SCM may also be a reuse option for these materials, because even though BA have a dissimilar composition compared to FA on average, certain BA outlier samples may have a composition more akin to FA.

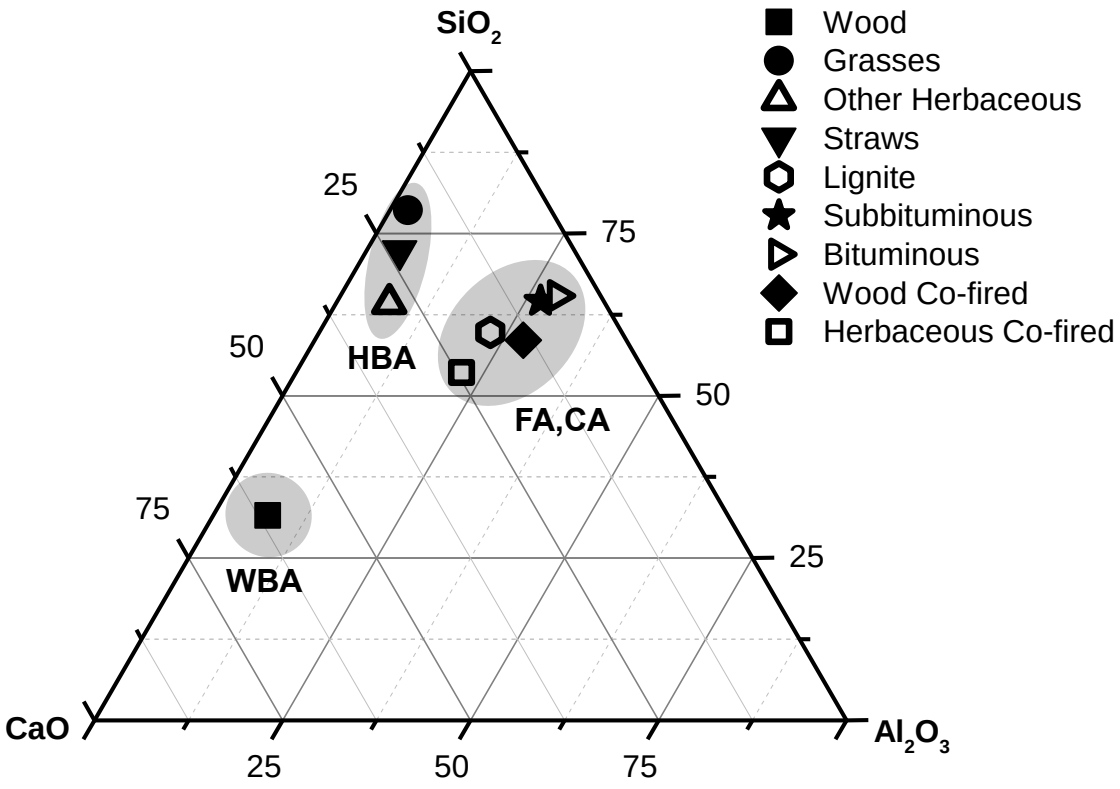

Figure 2.1: Ternary diagram for different ash types showing differences in their average composition. The wt. % of three primary oxides (CaO, SiO_2 and Al_2O_3) were normalized to sum to 100% using the average values presented in Table 2.2. FA = coal fly ashes, CA = co-fired fly ashes, HBA = herbaceous biomass ashes, WBA = wood biomass ashes

2.2 Coal, Biomass and Co-fired Fly Ash for Use in Concrete

Two of the primary constituent phases of portland cement—tricalcium silicate (C_3S) and dicalcium silicate (C_2S)—form calcium silicate hydrates (C-S-H) and calcium

hydroxide (CH) upon hydration as described by these reactions in cement chemistry notation[1] [49]:

$$2C_3S + 6H \rightarrow C\text{-}S\text{-}H + 3CH$$
$$2C_2S + 4H \rightarrow C\text{-}S\text{-}H + CH \quad (2.1)$$

C-S-H is the amorphous to crystalline main product of portland cement hydration and the primary strength-giving phase of hydrated cement [50]. CH (also known as portlandite) is the second most abundant reaction product, and is identifiable by its hexagonal plate-shaped crystals [51]. The strength-contribution of CH is much less than C-S-H due to its lower surface area and sometimes large crystalline structure (which can be more prone to cleavage) among other factors [52]. CH can also present durability concerns when it leaches from the paste resulting in increased porosity and permeability, and is also prone to chemical attack. Low-calcium pozzolans, which in themselves have little to any cementitious properties, chemically react with CH in the presence of moisture to form cementitious products:

$$\text{Pozzolan} + CH + H \rightarrow C\text{-}S\text{-}H \quad (2.2)$$

This reaction is advantages in cementitious systems because the CH phase is consumed to form strength-providing secondary C-S-H that fills up capillary spaces, thus reducing permeability [52]. The pozzolanic reaction is slow at ambient temperatures in comparison

[1] C=CaO, S=SiO_2, H=H_2O, A=Al_2O_3, F=Fe_2O_3, Š=SO_3, Č=$CaCO_3$, CH=$Ca(OH)_2$, C-S-H=$C_xS_2H_y$ where x and y vary

to the hydration of C_3S or C_2S, and the lime liberated through cement hydration may never be completely exhausted [49]. Al_2O_3 released from the pozzolans can also react to form additional monosulfate ($C_4A\check{S}H_{12}$) and hydrogarnet (C_3AH_6) phases, and monocarbonate ($C_4A\check{C}H_{11}$) and hemicarbonate ($C_4A\check{C}_{0.5}H_{12}$) phases in the presence of calcium carbonate [50, 53].

FA is categorized as a type of artificial pozzolan because its primary phase—amorphous aluminosilicate glass—reacts similarly to natural pozzolans (e.g., volcanic ashes, diatomaceous earth), but it is derived from an industrial process. The effect of using FA as an SCM on concrete properties has been extensively researched, but limited research has been conducted on reuse pathways for BA and CA. However, recent studies have begun to study their reuse in concrete as a partial replacement of cement, and these studies are presented in Table 2.4 and Table 2.5.[2]

2.2.1 Early-Age Properties

2.2.1.1 Heat of Hydration

The highly exothermic early-age hydration kinetics of cementitious materials can be linked to important long-term strength and durability properties of concrete. For example, a high heat of hydration can indicate high early strength, but sometimes can result in decreased durability performance [54]. On the other hand, a lower heat of hydration has the opposite effect by reducing early strength, but increasing the lifespan of the concrete through improving long-term durability performance. The addition of FA

[2] Rice husk ash is not included in this thesis as a BA because it typically has a significantly different chemical composition (i.e., high SiO_2 content) compared to most other wood and herbaceous biomass sources, and has been frequently studied for use as a pozzolanic material.