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Beneficial Use of Boiler Ash in Alkali-Activated Bricks

Thomas Poinot^a, Michael E. Laracy^a, Cecilio Aponte^b, Hamlin M. Jennings^a, John A. Ochsendorf^{a,c}, Elsa A. Olivetti^{b*}

a: Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts

b: Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts

c: Architecture, Massachusetts Institute of Technology, Cambridge, Massachusetts

*: elsao@mit.edu - phone number: 617-253-0877

ABSTRACT

This research incorporates waste boiler ash into masonry construction materials using alkali-activation. The boiler ash, derived from three different Indian pulp and paper mills, has many undesirable characteristics for alkali-activation, including varying shape, large particle sizes ranging from 5-600 μm , loss on ignition between 8-35%, and less than 4% alumina. When combined with supplementary materials in the form of clay and lime, high compressive strengths are observed in the bricks made with all three ashes, demonstrating the robustness of the proposed mix design. A brick formulation with a solids phase weight ratio of ash(70):clay(20):lime(10), liquid to solid ratio of 0.45, and 2M NaOH produces bricks with compressive strengths between 11-15 MPa after 28 days curing at 30°C. Furthermore, early strength development is observed, as more than 55% of the 28 day strength is achieved after one day curing. An economic and environmental analysis indicates that these bricks can be produced for similar costs as the clay fired brick with reduced environmental impact, making them a viable alternative in the market.

1. INTRODUCTION

Significant rapid growth in both population and industrial activity in India has offered great development opportunity but has been accompanied by substantial environmental challenges. With this research we aim to address one challenge, namely the unprecedented demand for building materials stemming from population growth, by leveraging another, the production of vast quantities of non-hazardous waste from industrial activity.

On the population side, India is home to over 1.26 billion people, making it the second most populous nation in the world with studies predicting that India will surpass China for the largest population by 2030 (Chandramouli, 2001, James, 2011). This spike in population leads to an inevitable increase in the demand for buildings and infrastructure at an annual growth rate of 7% thereby increasing housing stock by five times the current quantity from 2005 to 2030, leading to extraordinary materials use (Maithel et al. , 2012).

Historically, the fired clay brick is the most commonly used building material in India due to its low manufacturing cost and the availability of clay throughout the country (Maity, 2015). Despite the fired clay brick's long standing dominance as the building material of choice for housing, a number of environmental concerns surrounding its production have raised concern about future use (Maithel, Uma, 2012). The manufacturing of fired clay bricks is an energy intensive process as the bricks are fired at temperatures over 1000°C, making this industry the third largest consumer of coal in India as upwards of 150 billion bricks are produced annually (Maity, 2015). Furthermore, the frequent use of outdated kiln technology for firing leads to significant air pollution in the form of carbon dioxide, carbon monoxide, sulfur dioxide, nitrogen oxides, black carbon, and particulate matter (Maithel, Uma, 2012). Another serious environmental concern associated with the brick making industry is the degradation of topsoil extracted to make the bricks, which is quickly reducing the amount of irrigable land in India (Kathuria, 2015). The above mentioned problems, among others including extreme, labor-intensive working conditions, have prompted the search for alternative brick manufacture solutions, such as concrete or cement stabilized earth blocks.

In parallel with the growing population, there has been significant growth in industry within India. To date, this rapid industrialization has generated vast quantities of industrial wastes or byproducts. For instance, due to the lack

of energy access in rural India, (Balachandra, 2011, Bhattacharyya, 2006, Srivastava et al. , 2012) many small to medium sized factories produce their own energy by burning a variety of raw materials in industrial boilers, generating a byproduct called boiler ash. The raw materials these factories use fluctuate because their goal is to use the cheapest materials on the market. Some of the materials burned include petroleum coke, coal, and biomass/agricultural residues in the forms of rice husk, bagasse, and mustard straw (Cardoen et al. , 2015) where materials may be burned individually or co-combusted (Kalembkiewicz and Chmielarz, 2012). The ongoing changes in the quantity and quality of raw material sources produce ash with high variability in its physical and chemical properties. Furthermore, the inefficiency of the boiler where the raw materials are combusted produces ash with a large amount of unburnt material. Also, due to small-scale local production of boiler ash (as compared with coal-derived fly ash production from large thermal power plants), there has been low interest among entrepreneurs to make use of it, despite its large collective impact. To date, these issues have been a barrier to finding a beneficial use for boiler ash (Pappu et al. , 2007). Therefore, much of this boiler ash is being dumped into landfills or disposed of illegally, occupying valuable farmland and posing serious hazards to both the environment and human health. Furthermore, landfilling this ash comes at an expense to factory owners who need to purchase land, transport the ash to the site, and finally wet and level the ash.

One potential method of addressing both of the aforementioned problems (increase demand for housing materials and increased volume of industrial waste) is to use industrial ash byproducts as raw materials in bricks. Zhang defines three technological strategies for doing this: firing, cementing, and alkali-activation of waste (Zhang, 2013). Firing follows the same procedure necessary for the traditional fired clay brick, the only difference being a partial substitution of industrial waste for clay. However, studies show that as the waste substitution percentage increases, the strength of the brick decreases (Velasco et al. , 2014). Moreover the bricks still need to be fired at high temperatures using traditional kiln technology, thus the energy consumption and air pollution are equal to that of traditional fired clay brick production (Zhang, 2013). The second strategy, cementing, avoids the use of a kiln for high firing temperatures (Abdalqader et al. , 2016, Antunes Boca Santa et al. , 2013). Still, with the use of cement in the mix design, the carbon footprint of these bricks is greatly increased as around 0.92 tons CO₂ are released for each ton of clinker produced (Komnitsas, 2011). Previous work has explored the use of coal bottom ash as a sand replacement in concrete where it does not have significant reactivity (Singh and Siddique, 2013). The third strategy, alkali-activation, depends on a chemical reaction between amorphous alumina and silica rich solids and an alkaline activator (Provis and Van Deventer, 2014). This strategy uses a low energy curing process allowing the bricks to gain strength at ambient temperature. Due to the increased interest in the field of alkali-activation, the research presented here focuses on this third strategy to make beneficial use of ash in bricks.

