2009 World of Coal Ash (WOCA) Conference - May 4-7, 2009 in Lexington, KY, USA
http://www.flyash.info/

Stabilization of FGD By-products by Using Fly Ash, Cement and Sialite

Xiaoming Liu[1, 4], Haifang Wen[*, 2], Tuncer B Edil[1], Craig H Benson[3]

1 Department of Civil & Environmental Engineering, University of Wisconsin - Madison, WI 53706

2 Department of Civil & Environmental Engineering, Washington State University, Pullman, WA 99164

3 Department of Civil & Environmental Engineering, University of Washington, Seattle, WA 98195

4 School of Resource and Safety Engineering, China University of Mining & Technology, Beijing 100083, China

ABSTRACT: Flue gas desulphurization (FGD) sludge is a by-product from the air pollution control systems used in coal-fired power plants. The objective of this work was to stabilize FGD gypsum and FGD filter cake with class C fly ash. The effectiveness of other additive, such as cement, cement kiln dust, and sialite to investigate its possibility of utilization in road construction. In this work, the chemical, physical and mineralogical properties of FGD gypsum and FGD filter cake were analyzed. Compaction, California Bearing Ratio (CBR) test and unconfined compressive strength (UCS) test were conducted on FGD gypsum and FGD filter cake with fly ash. The UCS tests were also conducted on FGD materials stabilized with cement, cement kiln dust, and sialite,

[*] Corresponding author, Assistant Professor, e-mail: Haifang_wen@wsu.edu

respectively. This study also investigated the environmental implications of these two types of FGD by-products with different additives. The test results indicated that both CBR values and UCS for FGD gypsum and filter cake increased with the increase of fly ash contents. FGD gypsum has the potential to be used in geotechnical fill and embankment directly, while FGD filter cake can not be used directly in pavements without stabilization.

Keywords: FGD gypsum, FGD filter cake, Stabilization, fly ash

1. Introduction

Flue gas desulphurization (FGD) sludge is a by-product from the air pollution control systems used in coal-fired power plants. Use of FGD material, especially the FGD gypsum, has increased over the past decade because FGD gypsum can be used for wallboard and Portland cement production. In 2006, FGD scrubber systems at coal-fired power plants generated approximately 27.4 million metric tons (30.2 million tons) of material, or 24.2 percent of all coal combustion products[(1)]. Due to the expected increase in scrubbing applications, the amount of FGD produced is expected to grow during the next few decades[(2)]. Approximately 30 percent of the FGD material produced in 2006 was beneficially used[(1)]. Fixated or stabilized calcium sulfite FGD scrubber material has been used as an embankment and road base material[(4,5)]. FGD products have also been used in place of gypsum, as feed material for the production of Portland cement. In addition, FGD material has been used in flowable fill in mine reclamation and in aerated concrete blocks[(6, 7)]. Oxidized FGD scrubber material (calcium sulfate high in gypsum content) is used in the manufacturing of wallboard[(3)]. Wallboard production represents the largest single market for FGD scrubber material[(1)]. However, to increase the amount of beneficial utilization of FGD materials, alternative applications have to be investigated. The objective of this work was to stabilize FGD gypsum and FGD filter cake with class C fly ash, cement, cement kiln dust, and sialite (cement made primarily from waste materials) to investigate its possibility of utilization in road construction.

2. Materials and Experimental Methods

2.1. Raw material

FGD gypsum and FGD filter cake used in this investigation were produced by the P4 power plant, We energies, Wisconsin. FGD gypsum is the byproduct of Sox control when lime is used as absorbent in the flue gas desulphurization system. FGD filter cake is the filtered solids out of waste water. The FGD gypsum used in this study is fine powder, with 33% water content, while FGD filter cake is brown clay-like chunk with 107% water content. Table 1 and Table 2 show the chemical and mineralogical composition of FGD gypsum and FGD filter cake. Optical micrograph of FGD gypsum and FGD filter cake were described by Table 1.

Cement used in this work is type I Portland cement. Class C fly ash was obtained from Columbia power plant, Wisconsin. Table 3 presents the chemical properties of fly ash. Sialite is a new class of high performance aluminum-silicon based cementitious material that is obtained from Liuzhou sialite factory, Guangxi, China, which utilizes industrial solid wastes as its main raw material (such as tailing, slag, fly ash, calcined gangue, waste bricks and waste glass, etc., which can make up >70% of the mass composition).

