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An Evaluation of Free-Lime Containing By-products to Produce CCB Grouts for Use in AMD Abatement

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ABSTRACT

In 1995, the Maryland Department of Natural Resources Power Plant Research Program (PPRP) and the Maryland Department of the Environment (MDE) Bureau of Mines initiated the Western Maryland Coal Combustion By-Products (CCBs)/Acid Mine Drainage (AMD) Initiative (the “Initiative”). The Initiative is a joint effort with private industry to demonstrate the beneficial application of CCBs to create flowable grouts to abate AMD from underground coal mines in Maryland.

In 1996, the Initiative undertook the Winding Ridge Project to demonstrate this technology. During the course of the Winding Ridge Project, 5,600 cubic yards of a 100 percent CCB-based cementitious, grout was injected into a small, underground coal mine in western Maryland. The grout consisted of Class F fly ash, flue gas desulfurization (FGD) material, fluidized bed combustion (FBC) ash, and mine water. The FBC ash was used as the source of free lime to activate the cementitious reaction with the fly ash and cause the grout to harden in the mine. The FBC material used in the demonstration project contained approximately five-percent free lime.

The current and future availability of FBC ash in western Maryland is limited and may not be of sufficient volume to support future grout injection projects under the Initiative. Accordingly, PPRP initiated a study in 1997 to identify, evaluate, and analyze other sources of free lime containing by-products that could be used with fly ash and FGD material to form cementitious, CCB-based grouts for AMD abatement in western Maryland. Based on acceptable lime content, consistent physical and chemical characteristics, and cost, lime kiln dust (LKD) was selected as the lime activator for this study. A laboratory program was developed using LKD, fly ash, FGD material and acid mine water to determine optimum grout mixes for high flowability/low strength and high strength grouts. This paper presents the free lime containing by-product study findings and the testing program used to develop optimum grout mixes.

INTRODUCTION

Free-Lime Containing By-product Study

In 1995, the Maryland Department of Natural Resources Power Plant Research Program (PPRP) and the Maryland Department of the Environment (MDE) Bureau of Mines initiated the Western Maryland Coal Combustion By-Products (CCBs)/Acid Mine Drainage (AMD) Initiative (the "Initiative"). The Initiative is a joint effort with private industry to demonstrate the beneficial application of CCBs to create flowable grouts to abate AMD from underground coal mines in Maryland.

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Purpose

This paper describes the identification and evaluation of by-product sources of free lime generated near the coal producing counties in western Maryland (Allegheny and Garrett). The paper presents the results of laboratory testing of the by-products to determine free lime content and other chemistry. The paper also presents the scope of work for a laboratory testing program to develop potential grout mixes. At the time of this writing, Phase I of the laboratory grout testing program is underway.

FREE LIME CONTAINING BY-PRODUCTS

Sources of Free-Lime Containing By-Products

Potential free-lime containing by-products near western Maryland were identified with assistance provided by the MDE, western Maryland coal companies, Internet searches, associations representing the ash, cement, lime, and steel industries. Sources of lime kiln dust (LKD), cement kiln dust (CKD), steel slag aggregate, fiber clay, and paper mill by-products were selected based on the potential for these by-products to contain sufficient free lime to activate cementitious reactions. Twelve free lime containing by-products from seven sources were evaluated under this Study.

Site visits were conducted at each source to observe the process creating the by-product. The grain size (fineness), overall appearance, degree of homogeneity/ heterogeneity, and consistency of each by-product was assessed from visual observations by a geologist. Replicate samples of the by-products (provided by the generators) were submitted to GAI Consultants, Inc. for laboratory tests using ASTM or other standard analytical laboratory methods. These tests included measuring free lime content by the ASTM C25 and C114 methods. Atomic adsorption, spectrophotometry, and ion chromatography methods were used to determine calcium, magnesium, sodium and sulfate concentrations. ASTM D4373 was used to determine the percentage of calcium carbonate in each sample.

Evaluation of Free-Lime Containing By-Products

Each by-product selected for the Study was evaluated for free lime content and chemical and physical characteristics. The key technical criterion evaluated was free lime content. Free lime is the catalyst in the grout that activates cementitious reactions with the pozzolan provided by the fly ash, and possibly the FGD material; therefore, the evaluation of free lime content is essential in by-product selection. Based on the work performed for the Winding Ridge Project, a minimum acceptable free lime concentration in the by-products was established at 5 percent as affirmed by both test methods (i.e., ASTM C25 and C114). Table 1 summarizes the laboratory test results.

