Green Cementitious Systems Based on Off-Spec Fly Ash

M. Kozhukhova[1,2] , R. Wittenberg[1,2], K. Sobolev[2]

[1]*Ramboll, 234 W Florida St, Milwaukee, 53204, WI, USA*
[2] *University of Wisconsin-Milwaukee, 3200 N Cramer St, Milwaukee, 53211, WI, USA*

Keywords: sulfate attack, spray dry absorber ash, harvested fly ash, concrete durability

INTRODUCTION

The amount of coal combustion by-products (CCPs) generated by power utilities is significant and anticipated to grow [1]. However, more than 30% of all generated CCPs in the USA are considered "off-spec" because they do not meet the ASTM C618 specification and are not utilized [2]. For example, CCPs with high carbon content and spray dryer absorber ash (SDA) containing high concentrations of gypsum compounds represent two primary off-spec CCP materials that need to be addressed. The development of innovative binders based on off-spec fly ash represents an opportunity for efficient and sustainable use of by-products.

To address the challenge with broader use of SDA, a ternary cementitious system consisting of portland cement combined with two types of off-spec ash is proposed. This cementitious system is based on SDA with high amounts of calcium sulfate/sulfite (CS) phases combined with harvested ash used as a pozzolanic component. Earlier studies confirmed that combining Class F fly ash with by-products containing calcium sulfates favorably affects durability performance [4]. Such composites demonstrated a very low degree of deterioration after long term exposure in a seawater environment. A feasibility study of the use of CCP with CS in road construction using Roller-Compacted Concrete (RCC) demonstrated improved workability and strength performance [5-7].

EXPERIMENTAL STUDY

The reported experimental study included an investigation of the effects of two off-spec CCPs, which were freshly collected SDA and harvested ash (HA) from landfills provided by the local power utility. These were used at up to 50% and 18%, respectively. Silica fume (SF) supplied from Elkem Microsilica was used at 7% as a model pozzolan material. Portland cement (PC) Type I/II supplied by LafargeHolcim, as well as chemical admixtures were used for the preparation of cementitious systems.

The oxide composition revealed that the SO_3 amount in SDA is 12.6%, which is almost double of that accepted by ASTM C618 for coal ash recommended for use in commercial concrete applications. The percentage of unburned carbon represented as LOI content was 10.4%, which is considerably higher than the 6% limit recommended by the ASTM C618. The SDA consists of spherical particles of fly ash of smaller size and tabular and prismatic particles of calcium sulfates and sulfites represented by minerals of bassanite ($CaSO_4 \cdot 0.6H_2O$), anhydrate ($CaSO_4$) and hannebachite ($CaSO_3 \cdot 0.5H_2O$) (Figure 1).

Five different mix designs (M1 – M5) were prepared with the following proportions of PC, SDA, HA and SF: M1, 100% PC used as a reference; M2, 60:40 PC:SDA mix; M2, 50:50 PC:SDA mix; M4, 50:43:7 PC:SDA:SF mix; M5, 50:32:18 PC:SDA:SF mix (Table 1).

For the compressive strength investigation, 50-mm cube mortar samples were cast, cured in accordance with ASTM C 109 and ASTM C305 and then tested at the age of 3, 7, and 28 days. The W/C of 0.35 and S/C of 1 were kept constant for all mixes. For the sulfate resistance study, prismatic mortar samples with a size of 25×25×285 mm were used. The prisms were cast and cured using the same standard procedure. The length change of investigated mortars due to expansion was measured and calculated according to ASTM C157 and ASTM C1012. The length change measurements to determine a sulfate expansion was performed for the test samples at the age of 7, 28, 90, and also 200 days.

Table 1. Mix design proportions

Mix ID	Cementitious components (%)				Amount of SO_3, %
	PC	SDA	HA	SF	
M1	50	-	-	-	2.7
M2	60	40	-	-	7.6
M3	50	50	-	-	3.8
M4	50	43	-	7	6.7
M5	50	32	18	-	6.6

