Waste Reduction Partners
Land-of-Sky Regional Council

Outdoor Patio Stones from Coal Ash Products

by

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Executive Summary

The development of stepping stones and architectural tiles from coal ash, combined with other byproduct materials, was explored. Fly ash and bottom ash from the Carolina Ash Products (CAP)[1] program were combined with off grade acrylic latex and various other wastes (both from mining operations and industrial uses) and molded into forms for outdoor use as stepping stones or decorative tiles. A range of additional components was investigated, including waste gypsum, feldspar, and perlite. Surplus organic dyes and unused inventories of pigment/latex dispersions, intended for latex paints, were also screened for use. The purpose was to combine these materials in search of the best composite for ease of formulation and product performance. Various shapes, sizes, and configurations of molded pieces were prepared with major emphasis on 12" x12" x1" stepping stones for placement in a lawn to form a walking pathway. Though no formal testing for compressive or tensile strengths was performed on these squares, they appeared to be adequate for the intended outdoor application. Among their attributes are low densities (30 – 40 % lighter weight than commercial concrete pavers), good stability after being submerged in water, and retention of structural integrity after drying. Some of these 12"x12"x1" examples, both black and pigmented (red, yellow, blue, and green), are now being use-tested alongside commercial concrete (12"x12"x2") patio pavers. These squares have functioned well as a normal walking pathway in a residential lawn over the past 9 months, including rainy and freezing weather. Use-testing is continuing.

If this project were pursued as a commercial venture to manufacture green pavers (up to 85% waste and reused materials), a hydraulic pressing would be necessary to achieve required ASTM compressive strengths. The tensile strength is sufficient for use as decorative tiles.

Introduction

The accumulation of large quantities of underutilized byproducts from the following sources - industrial processes, coal-fueled energy generation, and waste streams from mining operations in Western NC - gave impetus to this product-development project. The materials used in these experiments were those formerly sent to landfills, but had potential use in value-added secondary applications. The purpose of this work was to explore those possibilities for reuse and to formulate products from these waste/byproduct materials.

A variety of composites was created by mixing different combinations of these byproduct inventories and casting them into simple forms to be used as outdoor stepping stones, decorative tiles, or patio pavers. The byproducts used for this study are listed in the accompanying Table of Materials. The origins of the byproducts and the quantities available are cited along with additional comments for each item.

TABLE OF MATERIALS

Waste/Byproduct	Supplier	Amount Generated in NC	Comments
Fly ash (Fine, powdery component of coal ash mixture; most voluminous fraction of raw coal ash)	Coal-burning boiler operations; Progress Energy, Duke Energy, private cogeneration plants.	Millions of tons annually; large inventories in private monofill cells.	Utilization opportunities needed most urgently for fly ash.
Bottom ash (Lower volume, more granular aggregate, larger sized particles in raw coal ash)	Coal-burning boiler operations; same sources as above.	Thousands of tons annually.	Low-carbon bottom ash can be used directly in concrete block manufacture.
Gypsum (Crude mix of calcium sulfate/ calcium sulfite from Progress Energy lime scrubbers)	Progress Energy Skyland Plant	Millions of tons annually	Current supplies already contracted to out-of-state cement plant.
Perlite fines (Bag house waste from Perlite manufacture)	Miller Perlite, Morganton, NC	Multi-ton supplies	Currently land-applied for soil stabilization.
Feldspar tailings (granular, off-color, impure stream from mining operation)	KT Feldspar, Spruce Pine, NC	Multi-ton supplies	Has been found useful for green brick manufacture.
Acy acrylic emulsion [~55% of butyl acrylate/ methyl methacrylate (BA/MMA) in water]	Rohm & Haas	Off-grade batch produced occasionally; drum quantities available on irregular basis.	Used primarily as binder for latex paints.