Table 1 Chemical composition of FGD gypsum and FGD filter cake

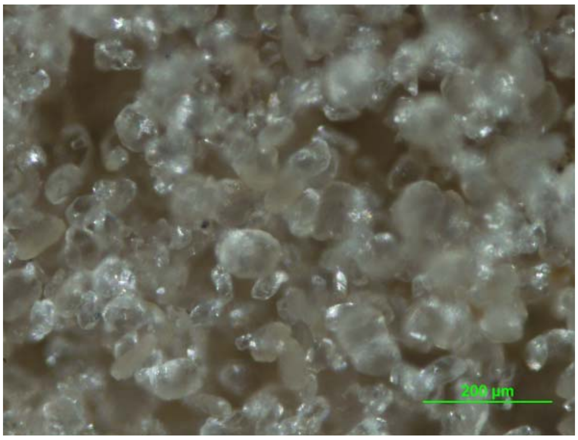
Samples	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	LOI	Total
FGD gypsum	0.81	0.05	0.17	38.74	0.26	0.06	0.02	7.74	47.88
FGD filter cake	16.66	4.43	7.33	13.01	11.54	0.6	1.37	29.8	86.28

Table 2 Mineralogical composition of FGD gypsum and FGD filter cake

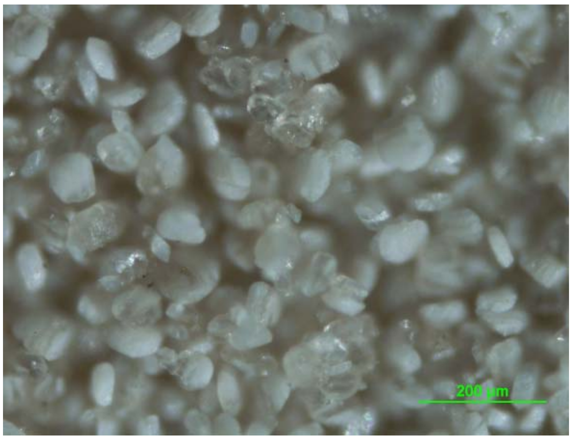
Samples	Dehydrated Gypsum	Quartz	Smectite	Calcite	Feldspar /Illite / Mica	Amorphous
FGD gypsum	93	0	6	1	0	0
Filter Cake	60	7	1	2	5	25

Table 3 Chemical composition of fly ash

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	LOI	Total
Fly ash	31.1	18.3	6.1	23.3	3.7	0.7	47.88



natural FGD gypsum



oven dried FGD gypsum

natural FGD filter cake

oven dried FGD filter cake

Fig. 1 Optical micrograph of FGD gypsum and FGD filter cake

2.2. Experimental Methods

2.2.1. Compaction test

The optimum moisture content and maximum dry density were determined based on ASTM D 698. These values were used to prepare specimens for CBR and strength tests.

2.2.2. California Bearing Ratio (CBR) Test

CBR test was preformed on untreated FGD gypsum and FGD filter cake in accordance with D 1883.

2.2.3. Unconfined Compressive Strength Test

Unconfined compressive strength (UCS) tests were conducted on treated and untreated FGD material. The specimens for UCS were prepared using Harvard compaction equipment following the procedure in ASTM D4609. The Harvard mold is 33 mm in diameter and 72 mm in height. Testing showed that 3 layers with 25 tamps/layer were adequate to achieve approximately the same dry unit weight as obtained with the standard Proctor effort. After compaction, the specimens were extruded, sealed in plastic, and stored in 100% humidity for 7 d curing. The specimens were tested in unconfined compression at a strain rate of 0.15 mm/min.

2.2.4. Leaching test

Leaching tests were conducted based on ASTM D 3987. The samples were placed in two-liter bottles after 18h rotation at a rate of 29 r/min, and then were filtered and stored for inductively-coupled plasma (ICP) tests.

3. Results and Discussion

3.1. Results of Compaction Test

Figures 2 and 3 show that the maximum dry unit weight increased with an increase of fly ash content. However, the optimum moisture contents decreased with the increase of fly ash content for both FGD gypsum and filter cake. It indicated that adding more fly ash can improve the dry unit weight of FGD material-fly ash admixtures.