Alkali-activation has been the subject of intense study across a broad range of wastes including those with relatively controlled compositions such as slag, lime kiln dust and fly ash (Arulrajah et al. , 2017a, b, Bernal, 2016). Broader wastes have been targeted such as those derived from the following four categories: 1) energy generation (i.e., coal and biomass-derived fly and bottom ash), 2) material and fuel production (i.e., mining (Ahmari and Zhang, 2012, Castro-Gomes et al. , 2012, Jiao et al. , 2013), metallurgical wastes such as red mud (Badanoiu et al. , 2015, Dimas et al. , 2009, He et al. , 2013, Kumar and Kumar, 2013), and paper production wastes (Santa et al. , 2013, Yan and Sagoe-Crentsil, 2012)), 3) waste treatment (i.e., incineration ash (Chen et al. , 2016, Garcia-Lodeiro et al. , 2016) and water treatment sludge (Geraldo et al. , 2017, Guo et al. , 2010)), as well as 4) end-of-life flows (i.e., glass waste (Novais et al. , 2016, Wang et al. , 2016) and ceramic waste (Reig et al. , 2013, Sun et al. , 2013)).

An issue hindering the implementation of alkali-activation is the inability to reliably predict the mechanical performance of the products formed based on the properties of the ash (Aughenbaugh et al. , 2015, Provis et al. , 2012). The reactivity of the ash will directly impact the final properties of the product formed (Diaz et al. , 2010, Van Jaarsveld et al. , 2003). The overall reactivity of the ash is dependent on a number of factors including the amount of reactive amorphous silica and alumina, calcium and iron content, unburnt material, as well as particle size and morphology. Since boiler ash has yet to be used in significant quantities in the application of alkali-activated materials, the desired properties of the boiler ash will be compared with the characteristics of fly ash, as the latter has been successfully used in the production of alkali-activated materials (Shi et al. , 2011). Characterizing the ash will determine its suitability for use in alkali-activated materials and identify solutions to improve its suitability if needed. Therefore, the contributions of this work are to characterize boiler ash from the pulp and paper industry,

identify whether it can be incorporated in bricks through alkali-activation, and measure the properties of the resulting bricks in comparison with fired clay alternatives along dimensions of technical, economic and environmental performance.

2. Materials and methods

Alkali-activated bricks were made out of boiler ash, clay, hydrated lime, sodium hydroxide pellets, and municipal water. The boiler ash samples were obtained from three different paper mills in the city of Muzaffarnagar, India. The paper mills were Bindlas, Silverton, and Siddhbadi, and we identify the boiler ash throughout this manuscript by the name of the paper mill from which it was obtained. A map of the study region including the paper mills of interest is provided in the appendix. The percentages by weight of raw materials combusted to produce the Bindlas boiler ash was 63% bagasse pit, 27% rice husk, and 10% petroleum coke. The Silverton and Siddhbadi ash were byproducts of combustion of 100% rice husk. Each of these energy sources was chosen by the paper producers within each mill and the mix will vary seasonally depending on their availability. The clay was also obtained from a field nearby the paper mills in Muzaffarnagar. Both the boiler ash and clay were placed in an oven at 105°C to remove any moisture from the specimens. The clay was then ground and sieved to pass the #35 sieve (0.5 mm) to break up any large agglomerates. Hydrated lime was a Graymont product obtained from Madigan Lime Corporation in Ayer, MA. The lime was also sieved to pass the #35 sieve to remove any large agglomerates. Laboratory grade >97% sodium hydroxide pellets were acquired from Sigma Aldrich. Municipal water was used throughout to attempt to represent field conditions.

The products formed using alkali-activation technology are heavily dependent on the boiler ash properties. The chemical composition of the ash is related to the raw materials burned, while the mineralogical properties depend on the design and operation of the boiler (Williams and Van Riessen, 2010). Common tests which were used to characterize ash include X-ray fluorescence (XRF), X-ray diffraction (XRD), particle size distribution (PSD), and scanning electron microscopy (SEM). A semi quantitative elemental chemical analysis was obtained via XRF using a Bruker S4 Explorer. A Leco SC632 Carbon Analyzer was used to determine carbon content in the ash. XRD data was collected using high speed Bragg-Brentano optics on the PANalytical X'Pert Pro MPD. The crystalline peaks were identified using the ICDD PDF4+ database. Data was obtained between 15° and 70° (2 θ). Particle size measurements on the boiler ash were conducted using a Horiba LA920 laser scattering particle size distribution analyzer. SEM images were taken on a Philips XL30 FEG ESEM to observe the morphology of the boiler ash particles.

Tests were performed to determine the mechanical characteristics of the bricks made using alkali-activation. To prepare the samples, first the sodium hydroxide pellets were dissolved in water by stirring until a homogenous solution was formed. Due to the exothermic reaction, this was done a day in advance to allow the solution to cool down to room temperature. Next, the dry materials (boiler ash, clay, and hydrated lime) were weighed, added to a bowl, and mixed using a planetary mixer for 3 minutes to attain a homogenous composition of the solids phase. The NaOH solution was then weighed and added to the bowl. This was mixed with the solids phase at maximum speed until a homogenous wet consistency was formed. This typically took between 20 and 30 minutes to achieve. The mixture was then transferred into 2" cubic molds where the samples were cast using tamping and vibration. Samples were cast in two layers which were each hand tamped and vibrated for 1 minute to compact the mixture and remove any air bubbles. Samples were then sealed using two layers of plastic wrap and placed in the oven to cure at 30°C. The temperature was chosen to mimic what ambient temperature would be like in India. Samples remained in the oven up until their designated testing days. There were a number of variables to consider related to both the mix design and the processing techniques. Individual studies were performed on several parameters to determine which had the most influence over the final properties of the brick. These included the type and quantity of supplementary materials, ash quantity, NaOH molarity, liquid to solid ratios, curing temperature, and mix time. Future work aims to optimize these parameters across the varied set of wastes. More details on the mixture proportion development can be found in Table A1 and Laracy et al.