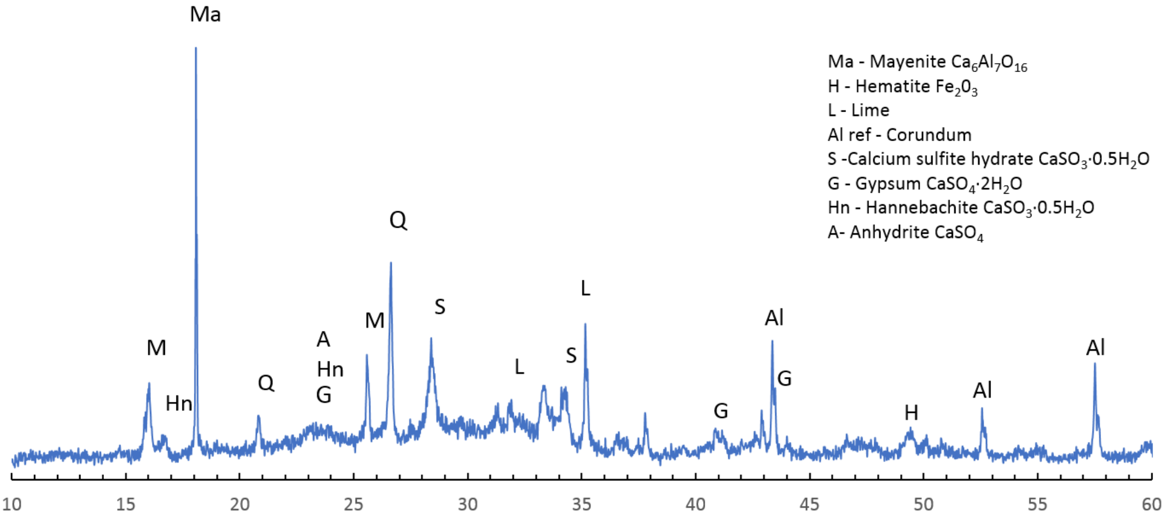

Figure 1. The XRD for SDA material used in the study

RESULTS AND DISCUSSION

The effect of partially replacing up to 50% of PC with a combination of SDA and HA (or SF) on compressive strength of mortar cubes demonstrated a positive trend of strength development for all tested compositions (Figure 2). Although the compressive strength for reference samples M1 developed steadily with time, all SDA containing samples (M2-M5) with the replacement of up to 50% of PC had about 12% strength reduction at all ages.

Mortars M4 and M5 with a pozzolanic component demonstrated considerably lower strength at 7 days, but at 90 days M5 gained strength of 83.5 MPa. Similarly, M4 mix with SF reached a 90-day strength of 106 MPa overperforming all tested mortars. Here, the pozzolanic reaction between the amorphous SiO_2 in HA and SF and portlandite can be responsible for the strength enhancement at later ages.

The evaluation of expansion data demonstrated a positive trend for all experimental mortars (Figure 3). The samples M4 and M5 with pozzolanic component compensating for SDA had a minimal total expansion of 0.020% and 0.028%, respectively vs. expansion of reference composition M1 of 0.043% over the tested period. The M2 with 40% of SDA, demonstrated 0.040% expansion, which is very close to that of the reference M1. On the contrary, the highest expansion of 0.054%. was observed for the M3 mortar prisms with 50% SDA. By the age of 200 days, all mortars satisfied the requirements for severe sulfate environment, except for the sample M3, which, after 150 days of the exposure, passed the minimal acceptance limit for moderate sulfate exposure.

