4) incorporation into the soil as fertilizer *(82)*. The study showed rice straw ethanol had the highest net GHG emission reduction (kg $CO_2$-eq/ton dry straw), followed by rice straw bio-dimethyl ether and rice straw electricity. Rice straw fertilizer had the least net GHG emission reduction.

Another study compared rice straw-based power generation with natural gas and coal *(83)*. Findings from the study showed that rice straw power generation could reduce GHG emissions by approximately 1.05 kg $CO_2$-eq/kWh and 1.79 kg $CO_2$-eq/kWh with natural gas and coal-based powered generation, respectively. Another study assessed and compared the environmental impacts of four rice straw utilization scenarios: (1) incorporation into the field as fertilizer, (2) animal fodder, (3) electricity, and (4) biogas *(84)*. The study showed that straw utilization for electricity and biogas production had the highest environmental benefits in terms of GWP. A study investigated and compared the energy, net GHG emission reduction, and economic impacts of a rice straw-based heat generating system (RBHG) with open-field burning and incorporation of straw into the soil *(85)*. The results show that RBHG had a greater net GHG reduction than soil incorporation and open-field burning.

## Life Cycle Assessment Performed by the UCPRC

A detailed LCA was undertaken to assess the environmental impacts of rice straw utilization for fertilizer production, ash for concrete products, and electricity generation. The functional unit of the study was 1.1 T (1 t) of rice straw. A commercial database, GaBi *(18)*, was used as the data source for the life cycle inventories of the production of materials, fuels, and electricity. Secondary data were derived from literature and standard articles. The California Air Resources Board (CARB) EMission FACtors (EMFAC) model was used to determine the fuel use of certain equipment *(86)*.

The scope of the study considered the field-to-gate model. The upstream processing included rice straw collection (raking, baling, and loading) and transportation, and downstream processing included rice straw pretreatment and processing into ash and electricity, water treatment, and reverse osmosis products transportation. Figure 2.9 shows the process flow diagram for the study.

The environmental impacts of the stages before collection or baling (cultivation and harvesting) and the land use changes were not included in the scope of this study. The environmental consequences of the plants' infrastructure, maintenance, human labor, and capital expenditure were not considered in this study. The following assumptions were made:

1. Leaching, drying, and filtration processes were assumed to occur on the farm.
2. The transportation of rice straw from the farm to the energy plant was assumed to be a distance of 25 miles.
3. The transportation of brine and waste from the reverse osmosis process to their relevant destinations was assumed to be a distance of 25 miles.

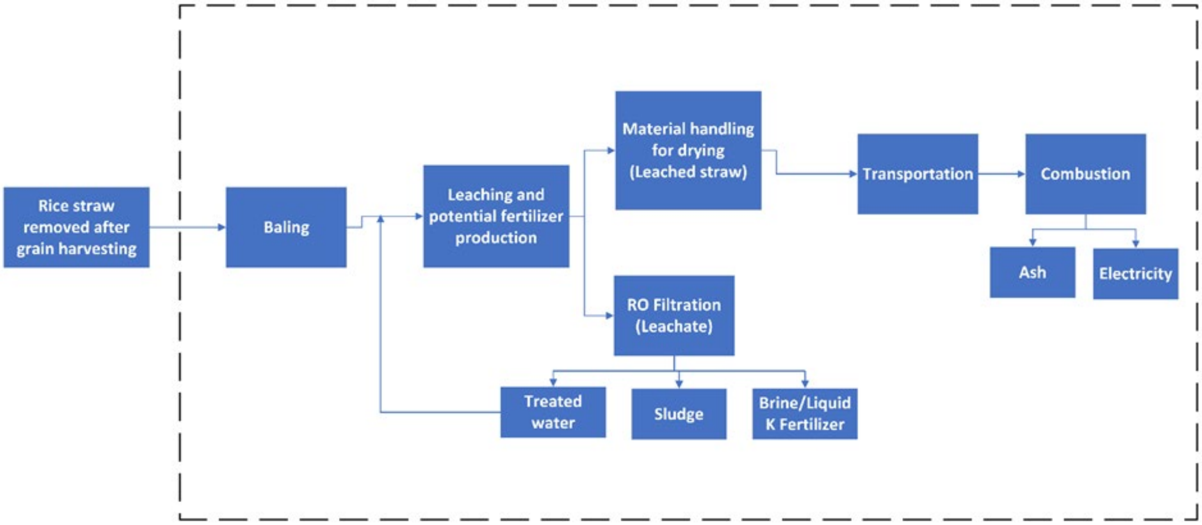


**Figure 2.9: Process flow diagram for ash and energy generation from rice straw.**

Data and references used in the study are presented in Table 2.6.

### Table 2.6: Inventory Data for Inputs and Outputs of Rice Straw Ash and Electricity Generation per 1 T (0.90 t) of Dry Rice Straw

| Process | Operation | Value | Unit | References |
|---|---|---|---|---|
| Baling Process | Bailer effective fuel consumption | 18 | lit/hr | California Air Resources Board (2022) *(86)* |
| | Fuel used | 0.8 | hr/tonne | Kemmerer and Liu (2012) *(87)* |
| | Total rice straw to process | 1 | tonne | Assumed |
| | Diesel fuel required | 14.4 | liters | Calculated |
| Rice Straw Loading into Pond | Front loader efficiency | 7.6 | lit/hr | John Deere (2022) *(88)* |
| | Fuel Used | 0.6 | hr/tonne | Calculated |
| | Total rice straw to process | 1 | tonne | Assumed |
| | Diesel fuel required | 4.56 | liters | Calculated |
| Water | Water required | 37.9 | $m^3$ | Experiment |
| Water Pumping | Pump water | 0.45 | $kWh/m^3$ of water | Energy Recovery Inc. (2020) *(89)* |
| | Electricity needed | 17.055 | $kWh/m^3$ of water | Calculated |
| Wastewater | Rice Straw | 1000 | kg | Experiment |
| | Water in the pond | 37,900 | kg | Calculated |
| | Moist rice straw | 3,850 | kg | Calculated |
| | Water in the pond | 35,050 | kg | Calculated |
| Reverse Osmosis | Pump water | 2 | $kWh/m^3$ of water | Energy Recovery (2020) *(89)* |
| | Electricity needed | 70.1 | $kWh/m^3$ of water | Energy Recovery (2020) *(89)* |
| Reverse Osmosis Process Output | Brine | 55 | % | Experiment |
| | Sewage | 5 | % | Experiment |
| | Treated water | 40 | % | Experiment |
| | Sludge water | 35,050 | kg | Experiment |
| | Brine | 19,277.5 | kg | Experiment |
| | Sewage | 1,752.5 | kg | Experiment |
| | Treated water | 14,020 | kg | Experiment |

| Process | Operation | Value | Unit | References |
|---|---|---|---|---|
| Rice Straw Loading to Field | Front loader efficiency | 7.6 | lit/hr | John Deere (2022) *(88)* |
| | Fuel used to spread the moist straw for sun drying | 0.6 | hr | Calculated |
| | Fuel used to load transport truck | 0.6 | hr | Calculated |
| | Total rice straw to process | 3.85 | tonnes | Calculated |
| | Diesel fuel required | 35.1 | liters | Calculated |
| Electricity Generation | Quantity of rice straw used | 700 | tonnes of straw/day | Enpower Corp. (2021) *(75)* |
| | Electricity produced in a biomass plant | 526.5 | MWh/day | |
| | Electricity consumed at a biomass plant | 48 | MWh/day | |
| | Net electricity production | 478.5 | kWh/tonne of straw | |
| | Net electricity production per tonne of straw | 683.6 | kWh/tonne of straw | |

The Tool for Reduction and Assessment of Chemicals and Other Environmental Impacts (TRACI) *(90)* was adopted for the impact assessment. TRACI provides a midpoint approach for life cycle impact assessment *(91)*. Impact categories considered in this study include ozone depletion, GWP, acidification, eutrophication, smog formation, ecotoxicity, and primary energy. The results from the impact assessment are presented in Table 2.7.

**Table 2.7: Impact Assessment Result for Upstream and Downstream Processes for Rice Straw Ash and Electricity Cogeneration**

| Impact Category | Value | Unit |
|---|---|---|
| Acidification | 3 | kg $SO_2$ eq |
| Ecotoxicity (recommended) | 643 | CTUe |
| Eutrophication | 0.18 | kg N eq |
| Global warming air, excluding biogenic carbon | 286 | kg $CO_2$-eq |
| Global warming air, including biogenic carbon | 294 | kg $CO_2$-eq |
| Human health particulate air | 0.06 | kg PM2.5 eq |
| Human toxicity, cancerous (recommended) | 0.00 | CTUh |
| Human toxicity, non-cancerous (recommended) | 0.00 | CTUh |
| Ozone depletion air | 0.00 | kg CFC 11 eq |
| Resources, fossil fuels | 529 | MJ |

| Impact Category | Value | Unit |
|---|---|---|
| Smog air | 90 | kg $O_3$ eq |
| Primary energy demand from Renewable and nonrenewable resources (gross cal. value) | 4785 | MJ |
| Primary energy demand from renewable and nonrenewable resources (net cal. value) | 4500 | MJ |
| Primary energy from nonrenewable resources (gross cal. value) | 4284 | MJ |
| Primary energy from nonrenewable resources (net cal. value) | 3999 | MJ |
| Primary energy from renewable resources (gross cal. value) | 501 | MJ |
| Primary energy from renewable resources (net cal. value) | 501 | MJ |

The environmental impact of coproducing ash and electricity from 1 T (0.90 t) of rice straw is presented in this study. Rice straw electricity with simultaneous ash production offsets all pollutants from the 2019 California electricity grid mix.

Material handling for drying, transporting materials, and straw baling had the highest GWP, representing 39%, 28%, and 16% of the entire process, respectively. Water use impact can be reduced by using river water instead of groundwater in the leaching process. Electric conveyance systems can replace diesel-powered loaders to minimize GHG emissions in the leaching and drying process. Optimizing transportation distances and using efficient transportation systems can help minimize the overall impact. As an example, Table 2.8 and Table 2.9 show the impact of using two different water sources on the net GWP of RSA concrete. Other optimizations and sensitivity analyses are required to lower the impacts of high water and diesel use. Further research is needed to compare the impact of different rice straw management options to determine the most feasible option.

**Table 2.8: Net GWP of RSA Concrete at 20% Replacement Rate Using Canal Water from the Reservoir**

| Item | kg $CO_2$-eq per 1 T (0.90 t) of Rice Straw |
|---|---|
| Production of 0.12 T (0.10 t) of RSA | 286 |
| Offset from energy production | -199 |
| Offset from cement replacement | -102 |
| **Net GWP** | **-15** |

**Table 2.9: Net GWP of RSA Concrete at 20% Replacement Rate Using Pumped River Water**

| Item | kg $CO_2$-eq 1 T (0.90 t) of Rice Straw |
|---|---|
| Production of 0.12 T (0.10 t) of RSA | 270 |
| Offset from energy production | -199 |
| Offset from cement replacement | -102 |
| **Net GWP** | **-31** |

### 2.2.8 *Cost Considerations*

Generating ash from rice straw involves bale collection, transportation, storage, pretreatment costs (e.g., leaching, drying), and combustion. Capital costs may include the cost of buildings and installation of devices (e.g., pumps), while operation and maintenance costs are associated with labor costs, fuel consumption, water consumption, and electricity consumption. The depreciation cost should also be considered.

Costs are expected for water, energy, labor, and loader rental costs in California. Apart from labor, fuel is expected to be a major driver of cost, considering its use for baling, loading, material handling, and transportation.

## 2.3 Biochar

### 2.3.1 *Product Description*

Biochar is produced by pyrolysis, a thermochemical process in which biomass is heated without oxygen or partially combusted with a limited oxygen supply *(92)*. Other processing methods are gasification, hydrothermal carbonization, and flash carbonization *(93)*. Thermochemical decomposition of biomass has the benefits of reducing carbon emissions from open burning and producing biochar that can replace activated carbon and other carbon materials applications *(94)*.

### 2.3.2 *Acting Mechanism in Concrete*

The use of biochar in concrete has recently gained attention for its potential to sequester carbon in long-life concrete infrastructure. In addition, biochar from agricultural feedstock such as rice hull and sugarcane bagasse could have pozzolanic reactivity from amorphous silica and alumina contents *(95)*. However, without siliceous and aluminous constituents in the source biomass, the produced biochar will likely have low pozzolanic reactivity *(96)*. Biochar is a highly porous substance with high water retention. Biochar-absorbed water does not chemically bond with carbon and remains free in the matrix. Later, this water could aid in the hydration reaction of concrete.

The impact of biomass-based materials on cement hydration depends on the saccharide content from cellulose and hemicellulose, which has been shown to hinder the hydration of portland cement *(97)*. Also, fine biochar particles with a high specific surface area could act as nucleation sites for cement hydration, resulting in the generation of additional hydration products.

### 2.3.3 *Chemical and Physical Properties*

The chemical and physical characteristics of biochar depend on the feedstock and method of production. The University of California Davis has developed an open-access tool that contains a large database of various biochars along with their production temperatures, feedstock sources, ash content, and other information.[2] Some of the common physical features of biochar are high porosity, high surface area, high water retention, low thermal conductivity, and low flammability *(98,99)*. The pore structure of biochar inhibits thermal bridging when used in concrete, thus leading to thermal insulation, which could be beneficial in building applications where building material with better thermal insulating properties could lead to energy savings from reduced cooling and heating needs *(100)*.

The chemical properties of biochar include a high affinity to nonpolar substances, which shows its potential for carbon sequestration. Free radicals react with ambient air when biochar is stored after production, and the carbon planes get restructured. As a result, the flammability is reduced *(99)*. Depending on the feedstock and method of production, biochars may also have a high pH and chemical stability.

### 2.3.4 *Feedstock Description and Supply*

There is an unlimited abundance of biomass feedstock for biochar production. Many producers receive tons of biomass from forestry restoration and wildfire suppression activities. Other

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[2] More information is available at biochar.ucdavis.edu/.

feedstocks include agro-based biomass, construction and demolition wastes, food waste, industrial waste, sawmill dust, pig manure, willow, palm shell, corn stover, peat, wood chips, and wastewater sludge *(101)*.

### 2.3.5 *Process Description, Technology Readiness Level, and Potential Suppliers*

#### Process Description

The general process of biochar production can be divided into four steps, which are summarized graphically in the system diagram in Figure A.3:

(1) Drying
(2) Pyrolysis
(3) Combustion/oxidation
(4) Gasification

In Step 1, drying occurs and the moisture content of the biomass varies according to the biomass material that is to be gasified. In this step, the moisture in the biomass is evaporated and the energy used for drying is not recovered *(94)*.

In Step 2, pyrolysis is used to decompose organic material thermally in the absence of oxygen in the temperature range of 572°F to 1652°F (300°C to 900°C). During this process, the cellulose, hemicellulose, and lignin in the biomass undergo reaction pathways like crosslinking, depolymerization, and fragmentation at their own temperatures, resulting in solid, liquid, and gaseous products. The solid products are usually biochar, the liquid products are bio-oil, and the gaseous products are usually a mixture of CO, $CO_2$, $H_2$, and syngas (Equation 1).

$$\text{Biomass} + \text{Heat} \rightarrow \text{Biochar} + \text{Bio-Oil} + \text{Syngas} \qquad [1]$$

The composition of the biochar and bio-oil depends on the reaction temperature pressure and the temperature rising rate *(94)*. In Step 3, combustion/oxidation is usually adopted for additional combustion and oxidation of gases, and biochar is generated due to the pyrolysis process. In this step, the gasification agents—such as air, steam, oxygen, and gas mixtures in the gasifier—react with the combustible species and produce CO, $CO_2$, and $H_2O$, along with the biochar produced during the previous step. Gasifiers are the reactors in which this combustion and oxidation reaction occurs *(94)*.

In Step 4, gasification occurs, a thermochemical process where carbonaceous materials such as biomass are converted into gaseous products using gasification agents. By the end of the gasification process, gaseous products such as $H_2$, CO, $CO_2$, and $N_2$; liquid products such as biotar and bio-oil; and solid products such as biochar and bioash are formed. Sometimes the biochar that is produced during the pyrolysis step is also converted into CO, $CH_4$, and $H_2$ through various gasification reactions at this step *(94)*.

Other thermochemical technologies are also adopted to produce biochar, including hydrothermal carbonation, flash carbonization, and torrefaction. Hydrothermal carbonization is the process that converts wet biomass to hydrochar using heat. In this process, biomass mixed with water is placed in the closed reactor and the temperature is raised for a certain time for stabilization. At the same time, the pressure of the water is raised to maintain a liquid state above 212°F (100°C). Depending on the temperature under saturated conditions, products are formed. At temperatures below 482°F (250°C), biochar is formed at temperatures between 482°F and 752°F (250°C and 400°C), bio-oil is formed at temperatures above 752°F (400°C), and gaseous products are formed between 392°F and 752°F (200°C to 400°C). The biochar produced by the hydrothermal carbonization process has a higher carbon content than other processes. Factors like reaction temperature, pressure, residence time, and water-to-biomass ratio affect the characteristics of biochar *(94)*.

Flash carbonization is a process where a flash fire is ignited on packed-bed biomass at a higher pressure of 1 to 2 MPa to convert the biomass into the gas phase and solid phase products. The temperature is usually 572°F to 1112°F (300°C to 600°C), and the reaction time is less than 30 minutes *(94)*.

Torrefaction is a process where moisture, carbon dioxide, and oxygen in the biomass are removed under an inert condition at 392°F to 572°F (200°C to 300°C). The long polysaccharide chain is also depolymerized to produce a hydrophobic solid product with a low oxygen-to-carbon (O/C) ratio. This process is usually conducted at a slow heating rate and is also referred to as mild pyrolysis. The main focus of torrefaction is gas production *(94)*.

## Technology Readiness Level

The main use of biochar is as a soil amendment to increase soil fertility and water retention. Therefore, its technology readiness is at TRL 5 as a soil amendment. However, the use of biochar for GWP reduction and carbon sequestration in concrete while maintaining concrete performance is still in the early phase of research. Therefore, its technology readiness is estimated at TRL 2 to TRL 3 as a concrete admixture (technology concept and/or application formulated proof-of -concept demonstrated, analytically, and/or experimentally).

## Potential Suppliers

Many biochar suppliers exist in California and other neighboring states. The full list of biochar producers is available from the US Biochar Initiative.[3]

## Current Use of Product

Biochar is a carbonized organic matter used predominantly as a soil amendment that enhances plant growth. Other applications include pollutant adsorbents in air and water filters and energy carriers. Based on conversations with biochar producers, new markets are being sought as more biochar is produced either as a primary product or a coproduct of energy production.

## Agents Involved in Production and Distribution

The main biochar producers are biochar manufacturers, energy cogeneration plants, and the energy sector, such as Pacific Gas and Electric (PG&E). Public agencies involved with the feedstock are the California Department of Forestry and Fire Protection (CAL FIRE) and the US Department of Agriculture (USDA).

## Product Consideration in Caltrans Specifications

Caltrans specifications currently do not include biochar as an accepted SCM for concrete.

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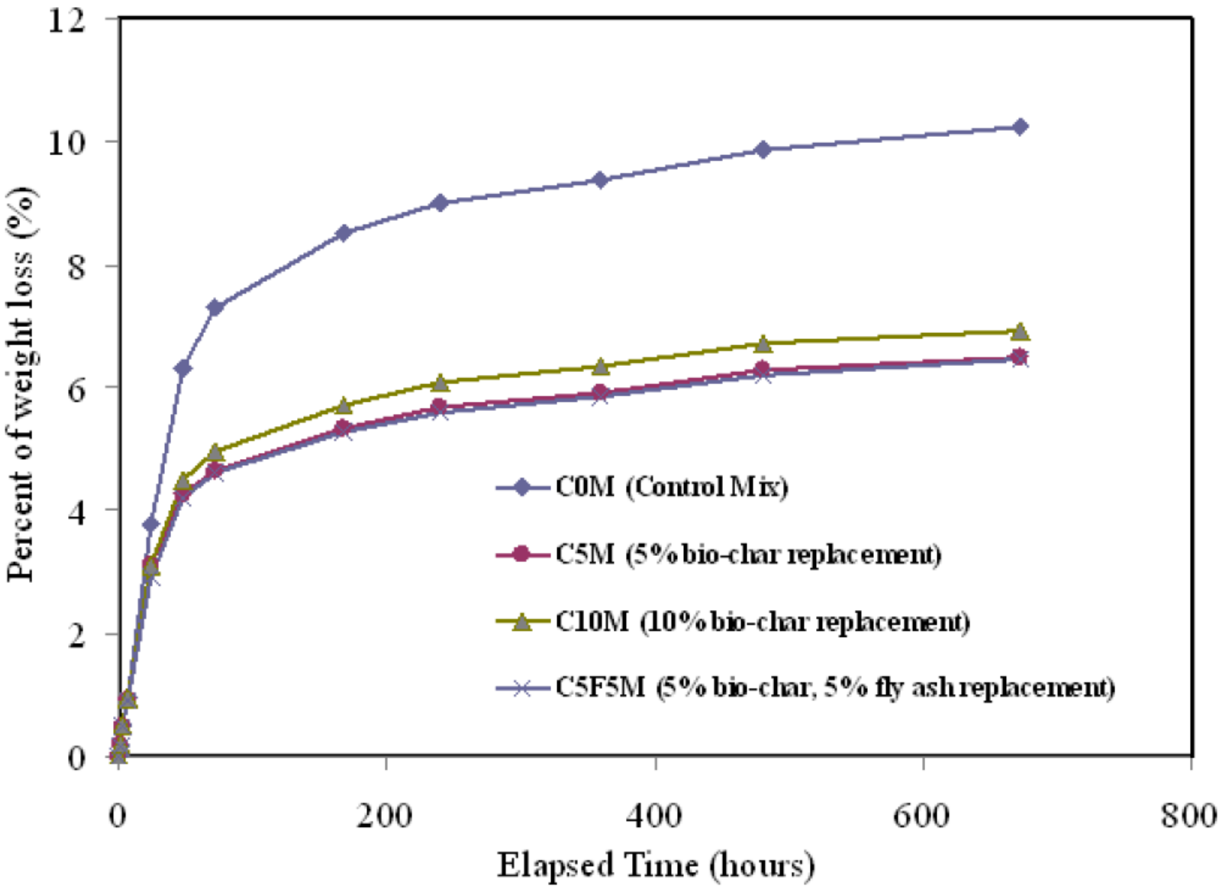
[3] More information is available at biochar-us.org/directory.

### 2.3.6 *Performance in Concrete Based on the Literature*

Research on the use of biochar in concrete is fragmented and empirical and at an early stage. The limited available research has shown that some biochar may reduce workability due to the high moisture absorption of biochar compared to portland cement and sand. Biochar could reduce autogenous shrinkage through internal curing functionality, increase the heat of hydration, and reduce setting times due to the dilution effect.

#### Impact on Fresh Properties

One study evaluated the effects of substituting portland cement in mortar mixes with biochar from hardwood and switchgrass produced by slow pyrolysis *(98)*. The substitutions were 0%, 5%, 10%, 15%, and 20% by the weight of cement. Fresh properties tested were workability based on the flow table test. The flow rate at 5% substitution was around 17%, comparable to the mixes with 5% coal fly ash replacement. However, replacement rates greater than 5% drastically reduced workability. To investigate the water retention capacity of the mixes with biochar, the weight loss with time from evaporation was recorded (Figure 2.10). Results indicated that mortar mixes with biochar retained water better than the non-biochar mixes and exhibited lower percent weight loss. Another study reported that workability generally decreases upon applying biochar in concrete. However, a moderate increase in the superplasticizer dosage can counterbalance this issue *(102)*.



Source: Choi et al. (2012) *(103)*.

**Figure 2.10: Weight loss with time from air drying.**

## Impact on Strength

The previously mentioned study also showed that biochar reduced the 28-day compressive strength of mortar cubes when used at higher than 5% replacement rates. The 5% replacement had a slightly higher 28-day compressive strength of 46.5 MPa compared to the 43.7 MPa of the control (0% biochar) *(98)*. Another study applied biochar from the pyrolysis of hazelnut shells in cement-based composites *(104)*. The three-point bending test indicated that with a 0.8% replacement rate, there was some post-peak bending strength. Such material behavior was attributed to the high surface area-to-volume ratio. The fracture energy also improved by about 130% compared to the control cement mixture. A scanning electron microscope (SEM) analysis showed that a nonlinear cracking pattern was responsible for this higher fracture energy in biochar cement mixtures than a linear cracking pattern in the control cement mixtures. A similar study examined char particles produced from bamboo. Results indicated that 0.08% substitution of cement with bamboo char particles could increase the flexural strength and toughness of cement composites by 66% and 103%, respectively *(105)*. Biochar produced from wood waste at 932°F (500°C), when replaced by 0.5% in cement concrete, increased the 7-day and 28-day compressive strength by 17% and 16%, respectively, compared to plain cement concrete *(106)*. Another study showed that biochar from pyro-gasifier wood wastes, when used at 2% weight of cement in concrete, can increase the 28-day compressive strength marginally *(102)*. Long-term flexural strength and fracture energy also improved.

### Impact on Durability

Overall, adding biochar does not significantly affect the drying shrinkage of concrete *(107)*. Wood biochar, when added as a replacement for cement in concrete at a rate of 1 wt% to 2 wt%., resulted in densification of concrete. As a result, capillary absorption and water penetration were decreased, leading to reduced seepage and durability issues *(106)*. Optimum usage of biochar in concrete reduced the degradation of compressive strength from exposure to sulfate attack from an 8% reduction to a 6.9% and 7.4% reduction in strength. The reason for this better performance in sulfate attack resistance was believed to be increased packing density from using biochar, which reduced permeability and blocked the penetration of sulfate ions into the concrete. However, a higher dosage of biochar addition reduced the compressive strength of concrete and made the matrix prone to sulfate attack *(108)*. The addition of biochar at a higher proportion in concrete (>5%) enhances the freeze-thaw durability of cement composite by allowing enough space for the expanding water during freezing and thus reducing cracking *(109)*. Limited data are available on the influence of biochar on other durability properties, such as acid attack and alkali-silica reaction *(110)*.

A summary of the impact of biochar on various properties of cement-based systems based on a literature review is shown in Table 2.10.

**Table 2.10: Summary of the Effect of Biochar on Various Properties of Cement-Based Systems**

| Property of Concrete | Comparison to 100% OPC Concrete |
|---|---|
| Water demand | Increase |
| Early strength | Increase, up to a certain replacement rate (<5%) |
| Late strength | Increase, up to a certain replacement rate (<5%) |
| Pozzolanic reactivity | Low, needs more research |
| Setting time | Not found |
| Drying shrinkage | No change or decrease, needs more research |
| Alkali-silica reaction | No information found |
| Sulfate attack resistance | Increase, but need more research |
| Freeze-thaw durability | Increase, but need more research |

### 2.3.7 *Environmental Considerations*

#### Global Warming Potential

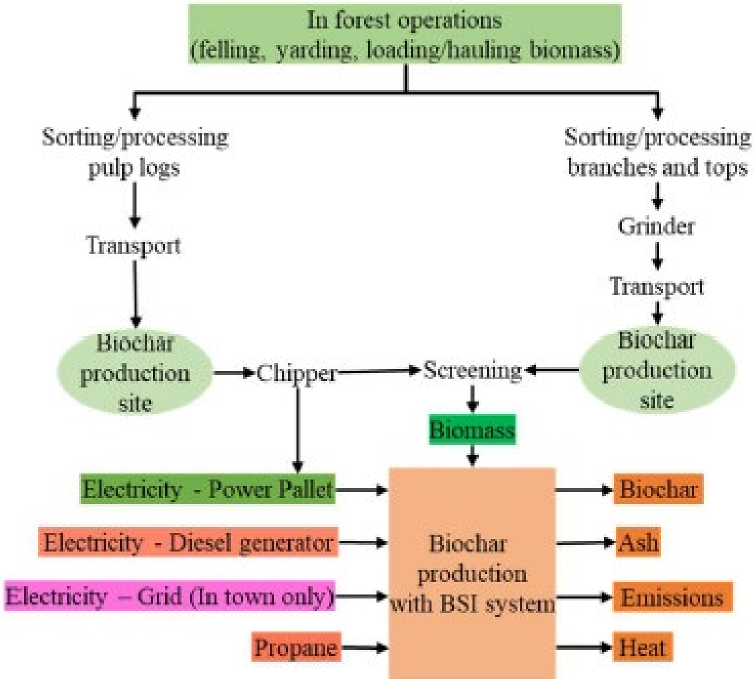
Several studies have developed an LCA for biochar production *(101,111–114)*. One study performed an LCA for 1 kg of biochar production using various pyrolysis methods suitable for rural tropical conditions *(114)*. The researchers' focus was on biochar production from flame curtain kilns, earth mound non-improved kilns, retort kilns with off-gases combustion, pyrolytic cookstoves allowing the use of the gas flame for cooking purposes, and gasifiers with electricity production. The pyrolytic cookstoves and gasifiers had positive impacts due to the avoidance of firewood consumption and emissions from electricity generation. Other kilns were not found to have direct environmental benefits. A literature review study synthesized LCA studies of biochar from different feedstocks that reported reduced $CO_2$-eq emissions compared to fossil fuel; however, the lack of a unified system for LCA boundaries made it difficult to make comparisons among studies and draw conclusions *(101)*. The conclusion was that there is variability in biochar properties, which makes finding use applications challenging, especially where consistency is required.

A USDA study carried out an LCA of biochar from waste woody biomass/wood chips *(111)*. The study's results using mass allocation for syngas and biochar produced in the process are shown in Table 2.11.

### Table 2.11: Cradle-to-Gate Environmental Outputs from Pyrolyzing 2.2 lb. (1.0 oven-dry kg) Wood Chips

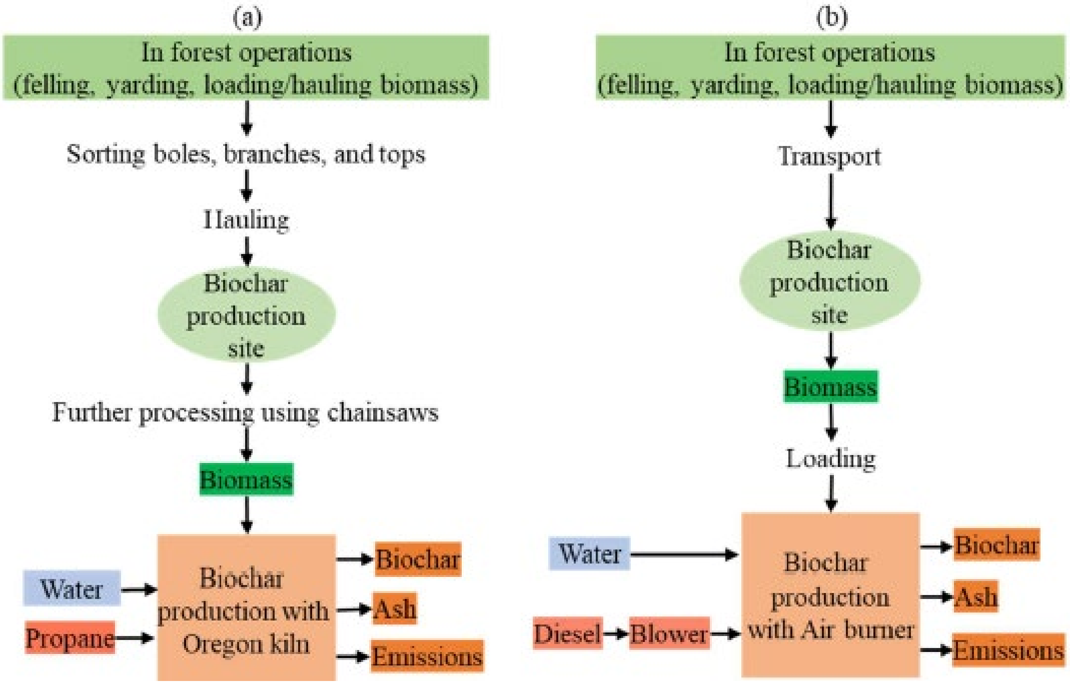
| Substance | Quantity | | | |
|---|---|---|---|---|
| | Unit | Syngas | Biochar | Total |
| **Air Emission** | | | | |
| Carbon dioxide, fossil | g | 447 | 94.9 | 542 |
| Carbon dioxide, biogenic | g | 272 | 57.8 | 330 |
| Sulfur dioxide | g | 3.82 | 0.81 | 4.64 |
| Methane | g | 1.77 | 0.38 | 2.15 |
| Nitrogen oxides | g | 1.18 | 0.25 | 1.43 |
| Carbon monoxide | g | 0.83 | 0.18 | 1.01 |
| Particulates, > 2.5 um, and < 10 um | g | 0.73 | 0.16 | 0.89 |
| Carbon monoxide, fossil | g | 0.61 | 0.13 | 0.74 |
| Methane, fossil | g | 0.34 | 0.07 | 0.41 |
| VOC, volatile organic compounds | g | 0.13 | 0.03 | 0.15 |
| **Water Effluent** | | | | |
| Suspended solids, unspecified | g | 26.93 | 5.72 | 32.65 |
| Chloride | g | 21.5 | 4.57 | 26.07 |
| Sodium | g | 6.069 | 1.29 | 7.35 |
| BOD5, biological oxygen demand | g | 2.81 | 0.6 | 3.41 |
| Calcium | g | 1.91 | 0.41 | 2.32 |
| Lithium | g | 0.614 | 0.13 | 0.74 |
| COD, chemical oxygen demand | g | 0.17 | 0.04 | 0.21 |
| **Industrial Waste** | | | | |
| Bark | g | 1.19 | 0.253 | 1.44 |
| Tar | g | 35.1 | 7.5 | 42.6 |

A detailed study on the cradle-to-gate LCA of biochar production using three portable systems, including the Oregon kiln, the air curtain burner, and the Biochar Solutions Inc. (BSI) production equipment *(115)*. The Oregon kiln and air curtain burner systems are batch-based kilns and require small fuel quantities to start up the systems, whereas the BSI system requires power that could be provided by the nearby grid, diesel generator, or woodchips (gasifier-based power). All three systems are portable and can be installed or parked nearby (maximum of two to four hours) from the forest location or in town. SimaPro *(17)* was used to develop the LCIs. The functional unit was defined as 1 metric ton of biochar production. The three systems are shown in Figure 2.11 and Figure 2.12.



Source: Puettmann et al. (2020) *(115)*.

**Figure 2.11: The system boundary of biochar production using the BSI process.**



Source: Puettmann et al. (2020) *(115)*.

**Figure 2.12: System boundaries of biochar production using (a) the Oregon kiln and (b) the air curtain burner.**

Biochar production from a BSI system is 0.045 T (0.04 t)/hr and requires 20 kW power. Usually, BSI systems are in remote regions where access to the grid may not be possible. Therefore, diesel generators are commonly used.

The Oregon kiln is a cone-shaped kiln that makes well-carbonized biochar with a conversion efficiency of 13% to 20%, depending on the feedstock used. The air curtain burner is like the Oregon kiln but much larger, contains refractory insulation (operates at higher temperatures), and uses a diesel engine of 36.5 kW to operate a continuous fan.

The feedstock in the study was generated from timberland during commercial logging operations based on the weighted average volume available from five regions in the state of California *(116)*. All feedstock sites produced more than 24 T (22.4 oven-dry t) biomass/ha, and it was assumed that 50% of the biomass is accessible. The feedstock is shown in Table 2.12.

**Table 2.12: Woody Feedstocks Used in BSI**

| Species | Contaminant | Comminution Method | Ash Content (%) | Moisture Content (wet basis) (%) |
|---|---|---|---|---|
| Conifer | None | Ground | 1.68 | 16.93 |
| Conifer | 9% soil | Ground | 11.45 | 14.91 |
| Conifer | None | Chip, medium | 0.08 | 25.18 |
| Conifer | None | Chip, small | 2.13 | 20.66 |
| Conifer | 2/3 bole, 1/3 tops | Ground | 3.65 | 16.20 |

Source: Puettmann et al. (2020) *(115)*.

The gate-to-gate life cycle inventory (LCI) data for the systems is shown in Table 2.13.

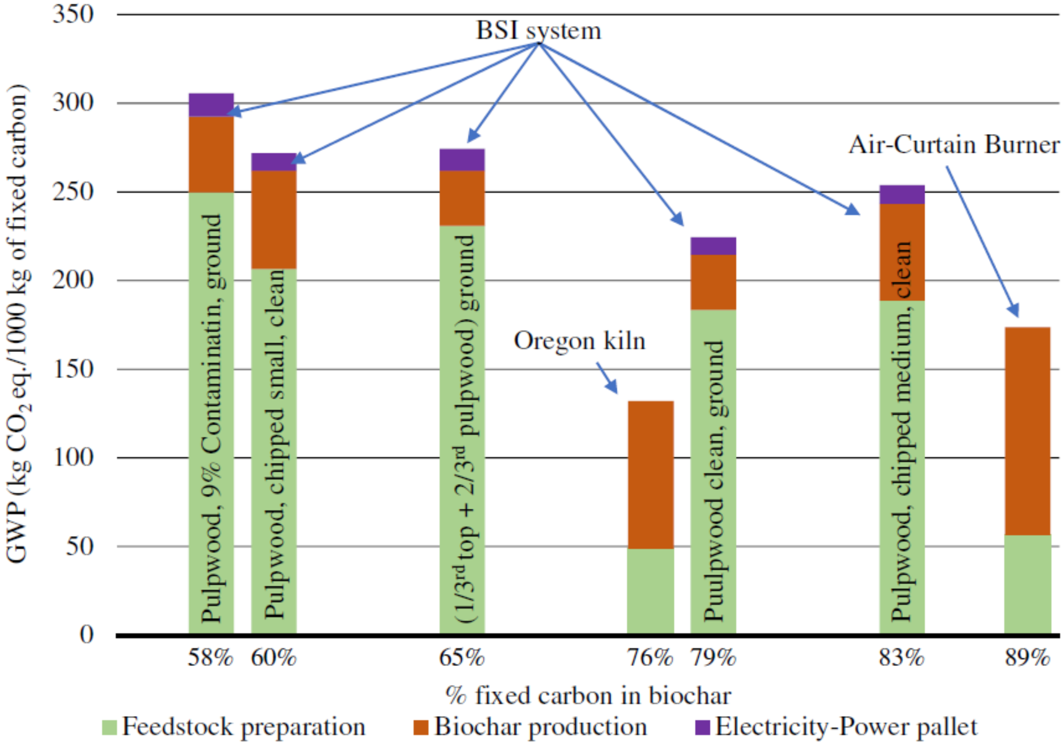
**Table 2.13: Gate-to-Gate LCI Data per Tonne of Biochar Production**

| Input Resources | Units | BSI Ground, clean | BSI Ground, 9% soil | BSI Chipped, medium, clean | BSI Chipped, small, clean | BSI Ground, 2/3 bole, 1/3 tops |
|---|---|---|---|---|---|---|
| Feedstock | kg (dry) | 6937[a]/ 6,550[b,c] | 7,934[a]/ 7,575[b,c] | 8,831[a] /8,392[b,c] | 5,361[a]/ 5,059[b,c] | 7,187[a] /6,781[b,c] |
| Biochar yield | % | 16 | 14 | 13 | 21 | 16 |
| Power pallet input | kg | 387[a]/0[b,c] | 359[a]/0[b,c] | 462[a]/0[b,c] | 302[a]/0[b,c] | 406[a]/0[b,c] |
| Diesel | L | 121[b]/0[a,c] | 158[b]/0[a,c] | 206[b]/0[a,c] | 110[b]/0[a,c] | 110[b]/0[a,c] |
| Electricity (from the grid) | kWh | 0[a,b]/223[c] | 0[a,b]/207[c] | 0[a,b]/266[c] | 0[a,b]/234[c] | 0[a,b]/234[c] |
| Propane | L | 3,005 | 1,037 | 7,760 | 4,578 | 1,727 |
| Water (for quenching) | L | NA | NA | NA | NA | NA |
| **Output Resources** | **Units** | **BSI Ground, clean** | **BSI Ground, 9% soil** | **BSI Chipped, medium, clean** | **BSI Chipped, small, clean** | **BSI Ground, 2/3 bole, 1/3 tops** |
| Biochar yield | kg | 1,000 | 1,000 | 1,000 | 1,000 | 1,000 |
| Fixed carbon | % | 79 | 58 | 83 | 60 | 65 |

[a] Includes wood chips required to operate the power pallet (gasifier-based electricity) to produce electricity for the BSI unit.
[b] Diesel generated is used to produce electricity to operate the BSI unit.
[c] Grid electricity is used to operate the BSI unit.

Source: Puettman et al. (2020) *(115)*.

The TRACI system was adopted to evaluate life cycle impact assessment (LCIA) for the systems, and the results are presented in Figure 2.13.



Source: Puettman et al. (2020) *(115)*.

