

BENEFICIAL REUSE OF REFINERY SPENT CAUSTIC SOLUTION IN ALKALI-ACTIVATED INFRASTRUCTURE MATERIALS

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Abstract

Over the past half-century, societal awareness of the detrimental effects of environmental pollution resulting from human activity has increased, and this newfound awakening has given an impetus to research on sustainable construction materials. In particular, research efforts are aimed at developing greener alternatives to portland cement, production of which accounts for 5-10% of global anthropogenic carbon dioxide emissions. Alkali-activated materials, which can be produced almost entirely from industrial by-products, have received considerable interest in this regard. Previous studies on waste-based alkali-activated materials have focused almost exclusively on reuse of solid waste (e.g., fly ash, slag); however, these materials require a highly-concentrated solution of alkali-hydroxides and/or alkali-silicates (typically 8-14M) to catalyze geopolymerization. Although the environmental and economic impact associated with consumption of excessive amounts of virgin alkalis and safety concerns associated with handling highly-alkaline solutions could substantially threaten the scalability of these materials, little work has been aimed at addressing these issues. In the current study, aqueous alkaline waste from industrial caustic washing of hydrocarbons (deemed unsuitable for regeneration or purification processes due to the presence of contaminants) was used as an activating solution for alkali-activated concrete in place of a conventional virgin alkali solution. The impact of impurities in the waste activator, particularly organics and heavy metals, on mechanical properties, temporal reactivity, mineralogy, and thermal stability of the materials was assessed. Results suggested that this toxic waste stream, for which there are currently few options available for beneficial reuse, could be used to produce alkali-activated materials in place of virgin alkalis without compromising performance.

Keywords:

Alkali-activated materials, sustainability, slag, post-industrial waste

1 INTRODUCTION

Alkali-activated materials (AAMs) have been widely recognized in the literature as a sustainable alternative for ordinary portland cement concrete [Provis 2015, Duxson 2007, McLellan 2011, van Deventer 2012]. Generally, the binding component of these materials (i.e., paste) is fabricated by mixing a fine aluminosilicate powder with a highly-concentrated solution of alkali-hydroxides and/or alkali-silicates. Reduction in environmental impact of AAMs is most commonly achieved through utilization of post-industrial waste materials such as fly ash or slag as the fine aluminosilicate powder component. While this approach is undoubtedly advantageous from an environmental and economic standpoint, the environmental footprint and cost of the activating solution remains a threat to the scalability of AAMs [Duxson 2007, Habert 2011]. Though many studies

have focused on use of solid waste materials to produce sustainable ACMS, little work has been done to identify suitable waste streams to replace the aqueous activator component. In this study, a hazardous refinery spent caustic solution (deemed unsuitable for regeneration or purification processes due to the presence of contaminants) was used in place of a typical virgin alkali solution as an activator for alkali-activated slag mortar in order to produce a more sustainable binder using 100% post-industrial waste materials.

2 MATERIALS

2.1 Activating solutions

Waste alkali-activator (WAA) was obtained from Veolia, a waste/ water management and energy services company. The WAA (Fig. 1), a byproduct of

industrial manufacturing processes, was yellow in color and exhibited a strong sulfide odor. A dense layer of organic material was observed floating on the surface of the liquid waste, which exhibited a viscosity similar to water. Veolia Lab analyzed the WAA using inductively coupled plasma emission spectroscopy (ICP-ES), which confirmed the presence of 0.02 ppm chromium and 62 g/L potassium [equivalent to ~8% w/w (~1.42M) as KOH]. Thus, due to the presence of organics and heavy metals, this particular waste stream was deemed unsuitable for typical regeneration or recycling processes. Upon receipt to our laboratory, WAA was further analyzed by titration to confirm the amount of KOH present in WAA. Titrations were performed in triplicate for WAA with 0.37M HCl and phenolphthalein as the pH indicator; it was determined that WAA contained $1.22\text{M} \pm 0.04\text{M}$ KOH. Finally, the alkalinity was verified using pH strips, which showed that WAA possessed a pH of approximately 14.