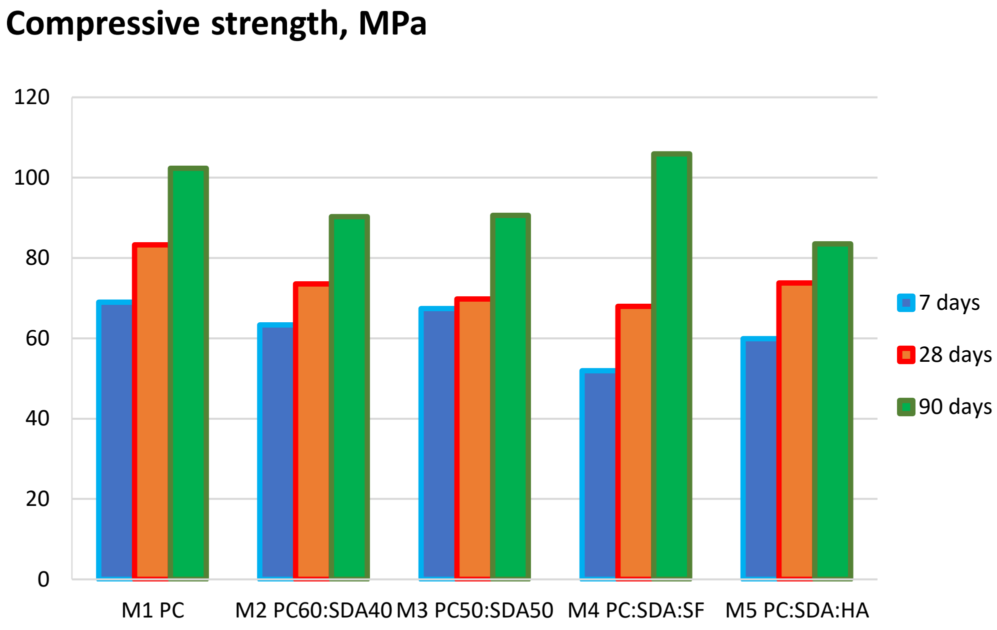

Figure 2. The Compressive Strength of Mortars

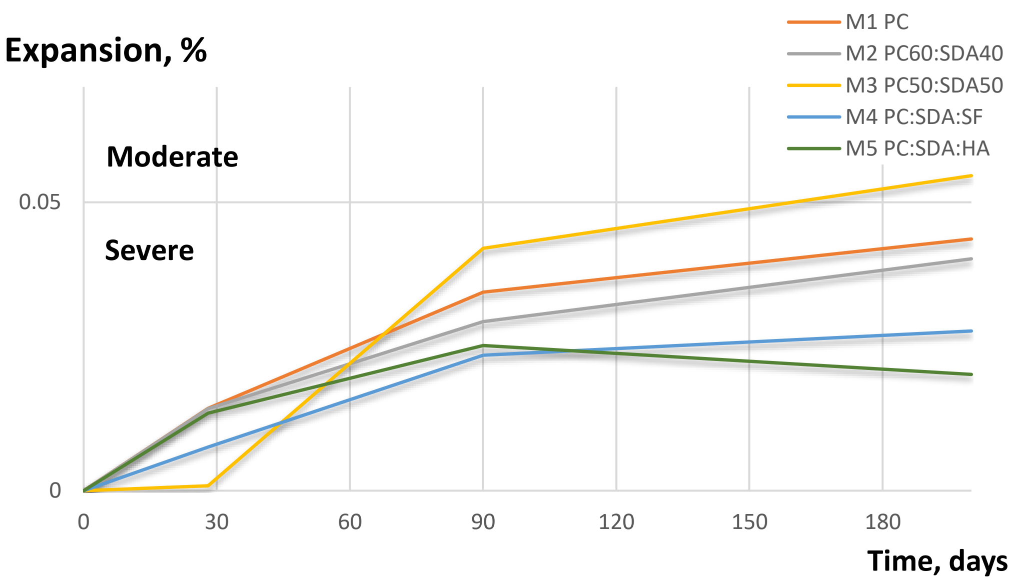

Figure 3. Sulfate Resistance of Investigated Compositions

CONCLUSIONS

The experimental results demonstrated a potential for application of two off-spec CCP, such as spray dry absorber fly ash and harvested ash in cement compositions at up to 50% replacement rates. Ternary blends with equivalent strength and long-term durability performance characteristics as required for conventional applications were developed. Strength and sulfate resistance results support the concept that combining SDA material with a pozzolanic component may help to offset the unfavorable effects of high concentrations of CS. Besides, harvested unprocessed pozzolanic fly ash from landfills and impoundments can be used in proposed systems. Bench-scale test results provide strong support for the application of ternary binder systems using conventional construction techniques that could streamline large scale applications in areas such as transportation, building materials, and environmental applications.

The critical objectives for these binder systems are to reduce the need for landfilling of off-spec CCP materials and turning waste into a commercially viable product. The opportunity for significant replacement of portland cement in concrete applications offers real benefits for the reductions in carbon emissions and efficient industrial waste utilization, which makes this approach green and sustainable. The replacement of portland cement could also have a significant economic benefit because of the high cost of portland cement that would be supplemented by lower-cost CCP materials.

Further bench and pilot-scale studies are underway to assess the long-term durability concerning sulfate resistance, freeze-thaw resistance, and field trials in pavement applications.

REFERENCES

[1] American Coal Ash Association, 2015 "Production of coal combustion products in the U.S."

[2] EPRI, 2007 "A review of literature related to the use of spray dryer absorber material-production, characterization, utilization applications, barriers, and recommendations," TR1014915.

[3] Shekhovtsova, J., Zhernovsky, I., Kovtun, M., Kozhukhova, N., Zhernovskaya, I., Kearsley, E.P., 2018 "Estimation of fly ash reactivity for use in alkali-activated cements - a step towards sustainable building material and waste utilization," Journal of Cleaner Production. Vol. 178. 22–33.

[4] Magallanes-Rivera, R.X., Escalante-García, J.I., 2014 "Anhydrite/hemihydrate-blast furnace slag cementitious composites," Construction and Building Materials. Vol. 65. 20–28.

[5] Jansen, T., Wittenberg, R., Sobolev, K., 2019 "Multi-layer design approach for the utilization of high-volumes of off-spec coal combustion products in transportation infrastructure," EPRI Ponded Ash Workshop: Harvesting and Beneficiation of Coal Combustion Products.

[6] Wittenberg, R., Kozhukhova, M., Jansen, T., 2019 "Multi-layer pavement design approach for effective utilization of off-spec coal combustion products," WOCA-2019.

[7] Jansen, T., Wittenberg, R., Kozhukhova, M., Sobolev, K., 2019 "Demonstration project: Roller Compacted Concrete pavement with high volumes of off-spec coal ash," WOCA-2019.