The results of the free lime analyses indicate that free lime is present at concentrations greater than five percent in four of the by-products. These by-products are the LKD and lime kiln scrapings from Source 1, fresh CKD from Source 2, and the lime grits from Source 5. The other by-products were found to contain negligible free lime content by one or both test methods; therefore, they were not considered by this Study to be suitable sources of free lime and were eliminated from further evaluation.

The by-products containing the highest concentration of free lime were the LKD and lime kiln scrapings from Source 1. The free lime content for these by-products ranged from 86 to 100 percent. The fresh CKD from Source 2 and the lime grits from Source 3 also contained acceptable, yet lower, concentrations of free lime, ranging from 10 to 30 percent.

High concentrations of sodium, magnesium, and sulfate can lead to excess swelling/expansion of grouts as they cure. As a point of reference, ASTM 618 standard for fly ash in concrete specifies limiting available total alkali (i.e., sodium was the only alkali tested) and magnesium to maximum concentrations of 1.5 and 5 percent, respectively. Low sulfate concentrations are also desirable in by-products because sulfate contributes to the formation of ettringite, which may lead to swelling of the hardened grout. However, some controlled swelling (1 to 3 percent for example), may be desirable for mine sealing applications.

In addition to containing a high concentration of free lime, the LKD and lime kiln scrapings from Source 1 contained negligible amounts (less than 0.03 percent) of sodium, magnesium and sulfate. Negligible amounts of calcium carbonate were also found in these two by-products, which is consistent with high free lime content and affirms that most of the calcium present is available for cementitious reactions. The CKD and lime grits also contained low levels of sodium, magnesium and sulfate, but at concentrations higher than the LKD and lime kiln scrapings. The calcium carbonate concentrations for these by-products were significantly higher than reported for the LKD and lime kiln scrapings, indicating that an appreciable amount of calcium in the material is unavailable for cementitious reactions.

The processes generating the LKD, lime kiln scrapings, and CKD are very consistent; therefore, the by-products generated are expected to have consistent physical and chemical characteristics. The properties of the lime grits depend on the source of lime used in the kiln, therefore, the free lime content and consistency may vary.

Cost Evaluation of Free-Lime Containing By-Products

The technical evaluation indicates that LKD and lime kiln scrapings from Source 1, CKD from Source 2 and Source 5 lime grits contain sufficient free lime to be an activator source for CCB grouts. With the exception of the lime kiln scrapings, each of these by-products were included in a cost evaluation. Lime kiln scrapings were not evaluated based on cost because the annual production of this by-product is only about 1,500 tons. Due to the low production rate, it is unlikely that lime kiln scrapings would be economically feasible to support full-scale injection.

The LKD from Source 1, CKD from Source 2 and lime grits from Source 5 were evaluated for cost-effectiveness by simulating a hypothetical CCB-based grout injection project in Garrett County. This hypothetical project was assumed to require 100,000 tons of grout, with 5 percent free lime content. The costs for this hypothetical project are a function of the price to purchase the by-products from the generator, transportation costs, and the amount of by-product that must be added to the grout to achieve a 5 percent free lime content. As a point of reference, a commercially available source of free lime, quicklime, was considered in the cost evaluation because it is virtually 100 percent lime and technically adequate for CCB grouts.

The most cost-effective by-product is LKD with a cost of about $165,000. The next lowest cost was for lime grits, which is about $245,000. In comparison, the cost using quicklime as the free lime source was $370,000. Quicklime is more than double the cost of LKD, which reflects the higher purchase price of quicklime ($55 per ton). CKD was the most costly by-product evaluated about at $715,000, due primarily to transportation costs (Source 2 is located about 150 miles one-way from Garrett County).