TABLE OF MATERIALS (cont.)			
Waste/Byproduct	Supplier	Amount Generated in NC	Comments
Numerous FDA approved, water-soluble organic dyes.	Ecusta Business Development	Research stock room leftovers, after Ecusta plant closed.	Small quantities, used only for testing feasibility of dyeing tiles.
Rhoplex E 330 acrylic polymer dispersion	Rohm & Haas	Batch, which does not meet all release quality specifications, occurs only irregularly. Availability of off-grade product must be checked frequently and in advance of needs.	Recommended for modifying Portland cement compositions. Has good compressive strength, enhanced elasticity.
Roplex 2500 Emulsion	Rohm & Haas	Off-grade batch generated only infrequently. Must check well in advance of needs for availability.	Designed for tough, water-resistant masonry paints and primers.
Rovace 661 Emulsion [Butyl acrylate/vinyl acetate (BA/Vac) copolymer at ~55% dispersion in water]	Rohm & Haas	Off-spec material available only on irregular basis.	High m.w. film former, intended for use as binder in latex paints.
Dye dispersions in Acy latex: BASF HI-Fast N Blue; BASF HI-Fast N Red; BASF Aquafine Yellow	BASF	From limited surplus inventory in storage at RPI, Davidson ,NC.	Concentrated dye dispersion, used to produce latex paints, formerly marketed by RPI. These dispersions are available from BASF.
Scrap plastic-coated wire clippings. Wire stems from bunches of artificial flowers.	Local cemeteries, which discard weathered artificial flowers from gravesites.	Variable amounts available, depending on normal trash collection schedules.	Cemetery management generally glad to get rid of these, rather than haul to landfill.

Formula Development

Initial experiments focused on using only waste stream materials or underutilized industrial byproducts; first quality commercial components were avoided in the mix formulations. Accordingly high proportions of fly ash (~60%), smaller amounts of bottom ash (~10%), and varying additions of scrubber-quality gypsum (5-10%) were the prominent ingredients. The only binder tested in these early trials was Acy latex (generally 25-30% of the total mix). The mixtures were easily scooped into small forms, such as empty tuna and sardine cans, which had been lined with aluminum foil and greased lightly with vegetable shortening. Curing at room temperature or in a laboratory oven at 150-170 deg. F. gave firm blocks/tiles, which demolded easily. All fly ash-containing blocks were dark gray in color, but could be decorated by adding small patches of dyed mixtures, which used no fly ash. Colored inserts, which used just gypsum, perlite, Acy latex binder, plus a water-soluble, ionic dye could be molded in the wet surface. These small round or rectangular configurations were attractive, very light-weight, and reasonably stable. However, for larger forms, such as stepping stones, a tough composite with higher compressive strength and tensile strength was needed.

Optimizing Latex Mix for Outdoor Use

Helpful conversations with a polymer specialist[2] at Rohm & Haas, who has extensive knowledge of architectural and functional coatings, and with the paint manufacturers[3], who supplied the Acy latex, suggested the use of low-cost Portland cement in the mix formulation. This strategy promised to raise the compressive and tensile strengths of the larger stepping stone configurations through cementitious bonding reactions and reduce the amount of latex needed for good structural integrity. Both these adjustments would also lower the over-all unit cost, while still preserving the very “green” classification of this home improvement product. Rohm & Haas furnished test samples of some additional acrylic polymer resins[4], more suited for use with concrete and masonry products. A series of experiments was carried out, using these materials to produce examples of stepping stones in the approximate size, 12”x12”x1”. These were formed in a homemade frame, also fashioned from scrap materials..

The scope of the project at this point was to generate light-weight (low density) stepping stones in dark gray ash colors, as well as dyed versions, which contained no ash. The dyed stones, instead, used waste feldspar and waste perlite fines (both white in color) as the medium and fine aggregates, respectively. Coarse aggregates, crushed to about one-half inch angular sizes, were from earlier prepared and reground ash/concrete/latex stepping stones for the gray version and from white feldspar mining residues for the colored stepping stones. The BASF dyed latex dispersions, supplied by RPI, were used to create red, yellow, blue, and green stepping stones; these dyes were also used to design colored features, embedded in the surface of the stones for decoration.

The dark gray fly ash stepping stones were made with both low-carbon fly ash (<3% carbon; very acceptable for ready-mix concrete products) and with high-carbon fly ash (LOI* 13.7%; high carbon content is generally detrimental to concrete products). The high-carbon ash was used only when processed ash, with the carbon removed, was no longer available. These versions were exceptionally light-weight, with densities in the range of 70-85 lb/cu ft. The dyed feldspar stones had slightly higher densities, in the range of 90-95 lb/cu ft.

In an effort to improve the compressive and tensile strengths, strands of plastic-coated wire scrap were embedded in a few of the final stepping stones.

All of these examples have been set out in a residential lawn to serve as a well-used pathway. For comparison, a number of commercial 12”x12”x2” concrete pavers from a home improvement store have been set alongside the experimental examples. All of these have supported much foot traffic throughout a 9-month time period, which included rainy and freezing weather conditions. Thus far, both sets of stepping stones have performed well.

A typical formulation for each of the dark gray and colored varieties of stepping stones is shown in the Experimental Section, page 7. Photos of some of these examples are shown in the Appendix.