After these individual experiments, the same mix design was determined for all three samples of boiler ash in order to test the robustness of the formulation. For all three samples, the solids phase by weight was 70% boiler ash, 20%

clay and 10% lime. The liquid to solid weight ratio was 0.45 for Bindlas ash and 0.46 for Silverton and Siddhbadi ash. This slight increase was to allow for the mixtures to all have the same consistency for molding. The concentration of the NaOH was 2M for Bindlas ash and 1.95M for Silverton and Siddhbadi in order to account for the increased liquid to solid ratio while keeping the alkali content constant. Samples were tested for their unconfined compressive strength at 1, 3, 7 and 28 days using a Baldwin Tate Emery Universal Testing Machine. Samples were prepared such that the sides being tested were both smooth and parallel.

For the environmental and economic analyses, a comparison was made between alkali-activated bricks and the fired clay equivalent. Based on the prototypes produced, the functional unit in this study was one brick that is 9" x 4" x 2.5" and the densities of the bricks compared in the analysis were the same (1.36 g/cm³). The system boundary only included the resources and processes involved in manufacturing the brick, and therefore the boundary did not include any impact regarding the bricks actual use or disposal. The primary reason for this exclusion was lack of data on the use phase of the alkali-activated bricks; this impact should be included in future investigations as leachate would potential impact the alkalinity of the surroundings. (Preliminary leaching tests through TCLP on the raw materials and final brick product have shown no significant leaching across the following elements: As, Ba, Ca, Cr, Pb, Hg, Se and Ag). This result is expected because of the bio-based nature of the ash) Transportation of clay was assumed to be equivalent between the bricks and therefore excluded, however the transportation of lime and sodium hydroxide for the alkali-activated bricks was included. The environmental analysis was done using the IMPACT 2002+ assessment method. The life cycle inventories were based on the ecoinvent 3 library modified for the context of Indian electricity grid and other energy sources(Frischknecht et al. , 2005) including an uncertainty analysis on each chosen inventory. The inventories used for the fired clay brick included: clay and tap water with bituminous coal with an upper bound heat value of 32 MJ/kg as an energy source for the kiln firing. The baseline kiln efficiency measured by the specific energy consumption parameter was assumed to be 1.22 MJ/kg. The inventories used for the alkali-activated brick include clay, a 2M sodium hydroxide solution and loose lime with Indian-based grid electricity for the heating and pressing of the brick and transport of 50 km by small truck. The full list of inventories is provided in Table A1.

3. Results

This work assessed the suitability of boiler ash from paper production for use in alkali-activated bricks. No standards for bricks currently exist for alkali-activated materials. According to Indian Standard (IS): 1077, traditional fired clay bricks are classified based on their average compressive strength with the minimum allowable strength being 3.5 MPa. To exceed this minimum, the goal of this research was to achieve at least 7.5 MPa, a target suggested by multiple sources on the ground in India. First, we characterized the boiler ash including both physical and chemical properties to understand how those might map to mechanical and durability properties of the final product. Based on these results a formulation was proposed to incorporate the ash into bricks. We then tested the resulting mechanical properties for the final product and conducted an economic and environmental impact assessment.

The particle size distribution (PSD) of the boiler ash is generally the most important physical characteristic influencing the reactivity of the ash (Fernández-Jiménez and Palomo, 2003). The benefit of smaller particles is the resultant higher total surface area, which increases ash reactivity as the reaction occurs at the particle-liquid interface (Diaz, Allouche, 2010). Furthermore, it is known that very small particles (< 20 µm) tend to have a more amorphous composition, as smaller particles quench faster than larger particles (Rickard et al. , 2011). The size of the particles for all three ash samples ranged from 5 - 600 µm. The Bindlas and Silverton ashes had nearly identical particle size distributions as seen in Figure 1b, while Siddhbadi was slightly larger. The mean particle size for the Bindlas, Silverton, and Siddhbadi ashes were 112 µm, 105 µm, and 118 µm, respectively.

The general morphology of the ash is also an important characteristic. Spherical-shaped particles are preferable in that they improve workability of the binder at lower liquid to solid mix ratios (Rickard, Williams, 2011). However, as shown in Figure 1a, the boiler ash particles were large angular pieces with a rough and bumpy surface.

From a chemical standpoint, silica and alumina are the two key components necessary for alkali-activation. The bulk elemental oxide analysis summarized in Table 1 found that more than 80% of the ash is made up of silica while alumina was found in much lower quantities, i.e., only 3.9%, 2.8%, and 2.6% for the Bindlas, Silverton, and Siddhbadi ashes, respectively. A high presence of iron can be detrimental as it has been observed to inhibit the dissolution of the aluminosilicates during alkali-activation (Chen-Tan et al. , 2009). Here, iron was present in sufficiently low quantities, less than 2% for all ashes. In contrast, the presence of calcium is desirable since it offers the benefits of rapid strength development and the ability to form the products calcium-silicate-hydrate gel (CSH) and/or calcium-aluminosilicate-hydrate (CASH) (Van Jaarsveld, Van Deventer, 2003, Yip et al. , 2005). Little calcium was found as only 1-3% of the elemental composition was calcium. Other elements found included sulfur (0-3%), sodium (0-1%), magnesium (1-2%), potassium (3-5%), phosphorus (1-2%), and titanium (0-1%). The sum of these elements did not equal 100% as other trace elements which were not tested for were likely present in the ash.

The presence of unburnt material in the ash is another critical factor when assessing the ashes suitability for alkali-activation, since it is not reactive and it absorbs the activator solution, requiring the mix design to have a higher liquid to solid ratio (Fernández-Jiménez and Palomo, 2003). This has been determined with a loss on ignition (LOI) test. The LOI value for all three ashes was higher than the allowable limit of 6% for fly ash prescribed by ASTM C 618: 8.75% for Siddhbadi, 13.1% for Silverton and an extremely high value of 34.9% for Bindlas. Values for the density of the ash were 2.23 g/cm³ (Bindlas), 2.49 g/cm³ (Silverton), and 2.58 g/cm³ (Siddhbadi), consistent with values seen in literature (Chancey et al. , 2010, Fernández-Jiménez and Palomo, 2003).