**Figure 2.13: GWP for a tonne of feedstocks for different systems.**

### 2.3.8 *Cost Consideration*

The price of biochar varies from \$158 to \$200 per t from various producers as a soil amendment product. The cost of biochar is dependent on feedstock acquisition, capital costs, operations costs, and the transportation of feedstock to the producer and the transportation of biochar to the consumer. A study determined that feedstock alone could make up 45% to 75% of the cost of biochar production (around \$63 to \$82 per ton) *(117)*. The authors suggested the feedstock procurement location be no more than 50 miles and product supply to consumers be less than 100 miles to reduce costs. Based on this study, the biochar cost was reported to be \$9 to \$42 per $ft^3$ (\$318 to \$1483 per $m^3$). They also projected biochar to reach a \$3 billion global market by 2025.

## 2.4 Cellulose Nanocrystals and Nanofibers

### 2.4.1 *Product Description*

Cellulose nanomaterials (CNMs) can be produced in several ways, leading to different physicochemical properties. The two primary forms of cellulose nanomaterials are cellulose nanocrystals (CNCs) and cellulose nanofibers (CNFs). CNFs can be produced by mechanical fibrillation or sulfuric acid hydrolysis using wood pulp. TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical)-mediated oxidation followed by mild disintegration in water using wood pulp has also been used for producing CNFs. Sulfuric acid hydrolysis with wood pulp, cotton fibers, algae, wood chips, and pulp sludge, among other precursors, has been used for producing CNCs *(118)*. CNCs and CNFs have recently been used at the research level in cement-based materials, such as paste, mortar, and concrete.

### 2.4.2 *Acting Mechanism in Concrete*

In cementitious systems, the following mechanisms may be at work: (1) bridging/reinforcing effect, (2) filling effect, (3) increased strength/stiffness with high modulus CNC/CNF, (4) more nucleation sites due to high surface area, and (5) internal curing by releasing adsorbed water to increase the degree of hydration. Two mechanisms were proposed to explain the contribution of CNCs to the increased degree of hydration. One mechanism is the steric stabilization effect of CNCs *(119)*. The other mechanism is a short-circuit diffusion effect *(120)*.

### 2.4.3 *Chemical and Physical Properties*

The chemical and physical properties of cellulose nanomaterials may differ based on the production procedures. A study characterized the two types of CNMs, TEMPO-oxidized CNC and mechanically fibrillated CNFs *(118)*. SEM observation showed the rod-like morphology of CNCs with an average width of 6 to 9 nm and length of 127 to 163 nm, depending on the sonication time.

In contrast, CNFs showed entangled fiber-like morphology with an average width of 30 nm. The crystallinity index (CI) was calculated from the X-ray diffraction (XRD) analysis. The CI for CNCs was 88.2%, whereas the CI for CNFs was 81.8%, meaning the presence of more amorphous regions in CNFs than in CNCs. CNCs pose a higher number of hydroxyl groups compared to CNFs because of the high specific surface area. The zeta potential of CNCs and CNFs were -47.5±2.31 mV (pH 7.4) and -50.6±1.48 mV (pH of around 5.6), respectively. In contrast to CNCs, CNFs have no carboxylate groups ($–COO^-$) groups because of their nonchemical mechanical fibrillation production process. The CNCs surface charge density ($OSO_3$) was between 0.241 and 0.261 mmol/g *(118)*.

### 2.4.4 *Feedstock Description and Supply*

CNMs are produced from cellulosic sources. The source of cellulose can be wood and non-wood plants, such as cotton, hemp, flax, and jute; algae; tunicate; and bacteria *(121)*. CNMs were also produced from old textiles *(122)*.

### 2.4.5 *Process Description, Technology Readiness Level, and Potential Suppliers*

#### Process Description

CNCs are usually isolated from semi-crystalline cellulose fibers using a strong sulfuric acid hydrolysis process where the amorphous region is digested and the crystalline region is intact. Thus, individual crystallites with a little amorphous phase remaining (CNCs have high crystallinity, >80%) are released with mechanical disintegration processes (e.g., ultrasonication) *(123)*. Sulfuric acid is one of the widely used inorganic acids for hydrolysis because of its low cost and its reactivity with the hydroxyl groups on the surface of crystallites; thus, it can introduce anionic sulfate groups. The resulting cellulose nanocrystals are often referred to as sulfated cellulose nanocrystals.

TEMPO-mediated oxidation is regarded as one of the most effective pretreatment processes of cellulose fibers because it can selectively oxidize primary C-6 hydroxyl groups into anionic carboxylate groups ($–COO^-$) under alkaline conditions *(124)*. This TEMPO-mediated oxidation reaction occurs on the surface of cellulose fibers and in their amorphous regions. As the carboxylate content increases to a certain amount, cellulose disperses in an aqueous solution *(124)*. In addition, the negative charges can induce interfibrillar electrostatic repulsion forces and thereby facilitate nano-fibrillation in the subsequent mechanical separation process, resulting in the production of fine and individualized CNFs with a diameter of 3 to 4 nm, a length of microns, and an aspect ratio greater than 100 *(125,126)*. The resulting carboxylated CNF is often referred to as TEMPO-oxidized CNF.

The mechanical fibrillation method does not involve any chemical treatment, and it is less effective in the defibrillation of cellulose fibers into nanofibers than chemical processes (i.e., strong acid hydrolysis and TEMPO-mediated oxidation). However, it may benefit from lower manufacturing costs and no chemical used to alleviate the environmental burdens compared to the TEMPO-mediated oxidation method for CNF and the strong sulfuric acid hydrolysis method for CNC. A friction grinding process is usually applied for the mechanical pretreatment of cellulose fibers *(124)*. The system diagrams for producing CNCs and CNFs are shown in Figure A.4

### Technology Readiness Level

Cellulose nanomaterials research in cement-based systems is still young and in the feasibility evaluation stage. Implementation in concrete still requires more research focused on concrete mixture optimization, sequence of adding the nanomaterials, and compatibility with chemical and mineral admixtures. This development phase places the technology at a TRL of 3 to 4.

### Potential Suppliers

Several manufacturers produce CNCs and CNFs at an industrial scale. The list of the suppliers is provided in Table 2.14.

**Table 2.14: List of Cellulose Nanocrystal and Cellulose Nanofiber Suppliers**

| Supplier | Production Capacity (MT) | Properties | Producer Links |
|---|---|---|---|
| US Forest Service R&D: Forest Product Laboratory | Pilot | CNC: 5 nm diameter and 150 nm long<br>CNF: 20 nm diameter and 2 µm long | fs.usda.gov/Internet/FSE_DOCUMENTS/fseprd499746.pdf |
| Kruger | 6000 | CNF: 80 to 300 nm wide, and 100 to 2,000 µm long, aspect ratio>1000 | biomaterials.kruger.com/products/the-filocell-advantage/ |
| Sappi North America | — | CNF product with the trademark name of Valida designed as concrete admixture | cdn-s3.sappi.com/s3fs-public/Sappi%20Valida%20Concrete%20Brochure.pdf |
| CelluForce | 300 | CNC: Average length of 150 nm and a diameter of 7.5 nm, aspect ratio 20 | celluforce.com/ |
| American Process | 175 | CNC: 2-20 nm diameter and 100-600 nm long<br>CNF: 5-30 nm diameter and >1 µm long | americanprocess.com/BiorefineryTechnologiesAndSolutions.aspx |
| Blue Goose Biorefineries Inc. | — | CNC: Length 100-150 nm, width 9-14 nm | bluegoosebiorefineries.com/product/ |
| Innotech Materials | — | CNC products with various surface functional groups available | innotechmaterials.com/ |
| US Forest Service R&D: Forest Product Laboratory | Pilot | CNC: 5 nm diameter and 150 nm long<br>CNF: 20 nm diameter and 2 µm long | fs.usda.gov/Internet/FSE_DOCUMENTS/fseprd499746.pdf |

## Current Use of Product

CNCs and CNFs are currently used in paints, adhesives, coatings, composites, gels, medical and pharmaceutical applications, and packing *(127)*. Some are marketed as a concrete admixture, such as the Valida product by Sappi, shown in Table 2.14.

**Agents Involved in Production and Distribution**

Public agencies involved with wood feedstock are the USDA and CAL FIRE. Cellulosic nanomaterials are produced by private manufacturing industries and other organizations such as the Forest Products Laboratory and the University of Maine Process Development Center.

**Product Consideration in Caltrans Specifications**

Caltrans specifications currently do not include cellulose nanocrystals and nanofibers as an accepted SCM for concrete.

### 2.4.6 *Performance in Concrete Based on the Literature*

Manifold characteristics of cellulose nanomaterials (high specific surface area, aspect ratio, reactive surface groups, and high water retention capacity) make cellulose nanomaterials an interesting additive for cementitious systems. Researchers have introduced cellulose nanomaterials derived from different sources and varied production methods discussed previously. The fresh-state properties and as well as hardened properties of cement paste and mortar have been reported in the literature. The properties of cement paste and mortar evaluated in the literature include the following:

- Setting time
- Degree of hydration
- Mechanical properties
- Rheology of cement paste
- Durability (drying shrinkage and others such as freeze-thaw cycling, sulfate attack, and ASR expansion)

**Impact on Fresh Properties**

CNMs have been found to alter the fresh properties and rheology of cement composites. One study reported a faster setting time incorporating different doses of CNFs (up to 0.5 wt%), indicating it is a set accelerator *(128)*. The study reported that the setting time decreased with increased CNF doses. However, other studies have demonstrated the retardation effect of CNCs and CNFs in cement composites. The impact of both CNMs on initial and final setting times was compared to the control *(118)*. The initial setting time was delayed up to 82 minutes, and the final setting time was delayed by up to 109 minutes by 0.05 wt% CNC. The retardation effect was more prominent for the final setting time for all concentrations of CNCs. CNFs had a lesser effect on initial and final setting time than CNCs. With CNFs, a maximum 56-minute delay was recorded at 0.055 wt%. The retarding effect of CNMs was also reported by other researchers based on calorimetry tests. One study demonstrated some retarding effect with CNFs where the final setting time was delayed by up to 24 minutes with 2% cellulose fiber *(129)*. Based on the calorimetry tests for 200 hours on cement paste, another study found a lower heat rate with more CNCs compared to the control mix for the first 25 hours *(120)*. The peak heat flow was delayed about 5 hours for the cement paste with 1.5 wt% CNC compared to the control. The researchers attributed this retardation to the reduction of the surface area of cement due to the adherence of CNCs on the cement particles blocking water to cement. However, a different study found no retardation effect with CNFs in cement paste *(129)*. Similarly, another study found the retardation effect was not prominent based on the isothermal calorimetry of CNF cement paste *(130)*. This study's findings suggested that CNFs may accelerate or retard the hydration reaction depending on the balance of two contrasting mechanisms. Including CNF provides additional nucleation sites for C-S-H formation, which may accelerate early-age hydration. On the contrary, active nucleation sites can be reduced due to the adsorption of CNF on cement particles because the negatively charged carboxyl group can bind with calcium ions on the cement particle, which may result in the retardation of the hydrations *(130)*.

A study of the effect of different CNC characteristics on the rheological aspect of CNC cement paste found two specific behaviors of CNCs based on the doses *(131)*. A CNC at a dose below 0.2 wt% works as a water-reducing admixture and reduces the yield stress; above 0.5 wt%, it works as a viscosity-modifying admixture by increasing the yield strength. At low volume fractions, CNCs reduce the network structure, thus decreasing yield strength. At higher doses, they increase the network structure, increasing the yield strength *(132)*. One study observed similar rheological behavior with CNCs in cement paste *(120)*. For paste with CNCs, yield stress decreased to the lowest level of 15.9 Pa for 0.04 vol% compared to the control (48.5 Pa) and then increased to the value of the control at 0.3 vol% and afterward increased drastically to 600 Pa at 1.5 vol%. The researchers attributed this behavior to two distinct mechanisms at low doses where steric stabilization takes place and reduces the yield strength, while at high doses agglomeration causes the increase in yield strength of cement paste.

Studies have shown that CNFs show different yield strengths and viscosity compared to CNCs *(118,133)*. A comparative study on both types of CNMs pointed out that, although CNCs show two distinct behaviors at two different dose ranges, CNFs increase the yield strength and plastic viscosity at all doses (*131*). Researchers have reported increased yield strengths and plastic viscosity with increasing doses *(129)*. Yield strengths were increased about 1.5, 2.2, 3.6, and 4.1 times for 0.05%, 0.1%, 0.2%, and 0.4% CNF, respectively, compared to the control mix. The corresponding plastic viscosity increase were 1.3, 1.7, 2.6, and 3.7 times, respectively. They pointed out that mixes with CNFs exhibit shear-thinning behaviors. This rheological behavior was attributed to the hydrophilic nature of CNFs, their morphology, and the presence of the OH group on the surface, which enables hydrogen bonding with water, thus binding water and increasing the yield strength and viscosity of the mix.

### Impact on Strength

The mechanical performance of CNM's added cement composites has been explored in recent literature. One study reported the greatest improvement of 13% in compressive strength at 0.05 wt% dose of CNF at 7 days, whereas the gain was reduced at 28 days *(130)*. The study reported a better compressive strength for a lower dose of 0.05 wt% compared to the 0.1 wt% doses of CNF, which was attributed to the agglomeration of CNFs. It also reported a maximum increase of 111% in flexural strength with 0.1 wt% CNF. Fracture toughness was not significantly affected using CNFs, which corroborated the low bridging capacity of nanoscale fibers. Additional research has shown that self-consolidating concrete (SCC) with CNF at 0.05 wt% increases compressive strength at 1 day, 7 days, and 28 days by 8%, 7%, and 12%, respectively, in self-consolidating concrete *(129)*. Indirect tensile and flexural strength were enhanced by 26% and 23%, respectively, with 0.05% CNF. Higher doses of CNFs yield less strength than the low dose because of the possible agglomeration. The improvement in strength, mainly in later ages, was attributed to the formation of hydrogen bonds between the active hydroxyl groups on the CNF surface and the hydrogen in the hydration products ($Ca(OH)_2$, C-S-H) produced in the cementitious composites. Flexural strength and indirect tensile strength improvement were derived from the reinforcement at the micro and nano level due to the fibrillated structure of CNFs.

In another study by the same authors, CNF performance in cement paste was evaluated *(129)*. The flexural strength was increased up to 28% for moist curing conditions and 38% for sealed curing conditions. Apart from the CNFs' nano-reinforcing action, they can work as an internal curing agent by retaining water and releasing it later. However, the researchers noticed the adverse effect of CNFs in the compressive strengths, which they believe is due to the air entrainment and agglomeration from including CNFs. A more recent study found about a 10% improvement in compressive strength and a 55% improvement in flexural strength at 90 days with CNFs *(134)*. Another study examined the flexural strength with different doses of CNCs in cement paste and found that flexural strength reached a maximum value at 0.2 wt% and decreased afterward *(120)*. It was hypothesized that this increase was due to the increase in the degree of hydration with the CNC addition. The optimum content is possible because higher doses cause agglomerations, thus reducing the effect after the optimum dose. One study demonstrated an impressive enhancement of 2.5 times in compressive strength at 1 day, which was reduced to a 30% improvement at 56 days for samples with CNCs compared to the control in oil well cement *(135)*.

A very similar trend was observed for the split tensile strength. One study showed that 1.5 wt% CNC improved compressive strength by 28% and flexural strength by 11% *(136)*. A comparative study on CNC and CNF in cement paste showed a similar improvement of 17% to 18% in compressive strength for both CNMs but at different doses (*117*). CNFs reached the maximum compressive strength at 0.065 wt%, whereas the maximum compressive strength for CNCs was obtained at 0.4 wt%. The morphology of the two CNMs was influential in this behavior. Due to the longer length of the fibrous CNFs, higher doses of CNFs were unsuitable for a workable mixture because of the agglomeration. The improvement was attributed to the improved degree of hydration, bonding of CNMs with hydrates, and internal curing due to the presence of CNMs.

CNMs are generally found to be beneficial for the degree of hydration of cement composites. Based on the calorimetry and thermogravimetric analysis of cement paste, researchers found that CNCs improved the degree of hydration at later ages of cement paste, which they described by a dual mechanism of steric stabilization similar to the way high-range, water-reducing admixture acts. The second mechanism is the so-called short-circuit diffusion, where CNCs enable water to diffuse through the hydration product on the outer shell of cement particles to the unhydrated core of cement and increase the high-density C-S-H and the degree of hydration *(120)*. They reported a 14% and 20% increase in the degree of hydration at 7 and 28 days, respectively, with 1.5% CNC compared to the control paste. Another study reported an improved degree of hydration for both CNCs and CNFs at 3, 7, and 28 days based on chemically bound water tests. The study found low doses of CNMs resulted in a higher degree of hydration compared to higher doses of CNMs *(118)*.

### Impact on Durability

Only a few researchers have explored the durability of CNM cement composites. One study investigated the effect of CNFs against sulfate resistance in cementitious composites *(137)*. In the study, up to 0.5 vol% CNF was used, and specimens were subjected to accelerated sulfate attack for 12 weeks. It was found that specimens with CNFs reduced the sulfate penetration depth, reduced the formation of ettringite, and refined the pore sizes. Another study examined the effect of CNCs on freeze-thaw and salt attack resistance, where three different doses of CNC (0.5 wt%, 1 wt%, and 1.5 wt%) were used. A 98% increase in freeze-thaw resistance for 50 freeze-thaw cycles was reported with 1.5 wt% CNC and 35-fold less mass loss from the sulfate attack for the same dose of CNC. The study also reported a 34% reduction in water vapor permeability and a 54% reduction in absorptivity. CNCs significantly reduced the pore numbers and microcracks and reduced ettringite formation while under a sulfate environment *(136)*.

In another study, CNCs and CNFs were used, and their effects on freeze-thaw resistance were compared *(136)*. After 100 freeze-thaw cycles, the mass loss was 58 and 14 times lower than the control mix for 1 wt% of CNF and CNC, respectively. Researchers attributed the better mechanical and durability performances to forming more C-S-H, denser composites, and pore size reduction and pore refinement, especially for pores larger than 10 nm. A more recent study looked at the effect of CNCs on ultra-high durability concrete in terms of durability performance. Researchers found about a 32% decrease in autogenous shrinkage at 100 days with the incorporation of CNCs compared to the control mix without CNCs. However, a significant difference was not observed in total drying shrinkage. They concluded that due to their internal curing capability, the CNCs work better to reduce autogenous shrinkage compared to drying shrinkage *(138)*. Other researchers also observed a significant influence of CNFs on autogenous shrinkage in ultra-high-performance concrete, which was more prominent at an early age *(139)*. The reduction of autogenous shrinkage was up to 75%, 53%, and 42% at 1, 7, and 14 days, respectively. Internal curing and nano reinforcing with the inclusion of CNFs were attributed to this improvement. A summary of the impact of CNCs and CNFs on various properties of cement-based systems is provided in Table 2.15.

**Table 2.15: Summary of the Effect of Cellulose Nanomaterials on the Properties of Cement-Based Materials**

| Property of Concrete | Comparison to 100% OPC Concrete |
|---|---|
| Water demand | Increase |
| Early strength | Increase up to a certain dosage |
| Late strength | Increase up to a certain dosage |
| Pozzolanic reactivity | None |
| Setting time | Increase |
| Drying shrinkage | Decrease needs more research |
| Alkali-silica reaction | Needs more research |
| Sulfate attack resistance | Increase, needs more research |
| Freeze-thaw durability | Increase, needs more research |

### 2.4.7 *Environmental Considerations*

One study included a summary of the studies that have assessed the environmental impact of the production of CNCs and CNFs using LCA *(140)*, and a summary of these results is presented in Table 2.16.

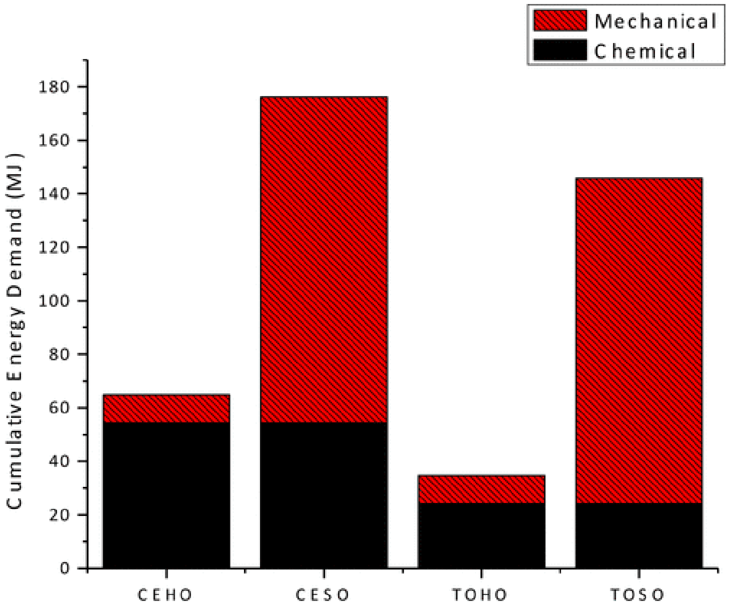
### Table 2.16: Summary of LCA Studies on the Production of Cellulose Nanocrystals/Cellulose Nanofibers

| Reference | Cellulose Type | Production Method | GWP (kg $CO_2$-eq) | ME/FE (kg N eq/ kg p eq) | TA (kg $SO_2$ eq) | CED Value | Human Toxicity (kg 1,4-DB eq) | Fossil Fuel Depletion (kg oil eq) | WD (kg or $m^3$ $H_2O$, other units specified) |
|---|---|---|---|---|---|---|---|---|---|
| Hohenthal et al. (2012) *(141)* | CNF | Enzymatic + HPH | 1.2–3.1 | 0.015–0.016 | 0.008–0.045 | — | — | 0.3–0.75 | 50 |
| | | TEMPO oxidation + HPH | 1.0–1.8 | 0.018–0.024 | 0.005–0.0065 | — | — | 0.25–0.5 | 158 |
| | | TEMPO oxidation + mechanical refinement | 0.75–1.0 | 0.014–0.015 | 0.0045–0.005 | — | — | 0.20–0.25 | 120 |
| Li et al. (2013) *(142)* | CMF | TEMPO oxidation + sonication + centrifuge purifying (TOSO) TEMPO | 980 (per kg NC) | — | — | 145.9 MJ | — | — | — |
| | | TEMPO oxidation + homogenization (TOHO) | 190 (per kg NC) | — | — | 34.7 MJ | — | — | — |
| | | Chloroacetic acid etherification + sonication + centrifuge purifying (CESO) | 1160 (per kg NC) | — | — | 176.1 MJ | — | — | — |
| | | Chloroacetic acid etherification + homogenization (CEHO) | 360 (per kg NC) | — | — | 64.9 MJ | — | — | — |
| Arvidsson et al. (2015) *(143)* | CNF | Enzymatic pretreatment + microfluidization | 0.79 | — | — | 87 MJ/kg | — | — | 240 |
| | | Carboxymethylation pretreatment + microfluidization | 99 | — | — | 1800 MJ/kg | — | — | 1000 |
| | | Without pretreatment + homogenization treatment | 1.2 | — | — | 240 MJ/kg | — | — | 130 L/g |

| Reference | Cellulose Type | Production Method | GWP (kg $CO_2$-eq) | ME/FE (kg N eq/ kg p eq) | TA (kg $SO_2$ eq) | CED Value | Human Toxicity (kg 1,4-DB eq) | Fossil Fuel Depletion (kg oil eq) | WD (kg or m$^3$ $H_2O$, other units specified) |
|---|---|---|---|---|---|---|---|---|---|
| Figueiredo et al. (2012) *(144)* | CNC | EUC system | 0.122171 | 0.000320/0.000134 | — | 15.943 MJ for the extraction of raw materials | 0.291122 | — | 131 L/g |
| | | EC system | | 0.000065/0.000024 | — | 1.8 MJ for the extraction of raw materials | 0.034797 | — | 138 L/g |
| Piccinno et al. (2015) *(145)* | CNF | MFC liberated (Enzymatic + homogenization) + coating MFC with GripX + wet spinning by adding sodium alginate (route 1a) | 1.5–1.6 (10 g of MFC) | — | — | 32.2 MJ for production of 10 gr MFC | — | — | (0.201 for MFC liberation) 0.253 L/g |
| | | MFC liberated (enzymatic + homogenization) + wet spinning by adding sodium alginate (without coating) (route 1b) | | — | — | | — | — | (0.201 for MFC liberation) 0.255 L/g |
| | | MFC liberated (enzymatic + homogenization) + electrospinning by adding PEO as a carrier polymer (route 2) | | — | — | | — | — | (0.201 for MFC liberation) 0.205 L/g |
| Nascimento et al. (2016) *(146)* | CNC | Extraction of CNC with high-powered ultrasound (CNU) | 0.207 | 5.68 × 10−5/3.03 × 10−5 | 0.00045 | — | 0.0477 | — | 0.0023 |

*Notes:* GWP: global warming potential; ME: marine eutrophication; FE: water body eutrophication; TA: terrestrial acidification; CED: cumulative energy demand; WD: water depletion; HPH: high-pressure homogenization; TEMPO: 2,2,6,6-tetramethylpiperidine-1-oxyl; EUC: extracted from unripe coconut fiber; EC: extracted from cotton fiber; MFC: microfibrillated cellulose; PEO: poly(ethylene) oxide.

The environmental impacts of producing wood-based CNFs from four different production routes were evaluated for two pretreatment and two treatment processes. The two pretreatments (chemical) processes considered were 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) oxidation (TO) and chloroacetic acid etherification (CE), and the two treatment (mechanical) processes were homogenization (HO) and sonication (SO) *(142)*. The scope of the study was cradle-to-gate, while the functional unit was defined as 10 g equivalent dry mass of the nanocellulose production. The impact categories assessed were cumulative energy demand (CED) and global warming potential. Results from the study showed that SO has a higher energy demand than HO, while CE is more energy-intensive than TO. The trend was observed to be similar for the GWP results. Figure 2.14 shows CED values for producing nanocellulose from the chemical pretreatments and mechanical treatments.



*Notes:* CEHO: Chloroacetic acid etherification and homogenization; CESO: chloroacetic acid etherification and sonication; TOHO: TEMPO oxidation and homogenization; TOSO: TEMPO oxidation and sonication.

Source: Li et al. (2013) *(142)*.

**Figure 2.14: Cumulative energy demand values for the production routes.**

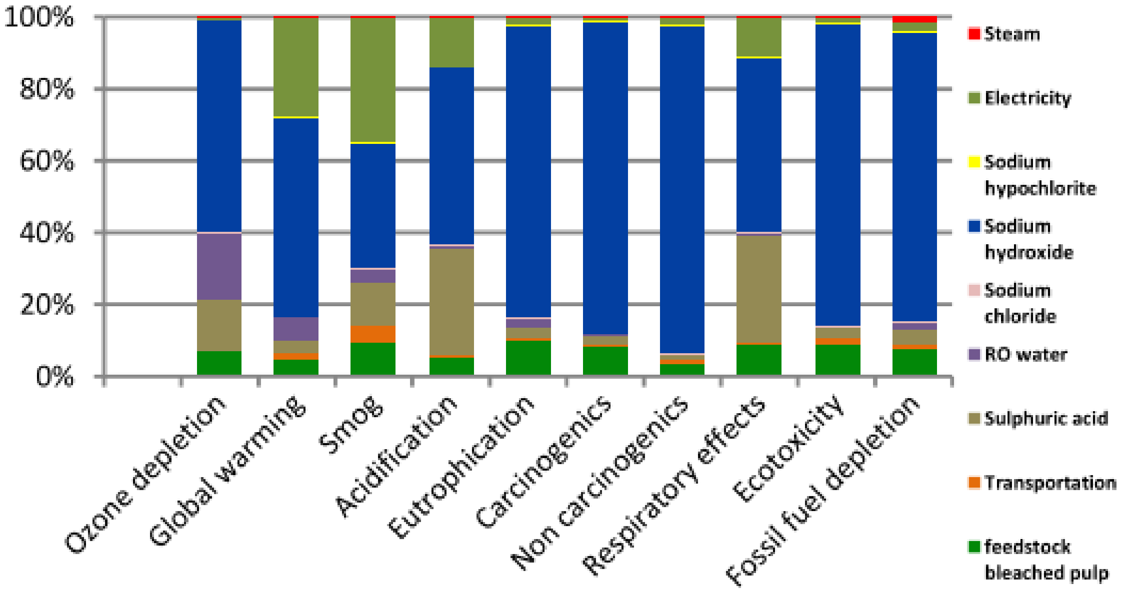
The environmental impacts of producing CNFs from wood pulp using three different production routes—the enzymatic route, the carboxymethylation route, and the no-pretreatment route—were evaluated in one study *(143)*. The scope of the study was cradle-to-gate using a functional unit of 1 kg of CNF produced. Four category indicators were chosen in this study: CED, GWP, water depletion (WD), and terrestrial acidification (TA) midpoint indicators from the ReCiPe impact assessment method *(147)*. Results of the study show that the carboxymethylation route had the highest energy demand and environmental impact. Similar results were obtained for the no-pretreatment and enzymatic route. Enzymatic treatment is the chief contributor to WD and TA, while pulp production is the main contributor to GWP and CED. The treatment process for the no-pretreatment route is the chief contributor to GWP, CED, and WD, while the pulp production contributes more to TA.

In another study *(147)*, the environmental impact of pilot-scale production of CNCs from wood pulp using LCA was assessed. The functional unit was set to be 0.0011 T (0.0009 t) of CNCs produced from the pilot acid hydrolysis process, and the scope of the study was from cradle-to-gate. Data for the manufacturing processes are based on estimates from the USDA Forest Product Laboratory pilot line. This line produces 0.025 T (0.023 t) CNC per batch from 0.050 T (0.045 t) oven-dry dissolving wood pulp. Results from the impact assessment showed that 992.7 MJ of cumulative energy is needed to produce 0.001 T (0.0009 t) of CNC. The production of sodium hydroxide for neutralizing acid used in hydrolysis and feedstock dissolving pulp was responsible for most water and air emissions. A summary of the impact assessment using the TRACI method is presented in Table 2.17, and Figure 2.15 shows the contribution of each activity to the impact categories considered. The highest contributors to GWP (kg $CO_2$-eq) were sodium hydroxide (55%) and electricity (28%).

**Table 2.17: The Impact of Producing 1 kg CNC with the USDA Forest Product Laboratory's Pilot Production Process**

| Impact Category | Unit (/kg CNC) | Total |
|---|---|---|
| Ozone depletion | kg CFC-11 eq | 1.11E-06 |
| Global warming | kg $CO_2$-eq | 29.64 |
| Smog | kg $O_3$ eq | 1.68 |
| Acidification | kg $SO_2$ eq | 0.54 |
| Eutrophication | kg N eq | 0.05 |
| Carcinogenic | CTUh | 8.25E-07 |
| Non-carcinogenic | CTUh | 8.71E-06 |
| Respiratory effects | kg PM2.5 eq | 0.03 |
| Ecotoxicity | CTUe | 96.81 |
| Fossil fuel depletion | MJ surplus | 72.11 |

Source: Gu et al. (2015) *(148)*.



Source: Gu et al. (2015) *(148)*.

**Figure 2.15: Percentage contribution from each activity to impact categories.**

## Toxicity

For commercialization or large-scale use of a product, it is necessary to assess its environmental impacts in terms of life cycle consideration, including the production process and use stage. In general, cellulosic materials are known as biocompatible, biodegradable, and nontoxic. One study examined the human health and aquatic toxicity of lignin-coated CNCs and CNFs. The observations showed that CNCs and CNFs have no oral, dermal, or ocular toxicity even at the highest tested level, which was an environmentally relevant concentration *(149)*. The study also analyzed aquatic toxicity and did not observe any aquatic toxicity.

### 2.4.8 *Cost Considerations*

The economics of making CNF materials primarily depends on the type of fiber pretreatment (e.g., enzymatic, carboxymethylation, TEMPO-modified CNF). The cheapest process is probably the enzymatic pretreatment process, where the cost of making CNFs from the pulp integrated into a pulp mill is 0.4 €/kg ($0.42/kg), a process which today is in operation in large-scale papermaking applications. For non-integrated use of CNFs in papermaking applications, the cost, including pulp cost and profits, should be lower than 2.5 €/kg ($2.64 /kg). Selling prices are expected to drop below 15 €/kg ($15.83/kg) for sulfuric acid hydrolyzed CNCs (and potentially cheaper for other processes) *(127)*. The price of 1 kg from a US manufacturer (University of Maine Process Development Center) was $34 for CNFs and $136 for CNCs. The price of 1 kg of CNC from CelluForce, a manufacturer in Canada, is $350 for 40 liters of aqueous suspension based on a quote from the manufacturer in 2022.

A techno-economic analysis was performed on the production of cellulose micro- and nanofibrils (CMNFs) from wood pulp *(150)*. Two scenarios were considered: (1) greenfield facilities (stand-alone manufacturing facilities) and (2) co-location manufacturing facilities. Findings from the study showed that the major cost driver for CMNF production is pulp production, representing 60% of manufacturing cost for both scenarios. The co-location scenario has lower minimum product selling prices (MPSPs) due to lower capital investment as well as the cost of electricity, pulp, and labor. In summary, the calculated manufacturing cost for a 55 T/day (50 t/day) (dry equivalent) facility using disk refining technology is $1,493/t CMNF (dry equivalent), while the MPSP is $1,893/t CMNF (dry equivalent).

## 2.5 Chitin Nanomaterials

### 2.5.1 *Product Description*

Chitin is the second most abundant amino polysaccharide polymer occurring in nature, providing strength to the exoskeletons of crustaceans and insects and the cell walls of fungi *(151,152,153)*. The native nanochitin in marine crustacean shells can be released and used as reinforcement components for various composites *(154)*. Chitin can be processed to yield chitin nanomaterials (ChNMs) in two forms: (1) rod-like chitin nanocrystal (ChNC) or (2) chitin nanofiber (ChNF) morphologies using chemical or chemo-mechanical extraction processes. ChNMs could be used in concrete as an admixture for setting time and rheology control and to reduce cement use.

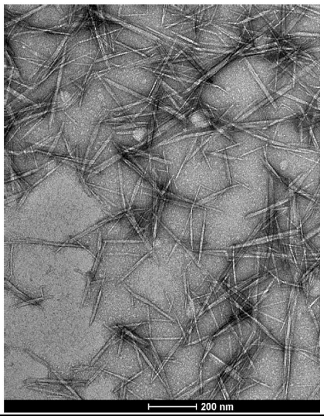
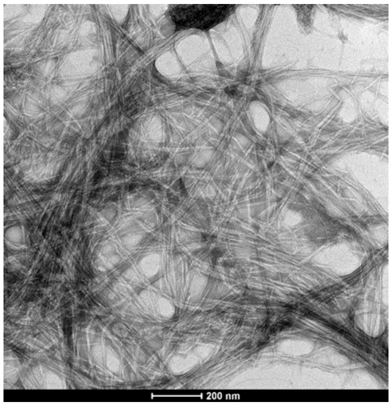
### 2.5.2 *Acting Mechanism in Concrete*

Chitin nanomaterials may boost cement hydration with their high surface area and act as heterogeneous nucleation sites, thereby accelerating the formation of C-S-H nuclei. ChNMs can also be used to regulate the setting time of cement by electrostatic repulsion, and they can refine the microstructure and reduce porosity, thus increasing strength. Crack bridging and reinforcing are possible, depending on the length of the ChNMs. Finally, an increase in the degree of crystallinity of the polymer matrix can contribute to the enhanced stiffness of the composites *(123, 124, 155)*.

### 2.5.3 *Physical and Chemical Properties*

The physical and chemical characteristics of chitin nanomaterials are shown in Table 2.18 *(156)*.

**Table 2.18: Physical and Chemical Properties of Chitin Nanocrystal and Chitin Nanofiber**

| | **Chitin Nanomaterial (ChNM) Type** | |
|---|---|---|
| | **Chitin Nanocrystal (ChNC)** | **Chitin Nanofiber (ChNF)** |
| **Physical Characteristics** | | |
| **Morphology** | Rod/whisker type<br> | Fibrillous<br> |
| **Size** | Length: 211±80 nm<br>Width: 8.7±4 nm<br>Aspect ratio: 24±20 nm | Length: 1063±765 nm<br>Width: 16±10 nm<br>Aspect ratio: 67±90 nm |
| **Chemical Characteristics** | | |
| **Crystallinity Index** | 92% | 92% |
| **Zeta Potential** | In deionized water: 56.1 ± 4.5 mV (at pH = 7.6)<br>In pore solution: -28.04 ± 2.6 mV | In deionized water: +3.9 ± 0.7 mV (pH = 6.9)<br>In pore solution: -24.02 ± 9.1 mV |
| **Surface Groups** | Carboxylate, OH | OH, NH4+ (trivial) |
| **Surface Charge Density** | 0.36 mmol | 0.01 mmol |

### 2.5.4 *Feedstock Description and Supply*

Chitin nanomaterials are produced from alpha-chitin (the most ubiquitous type of chitin) with remarkable structural possibilities due to its highly organized crystalline structure *(157)*. Chitin is produced in living organisms on a scale of $10^{10}$ to $10^{11}$ t per year. The fishing and seafood industry generates approximately 6.6 to 8.8 million T (6 to 8 million t) of waste annually *(158)*, mostly discarded or used as low-value-added products (animal feed and fertilizers) *(159)*. About 70% of the weight of the rejects is the bark, with 20% to 30% chitin depending on species and seasons *(160)*. If discarded without treatment, seafood waste can harm aquatic species due to high nitrogen, phosphorus, and other content *(159)*, and it is a source of marine coast pollution *(161)*.

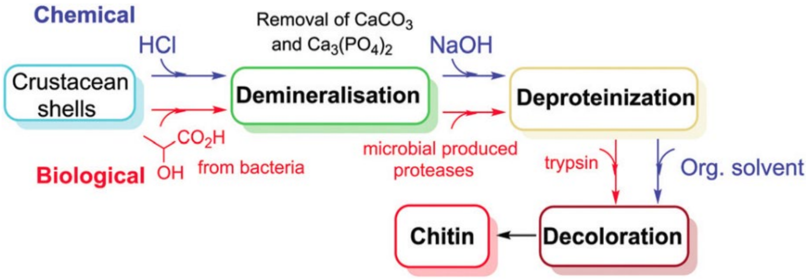
Shrimp, crab, and lobster shells are chemically and commercially valuable and are the main sources of chitin found in nature. About 200,000 T (181,437 t) of shrimp, 35,000 T (31,751 t) of lobster, and 90,000 tons of crab are processed in the United States. The waste from these can be processed to yield chitin. The United States is reported to be using 75 to 100 T (68 to 90.7 t) of chitin every year *(162)*.

Nanochitins can be released from shells by controlled chemo-mechanical refinement methods to produce ChNMs with fit-for-purpose morphology, size, surface groups, and ionic charge that have reinforcement possibilities for composites *(154)*. Their desirable properties are high specific area, stiffness, highly reactive surface chemistry, and low density. Chitin, the source material, is renewable, biodegradable, and a nontoxic source material *(161,163,164)*.

### 2.5.5 *Process Description, Technology Readiness Level, and Potential Suppliers*

#### Process Description

Conventional chitin extraction methods involve deproteination with an alkaline solution, demineralization with an acidic solution, and decolorization by removing astaxanthin pigments and lipids with organic solvents and bleaching to achieve white chitin fiber. The process is shown in Figure 2.16 *(159,163)*.



*Source:* Santos et al (2020); Maschmeyer, Luque, and Selva (2020) *(159,163)*.

**Figure 2.16: The process of extracting chitin from crustacean shells.**

The TEMPO-oxidation treatment method can be applied to pure industrial chitin to produce chitin-NC. Chitin is a polymer of poly(β-(1-4)-N-acetyl-D-glucosamine), which is structurally similar to cellulose but has acetamide groups at the C-2 positions *(165)*, shown in Figure 2.17a. In the TEMPO-oxidation method, the primary C-6 hydroxyl groups on the chitin surface or in amorphous regions can be selectively oxidized to carboxylate groups *(166)* (Figure 2.17b). The amount of oxidant (sodium hypochlorite, NaClO) can be tuned to deliver chitin-NCs with different morphologies, shown in Figure 2.17c and Figure 2.17d.