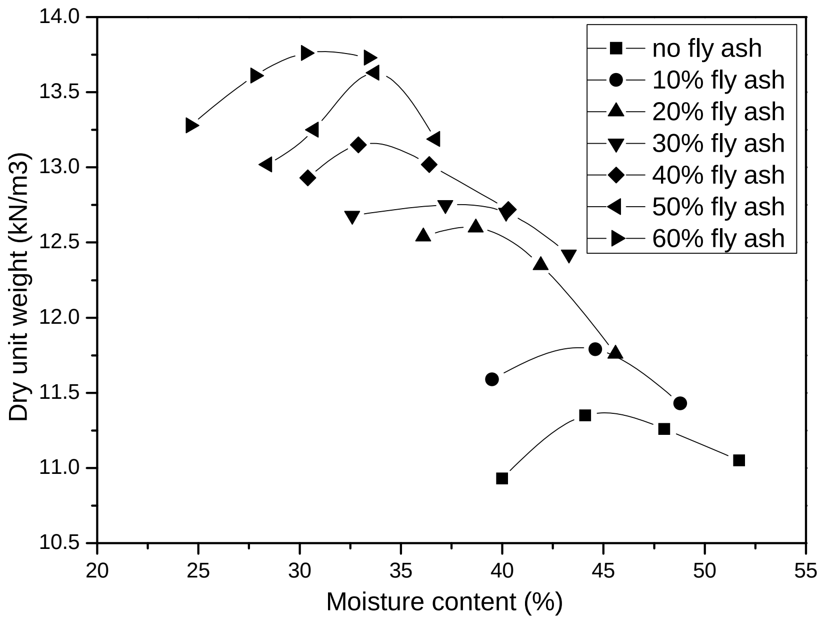


Fig.2 Compaction curves for FGD gypsum with varying fly ash content

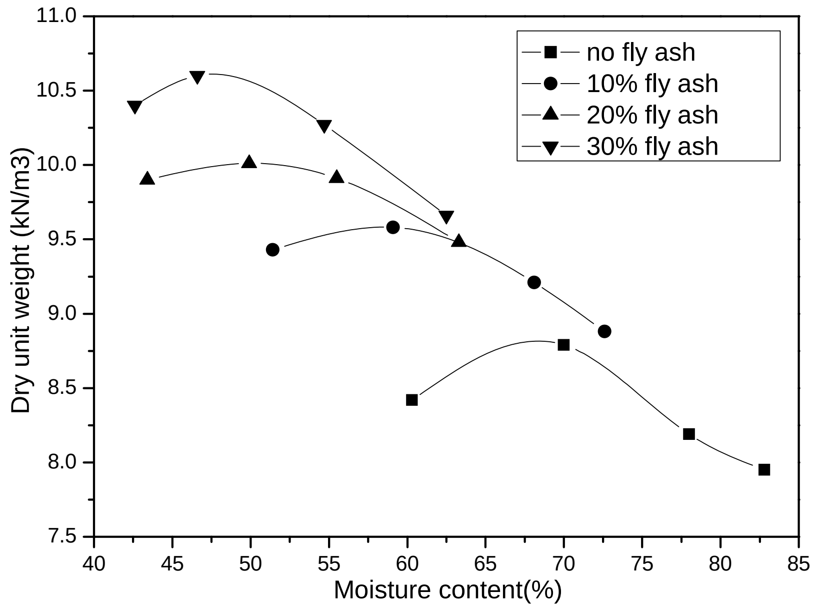


Fig.3 Compaction curves for FGD filter cake with varying fly ash content

3.2. Results of California Bearing Ratio (CBR)

CBR results for FGD gypsum at different moisture content are exhibited in Fig. 4. The maximum of CBR value was about 15 with an optimum moisture content of 39% which is less than the optimum moisture content for maximum dry density. The CBR value of FGD gypsum mixed with 10% fly ash at optimum moisture content of 40% was 20.7 after 7-day curing. The CBR test results indicated that treated and untreated FGD gypsum has the potential to be used as pavement subbase. Significant improvements are need for FGY gypsum to be used as pavement base materials.