The bulk elemental oxide analysis of the ash only provides a preliminary indication of the suitability of the ash, as it does not quantify the amount of reactive and nonreactive components (Rickard, Williams, 2011). In order to get a better understanding of the suitability of the ash, we quantified the reactive amorphous phases and nonreactive crystalline phases in the ash. Amorphous phases are desirable because they dissolve easier than crystalline phases during the early stages of alkali-activation, releasing more reactive silica and alumina (Diaz, Allouche, 2010). Figure 1c shows that all three boiler ash samples were similar and contained both crystalline and amorphous material. The crystalline material is represented by the sharp peaks along the diffractogram and the amorphous content is shown by the broad hump approximately located between 15 to 30 degrees (two-theta). The majority of crystalline materials were silica phases, primarily in the form of quartz, but also present as cristobalite and tridymite, in agreement with literature (Payá et al. , 2001). Traces of other crystalline phases included feldspar-type phases (albite, sodalite, anorthoclase), potassium sulfate (arcanite), calcium carbonate (calcite), as well as iron oxide (magnetite) and titanium dioxide (rutile). There were no traces of crystalline alumina phases, suggesting that the bulk alumina content from the XRF analysis was primarily amorphous material. An estimation based on the area of the peaks in the diffractogram found that the quantity of amorphous material is 62% for Bindlas, 66% for Silverton, and 52% for Siddhbadi. From this value, the reactive silica content was estimated by subtracting the reactive alumina content from the total amorphous content. It is then possible to estimate the amount of reactive silica compared to reactive alumina, often represented as a ratio of Si/Al that has been shown to be most effective at a value around 2 (Fernández-Jimenez et al. , 2006). In the case of the boiler ashes studied, conservatively assuming all the alumina was reactive would still yield a Si:Al ratio around 15 to 22.

Table 1: Bulk chemical analysis of the three boiler ashes using XRF

	Element as Oxide (wt. %)										LOI (%)	Carbon (%)	Density (g/cm ³)
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	CaO	Na ₂ O	MgO	K ₂ O	P ₂ O ₅	TiO ₂			
Bindlas	81.9	3.87	1.17	2.84	1.55	0.49	1.24	3.55	1.04	0.20	34.9	30.0	2.23
Silverton	82.7	2.80	1.90	0.97	1.45	0.45	1.35	4.68	1.52	0.16	13.1	10.8	2.49
Siddhbadi	85.2	2.61	0.79	0.49	2.24	0.59	1.03	3.98	1.06	0.14	8.75	5.97	2.58

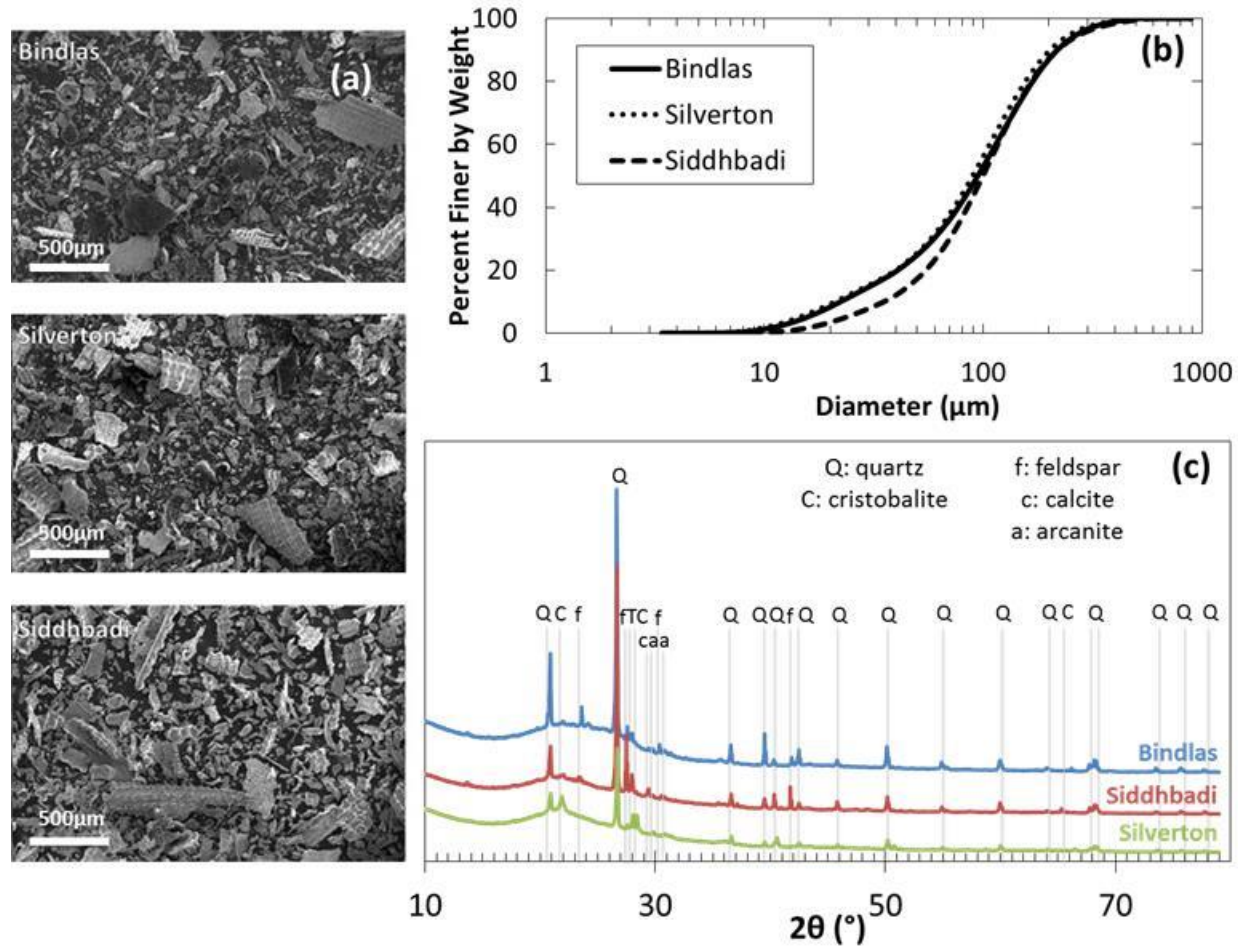


Figure 1: Characterization of the three boiler ashes a) SEM images, b) Particle size analysis showing that less than 25% of the ashes are under 45 µm and c) XRD patterns showing the relatively large amorphous content of the ashes and the crystalline phases

These results demonstrated that the three boiler ashes tested did not have many desirable characteristics to make the ash highly reactive including shape, particle size, LOI value, and reactive alumina content. The ashes were found to be similar especially regarding their chemical analyses and mineralogy. This was expected for Silverton and Siddhbadi ashes since they are both derived from the combustion of 100% rice husk, but Bindlas ash is derived from 63% bagasse pit, 27% rice husk, and 10% petcoke. However, 23% of the rice husk that is burned turns to ash, (Della et al. , 2002) whereas only 2% of bagasse pit turns to ash, (Montakarntiwong et al. , 2013) and combustion of petcoke produces no ash. Therefore, this ash was actually closer to 83% rice husk ash and 17% bagasse pit ash, explaining its similarities to the other ashes.