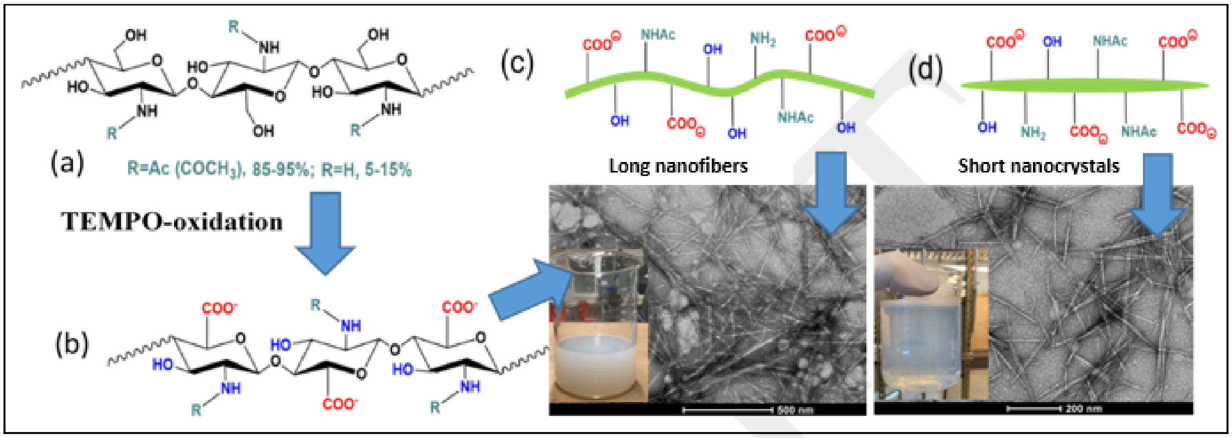
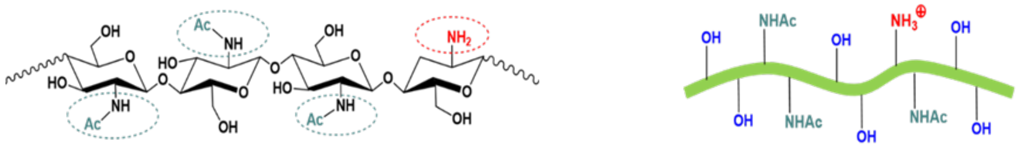


**Figure 2.17: Chemical structure of (a) source chitin, (b) carboxylated chitin, (c) carboxylated chitin nanocrystals with a low degree of oxidation, and (d) carboxylated chitin nanocrystals with a high degree of oxidation.**

Chitin-NF is produced by a mechanical fibrillation method that uses no chemicals. This method uses grinding discs to liberate nanofibers through massive compression and shearing forces. This method has little effect on the chemical structure because there is no chemical usage in the process, but the accessible reactive groups, such as hydroxyl and amino groups, will increase due to the significant increase in surface areas of chitin-NFs (Figure 2.18). The amino groups on the surface of chitin-NFs can be converted into positively charged ammonium ions ($-NH_3^+$) with the addition of acid because of the protonation under the pH of 3 to 4, leading to positively charged ChNF in an acidic aqueous medium *(167)*.



(a) (b)

**Figure 2.18: Figures showing (a) chemical structure of original chitin and (b) scheme of mechanically fibrillated cellulose nanofibers with positively charged ammonium ions at pH 3 to 4.**

A summary of the production process for ChNCs and ChNFs is provided in the system diagrams in Figure A.4 and Figure A.5.

## Technology Readiness Level

Using chitin nanomaterials as admixtures for concrete is still in the laboratory research and development stages at around TRL 3.

## Potential Suppliers

A full list of producers of chitin and chitosan across the United States and globally that were interviewed and contacted is provided in Table 2.19. Some suppliers produce chitosan, which is a derivative of chitin produced by removing acetyl groups of chitin using a concentrated NaOH solution *(168)*. Chitin and chitosan have the same molecular structure. However, the main difference between chitin and chitosan, which is important for commercial applications, is that chitin is insoluble in most aqueous acid solutions and dissolves only in toxic and corrosive solvents. On the contrary, chitosan is soluble in dilute acid solutions *(169)*. The information for the suppliers that were reached is summarized in Table 2.19. The full list of chitin/chitosan suppliers in the United States can be found on the American Chemical Suppliers website.[4] Chitin and chitosan is manufactured both domestically and internationally: "In the United States, there are several producers who manufacture and import chitosan. These include Vanson, Inc., DCV, Inc., Biopolymer Engineering, Inc., and Marine Polymer Technologies. There are also industries manufacturing chitin and chitosan in many countries on almost every continent. In particular, Japan, China, and Norway have well-established companies. Chitin and chitosan are still in the

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[4] More information is available at americanchemicalsuppliers.com/list/search?search=chitin.

stage of a specialty chemical and are sold mostly in the form of chitosan powder, at $25–50/kg, depending on purity. The primary uses are in the water treatment, paper, and agricultural industries. It is also sold as a dietary additive worldwide. Specialty producers offer very pure chitin and chitosan derived from algae and squid pens. These are primarily employed in biomedical research and biomedical products" *(170)*.

### Table 2.19: Information from Chitin Suppliers in the United States and Globally

| Company | Country | Annual Volume of Chitin Produced | Will It Increase? | Price (min. 1 MT) | Type of Agreement | Interested in Partnering with Project Team? | Interested in Making ChNFs at the Metric Ton Scale? | Any Challenges in Material Handling, Storage of Chitin? |
|---|---|---|---|---|---|---|---|---|
| Safimex Joint Stock Company | Vietnam | | | $3.29-4.09/kg (min. 10 MT) | | | | |
| Alibaba.com Lubon Industry | China | | | $4.4/kg (min. 5 MT) | | | | |
| Blueweight Biotech LLP | India | | | $5/kg (min. 1 kg) | | | | |
| Tidal Vision | USA | Nearly non-existent market for chitin since it is insoluble in everything other than strong ionic solutions (that are expensive and impractical). Most applications need a soluble form, which is why 99% of our business is selling chitosan (which is soluble in dilute organic acid solutions). | The market for chitin derivatives like chitosan is growing rapidly (many 3rd party market research reports mix up chitin and chitosan). In the US, we are the only commercial-scale producer (there are 1-2 other startups with websites that aren't commercially producing chitin or chitosan). Tidal is building an additional production line this summer, which will be able to produce about | $14.7/kg (>20 MT) | Happy to have an Off-take agreement. If the volumes required us to build additional production line(s) then we would need to have the Off-take agreement in hand ~twelve months in advance. If less than 100,000 lbs per year we wouldn't require any special agreement and could simply supply you with less than 30 day lead time once ramped up (we currently only | | Tidal is interested in manufacturing nanofibers, and we have some capital (and access to additional if it made sense) that could help move this project along potentially. | Chitin is stable for many (5+) years if stored out of direct sunlight and kept dry. We've tested samples older than 5 years old and there's no significant difference in polymerization. |

| Company | Country | Annual Volume of Chitin Produced | Will It Increase? | Price (min. 1 MT) | Type of Agreement | Interested in Partnering with Project Team? | Interested in Making ChNFs at the Metric Ton Scale? | Any Challenges in Material Handling, Storage of Chitin? |
|---|---|---|---|---|---|---|---|---|
| | | | 3,300 lbs per day of chitin (which can operate for ~300 days per year). However, we can build and run multiple additional production lines if the demand is there. These production lines take 9-12 months to construct, and we are starting construction of one this June or July 2021. | | maintain inventory on hand for chitosan, but can start stock chitin for you). | | | |
| Scandinavian Formulas | USA | Reseller not producer | Reseller not producer | $38.2/kg | None needed | We can supply with product. | No | No challenges |
| BOC Sciences | China | 1200 MT/year | Yes, based on demand | $39/kg | Depending on volume: $39/kg for >1 MT or $250 for 2 kg for research. | We do not have experts in this area. Most of our colleagues are PhD in chemistry in our tech team. | We can do customized manufacture if you can provide more information. Our chemist will check to see whether we can make it. | |

| Company | Country | Annual Volume of Chitin Produced | Will It Increase? | Price (min. 1 MT) | Type of Agreement | Interested in Partnering with Project Team? | Interested in Making ChNFs at the Metric Ton Scale? | Any Challenges in Material Handling, Storage of Chitin? |
|---|---|---|---|---|---|---|---|---|
| Creative Enzymes | USA | 2-5 ton/month | It will depend on demand | $69/kg (>200 kg) | We would like to have a Purchase Order to initiate the business. 60% upfront is needed if >100 kg. | We are only able to provide the chitin product for now. Training or involvement in development is not a part of our services. But if you have any questions regarding the product, please feel free to contact us. | Yes, we are open to it. | |
| Alfa-Chemistry | USA but supplier in China | | | NanoChitin<br>20-600 nm<br>$107.6/kg | Simple PO | | | |
| Kitozyme | Belgium | No response | | | | | | |
| Chitolytic | Canada | No response | | | | | | |

**Current Use of Product**

Some uses for chitosan and chitin are in medical applications: tissue engineering, wound healing, surgical sutures, bandages, food additives, supplements, vaccine adjuvants, and drug delivery *(152,153)*. Chitosan is used in stormwater treatment *(155)*.

**Agents Involved in Production and Distribution**

The private manufacturing industry is needed to produce nanomaterials from chitin. Other producers involved are producers of chitin and chitosan. The parties involved with the feedstock are the seafood and canning industries.

**Product Consideration in Caltrans Specifications**

Caltrans specifications currently do not include chitin nanomaterials as an accepted SCM for concrete.

### 2.5.6 *Performance in Concrete Based on the Literature*

Unlike cellulose nanomaterials, chitin nanomaterials are rarely used in cementitious composites. The following discussion provides a summary of the findings from three studies *(155,156,171)*.

**Impact on Fresh Properties**

The initial and final setting time was increased by adding ChNC up to a concentration of 0.055 wt%. The highest delay recorded was 56 minutes and 106 minutes for initial and final setting times, respectively, at this concentration. This delay was less prominent for ChNF, where the highest delay was 35 minutes and 78 minutes for initial and final setting times, respectively. The final and initial setting time of ChNF-cement decreases with ChNF concentrations beyond 0.035 wt% and reaches a plateau with concentrations higher than 0.075 wt%. ChNF at 0.035 wt% delays the initial and final setting by 35 minutes and 78 minutes, respectively. This retardation effect was attributed to the higher negative zeta potential and the presence of a reactive surface group causing electrostatic repulsion. The retardation was less with ChNF due to its tangled and long-fiber morphology.

The effect of ChNMs on rheological properties (i.e., viscosity and consistency) was studied. The addition of ChNC and ChNF either increased or did not affect consistency compared to the control mix. No specific concentration dependence was obtained for consistency or viscosity. ChNF had higher plastic viscosity than ChNC because of its fiber-like morphology that shows more thinning behavior and may cause entanglement, thus increasing the plastic viscosity *(156)*.

**Impact on Strength and Durability**

All the doses of both ChNC and ChNF increased the 7-day compressive strength with a maximum of 31% at 0.15 wt% of ChNC. For ChNF, the greatest improvement of 21% was measured for the 0.05 wt% concentration. However, the increase in 28-day compressive strength was less profound compared to the 7-day strength increase. At 28 days, the maximum 12% improvement was observed for ChNF at the 0.05 wt% concentration, which was reduced for higher doses mainly due to the fiber entanglement causing a stress concentration zone. The addition of ChNMs did not change the modulus of elasticity.

The most profound effect of ChNMs was observed in flexural strength and fracture energy. At 28 days, the enhancements in flexural strength with ChNC were between 16% and 40% for three tested concentrations and the increase was significant at a 95% confidence level. For ChNF, the greatest improvement in flexural strength was observed for the 0.05 wt% concentration (41%). The fracture energy was also reported, which was calculated from the load-deflection data of the flexure test. At 28 days, the greatest improvement in fracture energy was 1.8 times and 2.7 times for ChNC and ChNF, respectively, compared to the control mix. This improvement was attributed to the possible interactions between the reactive surface groups present in the chitin nanoparticles and the cement hydrates. In addition, a higher crystallinity index and nano reinforcement of cracks and porosity may have resulted in higher flexural strength and fracture toughness.

A summary of the overall impact of ChNMs on various properties of concrete is provided in Table 2.20.

**Table 2.20: Summary of the Effect of Chitin Nanomaterials on the Properties of Cement-Based Materials**

| Property of Concrete | Comparison to 100% OPC Concrete |
|---|---|
| Water demand | Increase |
| Early strength | Increase up to a certain dosage |
| Late strength | No change |
| Pozzolanic reactivity | Increase or decrease |
| Setting time | Increase |
| Drying shrinkage | Needs more research |
| Alkali-silica reaction | Needs more research |
| Sulfate attack resistance | Needs more research |
| Freeze-thaw durability | Needs more research |

### 2.5.7 *Environmental Considerations*

Chitin is a nontoxic, biocompatible, and biodegradable source material. The production methods of chitin nanomaterials are similar to those described for cellulose nanomaterials. Therefore, ChNMs are expected to have a similar environmental impact to cellulose nanomaterials. However, differences lie in the process of the source material (i.e., extraction of chitin and isolation from protein and calcium carbonates versus pulping of cellulose).

### 2.5.8 *Cost Considerations*

In an initial techno-economic analysis (TEA), a study identified the concrete pavement industry in Washington state as the end-user for ChNM admixture and obtained the annual volumes of concrete used in Washington state. Based on this information, the annual volumes and cost of chitin and TEMPO precursors were determined, and a TEA with two cost values for chitin powder was performed *(171)*. The study also included a second TEA for the mechanical approach to producing ChNFs. The mechanical process would produce ChNFs with an estimated cost of \$7.1 to 8.5/yd$^3$ (\$9.3 to \$11.1/m$^3$) of concrete depending on the cost of chitin powder, which corresponds to a 20% reduction compared to the TEMPO process [\$9.1 to 10.4/yd$^3$ (\$11.9 to \$13.6/ m$^3$) of concrete].

## 2.6 Seashell Powder

### 2.6.1 *Product Description*

Waste seashells could be reused for a circular economy rather than disposed of in landfills or the sea/oceans. Seashell waste primarily consists of oysters, clams, scallops, mollusks, and mussel shells, also called bivalves in the scientific literature *(172)*. Shells are nonbiodegradable, have a high disposal cost for the seafood industry, and are harmful to the environment *(173)*. Around 7 million tons of waste seashells end up in landfills and oceans worldwide, according to most of the literature, and a few studies have reported more than 10 million tons generated yearly in China alone *(174)*.

### 2.6.2 *Acting Mechanism in Concrete*

The primary function of ground seashells is expected to be a filler in cementitious systems. In addition, it is possible that the calcium carbonate produces new hydrate assemblage and further enhances the performance of the cementitious systems.

### 2.6.3 *Chemical and Physical Properties*

Seashells are made up of calcium carbonate in the mineral form of calcite or aragonite. They uniquely contain an intraskeletal organic matrix rich in carboxylate groups that allows covalent bonding with the cementitious matrix *(175)*. According to the literature, the calcium oxide content in oyster shells ranges from 48% to 86.8%. The morphology of seashell powder was found to be irregularly shaped particles in multi-angle shapes and some slender particles. The average particle size was reported to be 20.8, 29.9, 13.9, and 13.6 μm for clam, mussel, oyster, and cockle shells, respectively *(176).*

### 2.6.4 *Feedstock Description and Supply*

China is the largest producer of bivalves, followed by Chile, Korea, the United States, Spain, and France *(175)*. Shells such as those of mollusks are made up of over 95% calcium carbonate.

### 2.6.5 *Process Description, Technology Readiness Level, and Potential Suppliers*

#### Process Description

Most researchers have suggested washing and calcinating seashells during waste pretreatment to remove the organic matter and chloride content before using them in construction material. The process of washing and drying oyster seashell waste at about 105°C to 110°C has been reported in the literature. In some studies, sun drying was used. A wide variation in the calcination temperature and calcination duration of seashells has been reported, ranging from 190°C to 1000°C and for a few minutes to days *(177)*. The full process involved in implementing seashell powder in concrete as an SCM is shown in the system diagram in Figure A.6.

#### Technology Readiness Level

Seashells have been used in construction, such as in concrete as aggregates, in many coastal settlements around the globe. However, an industry-scale facility for processing seashells for use as an SCM (or aggregate) in concrete was not found in the United States. Therefore, the TRL is the laboratory research level around TRL 3 or 4.

#### Potential Suppliers

A supplier of processed seashell powder was not found.

#### Current Use of Product

A small fraction of seashells are used for fertilizers and handicrafts. Part of the seashell waste generated by the aquaculture industry is recycled as a lime substitute, wastewater decontaminant, soil conditioner, fertilizer constituent, feed additive, and liming agent *(177).* Researchers have proposed recycling seashell waste as an aggregate in mortars, substituting natural aggregates to replace limestone aggregates from quarries, and employing it as a silica sand substitute *(178).*

#### Agents Involved in Production and Distribution

Currently, no agents are producing seashell powder at the industry scale.

**Product Consideration in Caltrans Specifications**

Caltrans specifications currently do not include seashell powder as an accepted SCM for concrete.

### 2.6.6 *Performance in Concrete Based on the Literature*

Researchers have explored the effect of seashell waste as a replacement for cement or aggregates in cement composites. Seashell waste influences both the fresh and hardened properties of cement composites, summarized in the following sections.

**Impact on Fresh Properties**

The performance of seashell waste in cement composites varies depending on its size and substitution constituents. One study reported a reduction in water demand with increasing seashell waste content when replacing cement in the mortar *(173)*. Similarly, another study reported improved workability by including mussel seashell powder as cement replacement *(176)*. The finer size of the waste shell fills voids between cement particles and increases the amount of free water to improve workability. However, most studies found reduced workability by including seashell waste as a replacement for aggregates in the composites. The reduction in workability depends on the percentage of replacement with seashell waste. A study reviewed and summarized the workability results and possible reasons for the reduction in workability from the literature *(179)*. Using oyster seashells, the maximum decrease in workability was 94% for up to 20% replacement. Similarly, seashell waste from periwinkle and mussel caused an 87% and 92% reduction, respectively, in workability measured in terms of slump value. The decrease in workability was believed to be due to the irregular shape of the seashell waste. The angular shape of the seashell waste increases the interparticle frictions and reduces workability. However, one study reported a 15% increase in workability with up to 60% replacement of fine aggregate with scallop seashell waste *(180)*. The coarser size of the seashell waste increased the workability of the cement composites.

No common trends in setting time with the inclusion of seashell waste were observed across the literature. The influence of the addition of seashell waste depends on the replacing constituents (cement/aggregates), doses, and particle sizes of the waste. When replacing cement, seashell powder slows down the hydration process due to the dilution of cement and reduction of the surface area of the blended cement *(178)*. One study also reported delays in the initial and final setting time with seashell powder as a cement replacement *(181)*. Replacement of fine aggregate up to 20% with oyster seashell waste fines delayed the hydration due to the high water absorption of shell fines and organic matter in the shell fines *(182)*. Another study showed an increase in setting time with the increase in the percent replacement of sand with shell waste *(183)*. The presence of organic matter and chitin, a polysaccharide in the mussel shell, increases the setting time of concrete when replacing natural sand. Other research has also found an increase in setting time *(176,184)*. The reasons mentioned for an increased setting time were the formation of calcium hydroxide and a decrease in hydration when the seashell was replaced with cement. On the contrary, some studies reported reducing the setting time by replacing aggregate with seashell waste *(184,185)*. The formation of some early C-S-H gel was attributed to the early setting of the composites.

### Impact on Strength

A review article tabulated the effect of seashell waste on the mechanical properties of cement composites (Table 2.21) *(179)*. Most studies found a reduction in compressive strength with the addition of seashell waste either as a replacement for cement or aggregate. The decline in compressive strength was attributed to the higher surface area of the seashell waste requiring more cement for coating, less strength of seashell waste compared to the aggregate, poor interfacial bonding, and a more porous interface *(179)*. A reduction of 63% in compressive strength was recorded, with a replacement level of up to 20%. The highest reduction was 72% recorded for the 100% replacement level. Another study reported a decrease with the increasing amount of seashell powder and attributed this decrease to the increase in the effective water-to-cement (w/c) ratios. However, the study reported a higher compressive strength growth rate with seashell waste powder.

**Table 2.21: Summary of Effect of Seashell Waste on 28-Day Compressive Strength**

| Type of Seashell | Type of Replacement | Replacement Level | % Increase (+)/Decrease (-) in Strength |
|---|---|---|---|
| Oyster | Lime | Up to 15% | Up to 14% (+) |
| Oyster | Cement | Up to 20% | Up to 43% (-) |
| Oyster | Cement | 5% | 5% (+) |
| Oyster | Cement | 5-20% | Up to 21% (-) |
| Oyster | Fine aggregate | 5% | 5% (+) |
| Oyster | Fine aggregate | 5-20% | Up to 35% (-) |
| Oyster | Cement | Up to 22% | Up to 61% (-) |
| Oyster | Fine aggregate | Up to 50% | Up to 10% (-) |
| Oyster | Coarse aggregate | Up to 50% | Up to 50% (-) |
| Mussel | Fine aggregate | Up to 100% | Up to 72% (-) |
| Mussel | Coarse aggregate | Up to 50% | Up to 46% (-) |
| Mussel | Cement | Up to 20% | Up to 63% (-) |
| Cockle | Cement | Up to 20% | Up to 50% (-) |
| Cockle | Cement | Up to 50% | Up to 73% (-) |
| Cockle | Coarse aggregate | Up to 50% | Up to 19% (-) |
| Cockle | Fine aggregate | Up to 30% | Up to 17% (+) |
| Cockle | Fine aggregate | 30-50% | Up to 17% (-) |
| Scallop | Fine aggregate | 5% | 10% (+) |
| Scallop | Fine aggregate | 5-60% | Up to 10% (-) |
| Scallop | Fine aggregate | Up to 60% | Up to 27% (-) |
| Periwinkle | Coarse aggregate | Up to 50% | Up to 63% (-) |
| Periwinkle | Coarse aggregate | Up to 50% | Up to 30% (-) |
| Clam | Cement | Up to 20% | Up to 27% (-) |
| — | Fine aggregate | Up to 100% | Up to 17% (-) |
| — | Fine aggregate | Up to 50% | Up to 29% (-) |
| — | Coarse aggregate | Up to 50% | Up to 17% (-) |

Source: Haider et al. (2022) *(171)*.

Only a few studies found an increase in compressive strength with a smaller level of replacement of cement/lime or aggregate with seashell waste. One study reported a 7.5% increase in compressive strength with an 8% replacement of cement in the mortar *(178)*. Therefore, the researchers proposed 7% to 30% as the desirable dose for seashell waste powder. The reason for the improvement was mentioned as the filler effect of seashell waste because of its finer sizes compared to the portland cement filling the voids between cement particles. Replacement of coarse aggregate, even by 100%, with seashell waste was found to be feasible for developing low-strength concrete that meets the specification for lightweight concrete *(186)*. A study reported a 17% improvement in compressive strength with up to 30% replacement of fine aggregate *(187)*.

Most studies reported decreased flexural and split tensile strength with seashell waste inclusion *(179)*. One study reported a decrease in flexural strength with seashell waste powder replacing cement by up to 30% *(178)*. The highest 21% reduction was seen for a 30% replacement level, while the least was for an 8% replacement level. Another study found a decrease in split tensile strength, 46% lower at 7 days for 20% replacement of aggregate with seashell, and the smallest decrease at 28 days was 12% for 10% replacement *(188)*. Another study reported a 10% decrease in split tensile strength with a 40% aggregate replacement with crushed scallop shell *(189)*. Other research found a 10% reduction irrespective of the mussel shell doses used as aggregate *(183)*. This result was attributed to the higher absorption, shape of the mussel shell, and presence of organic matter in the mussel shell. However, a few studies reported increased flexural and tensile strength, attributed to the stronger interfacial bond between aggregate and cement paste due to high-calcium content *(190)*. A study reported an increase in split tensile strength with up to 10% of seashell and, afterward, a reduction of splitting tensile strength with increasing seashell powder with cement replacement *(181)*. Similarly, a study showed improvement in split tensile strength up to 10% aggregate replacement with seashell waste *(191)*.

## Impact on Durability

Researchers have reported both positive and negative effects from seashell waste on the shrinkage of cementitious composites. For example, studies have shown an increase in drying shrinkage by including oyster and mussel seashells as replacements for fine aggregate *(183,191).* Low rigidity of higher amounts of fines and moisture in the seashell particles were identified as the possible reasons for higher shrinkage. Contrarily, two other studies reported a decrease in the shrinkage for samples with seashells compared to the control, which was attributed to the pore refinement due to the fineness of the seashell powder *(176,192)*.

One study reported a significant reduction in water permeability in the concrete due to the incorporation of mussel shell aggregate, which has a flaky and elongated shape, preventing water penetration *(183)*. Other studies have shown reduced water transport using seashells as an aggregate replacement *(182,187)*. Researchers found a decrease in water permeability for samples with seashell ash powder compared to the control specimens after 120 days of curing due to the expansion of CaO hydrates refining the matrix *(190)*. However, other studies have shown differing findings, with an increase in the water transport in cement composites *(189,193)*. A study reported a negative impact of seashell powder when replaced with cement on concrete sulfate and alkaline attack *(181)*.

Similarly, no common finding was found among studies for freeze-thaw resistance of seashell-incorporated cement composites. Two studies found better performance with the inclusion of oyster seashells as a replacement for fine aggregate, attributed to the fine particles of seashell powder filing the voids and the reduction of the soluble calcium hydroxide *(191,194)*. However, two other studies reported a decrease in freeze-thaw resistance with seashell waste *(193,195)*.

A summary of the overall impact of seashell powder on various properties of concrete is provided in Table 2.22.

**Table 2.22: Summary of the Effect of Seashell Powder on the Properties of Cement-Based Materials**

| Property of Concrete | Comparison to 100% OPC Concrete |
|---|---|
| Workability | Increase |
| Early strength | Decrease |
| Late strength | Decrease |
| Setting time | Increase |
| Drying shrinkage | Increase |
| Alkali-silica reaction | Decrease |
| Sulfate attack resistance | Decrease |
| Freeze-thaw durability | Decrease |

### 2.6.7 *Environmental Considerations*

Waste seashells, if left untreated for an extended period, can cause foul odors due to the decay of the remaining flesh in the shells or the microbial decomposition of salts into gases, such as $H_2S$, $NH_3$, and amines. An enormous amount of waste seashells has been dumped into public waters and/or landfills by the seafood industry, causing many environmental problems, including pollution of coastal fisheries, management of public water surface, foul smells as a consequence of the decomposition of organics attached to the shells, damage of natural landscape, and health/sanitation problems *(172)*.

#### Global Warming Potential

Seashell is a waste material and will have negative environmental impacts when disposed of in the landfill. If used as an SCM or as other additives in any other material, required processing—such as cleaning, crushing, and grinding—will allocate environmental burdens to the material. Few studies have examined the environmental impacts of seashell processing into seashell powder.

One study determined that 1 kg of seashell powder has a GWP of 0.068 kg $CO_2$-eq compared to ordinary portland cement having a GWP of 0.875 kg $CO_2$-eq *(196)*. Researchers found that using seashell powder blended mortar brings down the GWP of the mortar. A reduction of 7% in the GWP was observed when comparing mortar made of blended cement (10% portland cement replaced with seashell powder) with mortar made of 100% portland cement. In one study*,* 1.12kg of $CO_2$ emissions were recorded from producing $CaCO_3$ from 100 metric tons of mussel shells, calculated to be 172.6 kg of $CO_2$ per ton of $CaCO_3$ from seashells *(197)*.

#### Toxicity

Besides $CaCO_3$ making up 95% of seashells, they also contain glycoproteins, polysaccharides, chitin, and other proteins that produce $NH_3$, $H_2S$, and other toxic, hazardous hydrocarbon gases under microbial decomposition at room temperature *(198)*. Some other toxic seashell examples include cone shells and shellfish (clams, oysters, mussels, scallops) *(199)*.

### 2.6.8 *Cost Considerations*

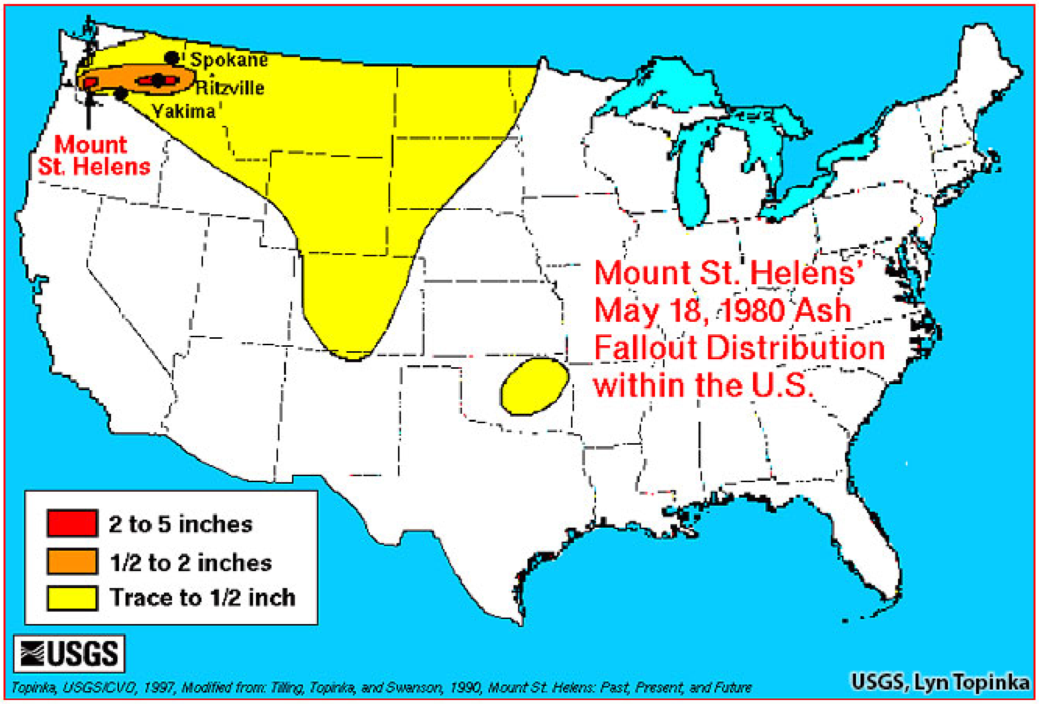
Seashell is not currently used as an SCM, so determining a definitive price is not straightforward. Seashell prices would vary highly depending on availability, region, and material transportation costs. In addition, processing—which could include cleaning, crushing, and grinding—are additional costs associated with seashell powder that could be used as an SCM. A few costs acquired from the literature include bulk crushed oyster shell and oyster shell flour at the cost of around $45.95 per 0.025 T ($41.68 t) *(200)*, clam shells at the cost of approximately $55.11 per T ($50 per t), and oyster shells at the cost of $424.4 per T ($385 per t) *(201)*.

# 3 NATURAL POZZOLANS

## 3.1 Natural Pozzolans with Volcanic Origins

### 3.1.1 *Product Description*

Natural pozzolans are aluminate-silicate materials with the potential to be used as an SCM in their naturally occurring state or with minimal treatment *(202)*. These materials originate from pyroclastic and sedimentary rocks, are processed mainly by sieving and grinding operations, and are found in areas with a history of volcanic activities. Natural pozzolans include a wide range of materials, such as calcined clay (metakaolin), calcined shale, diatomaceous earth, opaline shales, and volcanic materials *(203)*. This section discusses natural pozzolans of volcanic origin—that is, pozzolans formed from volcanic eruptions, including pumice, zeolite, perlite, volcanic ashes, and scoria. A volcanic eruption can be devastating; however, it brings out huge quantities of ash materials (i.e., volcanic ashes) that can be used as an ASCM. Figure 3.1 is an ash distribution fallout map showing that ash can reach areas far from the origin of the eruption. The ash depth contours give an estimate of the huge amounts of ash resulting from the eruption.



Source: Mount St. Helens Science & Learning Center (n.d.) *(204)*.

**Figure 3.1: Ash fallout distribution from Mount St. Helens eruption on May 18, 1980.**

### 3.1.2 *Acting Mechanism in Concrete*

Natural pozzolans of volcanic sources are typically used in concrete as an SCM. These materials—such as pumices, perlite, and volcanic ash—have high pozzolanic activity resulting from their rich glass content and highly vesicular or porous nature *(202)*. In addition, natural pozzolans, such as pumice and shale, can be used as lightweight aggregates *(205,206,207)*. Perlite has a highly amorphous and siliceous nature, which makes it an ideal pozzolan to be used in concrete. One study showed that the perlite fines that were stocked in Australian perlite mines had the potential to be considered for use as an SCM *(208)*. Another study implemented XRD and differential thermal analysis on mortar and found that perlite powder had a similar effect in mortar as traditional SCMs *(209)*. Volcanic ash is very similar to other volcanic pozzolans. Large plumes of hot gases and volcanic ashes are caused by explosive eruptions that make volcanic ash similar to perlite and pumice in terms of chemical components. However, volcanic ash may contain a large amount of mineral impurities, which increase the crystalline phase of the volcanic ash *(210)*.

### 3.1.3 *Chemical and Physical Properties*

Pumice, a highly porous pyroclastic material from the rapid cooling and solidification of volcanic matter, is a colorless or light-grayed igneous rock material *(203)*. Pumice ore comprises $SiO_2$ (60% to 75%), $Al_2O_3$ (13% to 17%), $Na_2O$-$K_2O$ (7% to 8%), $Fe_2O_3$ (1% to 3%), CaO (1% to 2%), and low amounts of $TiO_2$ and $SO_3$ *(211)*. Because of the high silica and amorphous phase content, pumice powder can be considered an ASCM *(213)*. The use of pumice powder as an SCM in concrete has a long history. Before the dominance of coal fly ash, it was implemented in many concrete structures, such as the Los Angeles aqueduct built in 1912 *(203)*.

Zeolites are formed from the diagenetic alteration of pyroclastic materials by alkaline waters under high pressure during deposition. However, alteration induced by less alkaline fluids results in the formation of clay minerals *(202)*. Zeolites are hydrated alumina-silicates with evenly stacked silica and alumina tetrahedra, resulting in an open, porous, and stable framework of consistent diameter channels *(203)*.

Perlite, unlike zeolite, is an unaltered pyroclastic rock or volcanic glass with high amounts of water *(202)*. Perlite can expand up to 35 times its original volume when subjected to a temperature of about 1100°C *(213)*. Perlites contain approximately 75% $SiO_2$, 10% to 15% $Al_2O_3$, and some amounts of alkalis.

Natural volcanic ash forms from the violent separation of molten rock into tiny pieces during explosive volcanic eruptions *(203)*. Volcanic ash comprises fragments of glass, minerals, and rock less than 0.08 in. (2 mm) in diameter *(214)*. Artificially, they are derived from crushing or grinding both loose and consolidated volcanic rocks such as pumice and scoria *(214)*. The mineralogical and chemical compositions, including the glass content and fineness of the volcanic ash, determine its pozzolanic reactivity *(203)*.

Volcanic scoria is the fragments of vesicular magma with a density lower than 1 g/cm$^3$. The internal structure of scoria contains tight pores and cells. Scoria is characterized by the high amount of vitreous components, and the high content of $SiO_2$ makes it a candidate for a reactive pozzolan. The $SiO_2$ in scoria can react with calcium hydroxide preset in cement, mortar, or concrete to form C-S-H gels *(215)*. One study showed that black scoria contains the required amounts of $SiO_2$ (46.52%), $Al_2O_3$ (13%), and $Fe_2O_3$ (11.4%) to be considered a pozzolan. Also, scoria has less than 10% loss on ignition (2.58%) and less than 4% $SO_3$ content (0.27%) *(216)*.

### 3.1.4 *Process Description, Technology Readiness Level, and Potential Suppliers*

#### Process Description

Using natural pozzolans in concrete is mainly influenced by the local availability of suitable deposits and the existing market of traditional industrial byproduct SCMs *(202)*. Some pyroclastic materials appropriate as natural pozzolan can be found in California and western states such as Utah and Nevada. Typical steps in the process of obtaining ash or aggregate from natural pozzolan of volcanic origin are mining, transporting, crushing, sorting/grading, and grinding *(217)*. Pretreatment is generally not a requirement. The full process is summarized in the system diagram in Figure A.7.

## Technology Readiness Level

As mentioned earlier, pumice powder was used in SCM concrete structures and has construction precedence like the Los Angeles aqueduct that was built in 1912 *(203)*, and it could be considered to be at a high TRL 8 (“technology has been tested and ready for implementation”) or 9 (“technology fully implemented”). However, after coal fly ash dominance of the concrete market, the uses of natural pozzolans in recent years have been very few. Several concrete suppliers incorporate natural pozzolans in their ready-mix concrete and other applications such as pavers and masonry. Overall, the TRL can be estimated to be at a ready-for-implementation level.

## Potential Suppliers

Various natural pozzolans, including pumice, have readily accessible sediments effectively used in industrial applications *(218)*. Natural pozzolan with pyroclastic nature is available in areas with a recent history of volcanic activities. The global distribution of volcanic rocks and deposits of natural pozzolans is shown in Figure 3.2.

Source: Snellings, Mertens, and Elsen (2012) *(202)*.

**Figure 3.2: Global distribution of volcanic rocks (shaded areas) and natural pozzolan deposits (dots).**

Reports of production amounts of some natural pozzolans are available from the US Geological Survey (USGS) mineral summary report *(5)*. The United States produced 580,000 tons of pumice in 2021, mined in California, Kansas, Idaho, Oregon, and New Mexico. Most of the mined pumices are concentrated in the western states. For zeolites, 87,000 tons of natural zeolites were produced in 2021 from nine zeolite mines across Arizona, California, New Mexico, Idaho, Texas, and Oregon. In 2021, 500,000 tons of perlite were produced from eight mines in six western states. Based on this report, an abundance of several pyroclastic natural pozzolans exists in California and neighboring states in the Western United States, indicating good potential for these materials to be used as ASCMs in California.

### Current Use of Product

Pumice is used as a lightweight aggregate for concrete blocks and assorted building materials and as an SCM. Other pumice applications include absorbents, abrasives, and filter aids *(203)*. Both natural and artificial volcanic ash have been used in lightweight concrete and as an SCM in ordinary concrete, high-strength concrete, and high-performance concrete applications *(214)*. Zeolites are predominantly used for animal feed, water purification, and odor control applications in the United States *(5)*. Perlite is mostly used in expanded form for building construction, horticultural aggregate, fillers, and filter aids *(5)*.

### Agents Involved in Production and Distribution

Agents involved in the production and distribution of natural pozzolans of volcanic origin are mining companies, which are usually responsible for mining, milling, and processing the material into different sizes and grades, after which they are transported for various industrial applications.

### Product Consideration in Caltrans Specifications

Caltrans approves using pumice in lightweight concrete as an aggregate *(76)*. It also allows the use of natural pozzolans complying with ASTM C618 (AASHTO M 295), Class N, in regular concrete. Some natural pozzolans are also included in the Caltrans Approved Cementitious

Materials list[5] for use in concrete. AASHTO M 295 and ASTM C618, the standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete, are currently used as the standard for other natural pozzolans such as pumice and zeolite by their suppliers *(219)*. Some suppliers of natural pozzolan in the Western United States are shown in Table 3.1.

**Table 3.1: Suppliers of Natural Pozzolan of Volcanic Origin in California and Western United States**

| Supplier | Product |
|---|---|
| 3M | NP200C |
| DMI | Global Pozzolan Class N - Pumice |
| Golden State Pozzolan | GSP Class N |
| Geofortis | Utah NP |
| KMI | Zeolite Class N |
| Nevada Cement | Fernley Class N Pozzolan |
| Sunrise Materials | Natural Pozzolan Class N |

Source: California Department of Transportation (2024) *(219)*.

### 3.1.5 *Performance in Concrete Based on the Literature*

**Impact on Fresh Properties**

Using pumice as an SCM decreases the workability of the concrete and increases the water demand because the interconnected vesicles of the pumice powder can hold and absorb water *(210)*. While the effect of some natural pozzolans, such as diatomite earth and zeolite, on the increase of water demand is noticeable, some natural pozzolans, such as pumice and volcanic ash, have a moderate impact on water demand and increase water demand only at high replacement rates *(220)*. Finely ground pumice contains particles with jagged edges, which requires more water to coat the surface *(210)*. Volcanic ash meets the ASTM C618 requirements to be considered an SCM.

One study found that increasing the replacement level of cement with perlite from 20% to 30% increases the required amount of water to maintain the same consistency based on the ASTM C187 method *(221)*. In addition, the initial and final setting time of mortar increased when

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[5] More information is available at mets.dot.ca.gov/aml/CementitiousList.php.

20% to 30% of cement was replaced with perlite. However, the delays were in the range of ASTM C595 and ASTM C1157 standards related to the performance of hydraulic cement. The main reason for the considerable increase in water demand by zeolite is the highly porous internal structure and higher surface area, which leads to higher water absorption *(220)*.

Another study used volcanic ash as the cement replacement and found that it did not have a noticeable effect on the initial setting time and final setting time *(222)*. The study also found that a 10% replacement of cement with volcanic ash resulted in similar initial and final setting times to the control. Based on a literature survey, increasing the cement replacement with volcanic ash increases the slump and decreases the compressive strength *(223)*. The results of this study are presented in Table 3.2, which shows that a 20% replacement level decreased compressive strength by around 15%. It was also observed that the amount of air void increases by increasing the replacement level, resulting in a slump increase and compressive strength decrease.