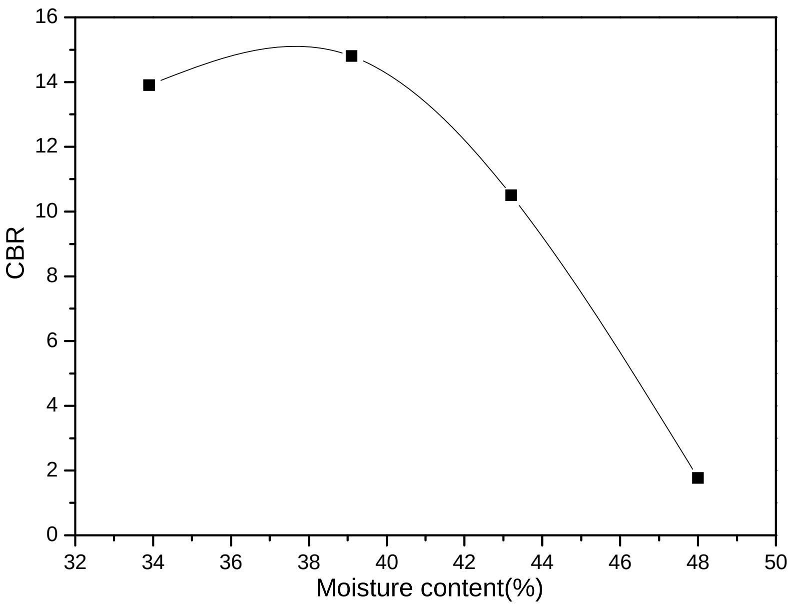


Fig. 4 CBR results for FGD gypsum at different moisture content

Fig. 5 shows CBR values of FGD filter cake at different moisture content. The moisture content of original FGD filter cake was 107.5%. A moisture content below 40% was difficult to achieve. It indicates that CBR value increases with the decrease of moisture content and the optimum water content is ranging from 40% to 60%. At the original moisture content, FGD filter cake had very low CBR values, less than 2.

The CBR value of FGD filter cake mixed with 10% fly ash at 107.5% water content was about 3.7 after 7 d curing. The CBR results indicated that FGD filter cake is a fairly weak material and has to be treated before it is used for construction.

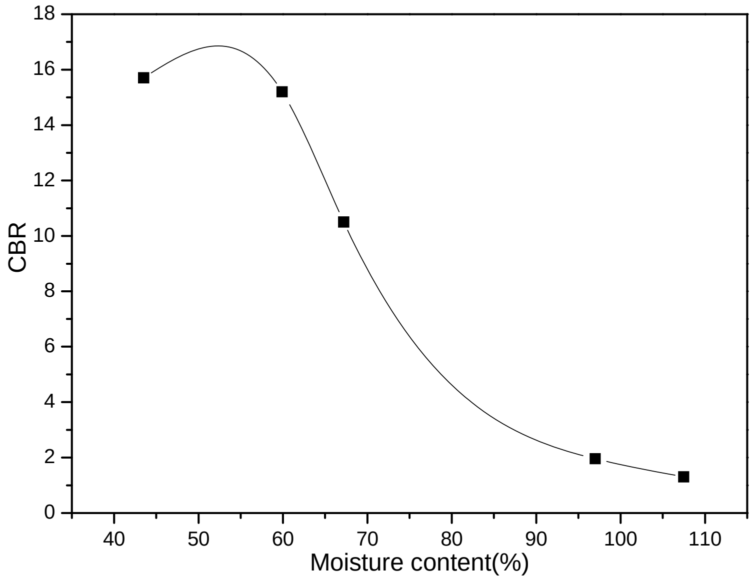


Fig. 5 CBR results for FGD filter cake at different moisture content

3.3. Results of Unconfined Compressive Strength Test

The UCS curves for FGD gypsum with varying fly ash content are shown in Fig. 6. The UCS increased with the increase of fly ash content and reached 1.3 Mpa with 60 percent fly ash in the admixture and at 27.5% moisture content after 7-day curing. It indicated that Columbia's class C fly ash was effective in increasing the strength of FGD gypsum, which has the potential, after treatment, to be used as pavement base materials.