Although the ashes were observed to have similar properties overall, there were a few key differences. First, the Bindlas ash had a significantly larger LOI than Silverton and Siddhbadi. Second, the Siddhbadi ash had larger particle sizes than the other two ashes. Third, the amount of amorphous content and reactive silica varied as Siddhbadi had far less than Bindlas and Silverton. The differences observed are more likely due to the differences in the boilers where the raw materials are combusted. The majority of the crystalline phases observed as quartz suggests that the boiler was operated at a temperature between 500-900°C. Yet, the presence of cristobalite and tridymite, which can be crystallized between 870-1470°C and 1470-1720°C, (Shinohara and Kohyama, 2004) respectively, indicate that the temperature varies in different locations of the boiler. Also, the fact that Bindlas has an LOI of 35% likely indicates that this boiler was very inefficient and low temperatures in locations of the boiler are leading to a large amount of unburnt material. Regarding the Siddhbadi boiler, the lower quantity of amorphous

content may have been due to slower cooling rate of the ash particles which is known to produce more crystalline phases (Diaz, Allouche, 2010, Fernández-Jiménez and Palomo, 2003).

Due to the overall poor qualities of the ash, the use of boiler ash as the only solid source for alkali-activation was not expected to produce a brick with good final properties. An option to improve the reactivity of the ash is to process the ash by means of fractionation, (Chindaprasirt et al. , 2004, Chindaprasirt et al. , 2005, Slanička, 1991) mechanical activation, (Fu et al. , 2008, Kumar et al. , 2007, Kumar and Kumar, 2011, Temuujin et al. , 2009) or combustion to reduce the loss on ignition to zero. Each of these processing techniques has been proven to increase the overall reactivity of the ash; however they are all associated with environmental and/or economic drawbacks. Despite the effectiveness of fractionation in increasing strength, the coarser particles must still be landfilled (Kiattikomol et al. , 2001). The drawbacks of mechanical activation and combustion are the energy inputs required to perform these techniques as well the costs associated with them. Most importantly, all of these techniques do not address the lack of reactive alumina, which needs to be increased in order to lower the Si/Al ratio. We instead proposed the addition of supplementary materials, rather than processing, which is known to increase the overall reactivity of the solid source (Provis, 2014). This mixture described above attained the maximum strength among various combinations of ash, clay and lime, and therefore, was chosen for this study. This proportion was fixed for different ashes to assess the robustness of formulation. There were a number of variables to consider related to both the mix design and the processing techniques. Individual studies were performed on several parameters to determine which had the most influence over the final properties of the brick. These included the type and quantity of supplementary materials, ash quantity, NaOH molarity, liquid to solid ratios, curing temperature, and mix time. Future work aims to optimize these parameters across the varied set of wastes. More details on the mixture proportion development can be found in Table A1 and in (Laracy, 2015).

The supplementary source can be an additional waste product, natural resource, or synthetically produced material. Additional sources of alumina in alkali-activated materials often come as metakaolin (calcined clay) or red mud (Provis, 2014). In this work, clay was used as the additional alumina source in its original state, because calcining the clay would be an energy intensive and costly process. The presence of calcium is also beneficial as it leads to more rapid strength development and it allows for a lower concentration of the alkali source (Yip, Lukey, 2005). Additional sources of calcium described in literature include blast furnace slag, cement, calcium hydroxide, calcium silicate, calcium carbonate, limestone, and class C fly ash (Provis and Van Deventer, 2014, Turgut, 2012). The additional source chosen in this work was calcium hydroxide (hydrated lime) as it is locally available throughout India and relatively inexpensive. With the addition of these two supplementary sources, boiler ash could be used in alkali-activation. This was demonstrated through testing of mechanical properties of the products formed. Given our interest in presenting an implementable solution for this waste, the analysis needed also to ensure that we were not shifting the environmental burden from heat in firing to the embodied energy associated with these supplemental materials. Additionally, the cost must be comparable with fired clay to be viable in the Indian market.

Figure 2 shows the compressive strength over curing time for cube samples made with all three ashes. Alkali-activated samples made with Silverton and Siddhbadi ashes achieved the 7.5 MPa goal after just 1 day of curing at 30°C, while the Bindlas ash bricks fell just short at 6.8 MPa. Still, the early strength development of these bricks was high, reaching 58% (Bindlas), 56% (Silverton), and 73% (Siddhbadi) of the 28 day strength after 1 day curing. At the end of 3 days curing the average strength of the bricks for each ash exceeded 9 MPa, with the lower bound of the standard deviations being all greater than 7.5 MPa. By 28 days curing the bricks were found to be 57% (Bindlas), 94% (Silverton), and 53% (Siddhbadi) stronger than the target goal of 7.5 MPa.

Silverton bricks had the highest strength and also the best ash properties (highest amorphous content at 62%, low LOI of 13%), demonstrating the correlation between the two. Bindlas and Siddhbadi bricks both had slightly less strength than Silverton, which can also be explained by their ash properties. While Bindlas ash did have a high amorphous content of 58%, the extremely high LOI of 35% likely is the cause of the reduction in strength as the unburnt material is not reactive. Although Siddhbadi ash had the lowest LOI at 8.75%, its low amorphous content of 52% and largest particle sizes likely lead to its reduction in strength compared to Silverton. All the cube samples exhibited a dark grey color, smooth surfaces, no efflorescence, no shrinkage (slight expansion at center of each side, less than 1%) and a minimal weight loss (less than 1%).