**Table 3.2: Mixture Details, Slump, and Compressive Strength of Volcanic Ash Concrete**

| Mixture ID | VA (%) | Water-to-binder ratio | Cement (kg/m$^3$) | Aggregates (kg/m$^3$) | | Air Content (%) | Slump (mm) | 28-Day Compressive Strength (MPa) |
|---|---|---|---|---|---|---|---|---|
| | | | | FA | CA | | | |
| VA-0 | 0 | 0.45 | 400 | 760 | 1020 | 2.5 | 80 | 41.4 |
| VA-05 | 5 | 0.45 | 380 | 755 | 1020 | 2.5 | 80 | 42.9 |
| VA-10 | 10 | 0.45 | 360 | 751 | 1020 | 2.6 | 90 | 40.8 |
| VA-20 | 20 | 0.45 | 320 | 743 | 1019 | 2.8 | 110 | 35.2 |
| VA-30 | 30 | 0.45 | 280 | 734 | 1019 | 2.9 | 86 | 30.7 |
| VA-40 | 40 | 0.45 | 240 | 725 | 1018 | 3.1 | 85 | 25.2 |

*Notes:* VA: volcanic ash (VA-05 means 5% replacement of cement with VA); FA: fine aggregate; CA: coarse aggregate.

Source: Hossain and Lachemi (2004) *(223)*.

A study on black, dark-red, red, and yellow scoria with 3600, 4500, 4700, and 5200 cm$^2$/g Blaine fineness, respectively, showed that replacing cement with scoria in mortar increases the initial and final setting times *(215)*. For example, replacing 15% of cement with red scoria increased the initial setting time by more than 100% and the final setting time by more than 50%. Also, the fresh and dried densities of samples changed slightly by increasing the replacement level of scoria to 35%.

## Impact on Strength

Different studies have evaluated the effect of replacing OPC with natural pozzolans of volcanic origin on the mechanical properties of concrete *(218,224,225)*. In one study, 25% of cement was replaced with different pumices in mortar *(226)*. Based on this study, the 28-day strength of only one out of ten specimens containing pumice was higher than the control sample. Also, the 90-day strength of only two pumices was higher than the control sample. Therefore, the study concluded that using calcined pumice in mortar mixes would cause higher strengths, while using uncalcined pumice would decrease the compressive strength of mortar.

Another study investigated the engineering properties of concrete containing zeolites at 10%, 20%, 40%, and 60% ordinary cement replacement *(227)*. The results showed that sufficient compressive strength, adequate fracture toughness, and compressive strength could be achieved with 20% zeolite content. However, another study showed that 15% and 25% replacement of ordinary cement with zeolite decreased 25-day and 36-day compressive strength relative to the control *(228)*.

The results of one study showed that using perlite as a cement replacement decreased the compressive strength of mortar *(221)*. Also, the 91-day compressive strength of perlite concrete was lower than the control. When the replacement rate was 20%, compressive strength decreased by 4% to 6%. Moreover, increasing the replacement percentage made the strength decrease more noticeable, and a 30% replacement level decreased the compressive strength of mortar by 13% to 20%. Also, by increasing the fineness of perlite from 320 to 370 $m^2$/kg, the performance of the concrete improved, which resulted in a lower decrease in strength.

A study on mortar with 10% pumice powder replacement revealed that 1-day and 28-day compressive strength decreased by 12% and 9%, respectively *(229)*. Another study showed that replacing 20% of cement with volcanic ash decreased the 28-day compressive strength of mortar by 43%, while replacing 20% of sand with volcanic ash increased the 28-day compressive strength of mortar by 25% *(230)*.

A study showed that by increasing the replacement level of cement with scoria in different colors of red, black, yellow, and dark red, the compressive strength of mortar decreased *(215)*. At 15% replacement, the compressive strength decreased by approximately 4% to 15.5%. At 25% replacement, the compressive strength decreased by approximately 10% to 28%., At 35% replacement, the compressive strength decreased by approximately 14% to 40%.

### Impact on Durability

Based on a study on the evaluation of pumice powder in concrete, adding pumice powder as an ASCM decreased the permeability of the high-strength concrete *(231)*. Another study showed the drying shrinkage of the concrete with pumice was slightly lower than control mixes *(232)*. While research has shown that incorporating natural zeolites into concrete generally decreases workability and compressive strength, it improves properties such as chloride penetration, shrinkage, sulfate resistance, water permeability, and carbonation resistance *(233)*. Concrete containing natural zeolite has also been shown to increase resistance to freeze-thaw and sulfate attacks *(227,233)*.

A study investigated the durability of self-consolidating concrete (SCC) with waste perlite powder replacement *(234)*. Based on the results, the compressive strength of SCC will increase by adding perlite, especially when combined with silica fume and metakaolin. Also, the performance of SCC containing perlite powder was higher than control mixes. Another study on mortar containing natural perlite and expanded perlite showed that both types of perlite mitigated ASR expansion *(235)*. Replacing 16% of cement with expanded perlite kept the ASR expansion, based on ASTM C1260, below the 0.1% expansion limit using reactive aggregate. One study showed that replacing 10% of cement with volcanic ash from Mount Tavurvur resulted in adequate ASR expansion control based on ASTM C311 *(222)*. Another study investigated the effect of cement replacement on the drying shrinkage of concrete *(236)*. In this study, the drying shrinkage of concrete with 20% cement replacement was 540 με, which was very close to the control at 493 με.

In another study, 15%, 25%, and 35% of cement were replaced with scoria powder, and carbonation resistance was measured based on the EN 13295 standard, where samples were exposed to 3% carbon dioxide at a temperature of 73.4°F (23±3°C) for 21 days *(215)*. Concrete carbonation is when atmospheric $CO_2$ consumes the $Ca(OH)_2$ content to produce more stable $CaCO_3$. The process reduces the pH below the passivation thresholds that protect the embedded steel in concrete. The carbonation depth of three test specimens of each mortar type was evaluated. First, the specimens were split, and then the surface was cleaned and sprayed with a phenolphthalein pH indicator. It was concluded that red and dark-red scoria samples with 15% replacement levels had better carbonation resistance than the control samples.

In another study, researchers examined the impact of different natural pozzolans—including zeolite, tuff, diatomite earth, perlite, scoria, bentonite, and siliceous sinters—on concrete properties, shown in Table 3.3 *(220)*. Based on these findings, replacing cement with natural pozzolans can increase the water demand and decrease the early compressive strength of the concrete, but it will increase the late compressive strength, chloride resistance, and, in some cases, sulfate resistance of the concrete.

**Table 3.3: Impact of Different Natural Pozzolans on Concrete Properties**

| Type of Pozzolan | Water Demand | Early Compressive Strength | Late Compressive Strength | Chloride Resistance | Sulfate Resistance |
|---|---|---|---|---|---|
| Zeolite | ↑ | ↓ | ↑ | ↑ | ↑ |
| Tuff | → | ↓ | ↑ |  | ↑↓ |
| Volcanic ash/pumice | ↑↓ | ↓ | ← | ↑ | ↑↓ |
| Diatomite | ↑ | ↑ | ↑ |  |  |
| Perlite | → | ↓ | ← |  |  |
| Scoria |  | ↑ | ↑ |  |  |
| Bentonite |  | ↓ | ↑ |  |  |
| Siliceous sinters | ↑ |  | ↑ |  |  |

*Notes:*
↑: increase
↓: decrease
←: slight decrease
→: slight increase
↑↓: both effects have been reported

Source: Dedeloudis et al. (2018) *(220)*.

### 3.1.6 *Environmental Considerations*

Using natural pozzolans as an ASCM is expected to reduce the environmental impact of concrete made with portland cement as they do not require the thermal processes of clinker production, and if they require some calcination, it is most likely at a lower temperature and does not directly emit $CO_2$. For natural pozzolans, energy consumption is from mining, crushing, sorting/grading, and milling. The full process is shown in the system diagram in Figure A.7. Transportation of natural pozzolan of volcanic origin is expected to be a significant source of pollution relative to other steps in the process, considering the use of diesel fuel in long-distance transport. However, local availability in California and the Western United States is expected to minimize the environmental impact of transportation. Moreover, the generation and disposal of reject fines in mining and milling pumice and other pozzolans may result in local dust issues at some operations *(5)*.

An EPD was developed by Lava Mining & Quarrying SA (Greece) after determining the environmental impacts of pumice production using LCA *(237)*. The functional unit of the study is 1 tonne of pumice stone, and the reference study year is 2020. Background data were collected from *ecoinvent* v3.7 from the Professional 2021 database *(238)*. *GaBi* modeling software was used for the impact assessment. The scope of the study was cradle-to-gate, covering the product stage, while the geographical scope was worldwide. The system boundary included the raw material production and supply (A1), internal transportation (A2), and production (A3) stages.

Of the natural aggregates produced in the Yali's island quarry, 100% are covered by the framework of the EPD. Processes in producing pumice stone include extraction, processing, deposit, and loading before it is shipped. The production process starts with using bulldozers to extract the material from the benches. The extracted materials are received by a conveyor belt and advanced to the processing plant, where they are sorted and graded into different sizes using crashers and sieves. The sorted materials are then deposited in open-air storage areas through conveyor belts, ready for shipping. Five different granulometry (or mixtures) are delivered to clients: 0 to 3mm, 0 to 8 mm, 2 to 10mm, 0 to 16mm, and 16 to 40mm. No packaging material is used since the product is delivered in bulk.

The environmental performance indicators considered in the study include global warming potential (GWP), ozone depletion potential (ODP), acidification potential (AP), eutrophication potential (EP), photochemical oxidant formation potential (POCP), abiotic depletion potential (elements, fossil resources), and water scarcity potential. A summary of the assessment is shown in Table 3.4. Table 3.5 shows the use of the resources for manufacturing 1 tonne of pumice stone from the EPD. Finally, output flows and waste categories from producing 1 tonne of pumice stone are presented in Table 3.6.

The environmental impacts associated with mining pumice are small. The main contributors to impacts are electricity and diesel consumption, along with land use activities. According to the EPD, electricity use during stages A1 to A3 is responsible for 49% of the climate change total indicator. Therefore, about half of the total $CO_2$ emissions are attributed to electricity consumption.

**Table 3.4: Environmental Impacts per Tonne of Pumice Stone**

| **Environmental Impacts (per tonne of pumice stone)** | | **Unit** | **Material Stage A1-A3** |
|---|---|---|---|
| GWP-total | Global warming potential – total | kg $CO_2$-eq | 2.196 |
| GWP-fossil | Global warming potential – fossil | kg $CO_2$-eq | 2.164 |
| GWP-biogenic | Global warming potential – biogenic | kg $CO_2$-eq | -0.039 |
| GWP-luluc | Global warming potential – luluc | kg $CO_2$-eq | 0.071 |
| GWP-GHG | Global warming potential – GHG | kg $CO_2$-eq | 2.144 |
| ODP | Ozone depletion potential | kg CFC-11 eq | 6.692E-15 |
| AP | Acidification potential | mol H+ eq | 0.04 |
| EP-freshwater | Eutrophication potential – freshwater | kg $PO_4^{-3}$ eq | 0.000185 |
| EP-freshwater | Eutrophication potential – freshwater | kg P eq | 6.027E-05 |
| EP-marine | Eutrophication potential – marine | kg N eq | 0.024 |
| EP-terrestrial | Eutrophication potential – terrestrial | mol N eq | 0.26 |
| POCP | Photochemical oxidant formation potential | kg NMVOC eq | 0.066 |
| ADPe | Abiotic depletion potential – elements | kg Sb eq | 5.243E-07 |
| ADPf | Abiotic depletion potential – fossil resources | MJ | 54.724 |
| WDP | Water deprivation potential | $m^3$eq | 0.085 |

Source: Lava Mining & Quarrying SA (2021) *(237)*.

**Table 3.5: Resource Use for Production of 1 Tonne of Pumice Stone**

| Resource Use (per tonne of pumice stone) | | Unit | Material Stage A1-A3 |
|---|---|---|---|
| PERE | Use of primary renewable energy, excluding renewable primary energy resources used as raw materials | MJ | 1.681 |
| PERM | Use of renewable primary energy resources used as raw materials | MJ | — |
| PERT | Total use of renewable primary energy resources | MJ | 1.681 |
| PENRE | Use of nonrenewable primary energy, excluding nonrenewable primary energy resources used as raw materials | MJ | 54.842 |
| PENRM | Use of nonrenewable primary energy resources used as raw materials | MJ | — |
| PENRT | Total use of nonrenewable primary energy resources | MJ | 54.842 |
| SM | Use of secondary material | kg | — |
| RSF | Use of renewable secondary fuels | MJ | — |
| NRSF | Use of nonrenewable secondary fuels | MJ | — |
| FW | Use of net fresh water | $m^3$ | 0.0030 |

Source: Lava Mining & Quarrying SA (2021) *(237)*.

**Table 3.6: Output Flows and Wastes from Producing 1 Tonne of Pumice Stone**

| Output Flows and Waste Categories (per tonne of pumice stone) | | Unit | Material Stage A1-A3 |
|---|---|---|---|
| HWD | Hazardous waste disposed | kg | 6.057E-10 |
| NHWD | Nonhazardous waste disposed | kg | 0.045 |
| RWD | Radioactive waste disposed | kg | 4.762E-04 |
| CRU | Components for reuse | kg | — |
| MFR | Materials for recycling | kg | — |
| MER | Materials for energy recovery | kg | — |
| EE | Exported energy | MJ | — |

Source: Lava Mining & Quarrying SA (2021) *(237)*.

In another study, it was determined that 1 kg of natural pozzolan powder has a GWP of 0.089 kg $CO_2$-eq compared to ordinary portland cement with a GWP of 0.875 kg $CO_2$-eq *(239)*. Therefore, using natural pozzolan as an SCM could be a viable solution to bring down GWP in concrete as minor processing (mainly grinding) is required.

### 3.1.7 *Cost Considerations*

Using natural pozzolans of volcanic origin may require higher use of superplasticizers, as these ASCMs could decrease workability due to their high surface area *(214)*. Superplasticizers are expected to increase the overall cost of concrete with natural pozzolan. Zeolite is also relatively expensive compared to other natural pozzolans of volcanic origin *(224)*.

## 3.2 Sedimentary Natural Pozzolans: Diatomaceous Earth

### 3.2.1 *Product Description*

Diatomaceous earth (DE), also called diatomite, is a biogenic material with a high level of pozzolanic reactivity *(240)*. DE mainly consists of siliceous frustules or skeletons of diatom micro-organisms (a type of hard-shell algae) and some amounts of calcareous (containing calcium carbonate) biogenic material and detrital sediment such as clay minerals *(202)*. DE has high silica content in nature *(241)*. However, deposits of calcareous materials on its siliceous diatoms can reduce the silica content *(202)*.

### 3.2.2 *Acting Mechanism in Concrete*

Diatom frustules or skeletons of DE compose to form opal-A (amorphous), a natural hydrous silica *(245)*. Pozzolanic activity and performance of DE largely depend on the amount of opal-A content. However, DE with high quantities of clay minerals can be improved using the thermal decomposition of the minerals *(202)*. The active mechanisms of DE in concrete are as a filler and SCM. DE can also be a lightweight aggregate *(243)*. The silica content of DE is approximately 86 to 94 wt%, with voids up to 80% and 90%, making it a highly porous material *(244)*.

### 3.2.3 *Chemical and Physical Properties*

Diatomaceous earth is siliceous sedimentary rocks consisting of fossilized skeletal remains of single-celled algae or aquatic plants *(245)*. Mineralogical studies of diatoms have shown that the main ingredient is opal-A, a reactive form of silica, quartz, calcite, clay minerals, and a small amount of feldspar *(246)*. Diatomaceous earth is naturally dull-white and can be blended with white portland cement to minimize the environmental impacts and cement cost. Low-grade DE has a relatively lower silica content, which can be 50 wt% intermixed with clay and calcite minerals *(240)*. This type of DE can be used as an adsorbent or filter and lightweight aggregate production. DE’s low density makes it highly suitable for producing lightweight aggregates *(247)*.

Because of diatomite's porous structure, its specific surface area is approximately 10 times greater than ordinary portland cement *(203)*. The silica content of a diatomite primarily depends on its geographical location and depositional environment. The silica content of pure diatomite is over 95%, while this content ranges from 25% to 95% for pure diatomite, and most of this content is considered reactive *(248,249)*. The concentration of CaO is normally less than 10% in diatomite, but it can be higher, up to 50%, which will create a calcareous diatomite *(202)*. Also, the $Al_2O_3$ and $Fe_2O_3$ contents of diatomite are less than 15% and the alkali content ($Na_2O + K_2O$) is mostly less than 2% *(202)*. Based on XRD analysis, diatomite is mostly amorphous *(249)*.

Various levels of grinding are applied to diatomite earth. In one study, DE from the Aceh Besar district in Indonesia was ground to finer than 250 µm to investigate the effect of ground diatomite earth on the splitting tensile strength and flexural strength of high-strength concrete *(250)*. Another study investigated the grinding level's effect on the diatomite's pozzolanic activity *(251)*. The materials were ground for 30, 60, and 240 minutes. After grinding, the 50% passing particle size (D50) was between 7 and 40 µm. This study showed that ultrafine diatomite with $D_{50}$ equal to or less than 10 µm resulted from low-energy grinding with a high surface area and was more soluble and pozzolanic.

### 3.2.4 *Process Description, Technology Readiness Level, and Potential Suppliers*

#### Process Description

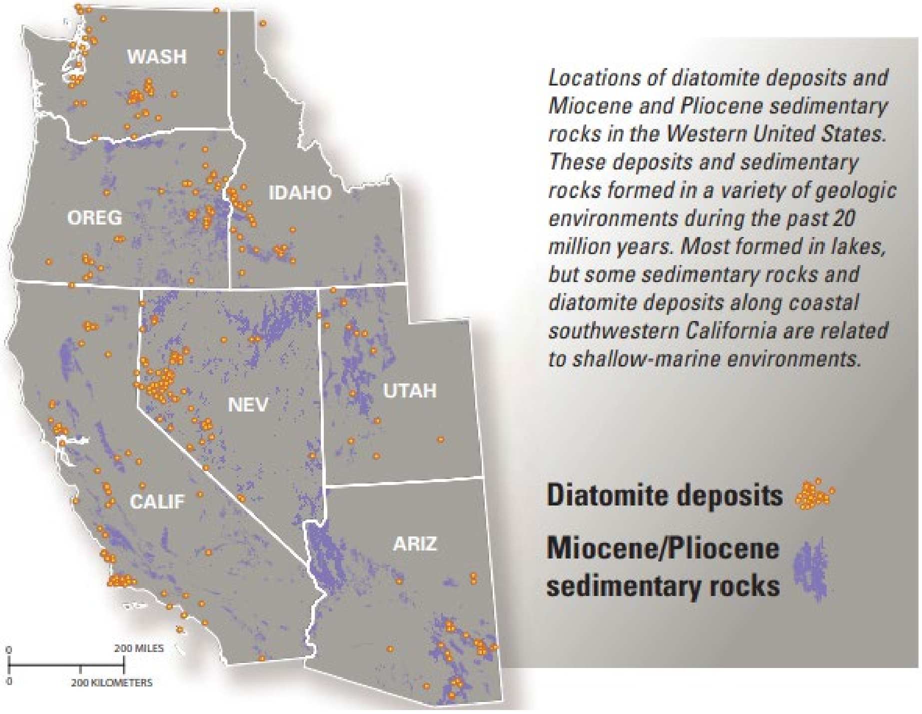
DE is abundantly available in California and other western states such as Washington, Oregon, and Nevada *(240)*. DE is categorized as a Class N natural pozzolan according to ASTM C618, making it suitable as a cement replacement. Like other natural pozzolans, DE requires no special treatment except grinding to present pozzolanic activity *(240)*. However, calcination may be required to activate the clay or calcite impurities. The process is similar to that shown for natural pozzolans in Figure A.7.

#### Technology Readiness Level

A few research studies have evaluated the effect of replacing ordinary portland cement with diatomaceous earth on the mechanical properties of concrete at the laboratory scale. Other studies have investigated the mechanical properties of concrete using diatomaceous earth as a lightweight aggregate. While these studies have demonstrated a proof-of-concept for DE as a mineral admixture experimentally, DE is not at a wide implementation stage in construction. Therefore, based on the TRL scale (with 1 being the least advanced and 9 the most advanced), the use of diatomaceous earth as a mineral admixture in concrete is at Level 3 ("proof-of-concept demonstrated, analytically and/or experimentally"). To advance to higher TRL levels, further research and development, including pilot-scale testing and validation in real-world applications, would be necessary. This would involve assessing factors such as the long-term durability, economic viability, and scalability of using diatomaceous earth in concrete production.

### Potential Suppliers

Around 300 million metric tons of diatomite are deposited in western North America *(252)*. US diatomite production in 2021 is estimated to be 830,000 tons, an estimated 36% of total world production *(5)*. Six companies in the United States produce diatomite at 12 mining areas and nine processing facilities in California, Nevada, Oregon, and Washington (Figure 3.3). Recovery of diatomite in the United States is achieved from low-cost, open-pit mining since it occurs at or near the earth's surface. Companies that mine diatomite in California include Imerys Minerals, California's Lompoc Plant, and the Celite Corporation. The exact quantity of DE mined at the Lompoc deposits, the world's leading source of diatomite, is unknown.



Source: Wallace, Frank, and Founie, (2006) *(253)*.

**Figure 3.3: Locations of diatomite deposits in the Western United States.**

## Current Use of Product

About 55% of DE is used in filtration products, while the remaining 45% is used in fillers, absorbents, lightweight aggregates, and other applications *(254)*. Less than 1% of diatomite is used for biomedical and pharmaceutical purposes. The unit cost of diatomite varies depending on the application. In 2021, the cost ranged from approximately $10 per tonne in the case of lightweight aggregate in PCC to over $1,000 per tonne for limited specialty markets, such as cosmetics, art supplies, and deoxyribonucleic acid (DNA) extraction *(254)*.

## Agents Involved in Production and Distribution

Agents involved in the production and distribution of diatomite are mining companies responsible for mining, milling, and processing the material into different sizes and grades, after which it is transported for different industrial applications.

**Product Consideration in Caltrans Standards**

Caltrans has not specified the use of diatomite as a source of SCM. However, it is approved as an absorbent material (resin) for bridge deck treatment *(57)*. It can also be used in cement mortars in joints for culverts and drainage pipes *(57)*.

### 3.2.5 *Performance in Concrete Based on the Literature*

**Impact on Fresh Properties**

Most studies have revealed that replacing cement with diatomite requires more water to achieve equal consistency, slump, and flow because of its high specific surface *(210)*. A study found replacing 5% and 20% of cement with diatomite increased the water demand by 6% and 30% compared to the control mixes *(249)*. To address the problem of workability, researchers have found that grinding diatomite powder to a high fineness will destroy the diatom's skeletal structure and reduce the water demand, especially if an air-entraining agent is added to the mixture *(255)*. Water demand has a direct impact on the drying shrinkage of the concrete. By increasing the water demand, the drying shrinkage of the concrete will increase *(220)*.

**Impact on Strength**

A study investigated the effect of DE on the workability, compressive strength, density, and environmental impacts of different mortar and concrete mixes, both binary (wPC-DE) and ternary (wPC-DE-LS) systems *(240)*. Results showed that the initial and final setting times of both systems increased as the DE level increased. The density of the mixes decreased as the DE level increased. Compressive strength increased in mortar mixes with DE at 7 and 90 days relative to the control mix. However, the mortar mix with 30%DE-5%LS had the highest strengths at 28 and 90 days. Results for DE-containing concrete mixes showed relatively higher compressive strength than the control at 28 days. C-30DE-5LS concrete mix had the highest compressive strength at 28 days, about 4% higher than the control mix.

Adding diatomite powder to mortar increases the pulse velocity in the pulse velocity test. By replacing 15% cement with diatomite powder, the maximum pulse velocity increase is 12%. Therefore, the pore structure of mortar improves by adding diatomite *(256)*.

One study investigated the effect of blended cement containing DE with a high content of reactive silica (over 45%) on the compressive strength of the mortar *(248)*. The study found the 1-day compressive strengths of the samples containing DE-blended cements were higher than the control mix when the clinker replacement dosage was up to 20%. Also, regardless of the content of reactive silica in DE, the 28-day compressive strengths of the mortar samples with DE-blended cements were higher than the control mix.

Another study investigated the mechanical performance of high-strength concrete containing DE microparticles calcined at 600°C for five hours *(250)*. The study found that the maximum flexural strength was attributed to the samples with a DE-to-binder ratio of 5%, and maximum splitting tensile strength was related to the control mix with 0% DE.

A study investigated the grinding level's effect on the DE's pozzolanic activity calcined at 900°C *(257)*. The study found higher $Ca(OH)_2$ consumption is an indicator of the pozzolanic reactivity of DE. It also found the higher surface area of DE will improve the compressive strength of the mortar.

**Impact on Durability**

A study evaluated the chloride-induced reinforcement corrosion of concrete with 20% diatomite replacement *(258)*. For 500 days, the steel-reinforced samples were exposed to a NaCl solution. Capillary and porosity spaces increase the diffusion rate of the water, which makes concrete more susceptible to cracking. Based on the results from this study, samples containing 20% diatomite performed better than control samples in the chloride corrosion test.

### 3.2.6 *Environmental Considerations*

Processing of DE for use in mortar and concrete has a low contribution to the overall GWP of concrete *(240)*. The energy used in processing diatomaceous earth is negligible compared to the total energy used in concrete production, as the only treatment required may be milling.

Calcination may be required when intermixed with clay or calcite minerals. Transportation of DE is another source of pollution from diesel fuel consumption in long-distance transport. The local availability of DE in California can help minimize environmental impact. In a study, the effect of DE on the consistency, strength, and environmental impacts of different mortar and concrete mixes of both binary (wPC-DE) and ternary (wPC-DE-LS) systems were investigated *(240)*. It was concluded that the control mix (with 100% wPC) had the highest total GWP, while the mortar mix 40DE-5LS-3C had the lowest total GWP. The energy consumption and GWP emissions of the produced concrete mixes decreased by reducing the cement content of the binder in a similar pattern to the mortar mixes.

A few studies examine the use of diatomite in cement production *(259)*, cement replacement in mortar *(245)*, or cement replacement in concrete *(255)*, or as a modifier in asphalt *(260)*. No studies of LCA or LCIA of diatomite and no EPDs were found in the literature. Two studies did look at the environmental benefits of using diatomite by performing LCA *(252,260)*. However, the diatomite LCIA results were not specifically reported. According to the National Pesticide Information Center, diatomaceous earth is nontoxic to fish and aquatic invertebrates *(261)*. According to the US Occupational Safety and Health Administration (OSHA), "Diatomaceous earth has been tested as a whole and evaluated as a Group 3 carcinogen by International Agency for Research on Cancer. A Group 3 listing indicates that diatomaceous earth is not classifiable as to its carcinogenicity to humans" *(262)*.

#### 3.2.7 *Cost Considerations*

Cost ranges from $10 per ton for lightweight aggregate in PCC to over $1,000 per ton for limited specialty markets *(5)* The price of SCMs will be different than these applications depending on the processing and use market.

### 3.3 Sedimentary Natural Pozzolans: Clays

#### 3.3.1 *Product Description*

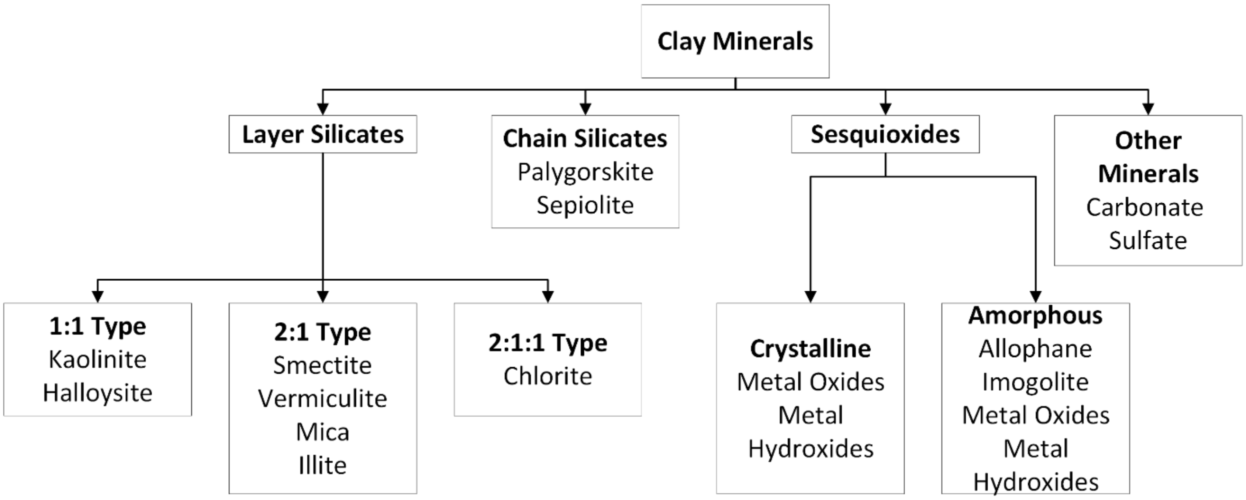
Clay is a naturally occurring material found almost everywhere worldwide. Clay particles are less than 2 µm in diameter and are produced through various geochemical processes, including weathering and metamorphosis *(263)*. Of the various classes of clay minerals, cement, and concrete, research has shown that kaolinitic clay has the best potential for activation, rendering pozzolanic reactions in concrete *(264)*. Many areas of the world, including the United States, have vast reserves of kaolinitic clay with high kaolin fractions.

### 3.3.2 *Acting Mechanism in Concrete*

A significant portion of high-grade kaolinite clay is made up of kaolinite ($Si_4Al_4O_{10}(OH)_8$) and is highly pozzolanic after calcined at the 1292°F to 1562°F (700°C to 850°C) temperature range *(265)*. Heat treatment decomposes the kaolinite crystals and forms a highly reactive amorphous pozzolan known as metakaolin (MK) *(266)*. Calcined clay's primary chemical reaction occurs through aluminosilicate reactions with $Ca(OH)_2$ from cement hydration to form C-S-H, calcium aluminate hydrate (C-A-H), and calcium aluminate silicate hydrate (C-A-S-H), depending on the Si/Al ratio in the metakaolin *(267)*.

### 3.3.3 *Chemical and Physical Properties*

Clay minerals are mainly known as complex silicates of various ions, such as aluminum, magnesium, and iron. Depending on how these ions are arranged, the two basic crystalline units for clay minerals are the silicon-oxygen tetrahedral unit and the aluminum or magnesium octahedral unit, which are the building blocks of the tetrahedral and octahedral sheets. The sheets are bonded by sharing $O_2^{2-}$ ions and also connected to some coordinated sheets that are made by cations like $Mg^{2+}$ and $Al^{3+}$ *(203)*. Based on the charge of the mentioned sheets, different interchangeable interlayer cations like $K^+$, $Na^+$, $Mg^{2+}$, and $Ca^{2+}$ will be present *(202,264)*. Classification of clay minerals based on the tetrahedral and octahedral sheets is shown in Figure 3.4 *(268)*. This figure shows that kaolinite is a clay mineral with a 1:1 layer silicate structure, meaning that each layer consists of tetrahedral $SiO_4$ and one octahedral $AlO_4$ sheet. In the 2:1 structure, two tetrahedral sheets of silica sandwich a central octahedral sheet of alumina.



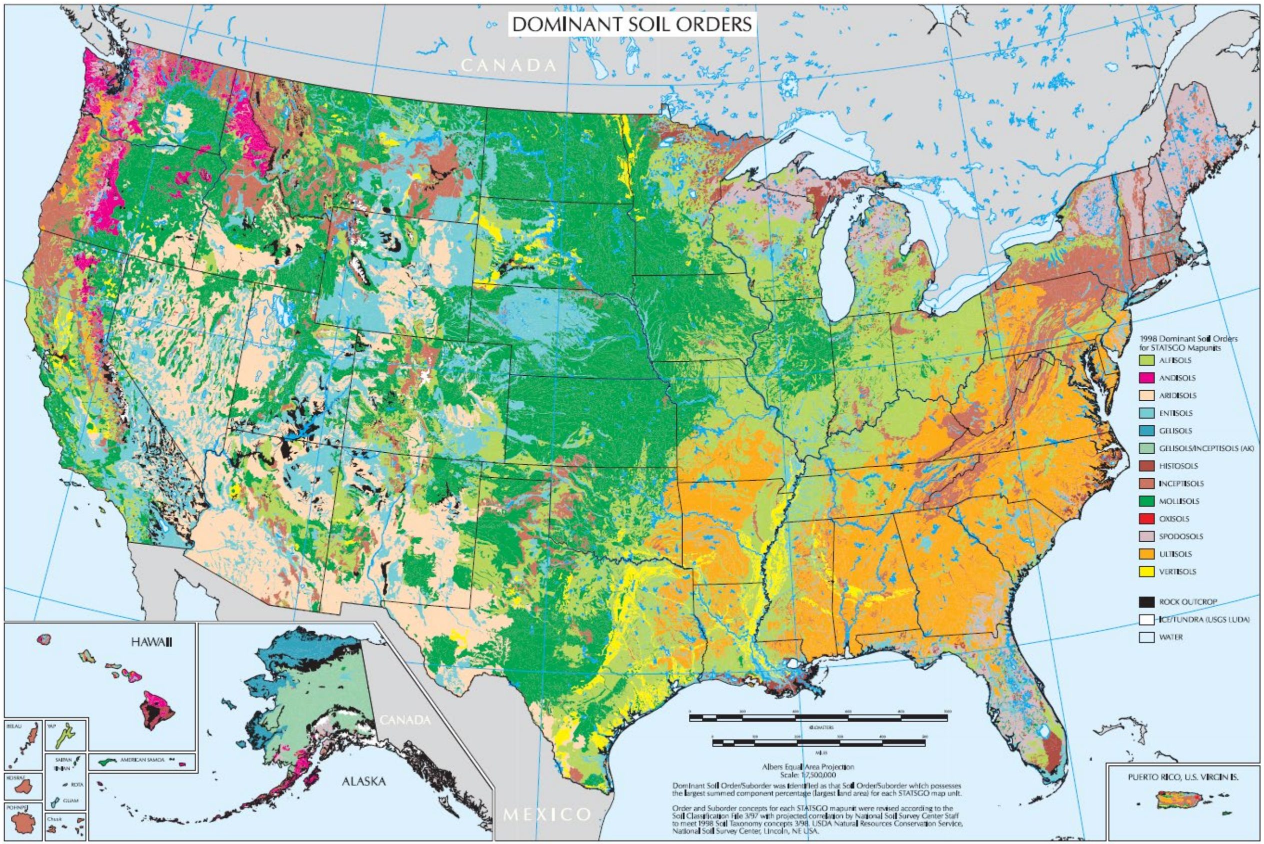
Source: Nascimento (2021) *(268)*.

**Figure 3.4: Clay mineral classifications.**

When water is added to clay, the interlayer cations from clay will shape adsorption complexes with the molecules of water, which will negatively charge the layers to repulse each other and consequently will cause the clay to swell *(264,269)*. This chemical behavior of clay with water plays an essential role in using clay as a pozzolan. The silicate layer structure of kaolinite with the OH groups connected by the octahedral layers placed at the interface between the repeat silicate layers facilities thermal activation, known as calcination, at lower temperatures as the OH groups are removed (the process known as dehydroxylation). The location of OH groups in kaolinite favors more disorder than other clays, such as 2:1 (illite and montmorillonite) and exposure of Al groups during the dehydroxylation process *(264)*. In one study, calcined illite and montmorillonite showed none or smaller amounts of contribution to the 28-day compressive strength of systems compared to kaolinite *(264,270)*. Therefore, as kaolinite is the most important ingredient of clay in reactivity, researchers have focused on calcined kaolinitic clay for concrete with various levels of kaolinite content. It should be noted that high-purity and highly reactive metakaolin (HRM) is a purified, manufactured, and thermally activated kaolinite different from calcined clays with impurities and is much more expensive *(271)*. However, for natural clay minerals, the amount of kaolinite present in the clay varies from region to region and impacts the reactivity and performance of the clay as an SCM in concrete *(265)*.

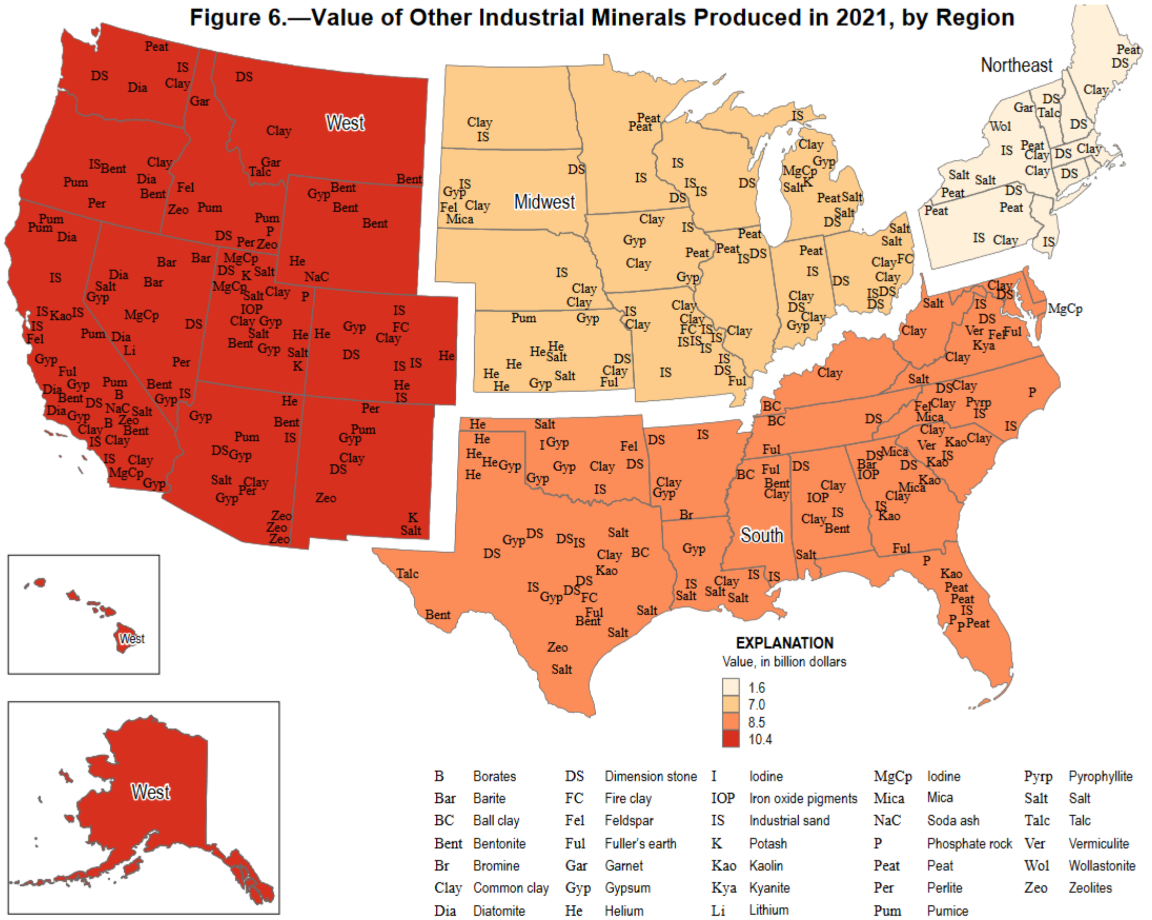
### 3.3.4 *Feedstock Description and Supply*

The soil order maps of the United States and the world are shown in Figure 3.6a. Kaolinitic soil is found in ultisol (orange) and oxisol (red) soils. Ultisols are primarily located in the southeastern region of the United States, and some are located in the mid-Atlantic region. Some reserves are also seen in Washington state and California. Kaolin (kao) mining is also marked for California in the USGS mineral production map shown in Figure 3.6b.