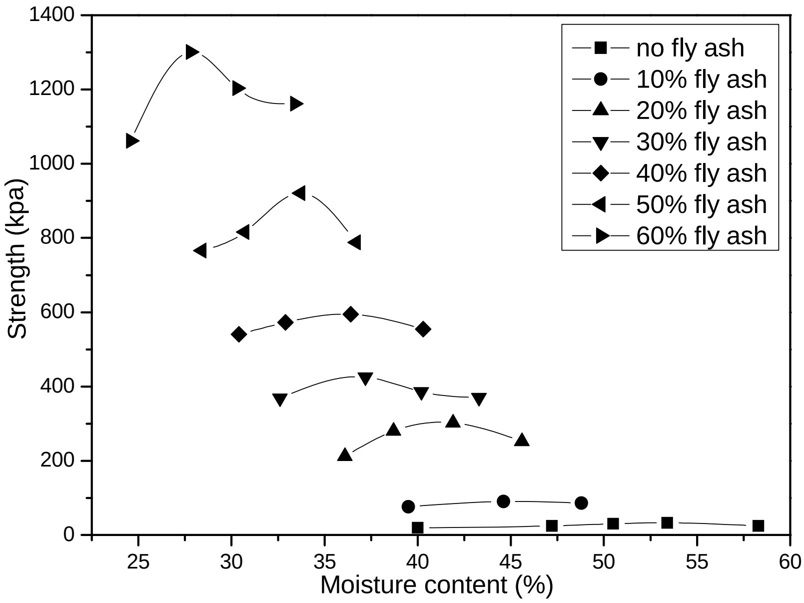


Fig. 6 UC strength curves for FGD gypsum with varying fly ash content

The UCS test results for FGD filter cake with different fly ash contents are shown in Fig. 7. It was also found that adding Class C fly ash significantly increased the UCS of FGD filter cake, but lower than that of FGD gypsum with fly ash.

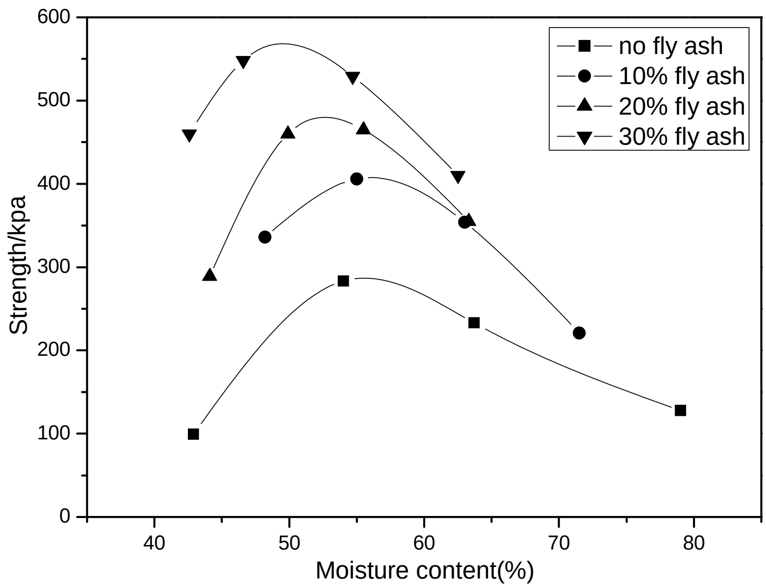


Fig. 7 UC strength curves for FGD filter cake with varying fly ash content

Fig. 8 indicated that the UCS for admixtures after 7-day curing were improved after mixed with different additives. It was found that adding 4% cement resulted in higherst

UCS, followed by 4% sialite, 2% cement, 2% sialite, 4% cement kiln dust (CKD), 10% fly ash, and 2% CKD. All these treated mixtures have potential to be used as pavement subbase materials, based on the mechanistic-empirical pavement design guide.