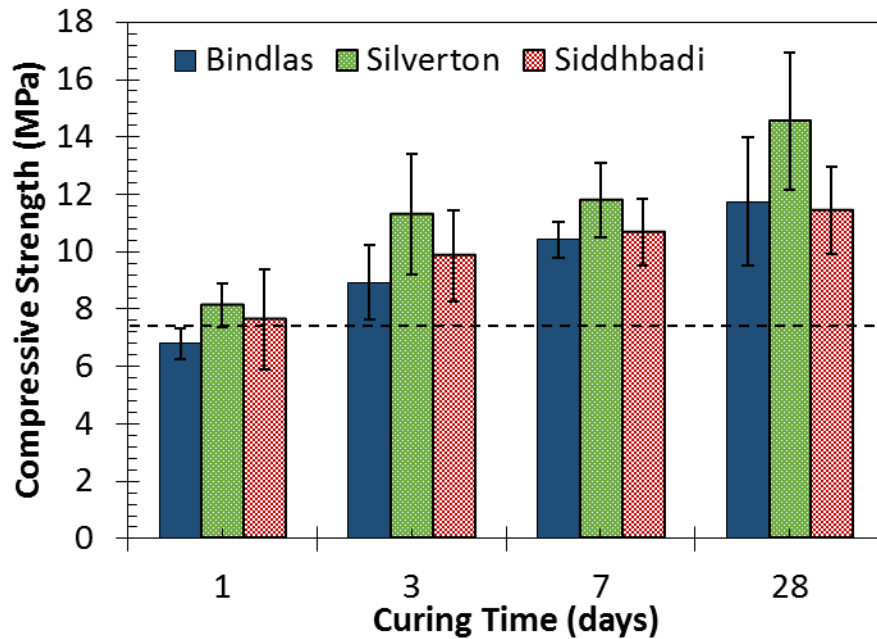


Figure 2: Compressive strength results for 1, 3, 7, and 28 days of 30°C curing for three sources of boiler ash- The goal of this research was to achieve at least 7.5 MPa, as shown as the dotted line on the figure. Samples were tested for their unconfined compressive strength using a Baldwin Tate Emery Universal Testing Machine. Samples were tested at a loading rate of 15000 N/min and otherwise in line with ASTM C109. The box and whiskers for each bar show the standard deviation across the samples tested and the table below shows the minimum and maximum compressive strength in MPa for Bindlas (B), Silverton (SI) and Siddhbadi (Sd).

Although boiler ash has many undesirable characteristics for alkali-activation, the use of supplementary materials in the form of clay and lime allowed the compressive strength results for the bricks made using all three boiler ashes to exceed the target goal of 7.5 MPa, validating the robustness of the brick formulation. Moreover, the lower bound of the standard deviation was at least 2 MPa higher than the target for all bricks, providing a comfortable buffer to account for variations in the ashes properties.

4. Discussion

In order to shed light on the economic and environmental performance of the final products, laboratory experiments were scaled up using industrial equipment in the city of Muzaffarnagar, India to produce full-size (9" x 4" x 2.5") prototypes. The performance of these bricks was similar to the laboratory-scale cube samples. The prototype conditions were used to assess economic and environmental performance.

In this analysis, the production costs were compared for a fired clay brick in the city of Muzaffarnagar and an alkali-activated brick molded with hydraulic pressure (as would be used in the field). According to local sources on the ground in India, the production cost of a fired clay brick in the city of Muzaffarnagar is 3 INR (about 0.05 USD), however brick prices vary throughout India. Muzaffarnagar is located on the fertile alluvial regions of the Indo-

Gangetic plain, where over 65% of the country's brick production occurs because of the high quality and availability of soil for brick making (Schuchman, 2014). Therefore, the availability of bricks in this area is high which reduces prices.

The costs included in this preliminary analysis were the materials, labor, and energy required in brick production based on local prices in Muzaffarnagar. The required amount of labor and wages were determined from a similar production scenario that uses automated machinery with a baseline forming pressure of 25 MPa (from five facilities that manufacture cement-based pavers using hydraulic presses). The energy demands were based on similar machinery to what would be required and the energy prices were based on Muzaffarnagar's rates. The analysis assumed the production of 10,000 bricks per day, a reasonable capacity for an automated machine, and under the assumption that the plant would operate for 26 days of the month (Sundays off) with one eight hour shift per day.

The resulting production cost for this brick formulation was 2.88 INR, not accounting for overhead costs. The appendix provides a full comparison of the breakdown by cost element between fired clay and alkali-activated approaches. 92% of the costs associated with the alkali-activated brick came from the materials (51% of that to NaOH, 35% lime, and 14% clay), whereas only 7% is labor, and 1% was energy. Ash was considered to be free, but could be considered a negative cost as it currently costs money to landfill (renting the land). These numbers can be compared to the cost breakdown of the fired clay brick which is 58% energy, 40% labor, and 2% materials (Schuchman, 2014). A significant difference is the cost of energy, which for alkali-activated bricks is a small amount of electricity to power a machine whereas the fired clay brick requires considerable amounts of coal to fire the bricks. These numbers do not represent the true production cost of the alkali-activated brick, but are meant as a proof of concept to show these bricks can be produced for similar costs to those for fired clay brick.

The final analysis was to compare the environmental performance of the alkali-activated brick to the traditional fired clay brick. LCAs of alkali-activated materials have produced varying results due to different raw materials and mix designs across studies (Gursel et al. , 2016, Jamieson et al. , 2015, Provis and Van Deventer, 2014). The estimated CO₂ savings compared to Portland cement, for example, ranges from 80% to 30 % (Habert et al. , 2011, McLellan et al. , 2011, Stengel et al. , 2009, Tempest et al. , 2009, von Weizsacker et al. , 2009). Previous has also found benefit of beneficial use of municipal solid waste incineration ash as a substitute alkali reagent in the Waelz process at an electric arc furnace (EAF) ash recycling plant, disposal in landfill after stabilization/solidification, reuse as part of raw material in a cement kiln, and reuse as part of aggregates in brick (Huang et al. , 2017). Here we focused instead on a rough comparison with the fired clay brick to gauge whether or not the burden of manufacture of supplementary materials used in the alkali-activated brick formulation outweighed the benefit of reduced curing temperature. Figure 3 shows a photograph comparing the cube samples used in compression testing with the full brick used in the LCA.