(a)

Source: US Department of Agriculture (n.d.) *(272).*

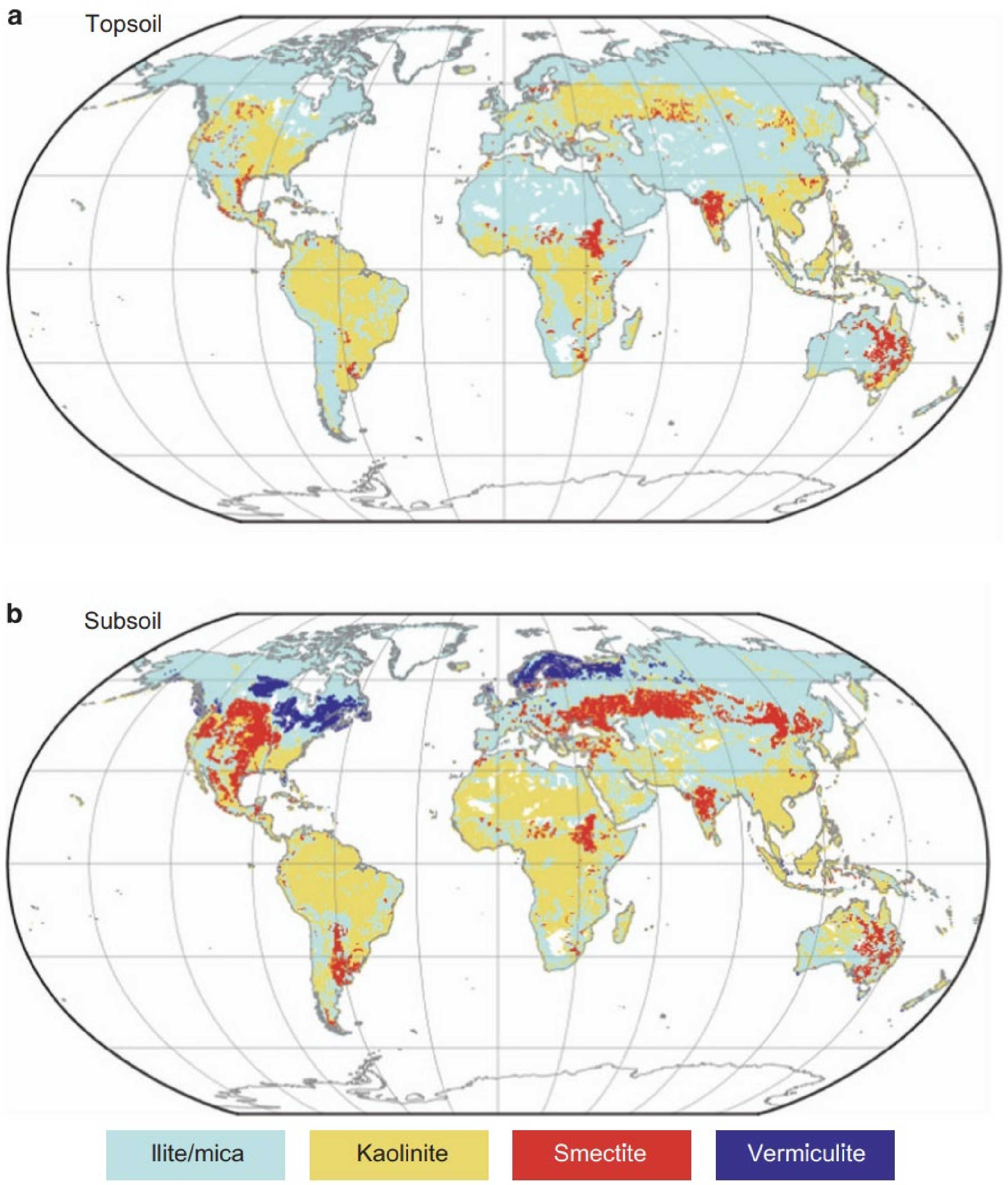


(b)

Source: US Geological Survey (2022) *(5)*.

**Figure 3.5: Maps showing (a) distribution of various soil orders across the United States and (b) value of industrial minerals produced in 2021 in the United States.**

The United States is among the leading kaolin producers and produced 4.5 million T (4.1 million t) of kaolin in 2021. Other countries such as China, India, Czechia, Germany, and Uzbekistan were the top producers of kaolin in 2020 and 2021 *(5)*. A map of the geographical distribution of kaolinite as topsoil and subsoil is shown in Figure 3.6 *(263)*. Vast reserves are located in South America and Africa. Despite large reserves on the continent of Africa, kaolinite clay exploitation and MK production are limited due to a reported lack of skills, capital, and other factors *(273)*.



Source: Ito and Wagai (2017) *(263)*.

**Figure 3.6: Distribution of the most abundant clay minerals, including kaolinite, worldwide for (a) topsoil and (b) subsoil.**

### 3.3.5 *Process Description, Technology Readiness Level, and Potential Suppliers*

**Process Description**

When the deposits are identified and the site is finalized, mining begins with excavation using earthmoving equipment. Sedimentary clays are mainly surface mined in an open pit with a stripping method. Clays vary widely within deposits as well as between deposits. Thus, blends are produced from one or more sites to homogenize final extraction and extend the existing reserve. The extraction and processing of clay can produce a large quantity of mineral waste or byproducts. For example, mining clay for calcination can generate around 20% to 50% of the waste during the process, while mining kaolin can generate approximately 90% of the waste during the process *(274)*.

Sometimes, additional homogenization takes place in addition to the homogenization on the mining site. Then, if the clay is relatively dry, it is passed through a coarse crusher to reduce the size of the raw material to <100 mm. Alternatively, a blade mill is used to reduce the particle size to <30 to 50 mm *(275)*.

Depending on the time of the year, location of the quarry, nature of the quarry, method of mining, and initial moisture content, the clay is either sun-dried or dried using thermal treatment. The thermal treatment is carried out either by rotary kiln or flash calcination. The raw and humid clay is dehydrated and deagglomerated to dry clay with an outlet temperature of around 302°F (150°C) and a final moisture content of <1 wt%. The clay is further ground to ensure a material fineness of <1 mm to ensure complete calcination *(274,275)*.

The calcination of clay is usually conducted either by static or rotary kiln or through flash calcination *(276)*. However, studies have demonstrated that in larger quantities of clay, when crushed to the size of a few centimeters, more uniform calcination can be achieved in the rotary kiln process as compared to the static kiln. The residence time is usually around one hour at the calcination temperature 1562°F (850°C) *(277)*. In the case of flash calcination, a gas-solid heat transfer is conducted to calcine the clay quickly with a residence time of 0.5 seconds. However, flash calcination requires pretreatment of grinding the raw clay into dry and fine powder to pneumatically suspend the feed with the carrier gas *(278)*.

Cooling is conducted to recover heat for subsequent processing. The cooling medium is either dry air or wet air with limited amounts of water. The cooling air is recirculated to enable heat recovery back to the calcinator's preheated combustion air. The clays are also cooled in rotary or fluidized bed coolers *(274)*. During the cooling process, clay tends to escape the system as dust (around 20 wt%.) and thus needs to be recovered. The dust is transported by spent gas, usually captured in bag filters. The dust collected in the bag filter is fed back to the raw feed. Dust generation is usually more in rotary kilns as compared to flash calciners *(274)*.

After calcination, depending on the intended application, the calcined clay might be reground to deagglomerate the clay clusters as well as to grind down quartz and other hard minerals present in the calcined clay. For applications in the cement industry, the regrinding is conducted to obtain a uniform mixture of clinker, limestone, and gypsum *(279,280,281)*.

The various steps involved in the production of calcined clay discussed above are shown in the system diagram in Figure A.8.

## Technology Readiness Level

Calcined clays blended with limestones are already used to substitute part of the clinkers in blended cement, also known as limestone calcined clay cement or $LC^3$ *(282)*. Trial production runs using $LC^3$ have been conducted in Cuba and India, and the results are quite promising. In India, roofing tiles made with $LC^3$ had higher breaking strength than tiles made with portland fly ash cement. In Cuba, the $LC^3$ was used in several applications, including making cement blocks and precast concrete culverts. Thus, the technology can be easily scaled to any capacity within an existing cement production system with essential capacity *(283,284,285)*. Based on the TRL scale, with 1 being the basic principles observed and reported and 9 actual systems being successfully operated, the use of calcined clay as an SCM in cement industries could potentially be a TRL 8 (the actual system has been tested in the industry) or 9 (technology fully implemented).

**Potential Suppliers**

Currently, Purebase in California is in the process of establishing a facility to produce calcined clay for concrete.

**Current Use of Product**

The primary uses for kaolin in the United States were reported as 30% paper coating and filling, 15% miscellaneous ceramics, and 15% refractory products *(5)*. Kaolin, mica, and talc are added to plastics. Kaolin, silica, and talc are also used in animal feed as anticaking and flow-control agents *(5)*. Kaolin is used in the state of Georgia in cement production *(5)*. The calcined clay is used to produce ceramics, whitewares, tiles, bricks, geopolymer concrete, SCM for portland cement, and concrete *(274,286)*. Projected growing demand for ceramics and paper, followed by paint and coatings, may limit the availability of MK for the construction industry *(273,287)*.

**Agents Involved in Production and Distribution**

Agents involved in the production and distribution of calcinated clay are basically mining companies responsible for mining, milling, and processing the material.

**Product Consideration in Caltrans Specifications**

Caltrans specifications do include natural pozzolan or fly ash complying with AASHTO M 295, Class F or N.

### 3.3.6 *Performance in Concrete Based on the Literature*

Many studies over the last two decades have evaluated the performance of MK as an SCM in concrete. The findings have shown a high potential for enhancing the durability and strength of concrete, mainly through pore refinement *(273,288)*. The primary use of metakaolin has been in high-performance concrete, mainly due to high water demand and higher heat evolution *(289)*. The overall optimal replacement rate of portland cement with MK is 10% to 20%, providing the concrete with the maximum strength *(290)*.

## Impact on Fresh Properties

Metakoline's ultrafine particles (1 to 2 μm) and the high surface area generally result in higher water demand and superplasticizer demand *(291)*. The irregular shape of metakaolin particles was also perceived to increase interparticle friction forces and reduce workability *(288)*. However, the workability reductions from MK were reported to be less than those from silica fume. It was shown that mixes with silica fume required 25% to 35% more amounts of superplasticizer to achieve the same level of workability at the same water-to-binder ratio *(292)*. However, another study reported that the workability of concrete mixes with 10% HRM was similar to those with 10% silica fume *(293)*. The heat of hydration of MK is expected to show higher peak heats and accelerated hydration reactions compared to 100% portland cement *(294)*.

One study showed that the setting time is delayed with adding MK up to 10% replacement and decreased at higher replacement rates *(288)*. Another study showed that blended cement with MK at a 10% replacement rate generally showed a similar setting time to the control, while a higher replacement rate at 20% with MK resulted in a delay in setting time *(295)*. Similarly, a retardation effect was seen in high-strength concrete with up to 10% replacement of cement with MK, but a reduction at higher replacement rates was reported *(296)*.

## Impact on Strength

One study compared the compressive strength of concrete with poor calcined kaolinite and commercially calcined kaolinite with high purity *(297)*. Based on the results, at the 3-day age, the strengths of concrete with both calcined kaolinites at 10% and 20% replacement rates were higher than the control. Another study found that concrete with HRM as the replacement of cement has a higher rate of strength development than control mixes *(298)*. After 3 days, the compressive strength of samples with 10% HRM replacement was higher than control mixes at any age. Although concrete with 10% silica fume showed a lower strength level compared to concrete with 10% HRM replacement at the first 7 days, the strength development of concrete samples with silica fume expedited after 28 days compared to the samples with HRM. Calcined clay can be used as a replacement for cement in concrete or as an ingredient in the production of cement to decrease the clinker content of the cement *(*299*)*. LC$^3$ showed higher compressive strength than control mixes with the same w/b ratio at all ages. Calcined clay form additional hydrated calcium aluminate phases in the presence of limestone, depending on the nature and amount of aluminate sources *(300)*.

Clay structures with the 2:1 layer structure, illite or montmorillonite, have also been researched as SCMs but showed less reactivity than kaolinite *(264)*. One study showed that calcination of bentonite (a clay primarily composed of montmorillonite) up to 302°F (150°C) would lead to higher strength development than untreated bentonite *(301)*. In another study, the 28-day strength of concrete with 20% untreated bentonite and 20% calcined bentonite at 932°F (500°C) replacements was lower, 12% untreated bentonite and 6% calcinated bentonite, than control concrete samples *(302)*.

## Impact on Durability

Metakaolin has been well known to result in pore refinement and lead to lower permeability and better durability in concrete *(290)*.

Based on previous research, HRM can decrease ASR. A study that measured the length change of concrete prisms due to ASR investigated the effect of replacing cement with HRM in concrete *(271)*. It was shown that using HRM as the cement replacement at the rate of 15%, the ASR using Spratt, a highly reactive aggregate after two years reduced to the 0.04% limit criterion by the CAN/CSA A23.2-14A Canadian standard. Therefore, HRM decreased the alkalinity of the concrete mixture significantly. However, based on the results of this research, the decrease in pH after replacing HRM was not enough to prohibit the corrosion of steel reinforcements *(271)*.

Replacing cement with HRM in concrete will decrease the drying shrinkage. Based on previous research on different w/c ratios, replacing more HRM will result in lower drying shrinkage *(303)*. Replacing cement with 20% metakaolin at w/c equal to 0.55 resulted in the drying shrinkage decreasing by 18% compared to control samples.

Metakaolin has been shown to enhance the sulfate resistance of concrete. A study evaluated the sulfate resistance of concrete containing HRM by measuring the compressive strength and expansion after exposure to a 5% sodium sulfate solution for 18 months *(304)*. It was observed that the control mixes disintegrated completely after this time, while the level of degradation of specimens with HRM was negligible. Specimens with 10% HRM experienced 0.1% expansion, while control mixes experienced 0.4% expansion. Another study evaluated the sulfate resistance of mortar with 30% untreated bentonite replacement after 90 days and found that its compressive strength was much higher than control samples *(305)*. Therefore, using calcined clay will generally increase the sulfate attack resistance of the concrete.

HRM was shown to increase the resistance of concrete against chloride ion penetration. Based on a study implementing the ASTM C1202 standard, the concrete with 10% cement replacement by HRM showed similar chloride ion penetration resistance to concrete with 10% silica fume but higher resistance than the control mixes *(298)*. In another study, concrete containing HRM was tested in ASTM C666 for freeze-thaw resistance and ASTM C672 for salt scaling test *(298)*. Based on the results, concrete with 10% HRM performed better with 89% residual flexural strength and 100.3% durability factor compared to the control mixes with 85% residual flexural strength and 98.3% durability factor.

**Table 3.7: Summary of Calcined Clay Performance in Cementitious Systems**

| Property of Concrete | Comparison to 100% OPC Concrete |
|---|---|
| Workability | Decrease |
| Early strength | No change |
| Late strength | No change |
| Setting time | Decrease |
| Drying shrinkage | Increase |
| Alkali-silica reaction | No information found |
| Sulfate attack resistance | No information found |
| Freeze-thaw durability | Increase |

### 3.3.7 *Environmental Considerations*

As no study was available in the literature that reported the TRACI impact assessment, the Institute of Environmental Sciences (CML), Leiden University, 2001 method *(306)* results are summarized here.

A detailed LCI was conducted by the Kaolin and Plastic Clay Association of Europe for the EPD, following ISO 14025 *(307)*. This study compared five different types of clay products: kaolin coarse, shredded clay, clay processed, kaolin fine, and kaolin calcined (calcined clay). The functional unit of the study was 1 T (0.9 t) of calcined clay, and the reference year of the study was 2015. *GaBi*, an LCA software, was used for LCA modeling. The system boundaries were defined as cradle-to-gate. The upstream processes included the production of raw materials, impacts due to electricity generation and fuels used in the raw materials supply, the production of auxiliary products such as explosives and lubricants, and the production of semi-products used in the core processes. The core processes included external transportation to the core processes, dry and wet extraction of clay, calcination, drying, material separation, treatment of waste generated during core processes, and the impacts due to the production of electricity and fuels used in the core processes *(307)*.

The environmental impact assessment was performed according to the procedure proposed by the ISO 2006a and 2006b standards. Different impact categories for environmental indicators were chosen based on the CML 2001 (baseline) characterization methods. The CML 2001, based on the European characterization factors, provides a midpoint orientation method for impact assessments. The EPD results for the study are presented in Table 3.8 and Table 3.9.

**Table 3.8: Use of Resources for Manufacturing 1 tonne of Calcined Clay**

| Category | Parameters | Category Indicator (Units) | Upstream (Cradle-to-Gate) | Core (Gate-to-Gate) | Total |
|---|---|---|---|---|---|
| Primary Energy Resources - Renewable | Use as Energy Carrier | MJ | 0.759 | 6,960 | 6,961 |
| | Used as Raw Materials | MJ | 0 | 0 | 0 |
| | Total | MJ | 0.759 | 6,960 | 6,961 |
| Primary Energy Resources - Nonrenewable | Use as Energy Carrier | MJ | 65.5 | 4,824 | 4,890 |
| | Used as Raw Materials | MJ | 0 | 0 | 0 |
| | Total | MJ | 65.5 | 4,824 | 4,890 |
| — | Secondary Material | kg | 0 | 0 | 0 |
| — | Renewable Secondary Fuel | MJ | 0 | 0 | 0 |
| — | Nonrenewable Secondary Fuel | MJ | 0 | 0 | 0 |
| — | Net Use of Fresh Water | m3 | 1.17E-03 | 1.43 | 1.43 |

*Note:* Calcinate clay is referred to as “kaolin calcinated” in the EPD.

Source: International EPD System (2021) *(307)*.

**Table 3.9: Environmental Impacts of Manufacturing 1 tonne of Calcined Clay**

| Category | Parameters | Category Indicator (Units) | Upstream (Cradle-to-Gate) | Core (Gate-to-Gate) | Total |
|---|---|---|---|---|---|
| GWP | Fossil | kg $CO_2$-eq | 1.37 | 348 | 350 |
| | Biogenic | kg $CO_2$-eq | 0 | 0 | 0 |
| | Land Use & Land Transformation | kg $CO_2$-eq | 2.95E-04 | 9.51 | 9.51 |
| | Total | kg $CO_2$-eq | 1.37 | 358 | 359.37 |
| — | Acidification Potential | kg $CO_2$-eq | 4.37E-03 | 2.09E+00 | 2.09 |
| — | Eutrophication Potential | kg $PO_4^{-3}$ eq | 3.68E-04 | 3.95E-01 | 0.4 |
| — | Formation Potential of Tropospheric Ozone | kg NMVOC eq | 3.69E-03 | 1.24 | 1.25 |
| Abiotic Depletion Potential | Elements | kg Sb eq | 1.57E-07 | 2.91E-04 | 2.91E-04 |
| | Fossil Resources | MJ | 64.7 | 4,410 | 4,475 |
| — | Water Scarcity Potential | $m^3$ eq | 2.98E-02 | 35.5 | 35.5 |

Source: International EPD System (2021) *(307)*.

### 3.3.8 *Cost Considerations*

Calcined clays can be produced using equipment similar to that used in portland cement production and thus require similar investment costs. However, clay calcination requires a much lower temperature [1382°F to 1472°F (750°C to 800°C)] than clinker production [2642°F (1450°C)], resulting in lower energy usage than clinker production.

# 4 CONSTRUCTION AND DEMOLITION WASTE

## 4.1 Fine Portion of Recycled Concrete and Crushed Concrete Aggregate

### 4.1.1 *Product Description*

More than 600 million T (544.3 million t) of waste from construction and demolition (C&D) activities were generated in the United States in 2018 *(308)*, making it one of the largest producers of C&D waste *(309)*. One major origin of C&D waste is concrete waste. Concrete recycling involves breaking, removing, crushing, and screening to generate recycled concrete aggregates (RCA) *(310)*. Most states use RCA as the aggregate base, and 11 states use RCA in concrete as aggregate *(311)*. Crushed concrete aggregate refers to the unused concrete returned to the plant, allowed to harden in a pile and crushed in the same way that RCA is produced.

### 4.1.2 *Acting Mechanism in Concrete*

The coarse fraction of RCA is currently accepted in pavement applications as the base, subbase, general fill material, and some pavement material (asphalt and concrete) in at least 43 states *(310)*. However, 20% to 30% is the fine fraction (<150 µm) from the production of recycled concrete *(312,313,314)*. If used directly in concrete as a replacement for virgin fine aggregate, the fines result in strength and durability loss and increased water demand due to the high content of both hydrated and anhydrate cement *(315,316)*. One way to overcome these barriers in using concrete waste fines in new concrete is to grind the fine fraction and use it either as raw material during cement production or as a blend with the cement during concrete production instead of an acceptable aggregate substitute, providing a potential recycling path for this waste stream. The microaggregate effect and pozzolanic effect make the RCA powder suitable to be considered as SCMs *(317)*.

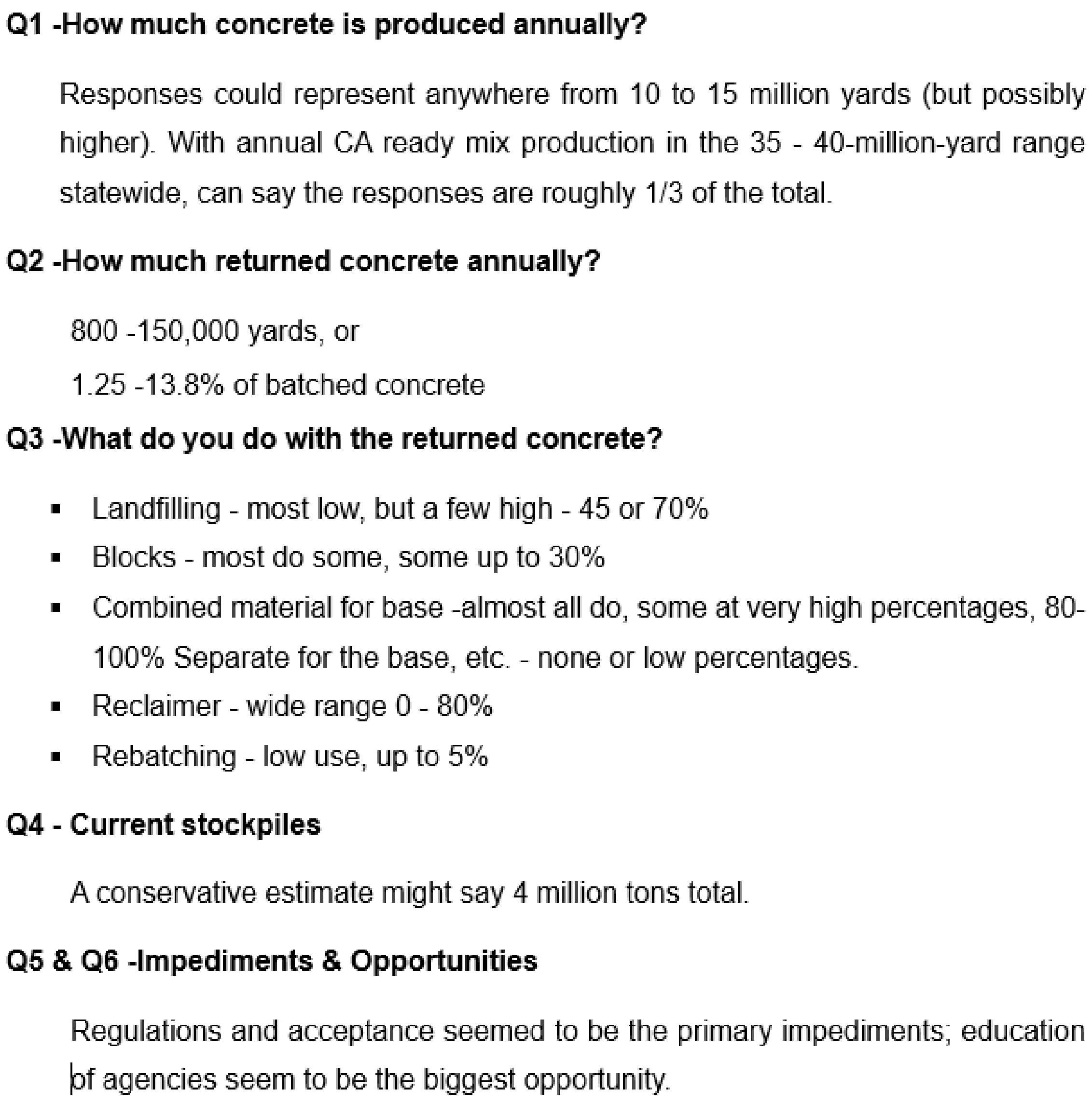
### 4.1.3 *Chemical and Physical Properties*

The chemical composition of RCA powder frequently has large amounts of $SiO_2$ and CaO. Together they constitute about 50% to 70% of the powder *(318,319)*. RCA powder has a specific gravity range of 2.4 to 2.6 and a chemical composition similar to portland cement, with a relatively higher loss on ignition (LOI) of 12% to 16%. This higher LOI is due to the thermal decomposition of the gel and calcite in the powder *(319,320,321)*. However, the density, particle size, and surface area of RCA powder depend on the properties of the concrete or the original C&D waste. RCA powder originates from crushed return concrete and usually has a higher surface area of about 500 $m^2$/kg, whereas C&D waste crushed RCA powder has a relatively lower specific surface area of 150 to 350 $m^2$/kg. These powders also have an angular grain shape when viewed with an SEM, like hexagonal $Ca(OH)_2$ crystals in cement, and a mean particle size of 5 to 8 µm *(321)*.

### 4.1.4 *Feedstock Description and Supply*

More than 367 million tons of concrete waste was produced in the United States, constituting about 70% of the C&D waste in 2018, and more than 64 million T (58.06 million t) of commercial concrete waste was landfilled *(322)*. Recycled concrete aggregate obtained from demolished concrete buildings and roads was reported to be 405.2 million T (367.6 million) in 2018, of which 334 million tons were reused while 71.2 million T (64.6 million t) went to landfills *(308)*. So far, RCA has been used in over 100 projects in the United States *(310)*.

The California Construction and Industrial Materials Association (CalCIMA) conducted a survey of 14 concrete suppliers in California, and the results are provided in Figure 4.1. According to the survey, about 70 to 80 million tons of concrete is batched in California each year, of which 1.25% to 13.8% (1600 to 300,000 tons) ends up as returned concrete. Returned concrete, by definition, is the amount of plastic or fresh concrete that is returned by the trucks to the batching plant. Figure A.9 graphically summarizes the various processing and uses of returned plastic concrete based on the CalCIMA survey of ready-mix concrete producers, and Figure A.10 shows the production process of recycled concrete aggregate.



**Q1 -How much concrete is produced annually?**

Responses could represent anywhere from 10 to 15 million yards (but possibly higher). With annual CA ready mix production in the 35 - 40-million-yard range statewide, can say the responses are roughly 1/3 of the total.

**Q2 -How much returned concrete annually?**

800 -150,000 yards, or
1.25 -13.8% of batched concrete

**Q3 -What do you do with the returned concrete?**

- Landfilling - most low, but a few high - 45 or 70%
- Blocks - most do some, some up to 30%
- Combined material for base -almost all do, some at very high percentages, 80-100% Separate for the base, etc. - none or low percentages.
- Reclaimer - wide range 0 - 80%
- Rebatching - low use, up to 5%

**Q4 - Current stockpiles**

A conservative estimate might say 4 million tons total.

**Q5 & Q6 -Impediments & Opportunities**

Regulations and acceptance seemed to be the primary impediments; education of agencies seem to be the biggest opportunity.

*Note:* 1 cubic yard= 2.03 US sh. Tons.

**Figure 4.1: Summary of survey of 14 concrete suppliers on returned plastic concrete by CalCIMA (shared by CalCIMA via personal communications).**

### 4.1.5 *Process Description, Technology Readiness Level, and Potential Suppliers*

**Process Description**

The production of RCA depends on various key factors like site location (on-site or off-site), project characteristics, and market. On-site processing of RCA can be further subdivided into two categories- (1) conventional stationary crushing and grading near the project location and (2) mobile on-grade processing using proper equipment *(310)*. Choosing between these two on-site RCA processing methods depends on the technical, environmental, and economic aspects of the project *(323)*. A description of the RCA production process is the following *(310)*:

> Mobile on-site processing is usually performed for unbound RCA base and fill uses. In this process, the existing pavement is broken into pieces, following which a hydraulic hammer breaks the oversized chunks into rubbles. Next, the rubblized material is fed into the mobile crusher on-site. Later, the crushed RCA is stockpiled alongside the project stretch. One drawback of this process is that it requires a lot of on-site space.

Stationary on-site processing is a more conventional process of RCA production that is used in PCC, base, and fill applications. The quality of RCA produced through this process varies depending on the pre- and post-processing of the material, production rate, and waste generation *(324)*. The main difference compared to mobile on-site processing is that this process involves a stationary crushing unit that stays on-site during the length of the project. This process also requires significant on-site space, but it does not require hauling C&D waste to a crushing plant, which is an advantage.

When the hauling distance of the C&D waste is short, off-site processing of RCA has been advantageous compared to the on-site processing. Larger off-site RCA production plants have lower RCA production costs and higher operational efficiencies *(323)*. One downside of off-site production is the contamination of RCA produced from various sources. However, one study reported that, with current advanced technology development, the risk of contamination is minimal in large off-site RCA processing facilities *(324)*.

## Technology Readiness Level

The use of RCA as the base aggregate is at TRL 9 as it has achieved full implementation and commercialization. However, the use of RCA fines as a ground powder as a mineral admixture in concrete is still in the proof-of-concept stage and requires further research, testing, and validation and is at TRL 3.

### Potential Suppliers

Potential suppliers are concrete ready-mix producers and concrete recycling plants.

### Current Use of Product

There is no everyday use for RCA fines, and they are currently stockpiled at recycling facilities.

### Agents Involved in Production and Distribution

The agents involved in production and distribution include concrete ready-mix plants, concrete recycling plants, landfills and waste management and recycling entities, Recology (a company based in San Francisco, California, that provides waste management and resource recovery services), California Department of Resources Recycling and Recovery (CalRecycle), and material recovery facilities.

### Product Consideration in Caltrans Specifications

Caltrans specifications currently do not include recycled concrete aggregate as an accepted SCM for concrete.

## 4.1.6 *Performance in Concrete Based on the Literature*

### Impact on Fresh Properties

RCA powder, when replaced in cement mortar as a supplement to cement, usually reduces the air content and flow of fresh mortar. This is due to the higher water demand of the micropores present in the RCA powder *(320,325)*. Overall, the source of RCA powder plays a significant role in the flow properties of cement mortar. According to one study, RCA powder acts as an accelerator to increase the initial hydration reaction rate of cement *(326)*. This is associated with the high fineness of RCA powders. Also, higher alkali content and a lower $SO_3$ level are also responsible for increased initial heat of hydration. The strength activity index of RCA powder is 68% to 72%. RCA powder also has a higher water demand (approximately 31%) when compared to plain cement paste (28%).

## Impact on Strength

The addition of RCA powder in cement mortar as a replacement for cement does not significantly increase the compressive or flexural strength of the cement mortar. A 10% replacement of cement with RCA powder in cement mortar resulted in a similar compressive strength of plain cement mortar at 28 days of curing *(320)*. A 30% replacement of cement with RCA powder resulted in no significant reduction in compressive strength and a slight improvement in the flexural strength of cement concrete *(317,321,327)*. Other researchers have noted that the optimum cement replacement with RCA powder should be limited to 20% in cement concrete *(318)*. A study reported that in the case of self-compacting concrete with a high-range water reducer, the addition of RCA powder resulted in a 30% increase in compressive strength *(321)*.

## Impact on Durability

RCA powder, when replacing cement, makes the concrete prone to early-age shrinkage cracking. This is a result of the combined effect of the high water demand of RCA and the lack of hydration products in RCA powder compared to plain cement *(327)*. RCA powder in concrete resulted in higher drying shrinkage for self-compacting concrete *(321)*. The water permeability and chloride permeability decreased upon the addition of RCA powder *(317)*. A summary of the performance of RCA powder in cementitious systems is shown in Table 4.1.

**Table 4.1: Summary of RCA Powder Performance in Cementitious Systems**

| Property of Concrete | Comparison to 100% OPC Concrete |
|---|---|
| Workability | Decrease |
| Early strength | No change |
| Late strength | No change |
| Setting time | Decrease |
| Drying shrinkage | Increase |
| Alkali-silica reaction | No information found |
| Sulfate attack resistance | No information found |
| Freeze-thaw durability | Increase |

### 4.1.7 *Environmental Considerations*

As no study was found regarding the LCA of recycled concrete fines, an EPD from the Vulcan Materials Company that reports LCA impacts of several aggregate sizes was reviewed. The nomenclature “rock dust LCA impacts” was used for the recycled concrete fines. The product description included fine sand-like material, a byproduct of crushing aggregate that can pass 100% through the 3/8” sieve *(328)*.

Two detailed LCIs were found, conducted by the Vulcan Materials Company, for the EPD following ISO 14025, ISAO 21930, and ASTM International’s EPD program operator rules. This study compared 12 concrete aggregates produced at the sites of Pleasanton, California, and Corona, California *(328)*. Another detailed LCI was found, conducted by Graniterock in Watsonville, California, for the EPD following ISO 14025, ISAO 21930, and ASTM International’s EPD program operator rules *(329)*.

These EPDs captured the mandatory cradle-to-gate life cycle product stages and included extraction and processing of raw materials—fuels used in the extraction and transport within processes, specific transportation of raw materials from the extraction site to the manufacturing site, and manufacturing of the product, including all energy and materials required and all emissions and wastes produced *(328,329)*. These EPDs excluded some processes from the study, such as the production, manufacture, and construction of manufacturing capital goods and infrastructure, equipment, delivery vehicles, and laboratory equipment. It also excluded fuel used to transport personnel around the facility and energy and water use related to the industry’s management and sales activities. The functional unit of the studies was 1 metric ton by dry weight.

These studies included the 15 LCA indicators, and TRACI v2.1 impact categories were used to calculate the mandatory category indicators. For calculating the electricity impacts, the 2013 resource mix at the level of North America Electricity Reliability Council (NERC) Western Electricity Coordinating Council (WECC) region data were used *(328,329)*. Table 4.2 summarizes the findings of the LCA for recycled aggregate fines.

**Table 4.2: LCA Results for the Recycled Aggregate Fines for 1 Metric Ton by Dry Weight**

| Impact Category | Unit | Pleasanton Site Values | Corona Site Values | Values |
|---|---|---|---|---|
| Global warming potential | kg $CO_2$-eq | 5.72 | 4.98 | 9.88 |
| Acidification potential | kg $SO_2$ eq | 0.03 | 0.10 | 0.10 |
| Eutrophication potential | kg N eq | 0.04 | 0.02 | 0.006 |
| Smog creation potential | kg $O_3$ eq | 0.72 | 2.47 | 2.63 |
| Ozone depletion potential | kg CFC - 11 eq | 4.71E-07 | 2.14E-07 | 1.46E-07 |
| Nonrenewable fossil | MJ (HHV) | 77.4 | 65.5 | 141.83 |
| Nonrenewable nuclear | MJ (HHV) | 11.3 | 6.66 | 9.27 |
| Renewable (biomass) | MJ (HHV) | 1.04 | 0.64 | 0.00 |
| Renewable (solar, wind, hydroelectric, and geothermal) | MJ (HHV) | 13.1 | 6.82 | 0.00 |
| Nonrenewable material resources | kg | 1000 | 1000 | 1000 |
| Renewable material resources | kg | 0.06 | 0.04 | 0.01 |
| Net fresh water | L | 0.63 | 0.10 | 1968.93 |
| Nonhazardous waste generated | kg | 0.07 | 0.08 | 0.02 |
| Hazardous waste generated | kg | 3.01E-04 | 1.33E-04 | 0.00 |

In another study, a reduction of 30% in $CO_2$ emissions was found by replacing portland cement with concrete demolition waste *(330,331)*. However, strength was reported to be negatively affected as well.

### 4.1.8 *Cost Considerations*

RCA fines do not have any value as they are considered a waste product of RCA production. However, several benefits could result from the increased use of RCA powder as a mineral admixture in concrete. Since RCA is locally available in most areas, the cost could be substantially lower than other SCMs if it can be ground on-site. Other major benefits are resource conservation and waste reduction, which lead to cost savings by offsetting landfill tipping fees or opening space at production facilities.

## 4.2 Rock Dust

### 4.2.1 *Product Description*

Rock dust, also called rock flour, is the powdered aggregate generated as part of the production of construction aggregates at a quarry site. In addition, rock dust is collected as baghouse fines from the exhaust gases of hot mix asphalt (HMA) plants. Rock dust is generated from batching as well as drum mix plants.

### 4.2.2 *Acting Mechanism in Concrete*

Pozzolanic reactivity is not necessarily expected from rock dust if it is from inert crystalline minerals. However, rock dust with amorphous silica content could render pozzolanic reactivity or could be calcined to increased reactivity. The inert rock dust could serve as suitable filler material for concrete to densify the matrix, increase packing density, and enhance strength *(332)*. As a filler, rock dust in a study was used to replace sand to improve the packing density of concrete, thus providing higher compressive strength than the reference concrete *(333)*. In addition, it has been shown that recycled rock dust might act as nucleation sites and enhance cement hydration *(334)*.

### 4.2.3 *Chemical and Physical Properties*

#### Aggregate Production

The physical and chemical properties of rock dust depend on the geological origin of the quarry rock. Granite fines were used in a previous study as quarry or rock dust along with rice husk ash (RHA) to replace cementitious materials in concrete *(335)*. The rock dust had a specific gravity of 2.56 and a water absorption of 2.32, and 16.8% of the materials were finer than 75 µm for the as-received rock dust from the granite quarry. No chemical characteristics of granite rock dust were reported in this study. Another study reported the characteristics of rock dust originated from a dolomite quarry. The as-received rock dust was manually ground using a pestle and mortar to obtain an average particle size of 90 µm. Dolomite rock dust had a higher CaO content (75%) compared to cement (64%). The other dominant oxide ingredient in the dolomite rock dust was MgO (18.3%) *(334)*. Another study in China applied recycled rock dust as SCM in low-carbon cement *(336)*. The exact source of this rock dust or the quarry material was not explicitly mentioned in this study. Results indicated that this rock dust had a CaO content of only 5%, whereas a noticeably high amount of $SiO_2$, 67%. The mean particle size of the rock dust was between 5 and 10 µm. In Nigeria, similar research was conducted by sampling rock dust from a local stone quarry. Characterization yielded a specific gravity of 2.6. *(337)*. Rock dust from granite quarries usually has low reactivity. As a result, the heat of hydration declines with an increase in rock dust content in the cement mixture *(338)*.

**Asphalt Production**

Baghouse fines are collected on the 0.6 mm (#30) sieve. Half of the plants in the United States collect 90% to 100% of the particles passing the 0.075 (#200) sieve, while others that do not have a primary collection system collect less than 50% *(339)*. Baghouse fines may have very little or no clay and usually meet the plasticity requirement for mineral filler *(340)*. The physical properties of typical baghouse fines are shown in Table 4.3. The pH of baghouse fines from granite and gravel ranges from 7.2 to 10.8 and from limestone and dolomite aggregates ranges from 11.0 to 12.4 *(339)*.

**Table 4.3: Physical Properties Typically Seen in Baghouse Fines**

| Range | Gradation of Passing | | | | Specific Gravity | Specific Surface[a] ($m^2/g$) | Hygroscopic Moisture (%) | Liquid Limit | Plasticity Index |
|---|---|---|---|---|---|---|---|---|---|
| | 0.600 mm (#30 sieve) | 0.300 mm (#50 sieve) | 0.075 mm (#200 sieve) | 0.01 mm | | | | | |
| Max | 100 | 100 | 100 | 78 | 2.87 | 2.18 | 1.9 | 39 | 4 |
| Min | 95 | 82 | 28 | 4 | 2.57 | 0.06 | 0.2 | NL | NP |

[a] Measured by air permeability

*Notes:* NL = Nonliquid; NP = Nonplastic

Source: Chesner et al. (2002) *(339)*.

### 4.2.4 *Feedstock Description and Supply*

**Aggregate Production**

Aggregates make up about 80% of the concrete volume. According to the USGS mineral report, the annual production of crushed stone in the United States was 1.6 billion T (1.5 billion t) in 2022. About 70% of the produced crushed stone is from limestone and dolomite geological origin. It was estimated that 71% of this amount was used as construction aggregate, 16% in cement manufacturing, 8% in lime manufacturing, and 2% in agricultural uses *(254)*. In addition to crushed stone or manufactured rock, the United States produced 1.1 billion T (1 billion t) of construction sand, gravel, or natural aggregate in 2022 *(254)*.

**Asphalt Production**

There are around 3,600 asphalt production plants in the United States, producing about 385 million T (350 million t) of asphalt mixture annually; about 420 million T (381 million t) were produced in 2019 alone *(341)*. Rock dust is produced during hot mix asphalt production. It is estimated that rock dust is about 5% of the total weight of produced aggregate. Thus, about 5,000 T (4535 t) of rock dust is produced at an average asphalt plant yearly *(332)* or 21 million T (19.05 t) of rock dust [0.05 x 420 million (US asphalt production)].

### 4.2.5 *Process Description, Technology Readiness Level, and Potential Suppliers*

**Process Description**

The crushed stone production process includes extraction, crushing, grinding, and screening. Another supply of rocks for construction is sand and gravel sourced from glacial deposits, river channels, and river flood basins.

As water is used during cutting, crushing, and grinding the rock, a waste sludge containing rock dust and fines is generated and stored in settling ponds and then landfilled when hardened *(332)*. Sand and gravel may contain clay and dust from the natural weathering process. The amounts of deleterious content and fine particles passing sieve #200 are restricted in the ASTM standard for concrete and asphalt aggregates. Therefore, aggregate needs to be washed before use if fines content exceeds the limits in the standard. The process of rock dust collection at an asphalt plant is shown in Figure A.11.

**Technology Readiness Level**

Aggregate dust is generated at scale as part of aggregate crushing operations and asphalt production. However, the use of aggregate dust in concrete is in the research and development phase at around TRL 4.

**Potential Suppliers**

Potential suppliers are aggregate quarries and ready-mix concrete producers. The full list of California Asphalt Pavement Association (CalAPA) members and asphalt producers can be obtained on its website.[6]

**Current Use of Product**

Almost 40% to 50% of HMA plants collect baghouse fines, which may be routed to the asphalt production facility or stored in a silo to be used as a mineral filler additive in asphalt mixes *(339)*. Rock dust is also used as remineralization material for agricultural soils. Applying rock dust to soils has been reported to stimulate plant growth and increase resistance to pests and diseases, among other benefits *(342,343)*.