Fig. 1: Waste alkali-activator (WAA) as-received from Veolia.

In order to examine the effects of chemical impurities on the performance of WAA in alkali-activated infrastructure materials, it was necessary to produce a pure KOH activating solution to serve as a control to WAA. Virgin alkali-activator (VAA) was produced by dissolving 70.1 g/L KOH (Sigma-Aldrich, St. Louis, MO, United States) in distilled, deionized (DDI) water to yield a pure 1.25M KOH solution. VAA solution was prepared at least 24 hours prior to mixing to allow the solution to reach equilibrium at ambient laboratory temperature (~23 °C). All experiments were performed in parallel with WAA and VAA.

2.2 Powdered materials

The binders examined in this study were fabricated from GGBFS and OPC. The GGBFS (Birmingham, AL, USA) conformed to ASTM C989 specifications and the OPC (St. Genevieve, MO, USA) conformed to ASTM C150 Type I and Type II specifications [ASTM 2015]. The oxide compositions for GGBFS and OPC are provided in Tab. 1.

2.3 Fine aggregate

Graded standard sand conforming to ASTM C778 [ASTM 2013] and C109 [ASTM 2016] specifications (Gilson Company, Inc., Lewis Center, OH, United States) was used for all mortar mixtures.

2.4 Sample preparation

Four different binder types were examined in this study:

- OPC – prepared by mixing OPC with DDI water;
- Slag: non-activated (S-NA) – prepared by mixing GGBFS with DDI water;
- Slag: virgin alkali-activated (S-VAA) – prepared by mixing GGBFS with VAA;

Slag: waste alkali-activated (S-WAA) – prepared by mixing GGBFS with WAA.

Tab. 1: Ordinary portland cement (OPC) and ground granulated blast-furnace slag (GGBFS) oxide compositions; LOI: Loss on ignition.

Oxides	Mass (%)	
	OPC	GGBFS
SiO ₂	21.66	40.92
Al ₂ O ₃	2.86	8.32
CaO	63.96	34.12
Fe ₂ O ₃	4.47	0.44
TiO ₂	0.19	0.23
MgO	2.69	10.99
Na ₂ O	0.09	0.14
K ₂ O	0.24	0.42
P ₂ O ₅	0.11	0.04
SO ₃	2.74	2.72
LOI	0.81	0.35

Both paste (i.e., powdered material and water or activating solution) and mortar (i.e., sand, powdered material, and water or activating solution) samples were fabricated for each binder type. Paste samples were prepared by stirring 25 g of OPC or GGBFS with 12.125 g of DDI water, VAA, or WAA by hand for two minutes such that the solution-to-powder (s/p) ratio was 0.485. 2 inch mortar cubes were prepared according to ASTM C305 [ASTM 2014].

3 METHODS

Paste samples were analyzed using isothermal calorimetry, X-ray diffraction (XRD), and thermogravimetric analysis (TGA); mortar samples were tested using compressive strength. All experiments were performed on triplicate samples except for isothermal calorimetry, which was performed on duplicate samples.

3.1 Isothermal calorimetry

Isothermal calorimetry was utilized to compare the cumulative heat generated by each binder type, which can be used to approximate the reaction rate. Immediately after mixing, approximately 30 g of paste sample were transferred to a 20 mL glass ampoule and inserted into a TAM air for testing at 23 °C for a duration of 48 hours.

3.2 TGA

TGA was utilized to compare the thermal decomposition behavior of the pastes. Following mixing, paste samples were cast in cylindrical molds and cured at 23 °C and 95% relative humidity (RH) for 24 hours, at which time the molds were removed. The samples were then returned to the 95% RH environment for curing until they reached 28 days of age. The pastes were crushed with a mortar and pestle and passed through a No. 325 sieve such that the resulting powder was finer than 45 μm . TGA was performed using a Netzsch STA 449 F1 Jupiter Thermal Analyzer (Burlington, MA, United States). For each sample, approximately 40 mg of ground powder was inserted in an aluminum oxide (Al_2O_3) crucible into the TGA for measurement. Highly-pure N_2 was used as the purge gas. The temperature was increased from ambient laboratory temperature to 1000 °C at a rate of 10 °C/min.