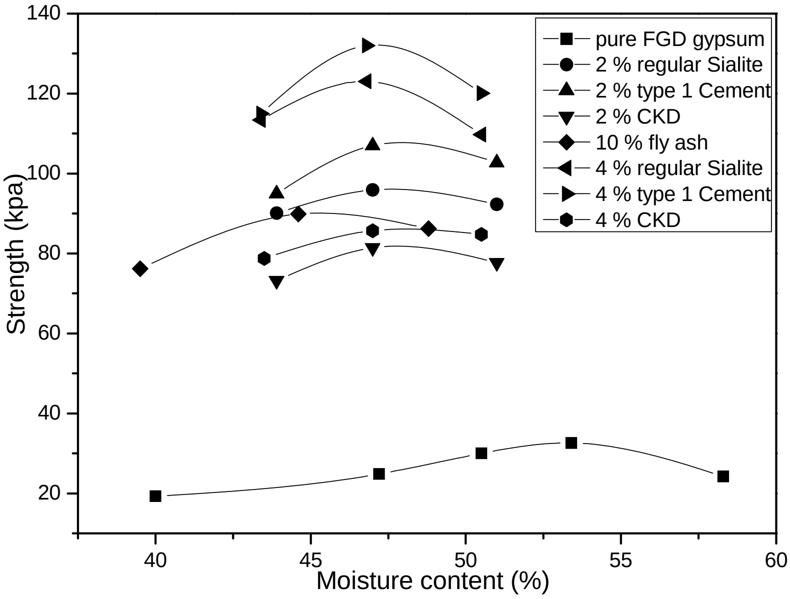


Fig. 8 UC strength curves for FGD gypsum plus fly ash, sialite, cement, CKD, respectively

3.4 Results of Modulus

The modulus of these materials was estimated based on UCS test results. Due to the implications of initial stage of stress/strain curve for UCS tests, two approaches were used, initial Young's modulus and modulus at 50 peak UCS (E50). Figure 9 shows the initial Young's modulus from UCS tests and E 50 (modulus at 50% of UCS) of FGD gypsum with different fly ash contents. Both curves in Figure 9 shows that the modulus could be up to 143 Mpa at 60% fly ash content.

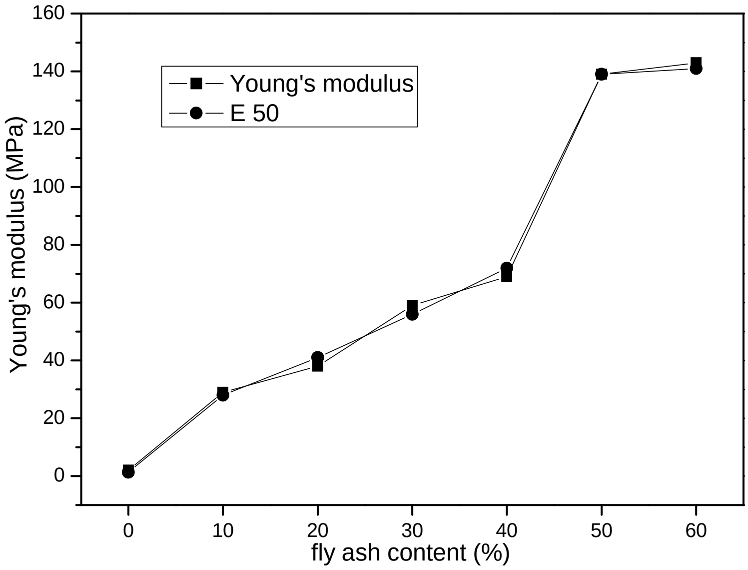


Fig. 9 Modulus of FGD gypsum with varying fly ash content

Fig.10 shows the Young’s modulus and E 50 of FGD filter cake with different fly ash contents. Both of them have a linear relationship with the fly ash content. The E 50 is slightly less than the relevant Young’s modulus.