**Agents Involved in Production and Distribution**

The agents involved in production and distribution include aggregate quarries, ready-mix concrete producers, local governments, and Caltrans.

**Product Consideration in Caltrans Specifications**

Caltrans specifications currently do not include rock dust as an accepted SCM for concrete.

### 4.2.6 *Performance in Concrete Based on the Literature*

**Impact on Fresh Properties**

Generally, the use of rock powder in replace of sand will reduce workability due to higher surface area *(344)*. However, one study used recycled rock dust to replace quartz sand with up to 80% replacement rates but did not report any significant changes in workability or the hydration process *(333)*. In another study, rock dust as SCM was found to affect the hydration reaction of cement-based mixtures *(334)*. Rock dust is non-reactive; however, due to fine particle size and high surface area, rock dust particles were shown to serve as nucleation sites,

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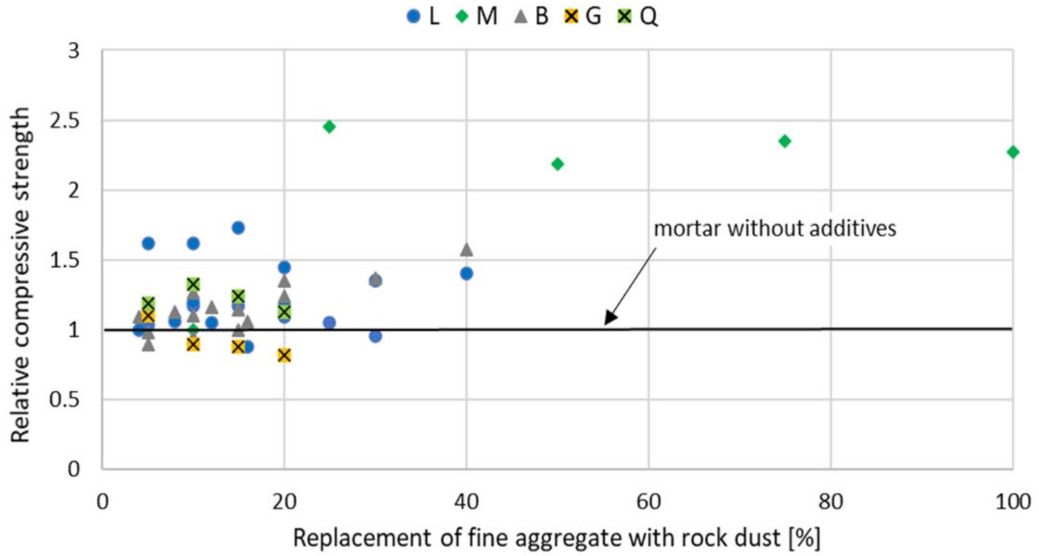
[6] More information is available at calapa.weblinkconnect.com/allcategories.

enhancing the hydration reaction. This study also suggested that dolomite-based rock dust, when used at a more than 20% replacement rate, may decrease the flow characteristics of the mix. The initial and final setting times of the cement paste increase as cement is partially replaced with rock dust *(337)*. This delay is most likely induced by the dilution of the cement in the mixture.

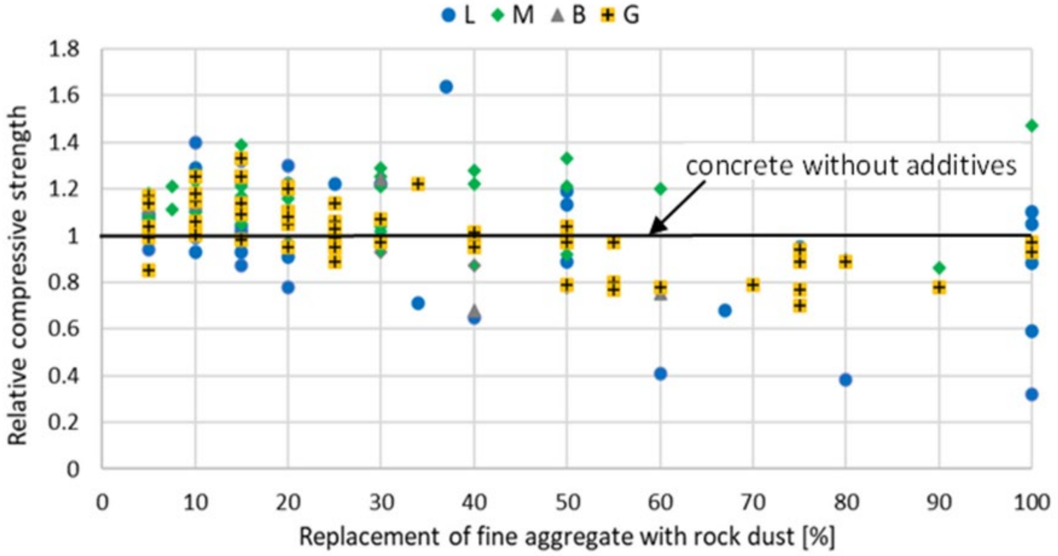
## Impact on Strength

Adding rock dust as a replacement for cement in concrete can reduce the compressive strength of concrete. An optimum dosage of 10% was suggested in a study with varying water-to-binder ratios from 0.3 to 0.6 *(345)*. Granite rock dust, along with RHA as SCM in self-compacting concrete, negatively affected the initial strength gain. However, with time, the difference in compressive strength between the control mix and the RHA and rock dust mix reduced significantly *(335)*. It was also shown that rock dust, when used as SCM by itself, reduces the 28-day compressive strength of concrete *(336)*. One study successfully produced ultra-high-performance concrete using recycled rock dust as 20%, 40%, 60%, 80%, and 100% replacement of quartz sand *(333)*. The ultra-high-performance concrete with 80% recycled rock dust achieved 22,349.5 psi (154.1) MPa compressive strength, even higher than the reference mix. The impact of the replacement of sand with rock dust in mortar and concrete is shown in Figure 4.2 *(332)*. Figure 4.2a shows that, overall, a positive impact is seen by replacing sand with rock dust in mortar. The same overall trend is seen for concrete in Figure 4.2b. However, at replacement rates, higher than 60% degradation in the strength is seen.



(a)

*Notes:* L: limestone dust, M: marble dust, B: basalt dust, G: granite dust, Q: quartz dust.



(b)

*Notes:* L: limestone dust, M: marble dust, B: basalt dust, G: granite dust, Q: quartz dust.

Source: Dobiszewska et al (2022) *(344)*.

**Figure 4.2: Summary of literature on the impact of rock dust as sand replacement on 28-day compressive strength in (a) mortar and (b) concrete.**

## Impact on Durability

Dolomite-based rock dust is highly susceptible to acid attack *(346)*. SEM analysis showed that adding rock dust reduces the average pore diameter and results in a more compact matrix *(336)*. In a study, the addition of granite rock dust reduced the drying shrinkage potential of cement composites and thus lowered the risk of early-age cracking *(338)*. It was also found that the granite rock dust had negligible alkali-silica reactivity. Sulfate resistance may increase when cement is partially replaced with rock dust (15% replacement level) *(347)*. Freeze-thaw durability increased when sandstone waste was applied to self-compacting concrete *(348)*.

**Table 4.4: Summary of the Effect of Biochar on Various Properties of Cement-Based Systems**

| Property of Concrete | Comparison to 100% OPC Concrete |
|---|---|
| Workability | Decrease |
| Early strength | Decrease |
| Late strength | Increases or no change |
| Setting time | Increase |
| Drying shrinkage | Reduce, More research needed |
| Alkali-silica reaction | No information found |
| Sulfate attack resistance | More research needed |
| Freeze-thaw durability | More research needed |

### 4.2.7 *Environmental Considerations*

#### Global Warming Potential

One study examined the life cycle cost savings and environmental benefits of partially replacing fine aggregate and/or cement in concrete with rock dust for roadway pavements *(332)*. The study determined that the strategy with 20% fine aggregate and 10% cement replacement with rock dust showed life cycle savings in terms of cost and environmental impacts. The material production stage was the place where most savings were observed.

It is uncommon to report each aggregate sieve/size environmental impact. However, using allocation methods and properly tracking and recording primary data are reasonably doable. Initially, due to the unavailability of a PCR from a program operator, the Vulcan Materials Company produced a nonverified EPD for 12 concrete aggregate products (basically different aggregate sizes) following the International EPD System's Product Category Rule (PCR). Rock dust was one of the products manufactured at the Vulcan sand and gravel facility in Pleasanton, California. The functional unit was set to cradle-to-gate analysis for 1 metric ton of concrete aggregate products. The primary data used were all for 2014, and electricity impacts were calculated based on the 2010 resource mix at the level of the NERC WECC region. The EPD does not report the characterization method used to compute the impacts, but based on the methodology, it appears the CML characterization factors were used. The theoretical electricity usage was assumed to be 746 watts/hp for the equipment used.

After the availability of a PCR published by ASTM, the Vulcan Materials Company developed and published another EPD following ISO 14025, ISO 21930, and ASTM International's EPD program operator rules *(328)*. The 2012 resource mix at the level of the NERC WECC region was used for electricity impacts, and the 2015 grid mix was used for electricity usage calculations. The EPD for rock dust material published in 2016 and 2017 is presented in Table 4.5.

**Table 4.5: LCI and LCIA of 1 Metric Ton of Rock Dust from the Vulcan Materials Company**

| Impact Categories | | Units | 2016 Rock Dust | 2017 Rock Dust |
|---|---|---|---|---|
| GWP | Global warming potential | kg $CO_2$-eq | 6.06 | 5.72 |
| AP | Acidification potential | kg $SO_2$ eq | 0.05 | 0.03 |
| EP | Eutrophication potential | kg N eq | 0.01 | 0.04 |
| POP | Photochemical ozone creation potential | kg $O_3$ eq | 0.73 | 0.72 |
| ODP | Ozone depletion potential | kg CFC-11 eq | 1.59E-07 | 4.71E-07 |
| rPE | Use of renewable primary energy | MJ | 7.54 | (1.04+13.1) HHV |
| nrPE | Use of nonrenewable primary energy | MJ | 90.7 | (77.4+11.3)HHV |
| rPEM | Use of renewable primary energy resources as raw materials | MJ or kg | 0 | 0.06 (kg) |
| nrPEM | Use of nonrenewable primary energy resources as raw materials | MJ or kg | 0 | 1000 (kg) |
| SM | Use of secondary materials | kg | 0 | — |
| rSF | Use of renewable secondary fuels | MJ | 0 | — |
| nrSF | Use of nonrenewable secondary fuels | MJ | 0 | — |
| nFW | Use of net fresh water | $m^3$ | 0.11 | — |
| nhW | Nonhazardous waste disposed | kg | 0.14 | 0.07 |
| hW | Hazardous waste disposed | kg | 7.84E-05 | 3.01E0-04 |
| rW | Radioactive waste disposed | kg | 1.20E-04 | — |

Source: Vulcan Materials Company (2016) *(328)*.

### 4.2.8 *Cost Considerations*

Rock dust is currently a waste produced during aggregate and asphalt production and has no economic value. Reusing rock dust as fine aggregate or cement replacement in mortar and concrete provides a reuse application for this byproduct. With the benefits reported in the performance of concrete with rock dust in concrete, its reuse in concrete could offer economic and environmental benefits.

## 4.3 Waste Brick Powder

### 4.3.1 *Product Description*

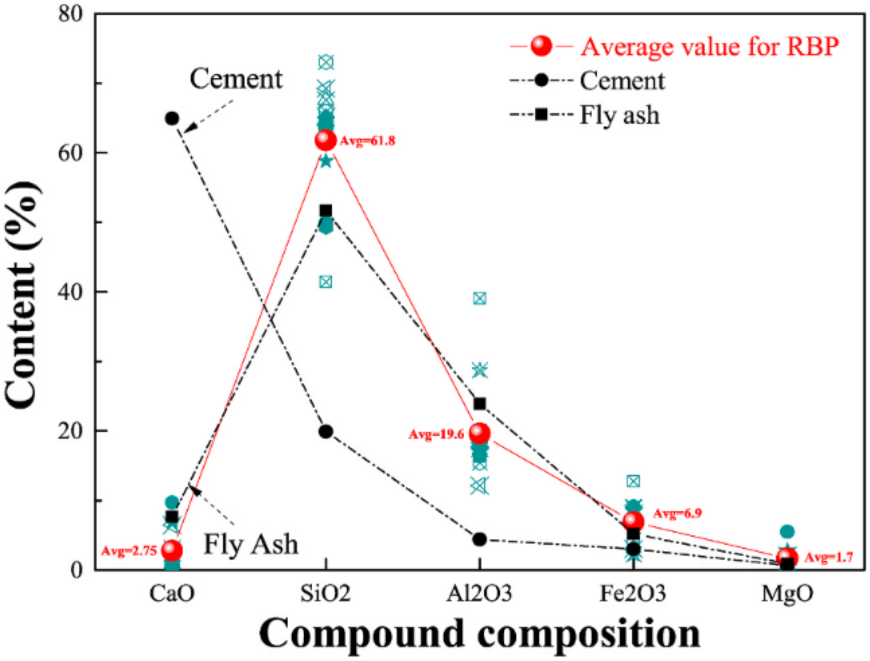
The United States produced 12.3 million T (11.16 million t) of brick and clay tile waste from C&D processes in 2018. However, only 1.6 T (1.5 t) of this amount was recycled or set for subsequent use *(322)*. It is well known that recycled brick as coarse aggregate replacement in concrete degrades the mechanical properties, durability, and workability of concrete due to the recycled brick's high porosity *(314)*. On the other hand, research has shown that recycled brick powder (RBP) could enhance these properties if used in the optimal replacement rates for portland cement *(349)*.

### 4.3.2 *Acting Mechanism in Concrete*

Bricks are produced by firing clay and are composed of high amounts of silica, alumina, and some lower levels of calcium oxide. The RBP has generally been shown to meet the oxide content requirements of ASTM C618 for $SiO_2$, $Al_2O_3$, and $Fe_2O_3$ *(350)*. Therefore, the mechanism by which RBP positively impacts concrete performance is expected to be a reactive pozzolanic SCM to reduce the requirement for portland cement *(351)*. However, the firing temperature must be in the proper range for adequate calcination to render pozzolanic reactivity because brick clay minerals (mainly illite and quartz) remain unchanged up to 1652°F (900°C) and do not dehydroxylate. These minerals undergo recrystallization at less than 1832°F (1000°C), producing mullite, cristobalite, and hematite. Finally, the sintering of some phases in the melt occurs at temperatures greater than 2012°F (1100°C) and brings about the phase transition from amorphous to crystalline, which gives the clay ceramic properties *(352,353)*. These latter phases, likely present in clay brick fired at less than 1832°F (1000°C), are crystalline and thus weak pozzolans.

### 4.3.3 *Chemical and Physical Properties*

The particle size of these powders varies in the literature, with the median particle size ($D_{50}$) ranging from about 3 µm to 27 µm, and in some cases, compared to coarser powders with a $D_{50}$ of 180 µm *(352,354–357)*. A summary of the chemical composition of RBP compared to cement and fly ash is shown in Figure 4.3 *(314)*. The figure shows that RBP is a potential pozzolanic material due to its high aluminosilicate content based on bulk oxide composition. The sum of the percentages of three relevant oxides ($Al_2O_3$, $SiO_2$, and $Fe_2O_3$) in brick passes the minimum prescribed level of 70% in ASTM C618. However, amorphousness and glass content should be considered because powders with low glass content and high crystalline mineral content are weak pozzolans *(358)*.



Source: Tang et al. (2020) *(314)*.

**Figure 4.3: Chemical composition of RBP gathered from various studies.**

### 4.3.4 *Feedstock Description and Supply*

More than 600 million T (544 million t) of waste from C&D activities were generated in the United States in 2018 *(322)*, making it one of the largest producers of C&D waste *(309)*. In addition, the United States produced 13.5 T (12.3 t) of brick waste from C&D processes in 2018. However, only 1.7 T (1.5 t) of this amount was recycled or set aside for subsequent use *(322)*.

### 4.3.5 *Process Description, Technology Readiness Level, and Potential Suppliers*

#### Process Description

The process of recovering brick waste and generating RBP is shown in Figure A.12 *(314)*. The process includes collecting and sorting brick waste at C&D waste recycling facilities. In addition, grinding can be done at cement plants or facilities.

#### Technology Readiness Level

The proof-of-concept demonstration of using RBP in concrete as SCM is available in laboratory-scale studies in the literature. However, its widespread use in construction has not been demonstrated. Therefore, it is still considered in the research and development phase, placing it at about TRL 4. Local and regional availability of RBP that is not mixed with other C&D waste could hinder its advancement to further TRLs in the United States.

#### Potential Suppliers

Potential suppliers are C&D recyclers and cement plants that can grind the brick waste supply into the right fineness to be used as SCM in concrete.

#### Current Use of Product

Based on conversations with GreenWaste/Zanker Recycling, not much brick waste is gathered separately and most brick waste is mixed with other C&D waste.

#### Agents Involved in Production and Distribution

The agents involved in production and distribution include C&D recyclers and CalRecycle.

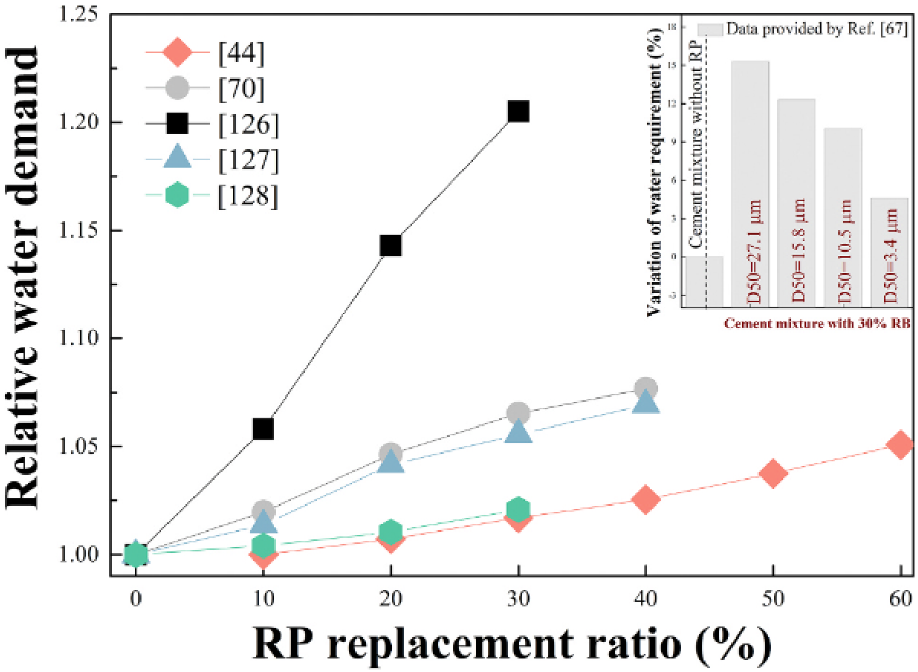
## Product Consideration in Caltrans Specifications

Caltrans specifications currently do not include waste brick as an accepted SCM for concrete.

### 4.3.6 *Performance in Concrete Based on the Literature*

## Impact on Fresh Properties

In general, RBP increases water demand due to irregular particle shape, but the impact is only substantial at replacement rates greater than 10% of OPC, shown in the summary graph in Figure 4.4. In terms of setting time, a study using ultrafine RBP found that early hydration is accelerated and setting time is shortened *(359)*. In contrast, another study with ultrafine RBP with hydrated lime increased the setting time. Another study specifically focused on the effect of RBP on the hydration of blended cement with RBP showed that RBP reduced the overall heat release duration of hydration but promoted cement hydration by nucleation and dilution. *(360)*



Source: Tang et al. (2020) *(314)*.

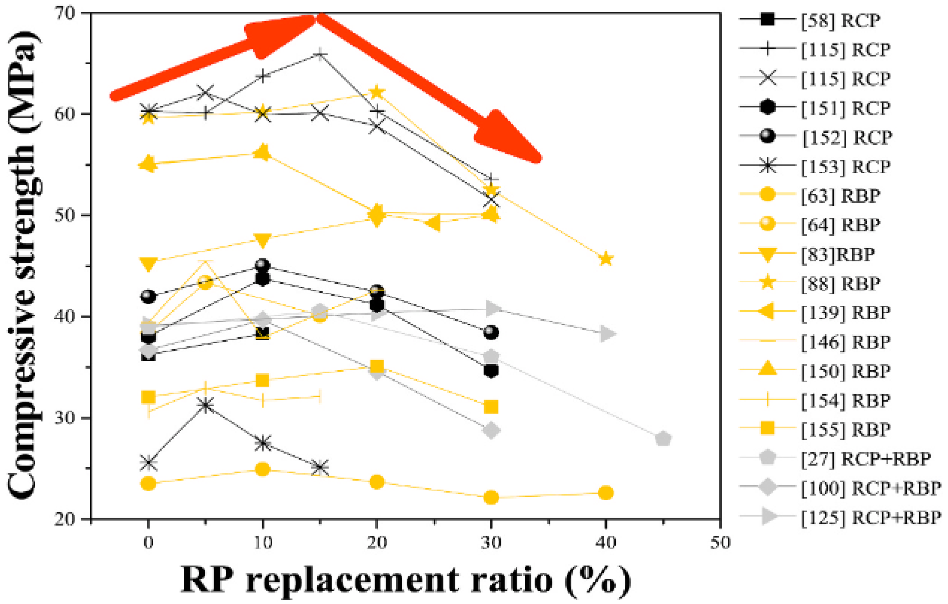
**Figure 4.4: Impact of RBP on water demand at various replacement rates.**

## Impact on Strength

The literature generally shows that replacing OPC with RBP in the 10% to 20% range leads to either an increase or equivalent compressive strength *(350)*. For example, in one study, researchers replaced 10% cement with RBP in cement pastes and observed a 5% increase in compressive strength at 60 days of curing *(361)*. The compressive strength decreased compared to the plain cement paste when cement replacement with RBP was done at or higher than 40%. In addition, it has been shown that alkali-activated RBP may positively impact the compressive strength of cement pastes *(362)*.

In mortars, the maximum compressive strength is achieved when cement is replaced with RBP at a moderate proportion of under 40% *(370)*. However, other researchers have shown that when the replacement proportion of RBP is 20%, the increase in both 28-day compressive and flexural strength is higher compared to plain cement mortar *(363)*.

A summary of the reported compressive strength for RBP concrete is shown in Figure 4.5 *(314)*. According to the figure, a decline in compressive strength is seen in most studies. However, in some studies, an increase in strength is achieved up to the optimum replacement rate of 5% to 15%. The increase may be due to the filler effect of RBP in concrete *(364,365,366)*.



Source: Tang et al. (2020) *(314)*.

**Figure 4.5: Impact of RBP and RCP on compressive strength of concrete at various replacement rates.**

## Impact on Durability

RBP with particles finer than cement was reported to increase the water tightness of concrete and reduce its water permeability and chloride permeability. However, the opposite impact on water and chloride permeability was seen with recycled powders with larger particles than cement *(314)*.

**Table 4.6: Summary of the Effect of Brick Powder on Various Properties of Cement-Based Systems**

| Property of Concrete | Comparison to 100% OPC Concrete |
|---|---|
| Workability | Decrease |
| Early strength | No change or increase with 10% to 20% replacement rate |
| Late strength | No change or increase with 10% to 20% replacement rate |
| Setting time | More research needed |
| Drying shrinkage | Reduce, More research needed |
| Alkali-silica reaction | No information found |
| Sulfate attack resistance | More research needed |
| Freeze-thaw durability | More research needed |

### 4.3.7 *Environmental Considerations*

Used and demolished bricks may be considered as having no GWP impacts as they are considered waste and have served the purpose for which they were manufactured. The GWP associated with recycled bricks is their transportation to the landfill or recycling facility or if any processing is required at any stage, such as grinding to produce an SCM.

Production of bricks produces air pollution due to the mining of clay material and burning of fossil fuels in the kiln *(367,368)*. However, waste bricks from demolition may not be a threat to the environment as clay is returned to nature in solidified form. Further grinding of recycled bricks may be required and, if not properly processed, could produce direct emissions such as particulate matter that may be harmful to nearby people.

Bricks are not toxic since they are made from a clay and water mixture *(369)*. However, they could be considered toxic if they have been contaminated. Construction demolition waste containing bricks may need to be tested for toxicity if contamination is expected.

### 4.3.8 *Cost Considerations*

RBP production would include energy for grinding and fineness improvement. However, this energy is much less than the energy and costs of portland cement production. Using RBP as cement replacement opens a new path for recycling this C&D waste in a circular economy, and at optimal replacement rates and fineness, enhancements of mechanical and durability properties of concrete are possible.

# 5 POST-CONSUMER WASTE

## 5.1 Municipal Solid Waste Ash

### 5.1.1 *Product Description*

Incineration is a waste management strategy for municipal solid waste (MSW). Municipal solid waste ash (MSWA) is the byproduct of incineration. However, managing large volumes of MSWA produced at incineration plants has created a challenge in some large cities worldwide as the volumes of generated MSW increase *(370)*. MSWA is usually a mixture of fly ash and bottom ash. Bottom ash is the noncombustible residue produced in the incinerator, while fly ash (also known as pollution controller residue) is the smaller particulate matter captured by the air pollution control system *(371)*. The bottom ash accounts for 85% to 95% of the residual remaining after incineration *(371)*.

### 5.1.2 *Acting Mechanism in Concrete*

MSW fly ash is 24% to 27% lime, some silicates, and some aluminosilicates *(370)*. The chemical composition has been found to be close to Class C fly ash, indicating potential reactivity to replace portland cement in concrete partially. Though the ash composition is expected to vary from facility to facility, several studies have demonstrated the potential for using MSWA in concrete as a filler material and as an SCM *(372,373,374)*.

### 5.1.3 *Chemical and Physical Properties*

MSWA is a lightweight material relative to natural sand, with specific gravity ranging from 2.3 to 2.5 *(375)*. It is highly absorbent, with absorption values ranging from 4% to 17% depending on the particle size *(370)*. MSWA is a gray-to-black amorphous glass-like material in appearance. Its properties and quality rely on the waste, the type of incineration unit, and the nature and type of pollution controller unit *(370)*. The chemical composition of MSWA plays an important role in reactivity as an SCM. Major chemical components in MSWA are CaO, $SiO_2$, and $Al_2O_3$ *(376)*. Quartz is the most abundant mineral phase in MSWA, followed by calcite, hematite, magnetite, and gehlenite *(375)*.

### 5.1.4 *Feedstock Description and Supply*

It is estimated that the burning of MSW produces around 0.275 to 0.325 T (0.250 to 0.295 t) of bottom ash and 0.02 to 0.03 T (0.018 to 0.027 t) of fly ash per ton of MSW *(377)*. The two MSW recovery plants in California and their ash production rates are provided in Table 5.1.

**Table 5.1: Municipal Solid Waste Recovery Plants in California and Their Ash Production Rates**

| Capacity/Ash Production/Facility | Southeast Resource Recovery Facility at Long Beach | Covanta Stanislaus Incinerator Facility at Stanislaus County |
|---|---|---|
| Waste processing capacity | 1300 T (1180 t) per day | 800 T (725 t) per day |
| Ash production | 400 T (362 t) per day | 250 T (226 t) per day |

### 5.1.5 *Process Description, Technology Readiness Level, and Potential Suppliers*

#### Process Description

While the MSW incineration process is unique to every incinerator, the general process description of the MSWA generation is provided below and shown in Figure A.13 *(372,377,378,379)*.

The tipping hall is the storage space where solid waste is delivered. The tipping hall is usually enclosed, and the air is continuously drawn from the pit area to remove dust and odor. The waste is lifted from the tipping hall by overhead cranes and dropped into the fuse hopper. The hydraulic ramp at the bottom of the feeding chute pushes the waste into the incinerator, where it is burned under controlled conditions. The floor of the incinerator contains moving grates that push the burning waste through the incinerators. The resulting ash is collected into the quench tank when the waste is passed through the incinerator. The quench tank is filled with water to cool and prevent ash dispersion.

The combustion gases generated in the incinerator travel through the dry scrubbing unit. The dry scrubbers in the unit neutralize the acid gases such as sulfur dioxide and hydrochloric acid by spraying a lime slurry in the exhaust unit. This process tends to remove around 95% of the sulfur dioxide and hydrochloric acid. The reacted lime and the fly ash are collected in the bottom of the scrubbing unit, which is later discarded along with other ashes.

The baghouse is like a large vacuum cleaner that traps particulate matter and fly ash. Each incinerator has a baghouse that contains 10 to 12 modules (depending on the manufacturer) with bags made of fiberglass. The particulate matter and the fly ash are trapped in the baghouse filters when the air is blown through them. The particulate and fly ash is then collected and removed from the bottom. The ash from the incinerator, dry scrubbing unit, and baghouse is treated and transported to the landfill, where it is mixed with the aggregates and used as road base material.

### Technology Readiness Level

The proof-of-concept demonstration of the use of MSWA as a mineral admixture in concrete is already available in many studies in the literature. However, MSWA use as an SCM in construction is not widespread. Part of this could be the lack of widespread availability and also concerns for leachate of heavy metals as form MSWA concrete, as will be discussed in the later sections. Therefore, the use of MSW ash as an SCM in concrete is at TRL 3 (“proof-of-concept demonstrated, analytically and/or experimentally”).

### Potential Suppliers

Two MSW recovery plants are active in California, the Southeast Resource Recovery Facility at Long Beach and Covanta Stanislaus Incinerator Facility at Stanislaus County.

### Current Use of Product

In California, MSWA is disposed of in a dual-layer landfill or used as a road base material. Based on communication with the California Nevada Cement Association (CNCA), “There isn’t municipal waste ash in California because waste is not incinerated here. There is engineered municipal solid waste produced in Southern California, but it is used as an alternative fuel in cement kilns, not as an SCM.” However, a conversation with the environmental officer at one of these plants suggested that the ash is still being produced as of June 2022.

**Agents Involved in Production and Distribution**

Agents involved in MSWA are MSW incineration plants and municipal waste management units.

**Product Consideration in Caltrans Specifications**

Caltrans specifications currently do not include municipal solid waste ash as an accepted SCM for concrete.

### 5.1.6 *Performance in Concrete Based on the Literature*

**Impact on Fresh Properties**

Mixed findings have been reported regarding the fresh properties of concrete with MSWA. An increase in a slump was reported in fresh concrete mixes with 30% MSWA when the ash was ground under dry conditions, while a decrease in the slump was observed when the ash was ground under wet conditions *(380)*. Another study evaluated the use of raw and washed MSW fly ash (to remove heavy metals and soluble salts) and bottom ash at 10%, 20%, 30%, 40%, and 50% replacement of portland cement. It was reported that washed fly ash increased the water demand to reach a normal consistency; however, the bottom ash decreased the water demand. The authors attributed this behavior to the porous structure of fly ash compared to bottom ash and the higher content of calcium in bottom ash that can use the water for the reaction. The water demand increased for both ashes as the replacement rates increased. In terms of setting time, the bottom ash retarded the setting due to the high content of heavy metals, while the washed fly ash set faster than the OPC control due to anionic ions such as Cl, $SO_4$, and $NO_3$ *(381)*.

The same study found as the replacement percent increased, the setting time also increased, with an initial setting time of 867 minutes and a final setting time of 989 minutes. Similar results were reported in another study *(381)*. Another study incorporated MSW bottom ash at a 20% replacement rate of OPC in concrete in different particle size fractions, shown in Figure 5.1 *(382)*. Overall, the MSW bottom ash fractions delayed the setting time. The heavy metals (chromium, zinc, and lead) were believed to have been released in the pore solution and inhibited the dissolution of $C_3S$ hydration. The smaller fractions contained more calcium-bearing substances and thus resulted in more delayed hydration. Other studies also reported MSWA results in a different hydration behavior and a significant delay in the onset of the acceleration reaction of $C_3S$ hydration and reduced maximum heat hydration *(382,383)*.

**Figure 5.1: Different size fractions of MSW bottom ash used as 20% portland cement replacement in concrete.**

## Impact on Strength

One study compared the effect of using 30% by weight of dry or wet ground MSWA on the mechanical properties of concrete *(380)*. The study demonstrated a considerable development in strength (around 95 MPa after 180 days). Another study assessed the effect of the MSWA milled to different particle sizes and concluded that greater milling time resulted in the improved strength of the concrete *(383)*. The study also reported that the compressive strength of the specimens with fine MSWA was equivalent to that of the control. Another study replaced the cement with 40% of MSWA and reported a decline in compressive strength by almost 50%

compared to controls *(384)*. The researchers explained this strength loss due to weaker bond development at the interfacial transition zone between the cement and aggregate.

**Impact on Durability**

Durability-related performance of the concrete with MSWA was studied by using an initial surface absorption test to measure the concrete's permeability *(384,385)*. The study reported that the absorption decreased from 0.55 $mL/m^2s$ (control) to 0.30 to 0.39 $mL/m^2s$ for ground MSWA mixes. The study also concluded increased drying shrinkage with a progressively higher content of MSWA (45% higher shrinkage for mixes with 40% MSW ash after 91 days). Regarding the corrosion resistance of the concrete, an evaluation of the chloride ion penetration was conducted *(380)*. Concrete containing 30% ground MSWA was tested using indirect electrical resistivity and direct chloride apparent diffusion coefficients. The study concluded that the MSWA mixes appeared to deliver a level of resistance to chloride attack comparable to control mixes of equivalent strength.

**Table 5.2: Summary of the Effect of MSWA on Various Properties of Cement-Based Systems**

| Property of Concrete | Comparison to 100% OPC Concrete |
|---|---|
| Workability | Depends on ash type and properties |
| Early strength | Decrease |
| Late strength | Decrease or no change |
| Setting time | Delay depending on calcium content and heavy metals |
| Drying shrinkage | More research needed |
| Alkali-silica reaction | No information found |
| Sulfate attack resistance | More research needed |
| Freeze-thaw durability | More research needed |

### 5.1.7 *Environmental Considerations*

There is no LCA or LCIA of MSWA as an SCM. Since MSWA is the waste material that is usually landfilled, no EPDs are available for this material. The disposal of MSW in the landfill is associated with concerns regarding the leachate of heavy metals and soluble salts (Cu, Pb, Zn, and Ni, and of the metalloids Sb, Cr, and Mo) into the nearby groundwater and soil *(386)*. The concentration of toxic elements in MSWA and the possibility of their leachate into the environment, if used in the concrete, should be carefully considered, as reviewed in the following discussion.

## Leachate of Heavy Metals

Infiltration of water through the cementitious system containing MSW ash could cause the leachate of the concentrations of heavy metals into the environment. The concentration of heavy metals in an MSW bottom ash sample available in one study is provided in Table 5.3. Only the cadmium concentration is close to the allowable limits *(387)*.

**Table 5.3: Requirements of Heavy Metal for Inert Classification**

| Element | Concentration in BA (mg/kg) | Error/LD (mg/kg) | Concentration Limits (mg/kg) |
|---|---|---|---|
| Ag | 1.01 | 0.15 | — |
| Al | 82,760 | 3,500 | — |
| As | 5.38 | 0.3 | 200 |
| Au | 0.292 | 0.01 | — |
| Ba | 1,294 | 47 | — |
| Br | 11.7 | 0.4 | — |
| Ca | 226,940 | 8,770 | — |
| Cd | 11 | 2.1 | 12 |
| Ce | 41.2 | 1.5 | — |
| Cl | 3,694 | 151 | — |
| Co | 16.2 | 0.6 | 250 |
| Cr | 281 | 12 | 500 |
| Cs | 3.7 | 0.1 | — |
| Cu | — | 54 | 500 |
| Dy | 2.49 | 0.16 | — |
| Eu | 0.69 | 0.08 | — |
| Fe | 16,900 | 593 | — |
| Ga | 38.5 | 5.4 | — |
| Hf | 4.54 | 0.16 | — |
| Hg | 0.11 | 0.02 | 10 |
| K | 7,926 | 807 | — |
| La | 22.4 | 0.8 | — |
| Mo | 10 | 1 | 500 |

| Element | Concentration in BA (mg/kg) | Error/LD (mg/kg) | Concentration Limits (mg/kg) |
|---|---|---|---|
| Mg | 21,481 | 1,981 | — |
| Mn | 574 | 20 | — |
| Na | 7,412 | 260 | — |
| Nd | 16.4 | 1.4 | — |
| Ni | — | — | 500 |
| Pb | — | — | 500 |
| Pt | — | 2 | — |
| Rb | 46.3 | 1.8 | — |
| Sb | 77.8 | 2.8 | — |
| Sc | 4.23 | 0.17 | — |
| Se | 1.33 | 0.11 | — |
| Si | — | 250,000 | — |
| Sm | 2.77 | 0.15 | — |
| Sn | — | 36 | — |
| Sr | 394 | 18 | — |
| Ta | 1.03 | 0.04 | — |
| Tb | 0.34 | 0.02 | — |
| Te | — | 2 | — |
| Th | 7.9 | 0.3 | — |
| Ti | 7,261 | 508 | — |
| Tm | — | 0.2 | — |
| U | 2.99 | 0.23 | — |
| V | 36 | 4.7 | — |
| W | 6.69 | 0.41 | — |
| Yb | 0.87 | 0.04 | — |
| Zn | 967 | 34 | 1,500 |
| Zr | 178 | 17 | — |

Source: Jurič et al. (2006) *(387)*.

The results of the leachate test from concrete with MSW bottom ash from the same study are provided in Table 5.4. As shown in the table, all the requirements for inert waste classification are met. However, the study suggests more research on the concentrations of toxic elements from MSWA concrete.

**Table 5.4: Leachate Test Results on Concrete with MSW Bottom Ash**

| Element | Leaching from Concrete (mg/kg) | Limits for Inert Waste Valid up to 2004 (mg/kg) | Limits for Inert Waste Valid from 2004 (mg/kg) |
|---|---|---|---|
| As | <0.01 | 1 | 0.5 |
| Ba | — | 20 | 10 |
| Cd | <0.03 | 0.5 | 0.04 |
| Cr | <1.5 | 10 | 0.5 |
| Co | <0.61 | 5 | — |
| Cu | 0.13 | 10 | 2 |
| Hg | — | 0.05 | 0.01 |
| Mo | — | — | 0.5 |
| Ni | 0.83 | 5 | 0.4 |
| Pb | <1.04 | 5 | 0.5 |
| Sb | — | 1 | 0.06 |
| Se | — | 0.5 | 0.1 |
| Zn | <0.17 | 30 | 4 |

Source: Jurič et al. (2006) *(387)*.

Another study similarly reported the MSW bottom ash is nontoxic; however, MSW fly ash has high concentrations of heavy metals from vaporized compounds adsorbed on the large surface area of fine fly ash *(388)*.

### 5.1.8 *Cost Considerations*

MSWA is considered a waste product without any economic value at this time. Any operations of collection and transportation of the material and disposal in the landfill are added costs.

## 5.2 Municipal Wastewater Sewage Sludge Ash

### 5.2.1 *Product Description*

Sewage sludge, also referred to as biosolids, is a solid to semi-solid residual material produced as a byproduct during the treatment of municipal wastewater. The sewage sludge is mostly organic wastewater solids used as soil amendments or fertilizers for crop growth *(389,390)*. Another sludge management practice is the incineration of sewage sludge. The incineration process reduces the waste by about 70% by mass and 90% by volume, leaving behind sewage sludge ash (SSA). With the increase in the processing capacities of wastewater treatment plants in the country, this practice is expected to generate a significant amount of SSA, requiring sustainable and appropriate secondary use. In addition, the cement industry is increasing rapidly and is expected to play a major role in meeting decarbonization targets, so evaluating SSA as an ASCM is useful and timely *(391,392)*.

### 5.2.2 *Acting Mechanism in Concrete*

According to a study of the cementing properties of SSA, the amorphous phases are rich in aluminum and iron phosphates that lead to the formation of amorphous hydroxyapatite. The study found that it is likely that these phases produce C-S-H in reaction with portlandite and contribute to strength development *(393)*. In another study, SSA was found to be a reactive pozzolan along with silica fume, MK, and fly ash *(394)*. Similarly, another study showed that if burned at 1472°F (800°C), SSA can possess high pozzolanic reactivity, but reactivity reduces at lower or higher temperatures *(395)*.

### 5.2.3 *Physical and Chemical Properties*

According to reported chemical compositions for SSA in the literature (Table 5.5), SSA is an aluminosilicate or silicate and calcium material with varied contents of other toxic and nontoxic element concentrations *(396,397 398)*. Crystalline phases of quartz, albite, calcite, magnetite, hematite, and other phases have been detected as the most abundant minerals in SSA, along with iron oxides, iron phosphates, calcium phosphates, and aluminum phosphates. SSA consists primarily of silica, iron, and calcium.