Figure 3. Photograph showing a cube sample used in the compression testing along side a full sized brick used in the LCA.

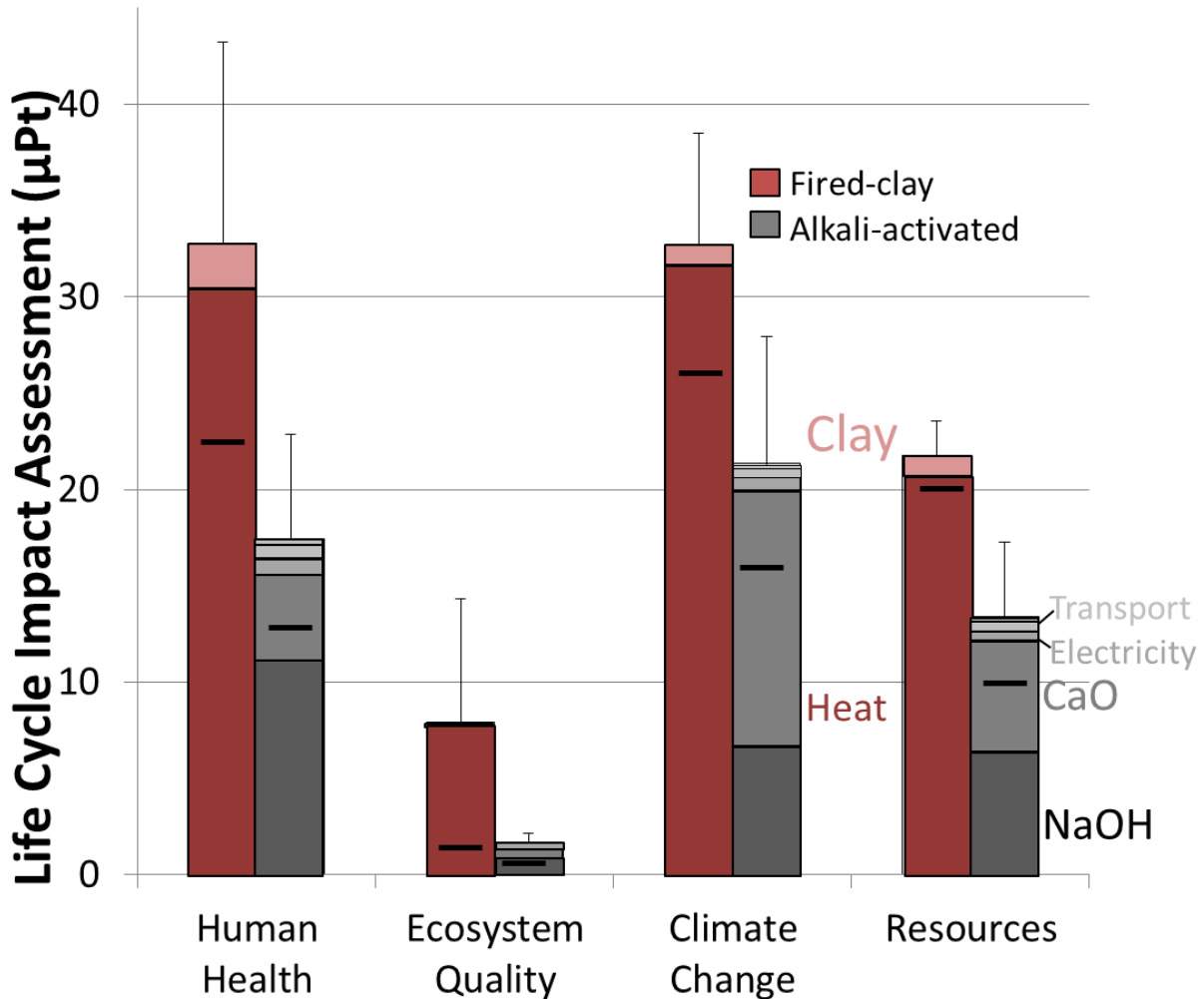


Figure 4: Life cycle impact assessment (LCIA) in points comparing fired clay to alkali-activated bricks for human health, climate change, and resources. Red stacked bars on the left of each category are for fired clay and include the mean-based breakdown of impact for coal-based heat in firing and clay as a raw material. Grey stacked bars on the right of each category are for alkali-activated and include the mean-based breakdown of impact for NaOH, CaO (lime), electricity and transport. The upper error bar provides the 95th percentile impact for each category and the solid black bar provides the 5th percentile.

Figure 4 shows the normalized Impact 2002+ life cycle impact assessment (LCIA) for each brick system, the fired clay brick in red on the left and the alkali-activated in grey on the right. The 5th and 95th percentile is shown as well based on the uncertainty analysis described in more detail below. These results indicated that the environmental burden of the alkali-activated brick was lower than the fired clay brick. The alkali-activated system performed better in all four damage assessment categories by almost a factor of 2 for all categories except for ecosystem quality (which has a larger reduction). The human health category was primarily driven by the production of respiratory inorganics, the climate change by CO₂ emissions, and the resources category by the depletion of nonrenewable resources. Given the lack of site-specific data for the background life cycle inventories for fuel sources and raw materials, an uncertainty analysis was performed. For the uncertainty, a range of possible inventories were chosen indicating variation in production approach for sodium hydroxide and lime, kiln efficiency and fuel source for the clay firing process. The resulting ranges in impacts led to a 20% coefficient of variation (COV, or the mean-normalized standard deviation) for all results except for the ecosystem quality of the clay brick, which had closer to a 50% COV). Even with uncertainty, the environmental impact of the alkali-activated brick exceeded (performs

worse than) the clay brick in only 6% of statistical trials for ecosystem quality and in only 2% of statistical trials for the other impact categories.

Environmental impact was also broken down by the system constituents in Figure 4 (mean-based only), indicating that the largest driver for the alkali-activated bricks was the lime (ranging from 30%-65%) and sodium hydroxide (ranging from 25%-60%). All other processes accounted for no more than 10% of the total. Regarding the fired clay brick, greater than 90% of the environmental impact across all categories stemmed from mining coal and from coal combustion during firing. The use of clay and water accounted for the remaining < 8% of the total impact. It should be noted that there is also significant regional land degradation from clay use not captured in the environmental metrics presented here based on data availability.