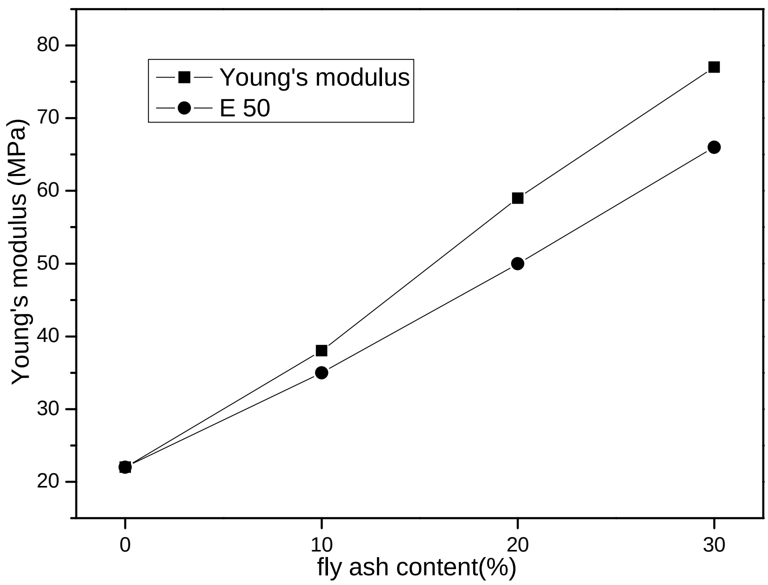


Fig. 10 Modulus of FGD filter cake with varying fly ash content

3.5 leaching test

3.5.1 PH values for raw materials

Table 4 and Table 5 show the PH values for various raw materials and mixtures with different water solid ratio. Results indicated that FGD gypsum and filtercake is weak acid while fly ash shows weak basic. The PH value of sialite is lower than cement.

Table 4 PH values for raw materials with different water solid ratio

Sample	PH	Sample	PH	Sample	PH	Sample	PH	sample	PH
FGD 3:1	6.15	FC 3:1	8.63	FA 3:1	12.22	Sialite 3:1	12.31	Cement 3:1	12.95
FGD 5:1	6.41	FC 5:1	8.54	FA 5:1	12.08	Sialite 5:1	12.25	Cement 5:1	12.92
FGD 10:1	6.44	FC 10:1	8.50	FA 10:1	11.96	Sialite 10:1	12.21	Cement 10:1	12.97
FGD 20:1	6.52	FC 20:1	8.42	FA 20:1	11.73	Sialite 20:1	12.06	Cement 20:1	13.01

FGD = FGD gypsum, FC = FGD filter cake, FA = fly ash

Table 5 PH values for admixtures with different water solid ratio

Sample	PH	Sample	PH	Sample	PH	Sample	PH
F+60 3:1	11.68	F+30 3:1	10.67	FC+30 3:1	9.78	F+4S 3:1	12.17
F+60 5:1	11.43	F+30 5:1	10.91	FC+30 5:1	9.41	F+4S 5:1	12.08
F+60 10:1	10.98	F+30 10:1	10.24	FC+30 10:1	9.33	F+4S 10:1	11.84
F+60 20:1	10.78	F+30 20:1	10.53	FC+30 20:1	9.23	F+4S 20:1	11.79

F + 60 = FGD gypsum + 60% fly ash, F + 30 = FGD gypsum + 30% fly ash, FC + 30 = FGD filter cake + 30% fly ash, F+4S = FGD gypsum + 4% Sialite

3.5.2 E-conductivity for raw materials

Table 6 and Table 7 show the Electronic-conductivity for various raw materials and mixtures with different water solid ratios. FGD filter cake and cement have a very high E-conductivity, reached 6087 us/cm and 11670 us/cm, respectively.

Table 6 Electronic-conductivity for raw materials with different water solid ratio

Sample	EC us/cm	Sample	EC us/cm	Sample	EC us/cm	Sample	EC us/cm	sample	EC us/cm
FGD 3:1	2212	FC 3:1	21970	FA 3:1	2347	Sialite 3:1	1170	Cement 3:1	14840
FGD 5:1	2168	FC 5:1	14620	FA 5:1	2037	Sialite 5:1	1144	Cement 5:1	12840
FGD 10:1	2197	FC 10:1	8985	FA 10:1	1976	Sialite 10:1	1071	Cement 10:1	12440
FGD 20:1	2179	FC 20:1	6078	FA 20:1	1821	Sialite 20:1	1012	Cement 20:1	11670

FGD = FGD gypsum, FC = FGD filter cake, FA = fly ash

Table 7 Electronic-conductivity for admixtures with different water solid ratio

Sample	EC us/cm	Sample	EC us/cm	Sample	EC us/cm	Sample	EC us/cm
F+60 3:1	2635	F+30 3:1	2691	FC+30 3:1	13820	F+4S 3:1	3758
F+60 5:1	2289	F+30 5:1	2443	FC+30 5:1	9893	F+4S 5:1	3366
F+60 10:1	2041	F+30 10:1	2376	FC+30 10:1	6211	F+4S 10:1	2974
F+60 20:1	1926	F+30 20:1	2257	FC+30 20:1	4377	F+4S 20:1	2553