**Table 5.5: Chemical Composition of SSA**

| Compounds | Weight (%) from Three Studies | | |
|---|---|---|---|
| | **Pérez-Carrión et al. (2014)** *(399)* | **Donatello et al. (2010)** *(394)* | **Tantawy et al. (2012)** *(395)* |
| $SiO_2$ | 19.2 | 35.8 | 39.03 |
| $Al_2O_3$ | 8.9 | 11.2 | 15.13 |
| CaO | 30.6 | 12.9 | 5.80 |
| $Fe_2O_3$ | 10.0 | 16.9 | 17.05 |
| $SO_3$ | 11.1 | 3.1 | 4.04 |
| $K_2O$ | 1.4 | 1.5 | 0.62 |
| $Na_2O$ | 0.8 | 0.2 | 0.43 |
| MgO | 2.7 | 1.9 | 1.93 |
| $TiO_2$ | 1.0 | 1.0 | — |
| $P_2O_5$ | 12.3 | 11.9 | 13.12 |
| $H_2O$ | 0.5 | — | — |
| LOI | 5.1 | 0.8 | 2.11 |

Source: Pérez-Carrión et al. (2014) *(399)*.

SSA comprises irregular particles with rough surface textures and porous microstructures *(391,393)*. The specific gravity of the SSA is in the range of 1.8 to 2.9, which is somewhat comparable to light sand and less dense than portland cement at 3.15 *(399,400,401)*. Studies have shown that density increases with increased incineration temperature up to 1832°F (1000 °C). SSA also has a low bulk density to particle density ratio, indicating its porous nature *(402,403)*. SSA was shown to have a mean particle size range from 50 to 260 µm and fell between silt-like material (2.5 to 62.5 µm) and fine sand (62.5 to 250 µm) *(391,399)*. SSA is consistent within the mean particle size and thus can be suitable for use as a filler or even fine aggregate in concrete with minor modifications. Brunauer-Emmett-Teller (BET) specific surface area and Blaine fineness varied over a wide range from 2,500 to 23,100 $m^2$/kg and 500 to 3,900 $m^2$/kg *(400,404,405)*. The marked variability and the discrepancies compared to the typical portland cement (BET of 350 to 380 $m^2$/kg) suggest that SSA is not ideally suited to be a potential SCM due to its irregular particle sizes and porous microstructures *(391)*.

The bulk chemical composition of SSA includes Si, Ca, Fe, Al, and P, along with heavy metal elements like Zn, Cu, Cr, Pb, Ni, and Cd. These elements are of greater importance in terms of the environmental impacts of the material. Studies have reported a large variability in the element concentrations in SSA *(399,400,*406*,407,408)*. This variability might be due to differences in the wastewater treatment systems or incineration conditions. The literature also suggests that supplementary processing treatments like aging and acid washing can be used to regulate the contents of SSA *(391)*.

### 5.2.4 *Feedstock Description and Supply*

As discussed earlier, biosolids or sewage sludge are generated during domestic wastewater treatment. According to CalRecycle, there are nearly 250 treatment facilities located throughout California. According to the California Title 40, Part 503 rule requirement, sewage sludge is classified as Class A sewage sludge (pathogen-free before land applications) or Class B sewage sludge (low pathogen concentrations rapidly dying off when applied to soils) *(409)*.

According to CalRecycle, California generated around 878,510 T (796,971 t) or 796,971 T bone dry (723,000 t) of biosolids in the year 2013, of which 36% was Class A and 20% Class B and used for land amendment/fertilizer, 19% was applied as final cover, 13% was disposed of in the landfill, 4% was another application, 3% was surface disposed, and 3% was incinerated and generated SSA. The ash generated was disposed of by landfilling. Thus, approximately 23,909 T (21,690 t) was incinerated in California to generate SSA *(409)*. Depending on the efficiency of the incinerator and assuming a 20% loss, California produced around 19,127 T (17,352 t) of SSA in 2013. However, according to CalRecycle, no active sewage sludge incinerators are operating in California.

### 5.2.5 *Process Description, Technology Readiness Level, and Potential Suppliers*

#### Process Description

Usually, the pretreatment operations of the sludge include sludge thickening, sludge dewatering (vacuum filter, centrifuge, or filter press), incineration, air pollution control, and ash handling/disposal. Sometimes, ferrous chloride, lime, or organic polymers enhance the dewatering process.

Presently, there are two major incineration systems in the United States to process sewage sludge: multiple hearth incinerators and fluidized bed incinerators. Most of the 72 incinerators are in Florida, New York, Minnesota, and Pennsylvania, and around 80% are multiple hearth incinerators *(339)*.

Multiple hearth incinerators consist of circular steel furnaces containing several solid refractory hearths and a central rotating shaft. Dewatered sludge enters at the top and proceeds downwards through the furnace from hearth to hearth. Cooled air is blown through the central column and hollow rabbles to prevent overheating in the chamber. The spent cooling air with its elevated temperature is recirculated and used as combustion air. Flue gases are typically routed to a wet scrubber for controlling particulate matter. The particulates are collected in the wet scrubber and are usually sent to the sewage plant *(410)*.

Fluidized bed incinerators consist of a vertical cylindrical vessel with a grid in lower sections to support a bed of sand. Dewatered sludge is injected into the lower section of the vessel above the sand bed. Combustion air flows upward and fluidizes the mixture of hot sand and sludge.

The incineration temperature varies depending on the furnace type but can be expected to be in the range of 1200°F (650°C) to 1800°F (980°C). High operating temperatures (above 1650°F [900°C]) can result in partial fusion of ash particles resulting in the formation of clinkers *(410)*. The ash generated from incinerators is either recycled to recover precious metals like copper or used as a soil conditioner by mixing it with lime *(339)*. However, most of the generated SSA is landfilled.

## Technology Readiness Level

SSA has been successfully used as a filler and as an SCM in concrete in the laboratory. Studies have also reported its use as fine aggregate in concrete. While some proof-of-concept studies are available, many various aspects of using SSA in concrete, including durability aspects, are still unknown. Wide stream field implementation of SSA in construction would require a standardization of the properties to ensure consistent high quality, but this requirement may not be possible due to inherent variability. Thus, SSA, as an SCM/filler in concrete, is estimated to be at TRL 3.

**Potential Suppliers**

SSA could be obtained directly from municipal wastewater treatment facilities with sludge incinerators or incinerator facilities or private companies responsible for the disposal of the SSA.

**Current Use of Product**

According to the California Association of Sanitation Agencies, California generated around 878,510 T (796,971 t) or 796,971 T bone dry (723,000 t) of biosolids in 2013, of which 36% was Class A and 20% was Class B and used for land amendment/fertilizer, 19% was applied as final cover, 13% was disposed of in the landfill, 4% was another application, 3% was surface disposed, and 3% was incinerated and generated SSA. The ash generated was disposed of by landfilling.

**Agents Involved in Production and Distribution**

Municipal wastewater treatment facilities with sludge incinerators or incinerator facilities or private companies responsible for the disposal of the SSA are involved in the production and distribution of municipal wastewater.

**Product Consideration in Caltrans Specifications**

Caltrans specifications currently do not include municipal wastewater sewage sludge ash as an accepted SCM for concrete.

### 5.2.6 *Performance in Concrete Based on the Literature*

**Impact on Fresh Properties**

Studies have demonstrated a decrease in the average workability when SSA was used as a partial replacement of portland cement *(401,406)*. The average rate of decrease in workability was calculated at 6% for every 10% SSA replacement and around 12% slump reduction per 10% of SSA replacement in concrete *(400,411,412)*. Studies have shown that SSA consists of irregular particles with rough surface textures and porous microstructures, which might lead to high absorption and an increase in the water demand for concrete using SSA *(401,406,413)*. Researchers have also reported an increase in the setting time with increased SSA content. An average increase of 35% per 10% replacement was reported for initial and final setting times *(414,415)*.

### Impact on Strength

Studies have shown a reduced 28-day compressive strength with increased SSA content. On average, a 1% replacement of OPC with SSA resulted in a 145 psi (1 MPa), 3.33% reduction in strength. Studies have also shown lower early-age strength development after adding SSA to cement concrete *(392,399)*. However, lower early strengths are typical after adding pozzolanic SCMs, with an average compressive strength of 92% more than that of the control after 90 days. This suggests that the positive strength develops after the addition of SSA in the long term *(416,417)*. SSA can also be used in lower contents to achieve comparable strengths by controlling the mix design parameters, increasing cement content in concrete using superplasticizers and/or nanomaterials, and increasing the fineness of SSA *(397,400,401,406,414,415)*. Similar results were also reported in the case of flexural strength. Studies have reported an evident reduction of 5% to 30% in strength with increased SSA content in concrete *(393,397,399,401,418)*.

### Impact on Durability

The high alumina content of SSA helps increase concrete resistance to chloride attacks *(391)*. Adding SSA (up to 20%) to concrete mixtures has been shown to increase corrosion resistance. However, adding SSA (up to 60%) has lowered the corrosion resistance capacity more than the control *(401,417)*. Studies on the susceptibility to sulfate attack revealed no significant change *(399)*. A decrease in the permeability and absorptivity of concrete was also reported *(399,411,419)*. In terms of drying shrinkage, the mortar with 30 wt% SSA had more than 30 % reduced drying shrinkage compared to the control mortar at 90 days *(420)*. On the other hand, studies have found contradictory results of an increase in the porosity of the concrete *(393,421,422)*. A summary of the overall impact of SSA on various properties of concrete is provided in Table 5.6.

**Table 5.6: Summary of the Effect of Sewage Sludge Ash on the Properties of Cement-Based Materials**

| Concrete Property | Compared to 100% OPC Concrete |
|---|---|
| Workability | Decrease |
| Early strength | Decrease |
| Late strength | Increase |
| Setting time | Increase |
| Drying shrinkage | Decrease, need more research |
| Alkali-silica reaction | Needs more research |
| Sulfate attack resistance | Increase, need more research |
| Freeze-thaw durability | Information not found |

### 5.2.7 *Environmental Considerations*

There is no LCA or LCIA of SSA as an SCM or filler. Since SSA is the waste material that is usually landfilled, no EPDs are available for this material. The leachate of toxic metals from SSA is regulated and needs to be under permissible levels for disposal in landfills. One study performed a chemical analysis of lachate from SSA concrete samples and found that the total concentration of heavy metals was under the permissible amounts set for landfill disposal but higher than concrete containing Class C and F fly ashes *(423)*. Recent work showed that leachate of heavy metals from SSA concrete is not a concern because heavy metals and other elements are immobilized and are stable in the cement matrix *(424)*. More research is required to confirm this recent finding.

### 5.2.8 *Cost Considerations*

SSA is the industrial ash left behind after the combustion of sewage sludge, and it is a waste material that has no monetary value. Currently, as discussed previously, it is used in zero to low-value applications such as soil amendment or soil stabilization. However, if standardized and distrusted by certified parties for use in concrete as an SCM, the price as an SCM could vary and can reach as high as other mineral admixtures for concrete, depending on market demand.

## 5.3 Carpet Backing Fines

### 5.3.1 *Product Description*

Tufted carpeting, the most common carpet type in the United States, is made of front face fibers (the tufts) sewn into backing materials. An adhesive, typically styrene butane rubber latex, is used to adhere the fibers to the primary and secondary backing materials *(425)*. Filler materials, predominantly $CaCO_3$-based, are mixed with the adhesive as a bulking agent to decrease costs and add weight to the carpet backing *(426)*. During the carpet recycling process, polymer fibers and textiles are mechanically separated from the $CaCO_3$ adhesive backing, resulting in post-consumer carpet calcium carbonate (PC4) as a byproduct.

A 2021 report indicated that 627,926 T (569,644 t) of carpet waste is discarded in landfills each year in California, and carpet waste has an almost 27.9% recycling rate *(427)*. California is the first state to require a statewide carpet recycling program designed and implemented by carpet manufacturers with CalRecycle's oversight. The Carpet America Recovery Effort (CARE) is the manufacturers' stewardship organization implementing the recycling program. Carpet recycling plants focus on sourcing materials by disassembling carpets *(428)*. PC4 is a powdered byproduct formed by separating beneficial polymer fiber and textile materials during carpet recycling and is associated with ash content (determined using an ash test). The byproduct could be a high PC4 product or a mix of coal fly ash, cured adhesives, and some residual fibers *(429)*.

### 5.3.2 *Acting Mechanism in Concrete*

The functioning mechanism of PC4 in concrete was shown to be a chemically inert mineral filler to improve particle packing, cement particle dispersion, and cement hydration *(427)*.

### 5.3.3 *Chemical and Physical Properties*

Calcium carbonate is a nontoxic, odorless, and low-oil-absorbing ingredient/powder commonly used for carpet backing to lower total manufacturing costs while maintaining excellent mechanical properties. In addition, calcium carbonate grades add weight to the backing so the carpet lies flat once installed *(426)*. PC4 is a predominantly $CaCO_3$ material of dolomite and calcite *(430)*. The amount of residual materials and polymers in PC4 varies by carpet type and recycling process. In a study, heat treatment of PC4 at 1112°F (600°C) led to the decomposition of dolomite and increased concentrations of calcite (about 86%, compared to limestone, >75%). PC4, before treatment, contains polystyrene and other polymer materials, which are eliminated by heat treatment *(430)*. However, PC4 is expected to have residual latex or backing binder because of the carpet manufacturing processes *(429)*.

### 5.3.4 *Feedstock Description and Supply*

Carpet is used in almost every residential and commercial sector, and it can produce several recycled components that can be reused if it is post-processed. Carpet comprised polymer fibers, textile backings, adhesive, and $CaCO_3$ filler materials; a typical carpet composition consists of 35% nylon, 15% polypropylene, and 50% calcium carbonate. The properties of PC4, including the presence and concentration of trace elements and impurities, depend on the carpeting type and the recycling process *(430)*.

Carpet recycling facilities in California are concentrated around population centers in Southern California (e.g., Los Angeles Fiber Co., Vernon), the Sacramento region (e.g., Circular Polymers, Lincoln; Aquafil, Woodland), and the greater bay area (e.g., Carpet Recycling Resources, Santa Clara) *(431)*. In 2020, 71% of recycling subsidies were paid to California recyclers, with the remaining subsidies paid to other states *(431)*.

### 5.3.5 *Process Description, Technology Readiness Level, and Potential Suppliers*

In California, CARE is responsible for driving carpet recycling. Most recycling begins with consumers or carpet installers dropping off the waste carpet at one of 131 carpet collection centers, which funnel waste carpet to five CARE-affiliated California recyclers (*412*). There are 14 CARE-affiliated recyclers across California, Arizona, Georgia, and South Carolina *(431)*.

The carpet waste is disassembled through advanced technology into three main components: polypropylene, calcium carbonate, and nylon 6 (*409*). Each component enters a different stream. Polypropylene enters the injection molding industry; calcium carbonate enters road construction or concrete streams; and nylon 6 feeds the ECONYL regeneration process. PC4 is currently considered a material that has a weak market. However, interest in and support for developing PC4-based products and pellets in California is encouraged by introducing market development programs and grants *(429)*.

## Process Description

Figure A.14 shows a simplified system diagram for recovery of the polymer and mineral components of waste carpet. Specifically, in the system, waste carpet is diverted from landfills to recyclers, where the polymer fractions of the carpet are separated and recovered. These polymers are then diverted for use in recycled polymer products. The remaining materials are then processed to remove remnant impurities in the PC4. As shown in Figure A.14, heat treatment is used to prepare PC4 for cement-based material applications.

Once the waste carpet is dropped off at a collection location, the carpet is sorted by fiber type so that the recovered polymer is not contaminated by divergent polymer types, which would impair the reuse of the polymer *(432)*. Carpets that are heavily soiled or include a mix of uncommon polymers that might threaten the quality of the recycled product are landfilled.

Due to concerns about fiber contamination and varying demand for different polymer types, some recycling facilities may specialize in only a specific polymer type. Although processing methods are often proprietary and parameters vary between recyclers, post-sorting methods typically involve the following phases *(428)*:

- Phase 1—Shredding: In this phase, the carpet is shredded, and the maximum amount of calcium carbonate is collected during the process. The polymer fibers and textiles are mechanically separated from the carpet backing.
- Phase 2—Bond breaking/size reduction: The size reduction of remnant backing material is performed in this phase.
- Phase 3—Nylon and polypropylene separation: Additional loose fibers are separated from the PC4 in this phase (i.e., sieving or settling off in the water).

These processes are designed to produce as high quality a recycled polymer product as possible, though residual impurities are often left in the PC4 byproduct. Due to the remnant impurities and variation in PC4 production, untreated PC4 can lead to reduced performance of cement-based materials. As such, further treatment might be required to remove these impurities. Initial investigations have shown heat treatment at 1112°F (600°C) is effective at reducing remnant polymers and latex, and this treatment results in PC4 influencing cement-based material performance similar to the effects of virgin limestone filler *(430)*. These treatment conditions also have the benefit of reducing perfluorinated compounds (PFCs) and brominated flame retardants (BFRs) to below-detectable levels *(433)*. However, post-treatments may impose high costs and additional environmental impacts.

## Technology Readiness Level

The use of treated PC4 in cement-based materials has been demonstrated in laboratory-scale testing. As noted previously, mechanical performance was achieved similar to conventionally accepted fillers. In addition, accelerated durability testing of untreated PC4 has also been performed. However, durability and larger-scale testing of treated PC4 in cement-based materials are needed. Therefore, the current TRL is estimated to be TRL 3.

## Potential Suppliers

According to CASA's 2021 annual report, PC4 recovered from 88.5 million pounds of post-consumer carpet was around 17 million pounds (about 8500 T) in 2021 (an approximately 29% increase from 2020) *(434)*. The reported annual US recycling capacity in 2020 was 147,000 T (134,000 t) of post-consumer carpet, of which approximately 65,000 T (59,000 t) is PC4 (assuming about 44% of the mass is PC4) *(431,432)*. In addition, legislation under consideration across the United States, along with existing regulations in California, will require increased carpet diversion from landfills and recycling *(435,436,437)*. Therefore, the production capacity and supply are expected to increase, including California's recycling capacity *(431)*.

## Current Use of Product

Most supplies of PC4 are currently landfilled or lost to the environment as unprocessed carpets *(432)*. PC4 has found few value-added applications, possibly due to remnant material impurities and toxicity concerns *(433)*. In 2020, the diversion of PC4 from landfills in California was subsidized at $0.17/lb ($0.37/kg) *(431)*.

Over 50 products use California-recycled post-consumer carpet materials (16+ vendors) *(431)*. Potential applications for PC4 could include the paper industry, a large consumer of ground calcium carbonate (GCC). Another industry that heavily uses GCC is the plastic industry. Plastics account for around 10% of European GCC consumption. Also, the paint market accounts for about 8% of Europe's GCC, and the adhesives and sealants industry consumes about 5% of European GCC production *(438)*. Animal and pet feed as vitamins and minerals use GCC as well. In one study, carpet waste was converted to alternative dye adsorbents for water management *(439)*. PC4 is sold as calcium carbonate fines and is also reported to be used in wheel stoppers *(440)* as well as transition ramps, cement, adsorbents, and lightweight aggregate *(434)*.

### Agents Involved in Production and Distribution

Carpet recycling regulations are enforced by CalRecycle. However, the recycling program is currently administered by CARE *(441,442)*. Carpet collection is done by the public, a nonprofit organization (CARE), and private collectors and sorters. Carpet recycling is performed by private recyclers who receive a subsidy based on the amount and types of material diverted from landfills *(431)*. Four additional states are actively considering legislation implementing carpet recycling programs similar to California's program *(427)*.

### Product Consideration in Caltrans Specifications

Caltrans specifications currently do not include carpet backing fines as an accepted SCM for concrete.

## 5.3.6 *Performance in Concrete Based on the Literature*

### Impact on Fresh Properties

One study examined the utilization of PC4 from carpet backing as a potential mineral admixture in concrete production *(427)*. The researchers found that the untreated PC4, when added to concrete, led to varied effects on slump and a consistent increase in air content by 3.5% to 10%. A reduction of about 11% in the unit weight of concrete was recorded. Cement replacement with PC4 led to an increase in the initial set time by 64% to 123% and the final set time by 74%

to 117%. The authors recommended further investigation and additional evaluation of heat-treated PC4 on the fresh properties of concrete.

**Impact on Strength**

One study reported a reduction in concrete compressive strength (up to 60%) when untreated PC4 was added to concrete (all mixtures; 5% and 15% replacement) as a mineral admixture *(427)*. In the same study, the researchers found a 35% reduction in the flexural strength of concrete containing PC4 as a partial replacement of fine aggregates. On the other hand, an improvement in flexural strength was observed when compared to the concrete with OPC and limestone filler.

**Impact on Durability**

A study found that the untreated PC4 increased shrinkage and permeable void volume and decreased bulk density in concrete compared to mixtures with similar amounts of limestone filler. The coefficient of thermal expansion was still within the normal ranges for concrete. The recommendation was further research on determining the effect of heat-treated PC4 on concrete durability properties *(427)*.

### 5.3.7 *Environmental Considerations*

Currently, PC4 is generated as part of polymer recycling from post-consumer carpets. As such, using PC4 in concrete is not anticipated to drive additional burdens from PC4 production. A study comparing the GHG emissions of ground limestone and PC4 as a partial replacement for portland cement found no notable differences between the two. If used to either lower OPC content in concrete or clinker content in the binder, PC4 can reduce GWP impacts associated with concrete production because portland cement is responsible for the majority of GHG emissions in concrete *(427)*. However, a robust LCA is needed to determine whether additional impacts from PC4 treatments would drive a net reduction of GWP.

**Air Pollution**

Carpet backing is commonly made with synthetic rubber derived from styrene and butadiene, both of which are respiratory irritants at low levels of exposure. Long-term exposure to high levels of styrene is associated with nerve damage, and long-term exposure to butadiene is associated with cancer and heart disease.

**Land Use**

PC4 has the potential to reduce land use in two ways. First, by substituting virgin limestone, PC4 could reduce the raw materials extraction required to produce concrete and its constituents. Second, by diverting it from landfills, PC4 could reduce landfill land use *(430)*.

**Water Consumption**

Neither direct water withdrawals nor water consumption has been evaluated for PC4 production or treatment. While water is not directly required for heat treatment, water demands associated with energy resources can be expected and need to be quantified to determine the net change compared to portland cement or PLC materials.

**Toxicity**

PC4 includes PFCs, BFRs, and antimony (Sb) from polymer and carpet manufacturing *(427,433)*. Treatment at 1112°F (600°C) has been validated as a method for reducing PFCs and BFRs from PC4 to below-detectable levels *(433)*. However, Sb is still present in the PC4. Leaching analyses have shown that Sb leaching from cement-based materials leads to concentrations well below US Environmental Protection Agency and European Union regulations *(427,430)*.

### 5.3.8 *Cost Considerations*

When buying carpet, the retailer pays \$0.35/yd$^2$ (\$0.29/m$^2$) of carpet, which is the funding to run CARE's stewardship program of carpet recycling *(431)*. According to CARE's report, the PC4 (post-consumer calcium carbonate) subsidy, added in 2015, "significantly increased recovery and use of PC4 carpet backing in the manufacture of recycled products totaling over 10.5 million pounds in 2017, up 337% from 2.5 million pounds in 2016" *(443)*. The diversion of PC4 from landfills started at \$0.07 per pound, then moved to \$0.12, and it is currently subsidized at a rate of \$0.17/pound (~\$0.37/kg) *(429,431)*. As PC4 is a byproduct of polymer recycling, PC4 material is not used or reused for manufacturing and must be disposed of or landfilled. In addition, PC4 treatment, to improve consistency, requires additional processing, which may add to the cost *(430)*.

# 6 CONCLUSIONS

This report reviewed 15 materials under the four categories of biomass, natural pozzolans, construction and demolition (C&D) waste, and post-consumer waste that might be used in concrete as alternative supplementary cementitious materials (ASCMs), mineral fillers, or admixtures that could reduce the portland cement demand in concrete. The information was gathered from various sources. Published literature, government reports and fact sheets, and online sources were used. In addition, professional organizations and associations and some suppliers were contacted and interviewed to determine the scale of the potential feedstock supply in California and the availability of suppliers at a large scale in California to estimate the technology readiness level. Other information gathered from the literature and the suppliers was about the type and extent of required treatment to produce an ASCM for concrete and the economic and environmental impacts of the treatment. System diagrams were also prepared for each SCM that presented the supply chain of the SCM and the type of treatment or treatments that may be needed to get ASCMs ready to use in concrete. Information from these system diagrams can help in building process diagrams when developing LCA models in the next tasks of this project. The information gathered is summarized for all the materials reviewed in Table 6.1 to Table 6.4.

As seen in in the tables, most of the materials studied have an abundance of feedstock supplies in California, much greater than the current demand for coal fly ash as an SCM in concrete, which is estimated to be around 500,000 to 600,000 T (453 to 553,000 t) per year, except small supplies of seashell waste *(45)*. However, many of the materials studied do not currently have a distributor in California. These include rice straw ash, chitin nanomaterials, metakaolin, RCA/CCA fines, rock dust, municipal solid waste ash, wastewater sludge ash, and brick waste. The materials studied are mostly at TRL 3 or 4 (i.e., initial research done to prove feasibility) and therefore require further laboratory testing at the concrete scale as a next step to further implementation at the industrial scale.

It is evident from the information gathered that, though many of the materials show promise, they are at the early stages of research and development. Thus, it is difficult to determine which ones should be prioritized for evaluation. Therefore, most of the materials reviewed in this report were selected for further pozzolanic reactivity testing in the next project task. Carpet fines were excluded as they are being investigated in another industry-funded contract. Seashell waste supply in California was difficult to identify, and its abundant and consistent availability was also questionable. Municipal solid waste incinerator plants in California had not provided samples when this report was written. If samples of these ashes become available during the project, they will be included in the laboratory evaluation.

**Table 6.1: Summary of Gathered Information for the Likely ASCMs Biomass Ashes Group**

| Studied ASCM | Annual Supplies | Suppliers in US | Distributor in California | Treatment | Technology Readiness Level | Function (filler, pozzolan, admixture) | Selected for Testing in the Project |
|---|---|---|---|---|---|---|---|
| 1 - Biomass energy plant ash | 419,045 T (380,151 t) | 25 biomass energy plants | N | Grinding for bottom ash | 4 | F/ P | Y |
| 2 - Rice straw ash | 200,000 T (181,436 t) | Rice grown in Sacramento Valley | N | Soaking and drying of feedstock, mild grinding of ash | 3 | P | Y |
| 3 - Biochar | Unlimited | Biochar Producers listed by US Biochar Initiative | N | Mild grinding | 3 | F/ P | Y |
| 4 - Cellulose nanomaterials | Unlimited | Kruger, Sappi North America, CelluForce, American Process Inc. | Y | Chemical or mechanical treatments of cellulose | 4 | AM | Y |
| 5 - Chitin nanomaterials | Annual US chitin market: 75 T (68 t) | Tidal Vision, Scandinavian Formulas, Creative Enzymes | N | Chemical or mechanical treatments of chitin | 3 | AM | Y |
| 6 - Seashell waste powder | Not known | None | N | Washing, calcinating, and grinding | 3 | F | N |

*Notes:* "T" = US short tons; "t" = metric tons; "Y" = Yes; "N" = No.

**Table 6.2: Summary of Gathered Information for the Likely ASCMs Natural Pozzolans Group**

| Studied ASCM | Annual Supplies | Suppliers in California | Distributor in California | Treatment | Technology Readiness Level | Function (filler, pozzolan, admixture) | Selected for Testing in the Project |
|---|---|---|---|---|---|---|---|
| 7 - Pumice, perlite, zeolite, volcanic ash | 580,000 T (526,000 t) of pumice and 500,000 T (453,000 t) of perlite | Mines across Arizona, California, New Mexico, Idaho, Texas, and Oregon | Y | Grinding | 8 | P | Y |
| 8 - Metakaolin | 4.5 million T (4.1 million t) | Mines across Arizona, California, Idaho, and Oregon | N | Calcinating, grinding | 8 | P | Y |
| 9 - Diatomaceous earth | 830,000 T (752,000 t) | Imerys Minerals California's Lompoc Plant and Celite Corporation | N | None | 3 | P | Y |

*Notes:* "T" = US short tons; "t" = metric tons; "Y" = Yes; "N" = No.

**Table 6.3: Summary of Gathered Information for Likely ASCMs Construction and Demolition Waste Materials Group**

| Studied ASCM | Annual Supplies | Suppliers in California | Distributor in California | Treatment | Technology Readiness Level | Function (filler, pozzolan, admixture) | Selected for Testing in the Project |
|---|---|---|---|---|---|---|---|
| 10 - Recycled concrete fines | 405.2 million T (367 million t) | Concrete ready-mix producers and concrete recycling plants | N | Grinding | 4 | F | Y |
| 11 - Rock dust | 21 million T (19.05 t) | Aggregate quarries, ready-mix concrete producers | N | None | 3 | F | Y |
| 12 - Brick waste powder | Not known | None | N | Grinding | 3 | P | Y |

*Notes:* "T" = US short tons; "t" = metric tons; "Y" = Yes; "N" = No.

**Table 6.4: Summary of Gathered Information for Likely ASCMs Post-Consumer Waste Materials Group**

| Studied ASCM | Annual Supplies | Suppliers in California | Distributor in California | Treatment | Technology Readiness Level | Function (filler, pozzolan, admixture) | Selected for Testing in the Project |
|---|---|---|---|---|---|---|---|
| 13 - Municipal solid waste ash | 237,250 T (215,229 t) | MSW incineration plant | N | None | 3 | P/ F | N |
| 14 - Wastewater treatment sludge ash | Not known | Several | N | None | 3 | P/ F | N |
| 15 - Calcium carbonate from recycled carpets | 65,000 T (59,000 t) | Aquafil and other carpet recycling industry | Y | Heat treatment | 3 | F | N |

*Notes:* “T” = US short tons; “t” = metric tons; “Y” = Yes; “N” = No.

The first round of laboratory evaluation will include pozzolanic reactivity testing according to ASRM C1897 and strength activity index ASTM C618. Those identified as promising as ASCMs after that next step of evaluation will be selected to determine their benefits and disbenefits by a detailed LCA and LCCA.

It should be noted that the ASCMs identified in this research, other than the natural pozzolans group, are mainly waste products that are likely currently going into landfills or have some limited reuse but with low value. Therefore, developing supply chains to reuse these waste products as value-added ASCMs to replace portland cement in concrete mixes has environmental and societal benefits. The reuse of waste materials has the potential to reduce the consumption of natural resources required to produce portland cement, help preserve landfill space, and reduce methane and other emissions (to air, water, and land) in landfills.

The local availability of the ASCMs is a consideration in their evaluation. Local availability may help reduce transportation distances, local landfill use, and pollution from unregulated processing and may also help create local employment opportunities. These waste products usually have zero environmental allocation of impacts in LCA if used without additional processing and minimal transportation of construction materials. However, some may require further processing, such as washing, drying, crushing, grinding, long transportation distances, and other steps that significantly diminish their environmental benefits or even make them worse than current practice. Continued improvement of the supply chain system definition and quantification of environmental and social impact and costs will help determine the best materials to pursue first.

# APPENDIX A SYSTEM DIAGRAMS FOR THE SCMS CONSIDERED IN THIS STUDY

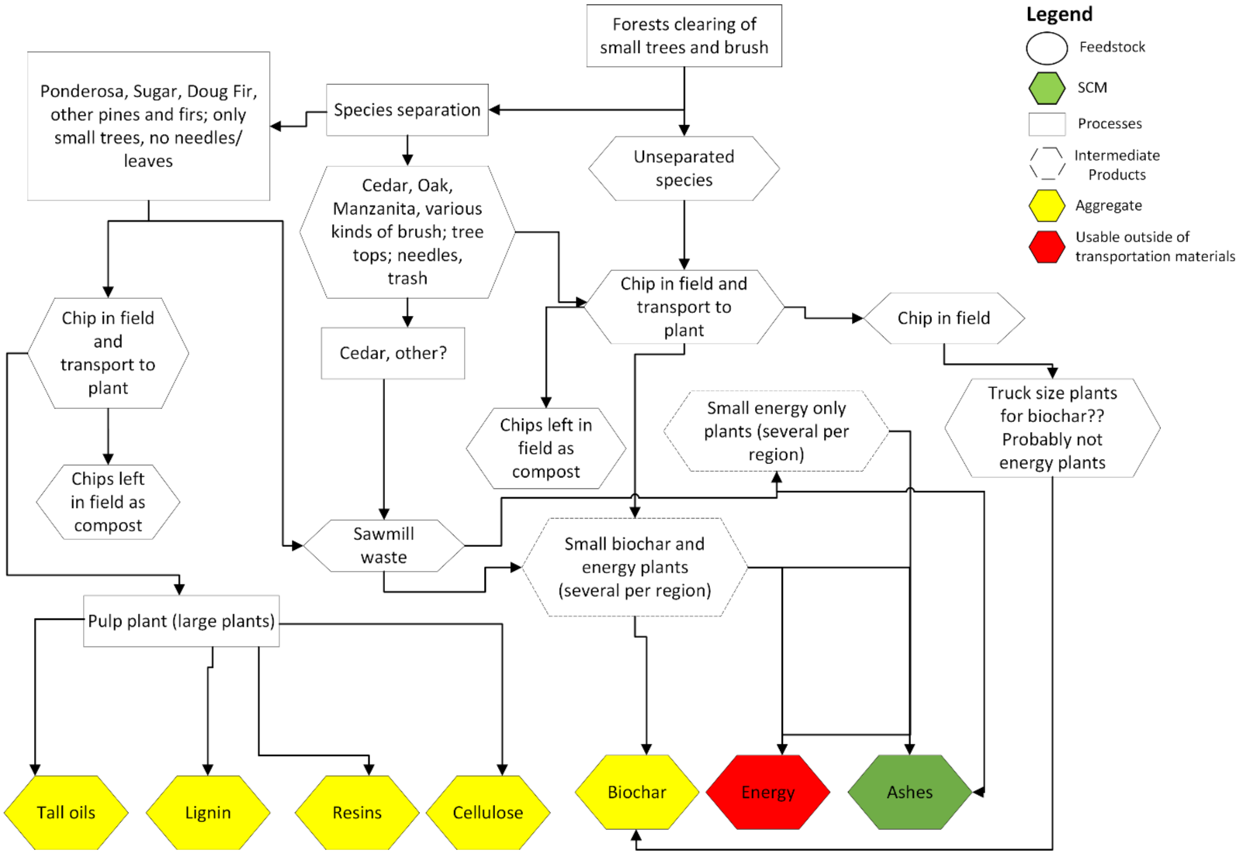


Figure A.1: System diagram of wood ash generation.

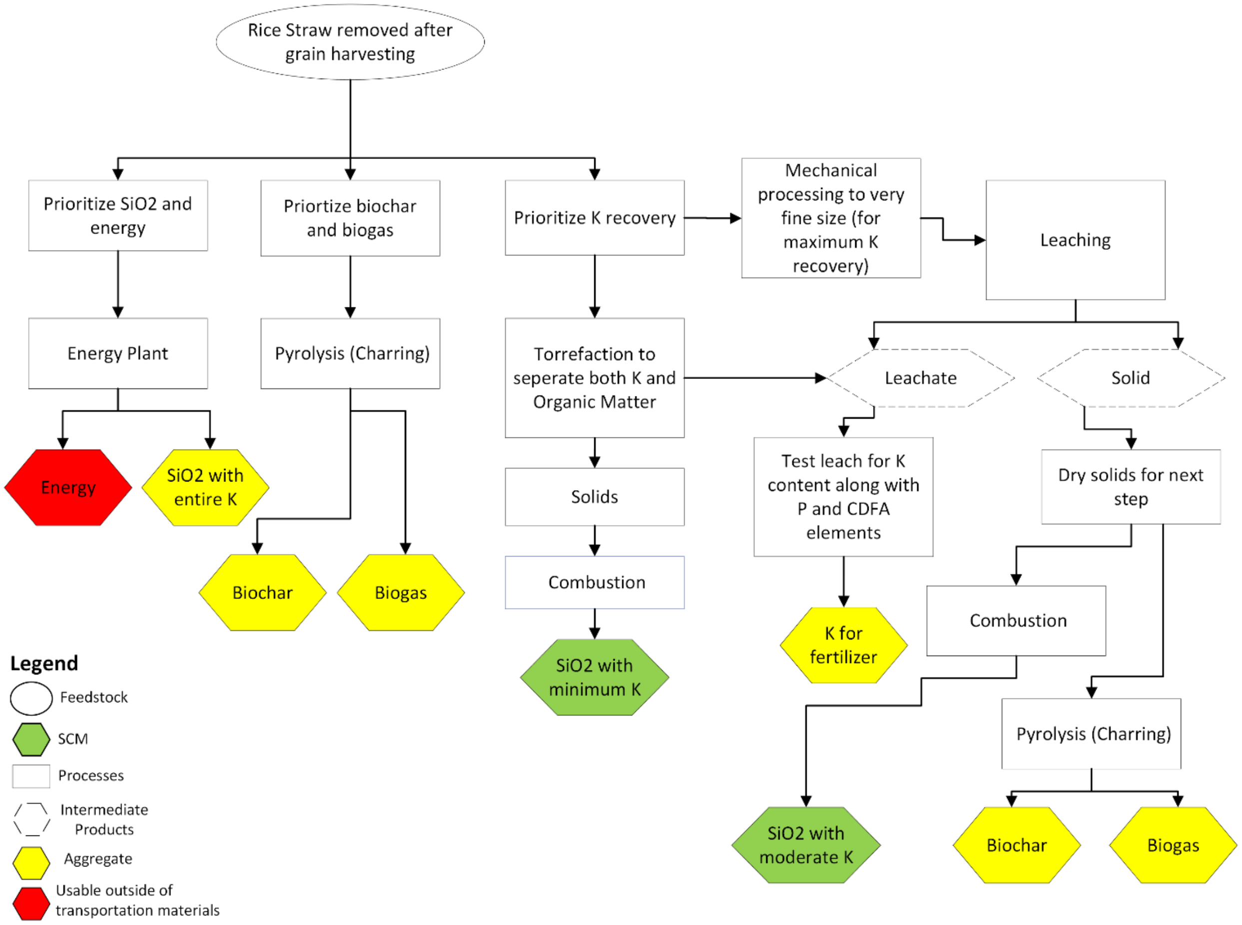
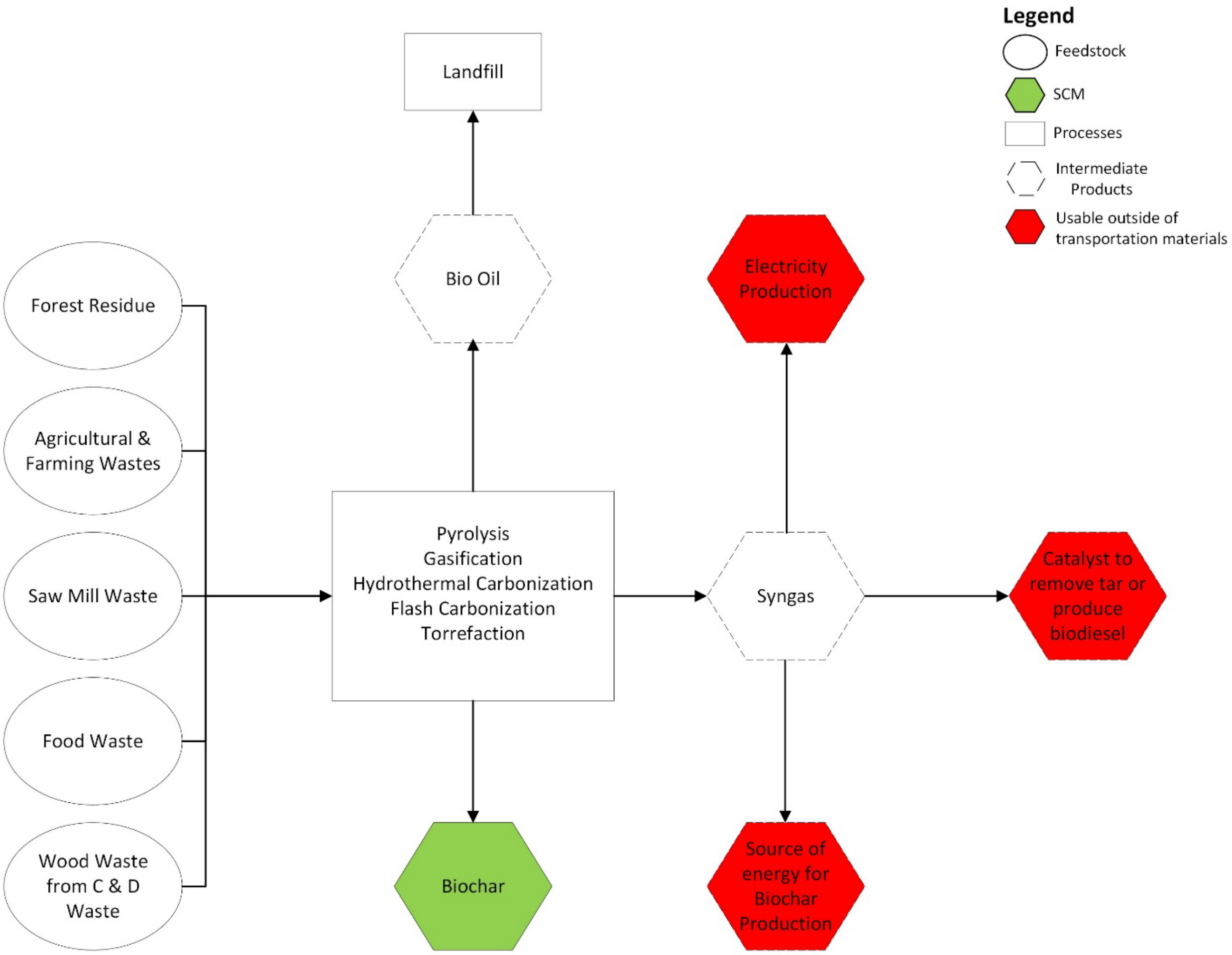
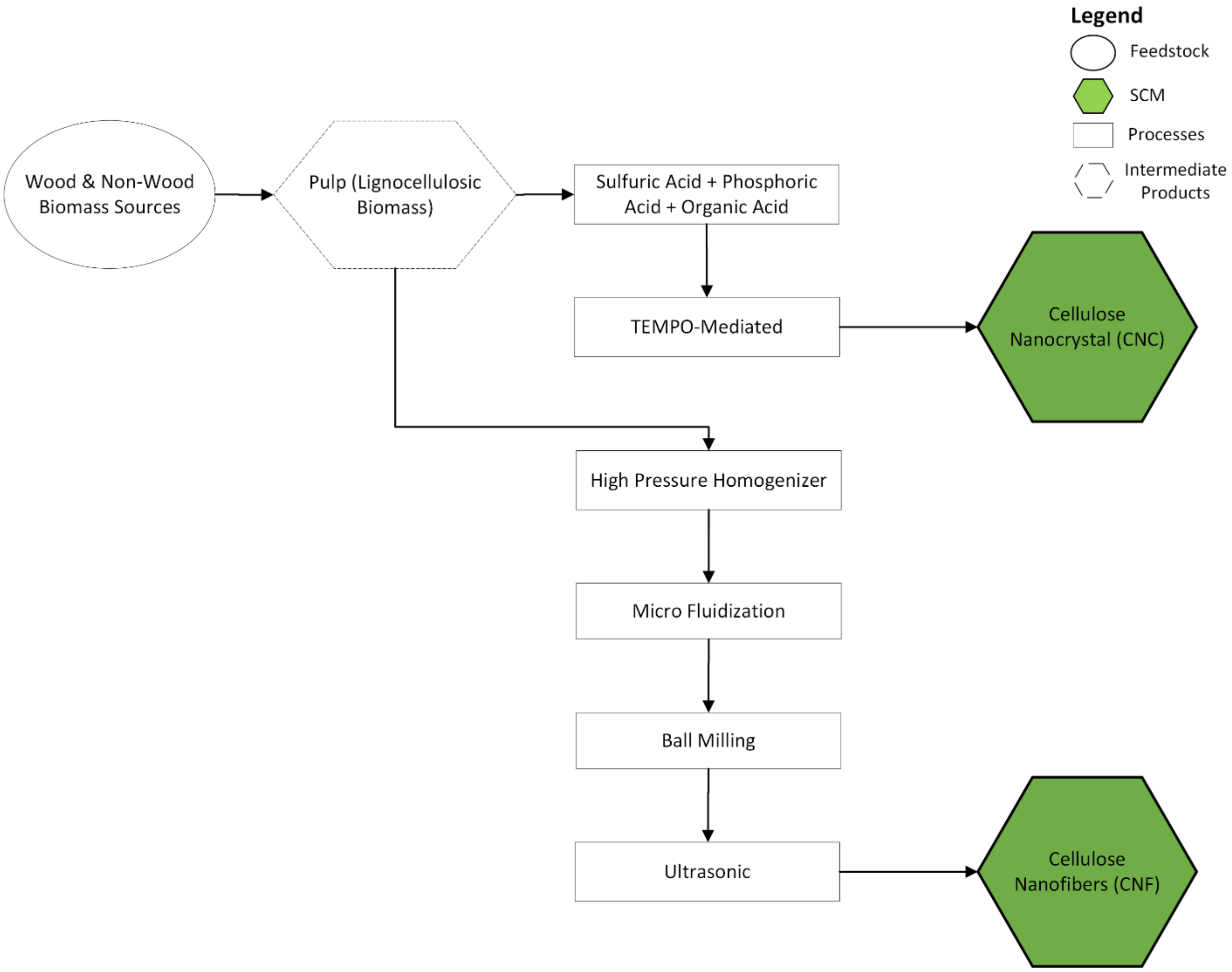


**Figure A.2: System diagram for treatment of rice straw ash.**



Source: Gaunt and Lehmann (2008); Meyer, Glaser, and Quicker (2011); Cha et al. (2016) *(92,93,94)*.