GROUT TESTING PROGRAM

Building upon the work of the Winding Ridge Project, LKD will be tested under laboratory conditions with the Class F fly ash and FGD by-product to determine optimum grout formulae for potential full-scale injection to abate AMD from significant AMD sources in Maryland. The principal objective of the proposed laboratory testing program is to develop CCB-based grout formulae using LKD as the free lime source for use at the Kempton Mine Complex (Kempton) and other significant AMD sources in Maryland. Accordingly, the laboratory goals are as follows:

- Develop a high flowability and low strength grout for mine injection in to areas where flow must occur around obstacles, such as collapsed roofs;
- Develop a high strength grout suitable for use as bulkheads or water diversion structures, and capable of withstanding large hydraulic pressures while maintaining adequate flowability;
- Develop the grouts using conventional concrete mixing equipment, and testing methods (preferably ASTM) to achieve cost-effective field implementation, and easy replication of grout mixes.

Candidate grout mixes will be prepared using Source 1 as the free lime containing activator. The other admixture(s) will be Class F fly ash and FGD by-product from a nearby generating station. Two grout types will be tested. One grout type will contain LKD, fly ash and FGD by-product. The other grout type will only use LKD and fly ash. All grouts will use mine water from Kempton as the mixing water, or synthetic mine water.

Phased Laboratory Testing Program

To achieve the project objectives and goals, a phased laboratory approach consisting of four phases will be implemented. Each phase will include certain geochemical and geotechnical laboratory tests. Table 2 summarizes the recommended laboratory tests for each respective phase of the testing program. The University of Maryland will spearhead the laboratory program under the direction of PPRP.

The objective of Phase 1 is to establish baseline physical and chemical characteristics of the LKD, fly ash, FGD by-product and mine water. The baseline conditions determined in Phase 1 will then be used during subsequent laboratory evaluations to assess changes in the physical and chemical characteristics of the admixtures and grout, and the possible reason(s) for these changes.

The Phase 2 objective is to develop an initial set of trial grout mixes that would cover a probable range of admixture proportions. The grouts should be evaluated based on a limited set of parameters to determine which mixes are most suitable for full scale application. Essentially, Phase 2 will be used to balance grout flowability, workability and strength to identify final grout mixes for detailed evaluation under Phase 3.

The objective of Phase 3 is to determine optimum grout mixes from the candidate trial grout mixes recommended under Phase 2. In Phase 3, flowability, set time, and unconfined compressive strength, will be conducted with additional conditions. Flowability will be evaluated under submerged conditions to more accurately simulate mine environments. Set time will be evaluated in both dry and submerged conditions to compare the behavior of the grout mixes in different conditions. Unconfined compressive strengths will be evaluated for samples cured under submerged conditions and for longer period of time, e.g., 7, 14, 28, 60, 90 and 270-day strength tests.

Additional tests that will be conducted on the final grout mixes under Phase 3 include: dimensional stability to evaluate shrink/swell potential; yield to determine the volume the grout will occupy once it is hardened; permeability to assess the rate of mine water flow through the cured grout; and acid neutralization potential to measure the potential for the grout to raise the pH of acidic mine water. In addition, the grouts will be tested for specific gravity, density and viscosity to assess grout consistency and workability in the field. The optimum grout mixes developed under Phase 3 will be submitted for Toxicity Characteristic Leaching Potential (TCLP) tests to assess the potential for the grout to leach heavy metals under acidic conditions, and ensure that the grouts are not characteristically hazardous from a regulatory perspective.

The objective of Phase 4 testing is to determine the long-term stability and potential leaching characteristics of the optimum grout mixes under acidic mine conditions. Phase 4 will be performed by placing the grout into a simulated mine environment, and assessing chemical and physical changes that may occur as the grout cures, and over the long-term as it is exposed to acid mine water. The objective of the simulated mine environment testing is to develop a scaled system that accelerates, to the extent practicable, the effects of the mine environment on an injected grout.

REFERENCES

The Western Maryland Coal Combustion By-Products/Acid Mine Initiative: The Winding Ridge Demonstration Project. L. Rafalko and P. Petzrick, in Proceedings: 13th International Symposium on Use and Management of Coal Combustion Products (CCPs), January 1999, The American Coal Ash Association.