3.3 Compressive strength

Generally, unconfined compressive strength testing of the 2 inch mortar cubes was performed at 3, 7, and 28 days according to ASTM C109 [ASTM 2016] using an Instron Industrial Series DX Model Static Hydraulic Universal Testing System (Norwood, MA, United States). Following mixing, mortar cubes were cured initially at 23 °C and 95% RH for 24 hours, at which time the molds were removed (exception: S-NA). The cubes were then returned to the 95% RH environment for curing until the time of testing. S-NA cubes remained in their molds in the 95% RH curing environment at 23 °C for 28 days and demolded immediately prior to testing.

4 RESULTS AND DISCUSSION

4.1 Isothermal calorimetry

Results of isothermal calorimetry for OPC, S-NA, S-VAA, and S-WAA pastes are presented in Fig. 2.

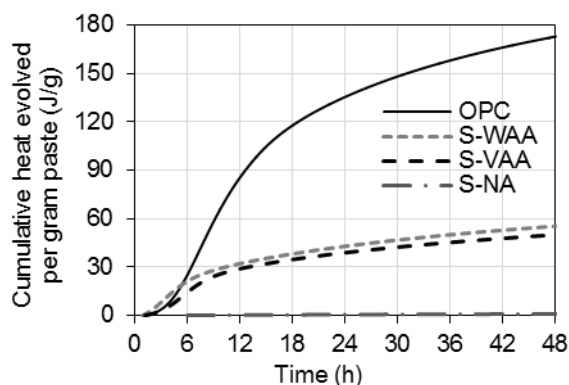


Fig. 2: Cumulative heat evolution (averaged from duplicate samples) for ordinary portland cement (OPC), slag: non-activated (S-NA), slag: virgin alkali-activated (S-VAA), and slag: waste alkali-activated (S-WAA) pastes at 23 °C for 48 hours.

The beginning of the acceleratory period, where the rate of heat generation increases rapidly, occurred within 3 h after mixing for OPC, S-VAA, and S-WAA. OPC generated the greatest amount of heat over 48 h; however, it should be noted that the OPC sample cannot be directly compared to the others since the mechanisms of hydration for portland cement and slag differ considerably [Glukhovskiy 1980, Lamond 2011]. Thus, comparative analysis can only be performed for

the slag-based pastes (S-NA, S-VAA, and S-WAA). From Fig. 2, it can be seen that the isothermal calorimetry profiles for S-VAA and S-WAA were similar with respect to the total quantity of heat evolved and the rate of heat evolution over 48 h. This indicated that WAA solution was able to promote reactivity in slag paste with similar efficacy as VAA solution. Contrastingly, S-NA exhibited no discernible heat generation for 48 h, indicating that reactivity was severely retarded as is typical for a slag binder without an activating agent [Kim 2011].

4.2 TGA

Fig. 3 shows results of TGA for OPC, S-NA, S-VAA, and S-WAA pastes. For each sample, mass loss observed up to 100 °C could be attributed to evaporation of free water inside the pore structure. Then, S-NA, S-VAA, and S-WAA continued to exhibit a steady mass loss up to 1000 °C; this could be attributed to evaporation of bound water from various hydrated phases in the range of 100-500 °C, and to loss of CO_2 from carbonated phases in the range of 500-1000 °C [Salman 2015]. Mass loss in OPC from 100-250 °C is attributable to loss of bound water from calcium silicate hydrate (C-S-H) gel and ettringite, while mass loss in the range of 450-550 °C is attributable to loss of bound water from calcium hydroxide. Finally, mass loss from 700-900 °C is attributable to decarbonation of calcium carbonate [Zhang 2011].