<u>Directions for a Future Commercial Product</u>

It is well-known that ram-pressed concrete, containing fine and coarse aggregates and Portland cement as binder, exhibits superior compressive strength. To demonstrate that technique with these materials, a small 4” diameter, 1.2” thick test block was made from fly ash, bottom ash, Portland cement, and Acy latex. This blend was pressed in a mold made from a 4” inner diameter cut-off steel pipe; hydraulic pressure up to 10,000 psi was applied to the disk. The round disk released easily from the form and had a density of 92 lb/cu ft and was extremely tough. It has been stable to soaking in water and to freeze-thaw cycles. This high-pressure molding would be the advised method for optimizing the product to pass ASTM specifications for concrete blocks. The equipment necessary to explore this technique was not available during the course of this study. Therefore, the examples made from these experiments would be useful for developing a ram-pressed commercial product with the needed hydraulic press equipment. For tile product applications, acceptance criteria are less demanding than for concrete blocks. Using the ash/concrete/latex or feldspar/concrete/latex mixes for tile purposes could probably be accomplished without the need for hydraulic pressing.[5]

* LOI = Loss on ignition: an estimate of the amount of carbon in the sample.

Experimental

The following components were well mixed by hand, and each pasty, dough-like mass was packed into a 12”x12”x1.5” frame, which had been lined with foil and greased with vegetable shortening. Both molds were reinforced with embedded pieces of plastic-coated wire scrap. The surface was flattened with gentle pressure, and smoothed with a trowel. Each surface was decorated with an embossed design of dyed feldspar mix, using a cookie cutter as a stencil.

Fly Ash (dark grey) Stepping Stone				
Component	Wt. (oz.)	Wt (g.)	W/w%	Comments
Fly ash (FA)	80	2272	61.1	13.7% carbon
Portland cement	26	738	19.8	Holsim Type 1
0.5” Aggregate	12	341	9.1	Crushed FA/cement/Acy block made previously
Rhoplex 330 latex	13	369	9.9	Intended for masonry paints
Water	66			To give spreadable mix

Feldspar (colored) Stepping Stone				
Component	Wt. (oz.)	Wt. (g.)	W/w%	Comments
Feldspar, Alaskite	14	397	8.2	Alaskite crushed to 0.5”
Feldspar, granular	112	3180	65.4	Sand-like mining waste stream
Perlite	3	85	1.8	Very fine aggregate
Rhoplex 330 + Aquafine yellow dye dispersion (6ml.)	14	397	8.2	Recommended for modifying Portland cement
Portland cement	28	795	16.4	Holsim Type 1
Water	9			To give spreadable mix

Each form was dried in the oven at 150 deg F. for 3 days. The thin stepping stones demolded easily. Each piece had final dimensions of about 11.3”x11.3”x1.4” after shrinkage and trimming the edges. As expected, the fly ash stone was lighter in weight than the feldspar stone.

The final dry weights of the stepping stones were as follows:

Fly ash stepping stone 6.9 lb   Feldspar stepping stone 9.7 lb

Densities of the stepping stones were as follows:

Fly ash stepping stone 70 lb/cu ft   Feldspar stepping stone 93 lb/cu ft.

Both stepping stones were stable to soaking in water overnight. Water absorption was about 5-6%. Upon redrying, each of the stepping stones returned to its original weight.

REFERENCES

1. Mensah-Biney, Robert, "An Integrated Separation Technology for Processing Coal Combustion By-Products and Organic Bio-Solids," NCSU Minerals Research Laboratory, College of Engineering, March, 2007.

2. Meeting with Mr. Steve Cooper, Sales Service manager, Architectural and Functional Coatings, Technical Services, North American Region, Rohm & Haas Company, Charlotte, NC, plant.

3. Mssrs. Allen and Todd Elliott at RPI, Davidson, NC.

4. Roplex and Rovace Emulsions, listed in Table of Materials.

5. Mishulovich, Alex; Evanko, James l., "Ceramic Tiles from High Carbon Fly Ash," Proceedings: 15th International American Coal Ash Association Symposium on Management & Use of Coal Combustion Products (CCPs), 2003.

Acknowledgements

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Appendix

Photographs of stepping stones from fly ash and feldspar

Above and Left: Gray fly ash tile/dyed feldspar stencils; colored feldspar tiles/dyed stencils

Right: Stepping stones positioned in lawn alongside commercial pavers for use tests

Above and Right: Fly ash and feldspar stepping stones reinforced with plastic coated scrap wire (flower stems)