Table 1: Laboratory Testing Results

Source/Generator	Type	Test Date	Moisture Content (%)	Free Lime Content ASTM C114	Free Lime Content ASTM C25	Calcium Carbonate (%)	Calcium (%)	Sodium (%)	Magnesium (%)	Sulfate (%)
Source 1	Fresh LKD	3/24/97	<0.01	100						
		3/28/97	<0.01	100						
		4/30/97	NM	100	86.5	<0.1	53.2	0.1	0.3	negligible
	Kiln Scrapings	3/24/97	<0.01	100						
		3/28/97	<0.01	100						
		4/30/97	NM	100	99.3	<0.1	49.5	<0.1	0.3	negligible
Source 2	Fresh CKD	3/28/97	<0.01	11.4						
		3/28/97	<0.01	10.8						
		5/1/97	NM	10.6	30.7	38	33.3	1	1.9	6.4
	stockpile CKD	3/24/97	0.04	1.2						
		3/28/97	0.01	0.4						
		5/1/97	NM	0.6	17.9	38	29.7	1	1.7	7.2
Source 3	Fresh CKD	3/24/97	0.04	0.4						
		3/28/97	0.01	0.8						
		4/30/97	NM	0.6	16.8	26	38.1	0.2	1.3	4
Source 4	Fresh CKD	3/24/97	0.05	0.4						
		3/28/97	0.01	0.3						
		4/30/97	NM	0.2	6.3	47	28.2	0.6	1.5	9
	stockpile CKD	3/24/97	13.7	0.4						
		3/28/97	13.0	0.4						
		4/30/97	NM	0.2	1.4	47	24.2	0.5	1.2	6.1
Source 5	lime mud	4/15/97	28.9	<0.01						
		4/15/97	28.7	<0.01						
		5/1/97	NM	<0.01	1	53	26	0.8	0.5	negligible
	lime grits	4/15/97	14.0	11.4						
		4/15/97	14.5	11.8						
		5/1/97	NM	11.2	12.7	20	34.4	0.9	0.5	negligible
	UPRC sludge	4/15/97	75.7	<0.01						
		4/15/97	75.8	<0.01						
		5/1/97	NM	<0.01	<0.01	<0.1	0.6	0.1	0.1	negligible
Source 6	fresh Recmix	4/16/97	16.8	1.0						
		4/16/97	17.1	0.8						
		4/16/97	16.3	1.0						
		4/16/97	16.0	0.6						
		5/1/97	NM	0.8	1.8	<0.1	25.8	0.1	5	0.3
Source 7	fiber clay	3/28/97	63.0	<0.01						
		3/28/97	63.4	<0.01						
		3/28/97	63.1	<0.01						
		3/28/97	63.3	<0.01						
		5/1/97	NM	<0.01	<0.01	<0.1	2.5	0.1	0.1	negligible

NM = Not Measured

Table 2: Sumary of Proposed Labaoratory Testing Program

Analysis	Test Method	Test Material(s)	Laboratory Test Phase			
			1	2	3	4
X-ray fluorescence (XRF)	ASTM D3682	LKD, fly ash, FGD material, grout	X			X
X-ray powder diffraction (XRD)	TBD	LKD, fly ash, FGD material, grout	X			X
Thermogravimetric analysis (TGA)	TBD	LKD, fly ash, FGD material, grout	X			X
Free Lime Content	ASTM C25	activator	X			
Moisture Content	ASTM D4643, D2216	LKD, fly ash, FGD material	X			
Grain Size	ASTM D422, C33, C117, C204, C330, C430	LKD, fly ash, FGD material	X			
pH	EPA SWA-846, 9040	LKD, fly ash, FGD material , mine water	X			X
Loss on Ignition	ASTM C618	fly ash, FGD material	X			
Major cations and anions	EPA SWA-846	LKD, fly ash, FGD material , mine water	X			
Trace Elements / Heavy Metals	EPA SWA-846	LKD, fly ash, FGD material , mine water	X			X
Total Dissolved Solids (TDS)	AWWA 2540	mine water	X			
Flowability	ASTM 143	grout mixes		X	X	
Set time	ASTM C953	grout mixes		X	X	
Bleed	ASTM C490 or C232	grout mixes		X	X	
Unconfined Compressive Strength	ASTM C942	grout mixes		X	X	X
Dimensional Stability	ASTM C490 or C232	grout mixes			X	
Yield	ASTM C940	grout mixes			X	
Specific Gravity / Density	ASTM C642	grout mixes			X	
Permeability	permeability apparatus	grout mixes			X	X
Modulus of Elasticity	ASTM C469	grout mixes			X	X
Acid Neutralization Potential	TBD	grout mixes			X	
Toxicity Characteristic Leaching Potential (TCLP)	EPA SWA-846	grout mixes			X	

TBD is to be determined.