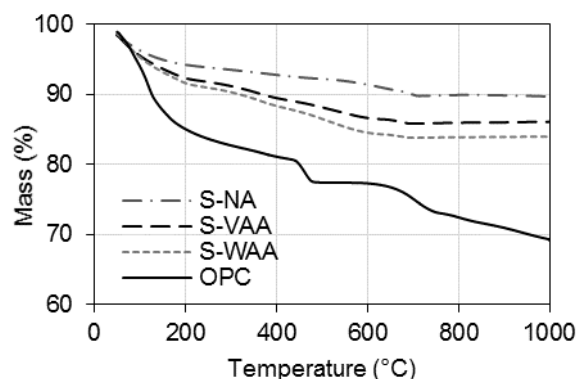


Fig. 3: Thermogravimetric analysis (TGA) of ordinary portland cement (OPC), slag: non-activated (S-NA), slag: virgin alkali-activated (S-VAA), and slag: waste alkali-activated (S-WAA) pastes.

From Fig. 3, it can be seen that S-VAA and S-WAA exhibited similar decomposition behavior up to 100 °C, indicating that impurities in the WAA solution did not substantially alter the phase composition in S-WAA as compared to S-VAA. Further, the slag pastes S-NA, S-VAA, and S-WAA each exhibited mass loss of less than 20% in the temperature range examined while OPC exhibited mass loss of greater than 30%. This indicated that the slag pastes possessed greater thermal stability than OPC paste.

4.3 Compressive strength

Results of compressive strength testing for OPC, S-NA, S-VAA, and S-WAA are displayed in Fig. 4. Testing at 3 and 7 days could not be performed on S-NA because the mortar cubes were too soft to demold. OPC mortar cubes exhibited the greatest compressive strength at 3, 7, and 28 days. While the strength of the slag mortar was substantially lesser than that of OPC mortar, each slag mortar achieved compressive strength in excess of 2000 psi at 28 days, which is

sufficient for many construction applications. The same trend observed in isothermal calorimetry and TGA data was evident with regard to compressive strength data; S-VAA and S-WAA mortar exhibited similar compressive strengths at each testing age. This indicated that impurities in WAA solution did not substantially influence the mechanical performance of the bulk material.

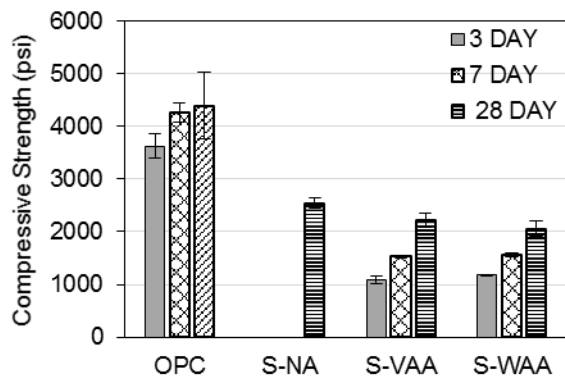


Fig. 4: Compressive strength for ordinary portland cement (OPC), slag: non-activated (S-NA), slag: virgin alkali-activated (S-VAA), and slag: waste alkali-activated (S-WAA) mortar cubes at 3, 7, and 28 days; error bars represent the standard deviation of triplicate samples.

5 CONCLUSIONS

In this study, a refinery spent caustic solution was utilized as an activating solution to fabricate an alkali activated slag binder composed of 100% post-industrial waste. Isothermal calorimetry was employed to verify that the temporal reactivity of slag activated with waste alkali-activator (S-WAA) was comparable to slag activated with a typical virgin alkali-activator (S-VAA). Thermal stability was analyzed using thermogravimetric analysis (TGA), which showed that both S-VAA and S-WAA were more stable than ordinary portland cement (OPC) paste. Finally, unconfined compressive strength testing showed that while OPC mortar possessed greater compressive strength, S-VAA and S-WAA each obtained in excess of 2000 psi compressive strength at 28 days which is acceptable for a variety of construction applications. However, future work should include optimization of mix designs to achieve greater strength to more broadly acceptable values for the field (ideally >3000 psi). One way this could be achieved is through partial replacement of slag with an aluminosilicate source (i.e., fly ash, metakaolin) to create a blended system. Incorporation of an additional aluminosilicate source might encourage geopolymerization, improving the ordered nature of the final material. Another important area for future work will be to determine the potential of harmful compounds (i.e., heavy metals, organics) to leach out from waste-activated materials.

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