As stated above, the main contributors to environmental impact for the alkali-activated brick were lime and sodium hydroxide. Therefore, as we optimize our mix design in future work through reduction in molar concentration of NaOH or use of alternate wastes to provide a source of calcium, the environmental burden (and potentially cost as well) will be further reduced relative to the fired clay brick. Future work will also address the water absorption performance of the alkali-activated bricks through cycling tests.

5. Conclusion

This work has demonstrated the further promise of alkali activation as a way to beneficially reuse boiler ash waste from industrial activity in northern India in masonry units. The authors are currently working to implement this technology in the field. Increases in compressive strength relative to the fired clay alternative were achieved through robust mix design given the relative particle size and compositional variation in three ash types from the region. Early strength development was observed as more than 55% of the 28 day strength is achieved after one day curing. To achieve these strengths, supplementary materials in the form of clay and lime were used, but through cost and environmental analysis this was shown to perform well relative to the comparator, fired clay bricks. Furthermore, there is opportunity to lower the environmental impact by reducing the lime and NaOH quantities and by using additional wastes in the mix design.

The investigation described in this manuscript invites future work along several dimensions. For the raw materials it would be of interest to further map the characteristics of the input byproduct streams (such as amorphous content and particle size) to the properties of the final product (such as compressive strength or density of reaction product). Further chemical analysis of the reaction product would provide insight into the role of clay and lime. This could be done not only through additional x-ray diffraction studies, but also via nuclear magnetic resonance techniques or other spectroscopic approaches. The role of bound water could be explored through thermogravimetric analysis. With regards to the final product, durability studies would be of interest including both water absorption studies over extended wetting and drying cycles as well as environmental durability studies through leaching investigations. As the results of these explorations prove promising further life cycle assessment studies should be performed that account for the availability of these materials and a detailed assessment of the scaled environmental impact.

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This manuscript is dedicated to the memory of Professor Hamlin Jennings, pioneer in cement science (1946-2015), his coauthors are grateful for his wisdom, enthusiasm and guidance.

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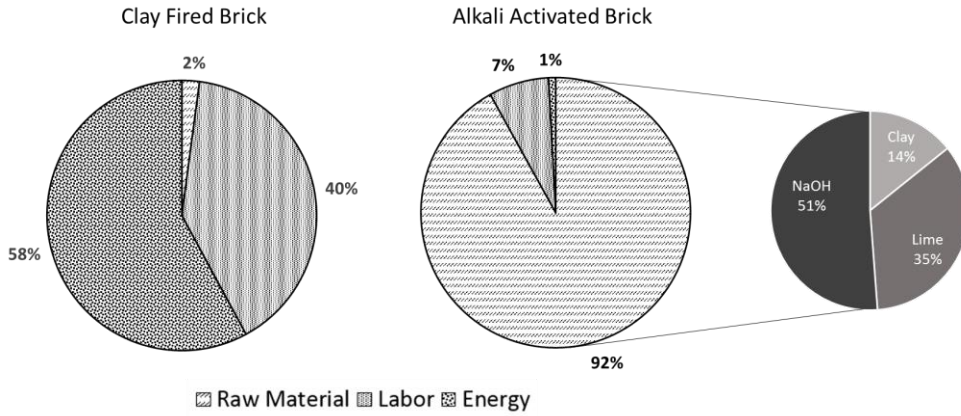
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Appendix

Figure A1: The upper three maps present the location of the city of Muzaffarnagar within India. The bottom figure is a google earth image showing the location of the three paper mills where boiler ash samples were obtained.



Figure A2: A breakdown of the costs associated with the production of fired clay bricks and alkali-activated bricks.



Production Costs		
MATERIALS		
Units/day	10000	
Operation days/month	26	
Units/month	260000	
Material cost/unit	2.648	INR
Material cost/month	688507.8	INR
LABOR		
Skilled Laborers	1	
Unskilled Laborers	7	
Skilled Labor Rate	12000	INR/month
Unskilled Labor Rate	6000	INR/month
Labor cost/month	54000	INR
Labor cost/brick	0.208	
ENERGY		
Units / 8 hr. shift	35	(1unit=1 kWh)
Number of shifts/day	1	
Cost/unit	7	INR/kWh
Cost/day	245	INR
Operation cost/month	6370	INR
Operational cost/brick	0.0245	
TOTAL		
Cost/month	748878	INR
Cost/brick	2.88	INR

Materials	Cost (INR/ton)
Ash	0
Clay	1000
Lime (80% purity)	4850
NaOH (pellets)	30000

Figure A3: Tables showing the materials costs in Muzaffarnagar and the breakdown of the production costs for one alkali activated brick.

Table A1: Parameters explored in the mix design

Ash: Clay	NaOH	Temp	L/S
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60/30, 70/20, 80/10, and 90/0.	0 M, 2 M, 5 M	30, 100	0.4, 0.45, 0.5, 0.55
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Table A2: Life cycle inventory for the LCA of alkali-activated brick

Item	Quantity	Assumed inventory (all market for alloc def, U)
NaOH: Water	0.926 kg	Tap water, at user (ROW)
NaOH: Sodium hydroxide	0.074 kg	Sodium hydroxide, without water 50% solution state (GLO)
Clay	0.310 kg	Clay {GLO}
NaOH solution 2M	0.506 kg	See first two rows
Lime	0.155 kg	Lime, hydrated, loose weight {GLO}
Electricity	0.0044 kWh	Electricity, high voltage {IN} electricity production, hard coal
Transport	0.01508 tkm	Transport, freight, lorry 3.5-7.5 metric ton, EURO3 {GLO}

Table A2: Life cycle inventory for the LCA of fired clay brick

Item	Quantity	Assumed inventory (all market for alloc def, U)
Clay	2.005 kg	Clay {GLO}
Water	0.46 kg	Tap water, at user (ROW)
Heat	2.44 MJ	Heat, central or small-scale, other than natural gas {RoW} heat production, hard coal briquette, stove 5-15kW