**Figure A.3: System diagram of biochar feedstock, processing, production methods, and usage.**



Source: Nagarajan et al. (2021); Jonoobi et al. (2015) *(444,445)*.

**Figure A.4: System diagram of cellulose nanocrystals (CNC) and cellulose nanofibers (CNF) production.**

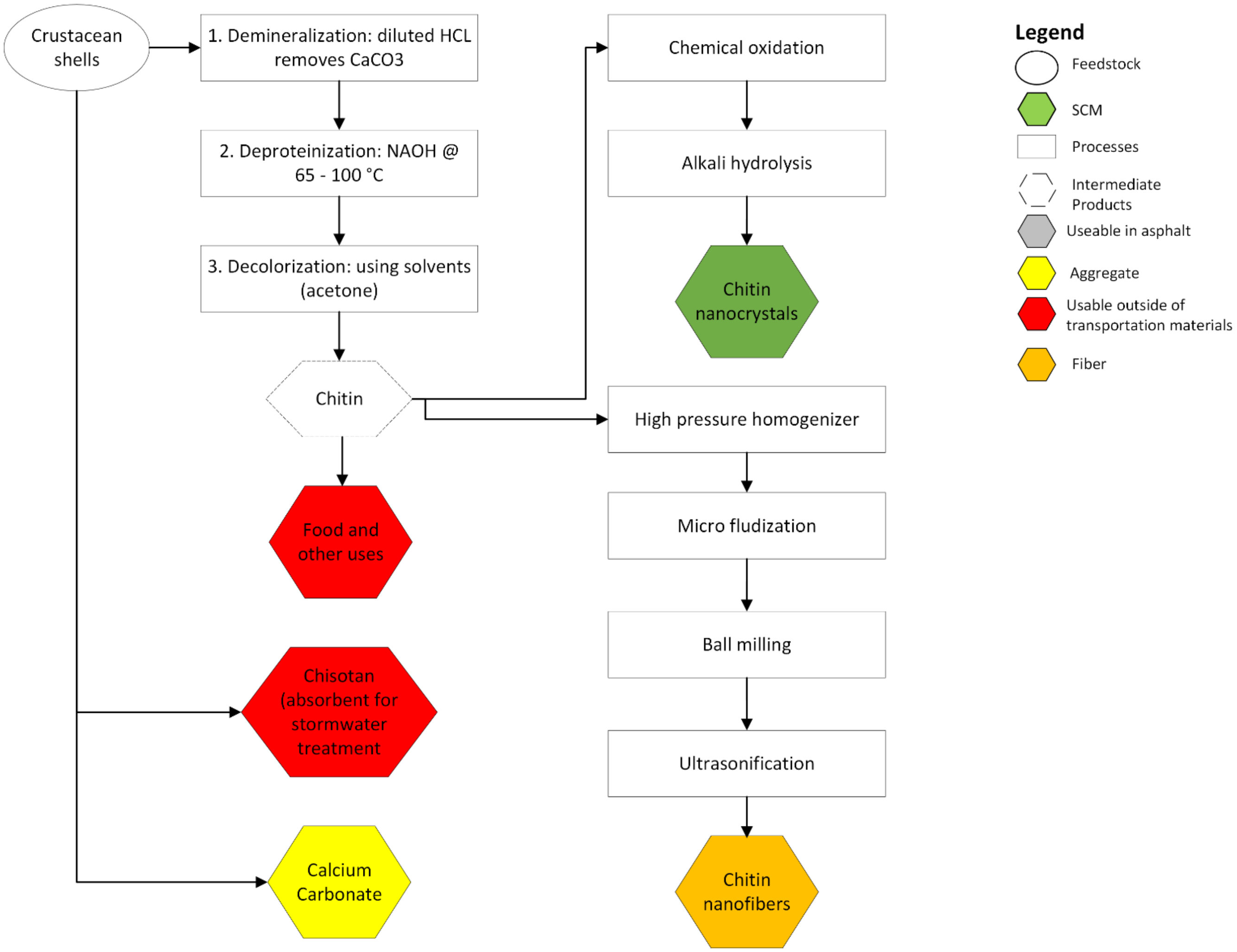


**Figure A.5: System diagram of the production process for chitin nanocrystals (ChNC) and nanofibers (ChNF).**

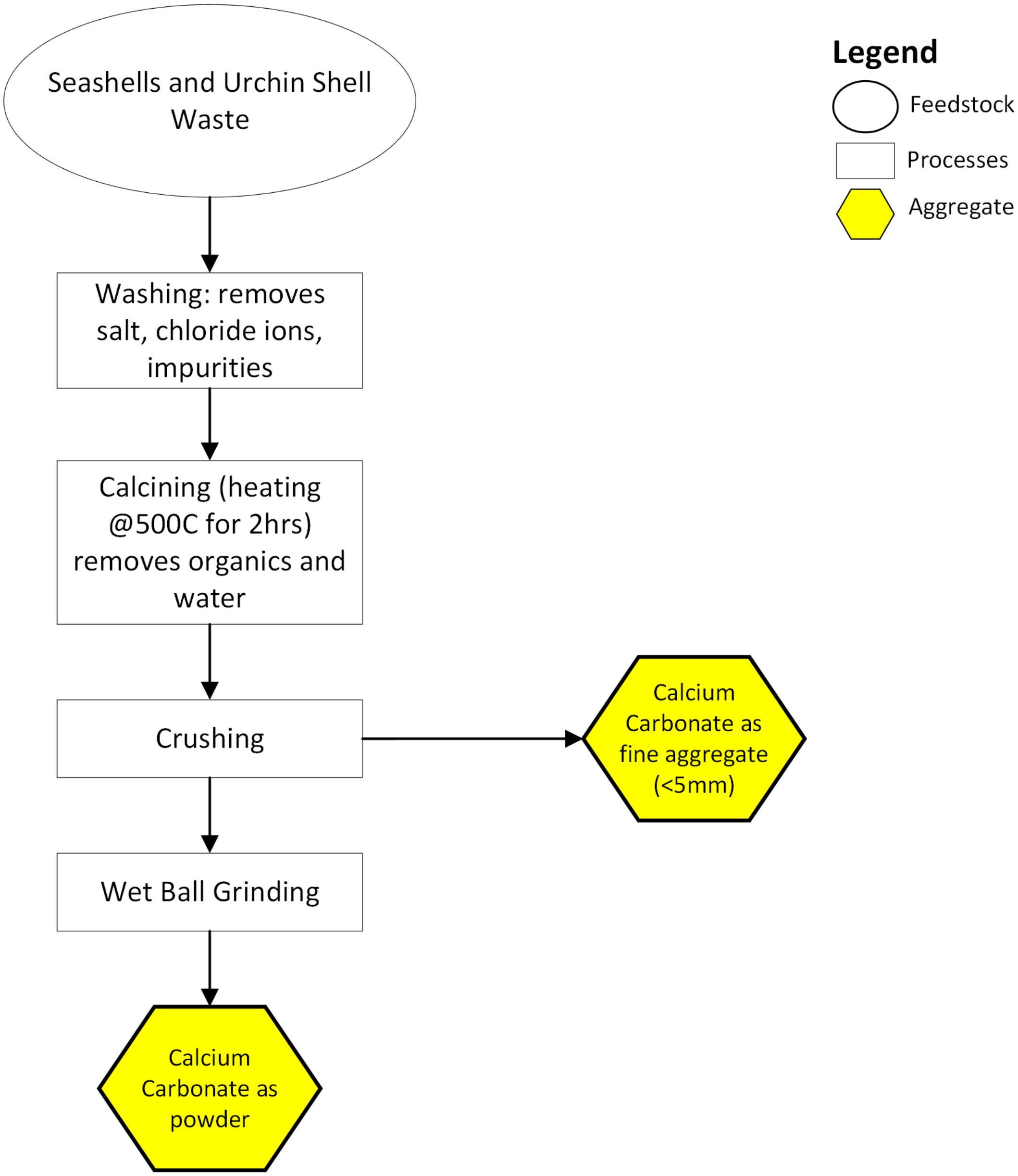


**Figure A.6: System diagram of seashell waste powder production for use as SCM in concrete.**

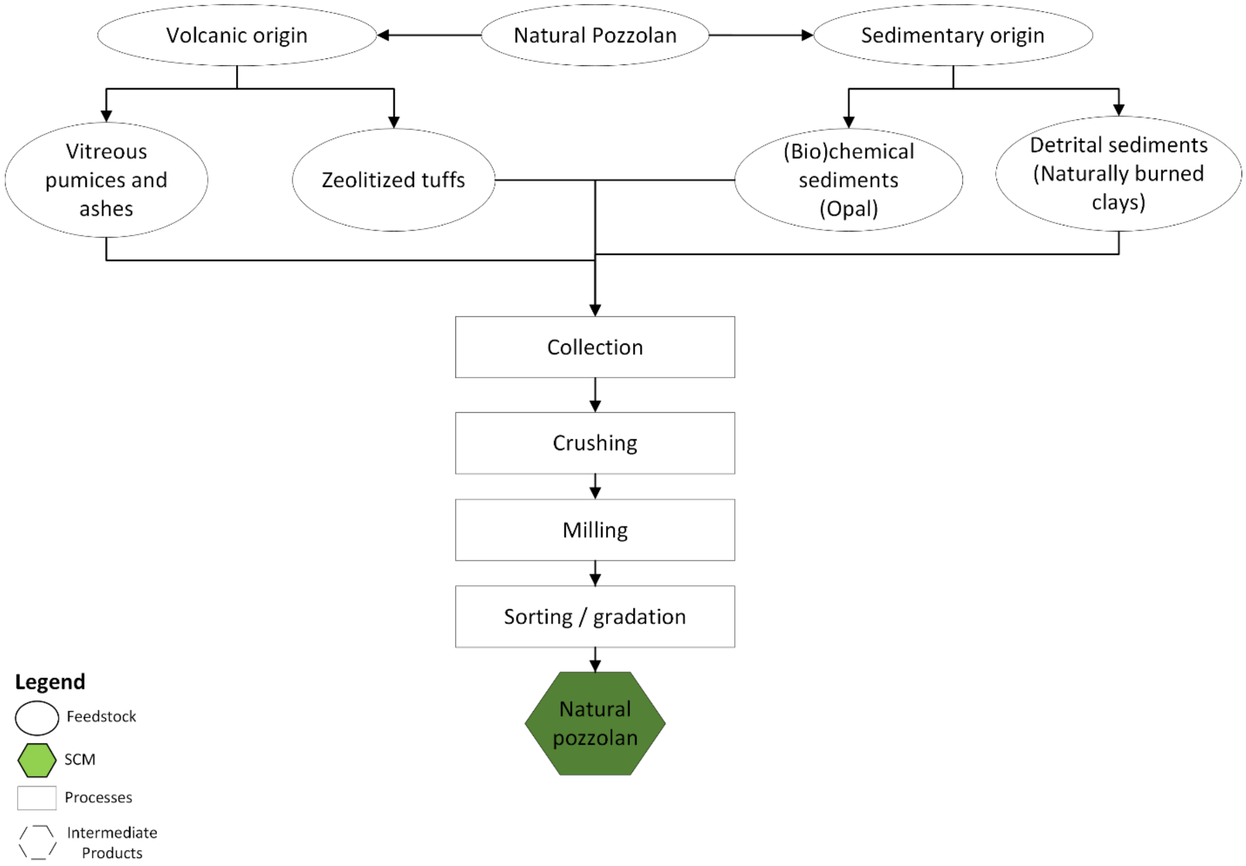
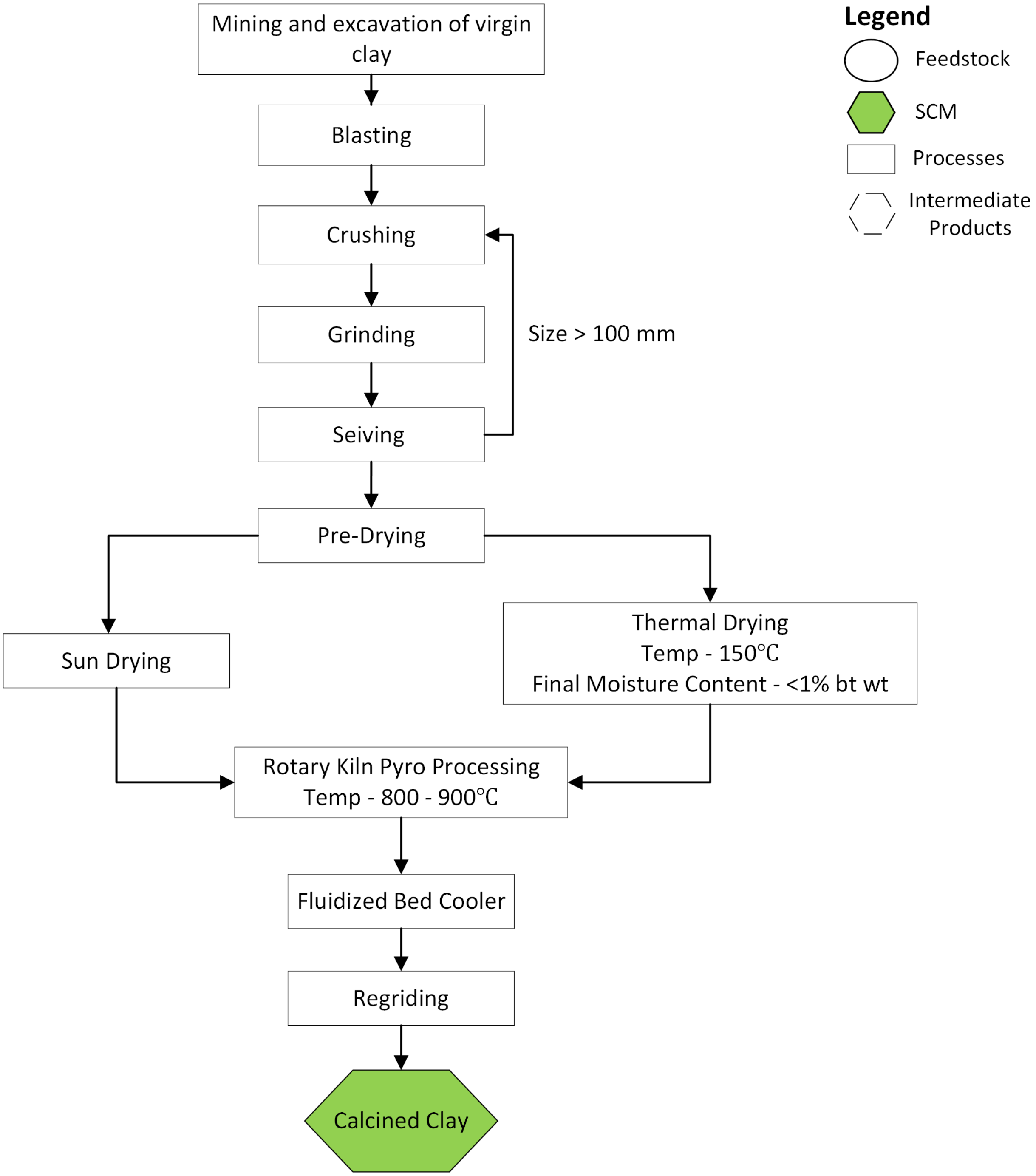


Figure A.7: System diagram of production of SCMs from natural pozzolans for concrete.



Source: Hanein et al. (2022) *(274)*.

**Figure A.8: System diagram of the production process of calcined clay.**

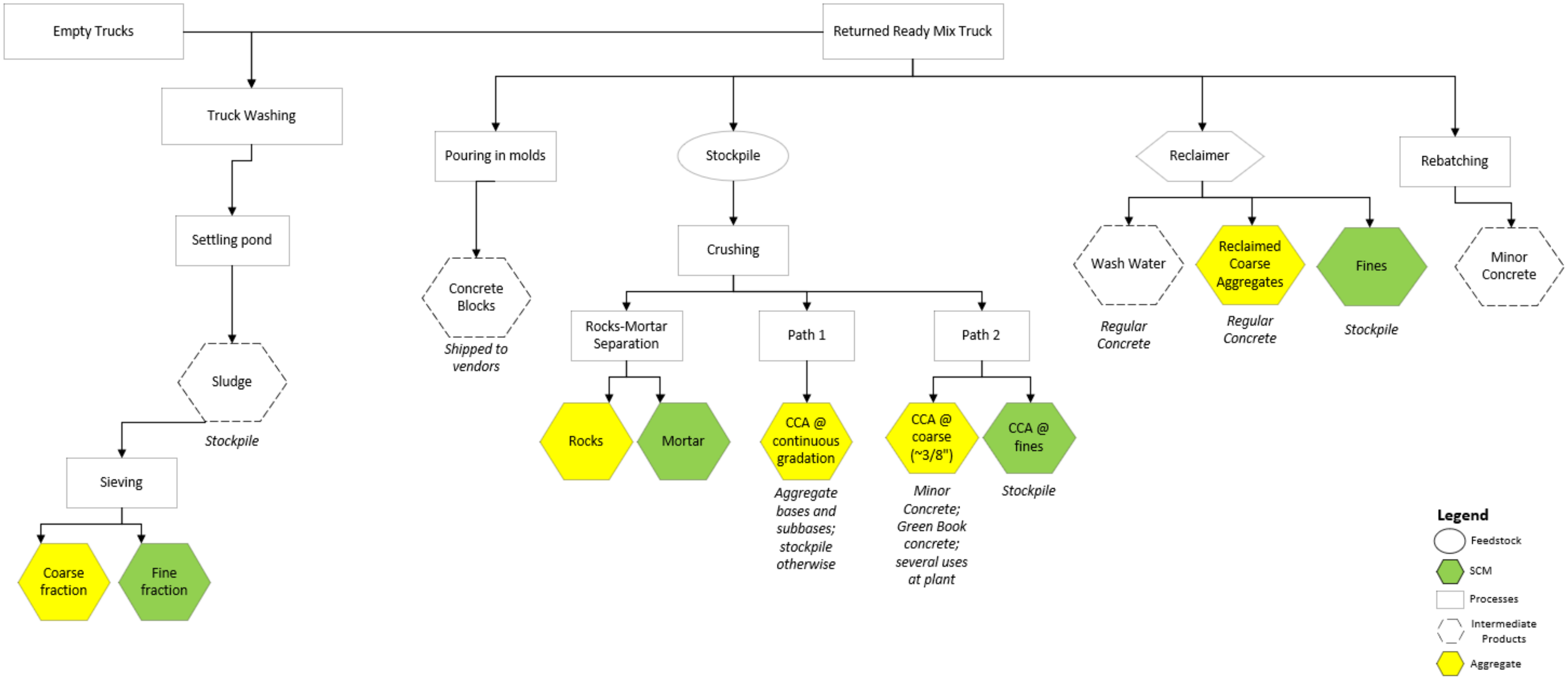
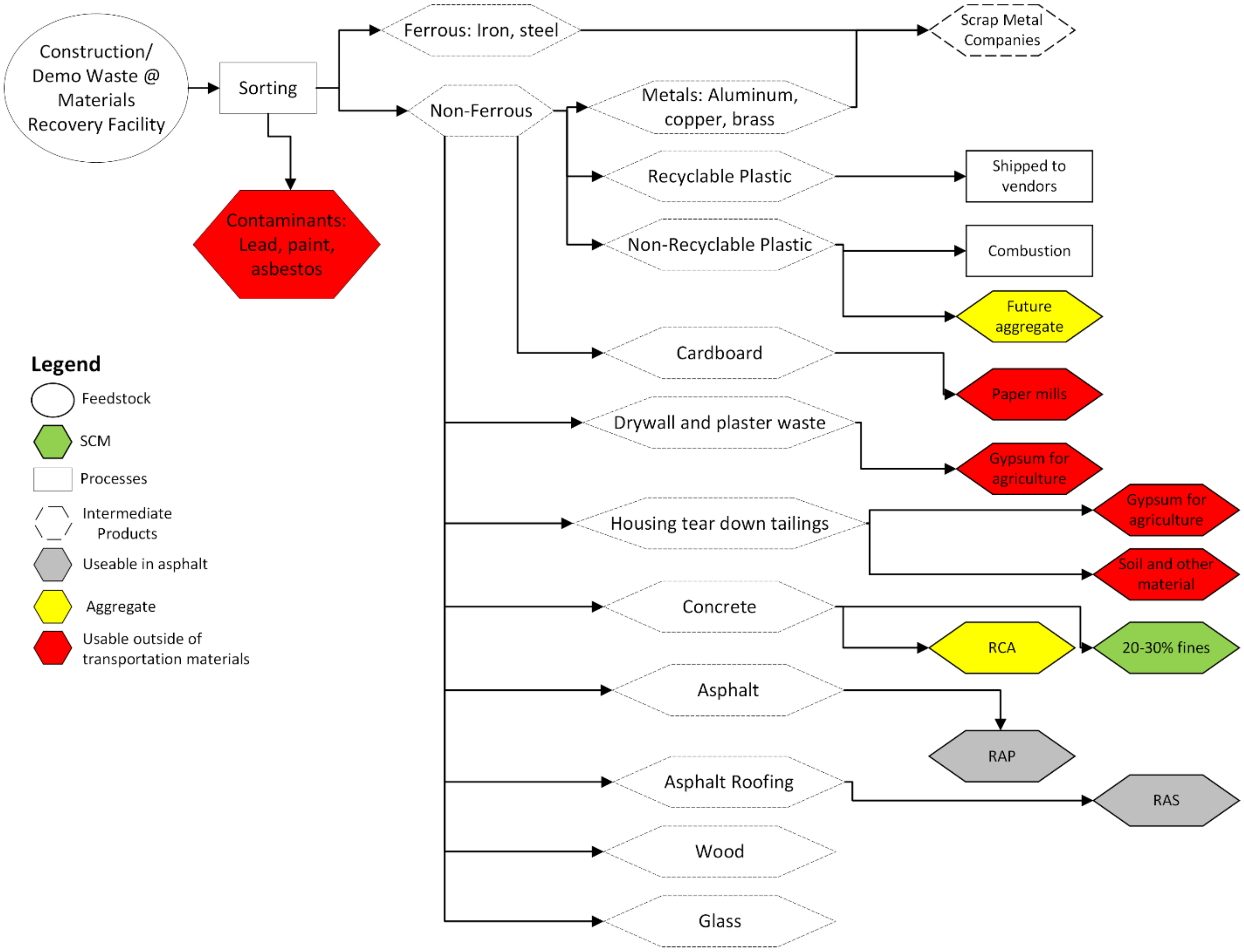


Figure A.9: System diagram of production and various uses for returned plastic concrete.



Source: STEINERT (2016); Van Dyk Recycling Solutions (2021) *(446,447)*.

**Figure A.10: System diagram of the production process of recycled concrete aggregate.**

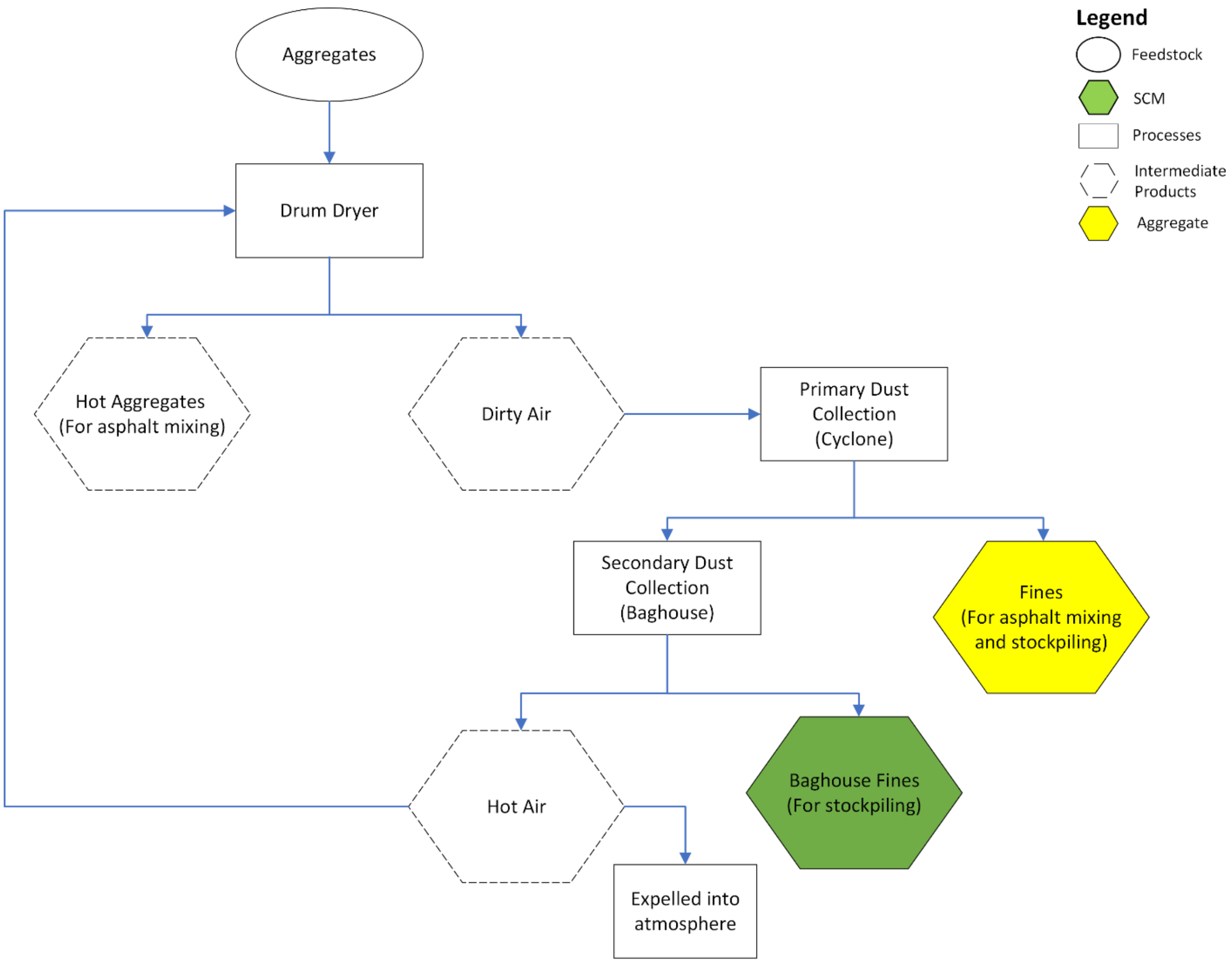


Figure A.11: System diagram of process of rock dust collection at asphalt plants.

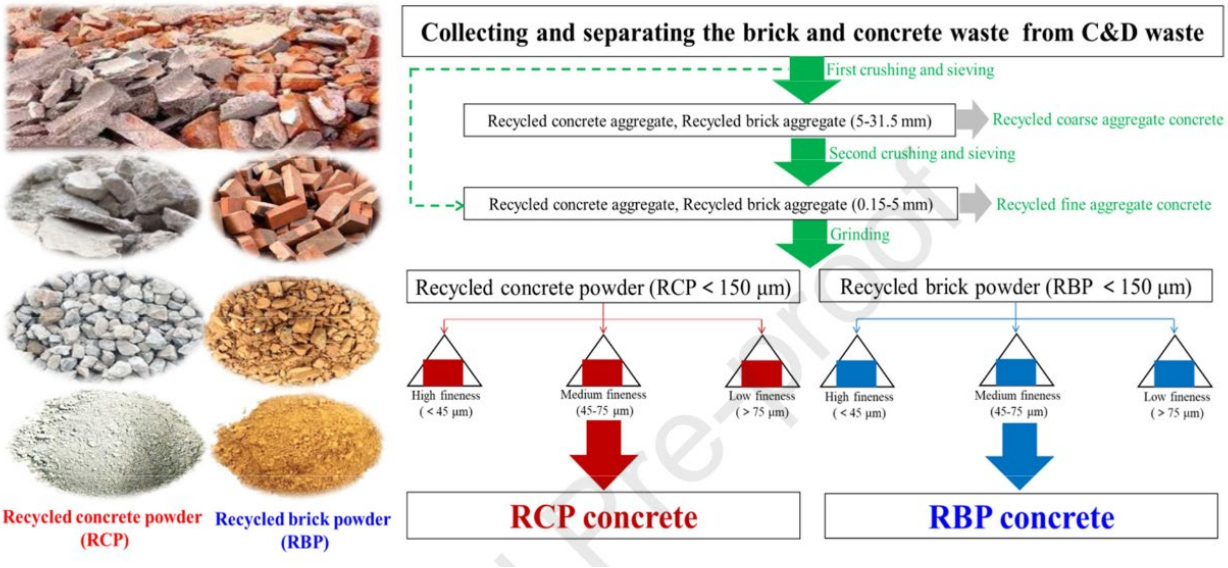
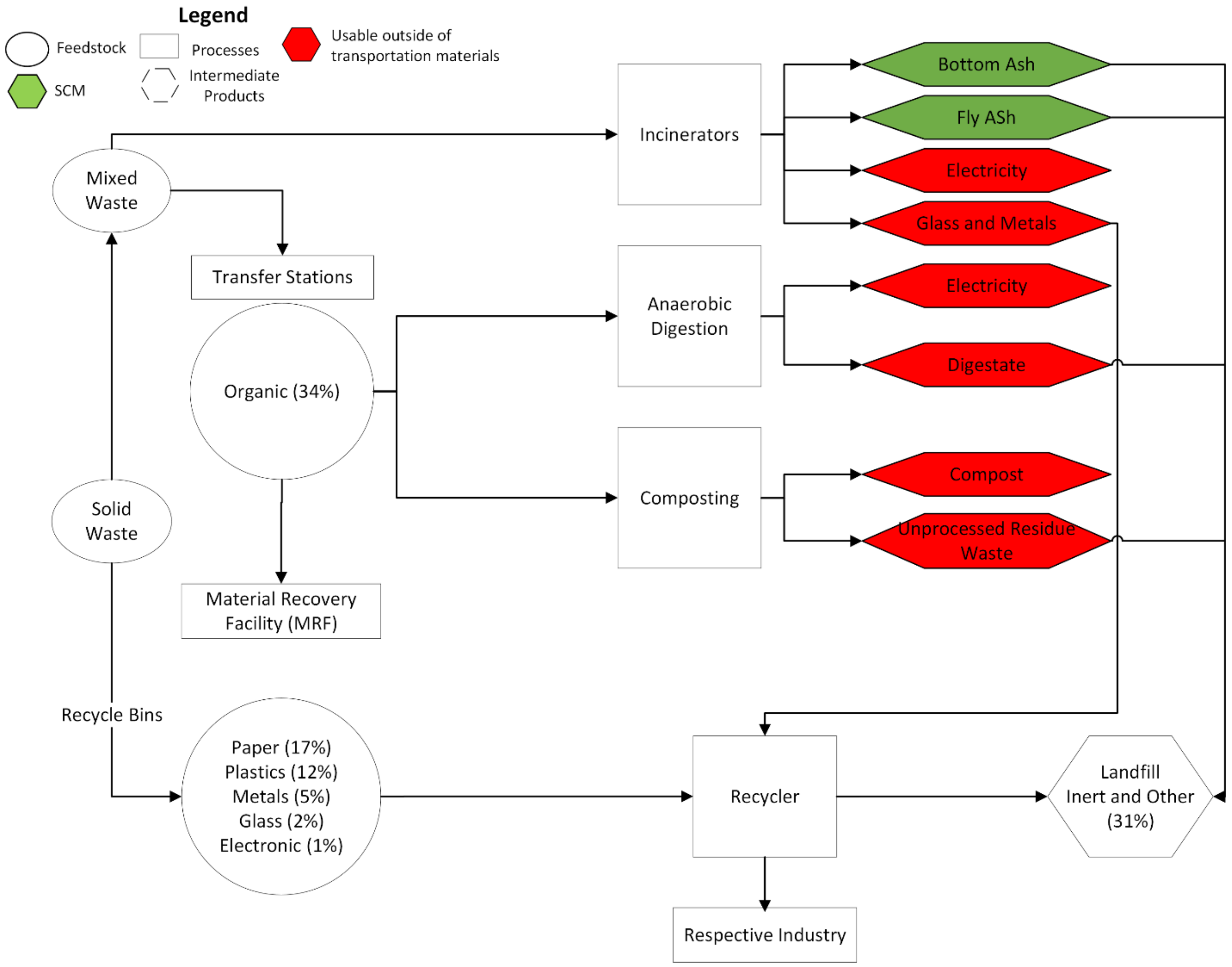


**Figure A.12: System diagram of sorting and grinding recycled brick powder for concrete use.**



Source: US Environmental Protection Agency *(308)*.

**Figure A.13: System diagram of municipal solid waste ash (MSWA) production.**

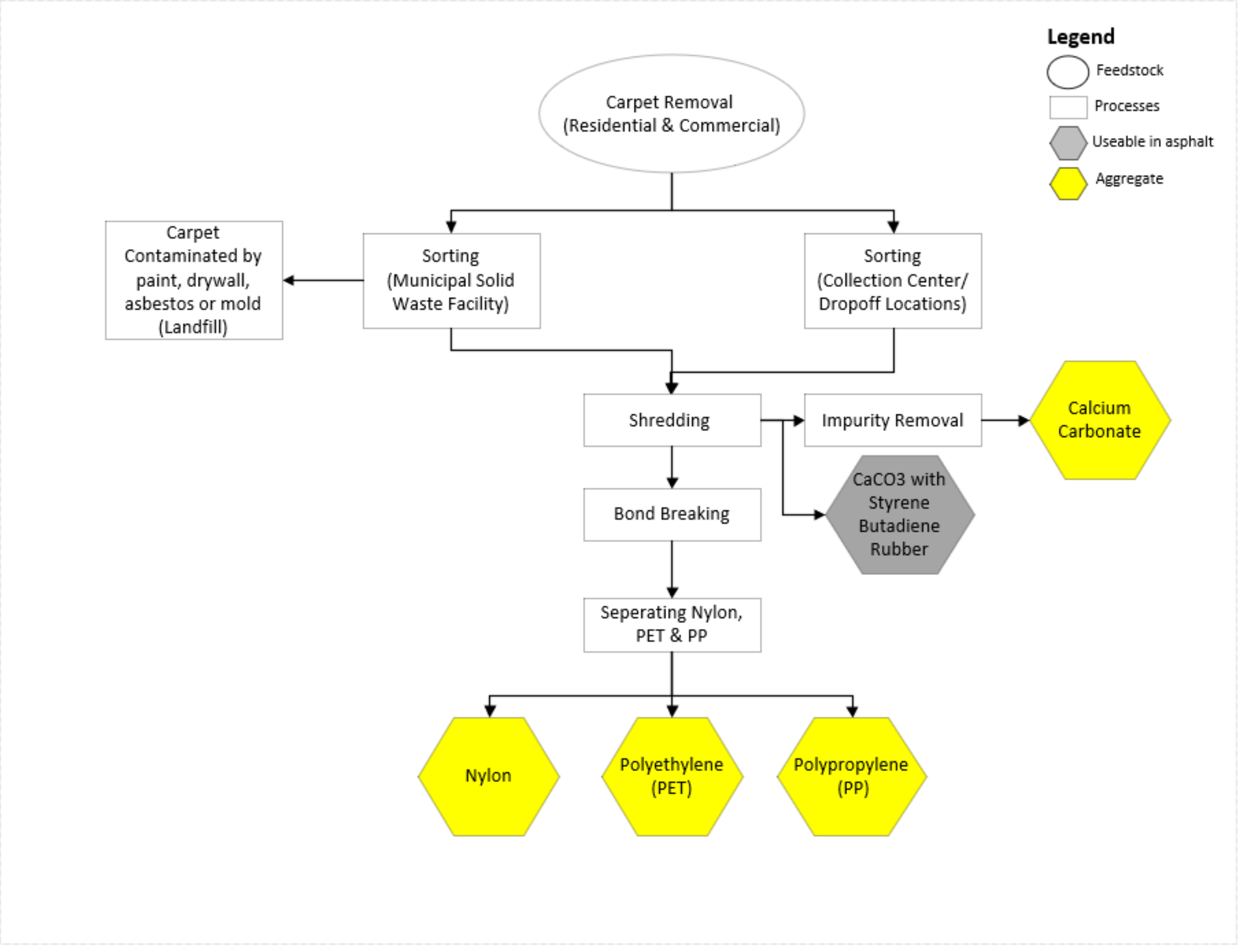


**Figure A.14: System diagram of the recovery of fibers and $CaCO_3$ from post-consumer carpet waste.**

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