F + 60 = FGD gypsum + 60% fly ash, F + 30 = FGD gypsum + 30% fly ash, FC + 30 = FGD filter cake + 30% fly ash, F+4S = FGD gypsum + 4% Sialite

3.5.3 ORP for raw materials

Table 8 Oxidation-Reduction potential for raw materials with different water solid ratio

Sample	ORP mV	Sample	ORP mV	Sample	ORP mV	Sample	ORP mV	sample	ORP mV
FGD 3:1	326	FC 3:1	97	FA 3:1	-51	Sialite 3:1	-266	Cement 3:1	-72
FGD 5:1	329	FC 5:1	107	FA 5:1	-42	Sialite 5:1	-219	Cement 5:1	-63
FGD 10:1	360	FC 10:1	112	FA 10:1	-56	Sialite 10:1	-130	Cement 10:1	-52
FGD 20:1	355	FC 20:1	122	FA 20:1	-33	Sialite 20:1	-131	Cement 20:1	-45

FGD = FGD gypsum, FC = FGD filter cake, FA = fly ash

Table 8 and Table 9 show the oxidation-reduction potential for various raw materials and mixtures with different water solid ratios. High potential indicates greater affinity for electrons and tendency to be reduced.

Table 9 Oxidation-Reduction potential for admixtures with different water solid ratio

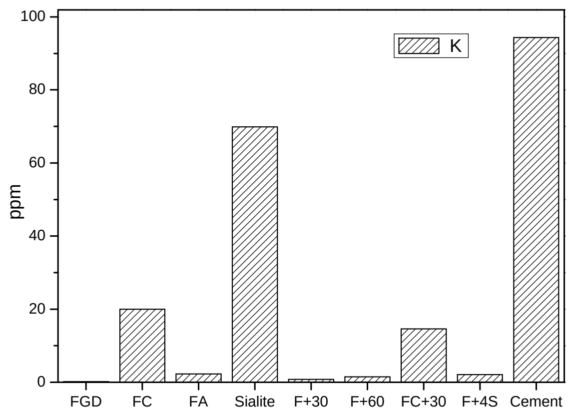
Sample	ORP mV	Sample	ORP mV	Sample	ORP mV	Sample	ORP mV
F+60 3:1	22	F+30 3:1	42	FC+30 3:1	48	F+4S 3:1	-85
F+60 5:1	30	F+30 5:1	45	FC+30 5:1	50	F+4S 5:1	-78
F+60 10:1	32	F+30 10:1	47	FC+30 10:1	55	F+4S 10:1	-68
F+60 20:1	35	F+30 20:1	49	FC+30 20:1	60	F+4S 20:1	-58

F + 60 = FGD gypsum + 60% fly ash, F + 30 = FGD gypsum + 30% fly ash, FC + 30 = FGD filter cake + 30% fly ash, F+4S = FGD gypsum + 4% Sialite

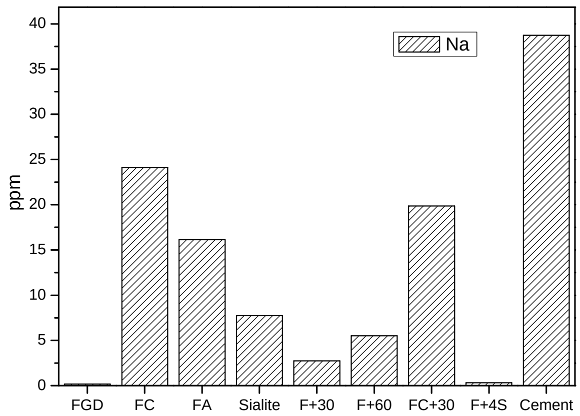
3.5.4 Basic cation

WisDNR NR 538 (Beneficial use of industrial byproducts), a regulation by Wisconsin department of natural resource, was considered as a standard for this work. A material complying with Category 4 of NR 538 can be used as confined geotechnical fill and transportation facility embankment. National drinking water standards and Wisconsin enforcement standard (NR140) for groundwater quality were used as a reference.

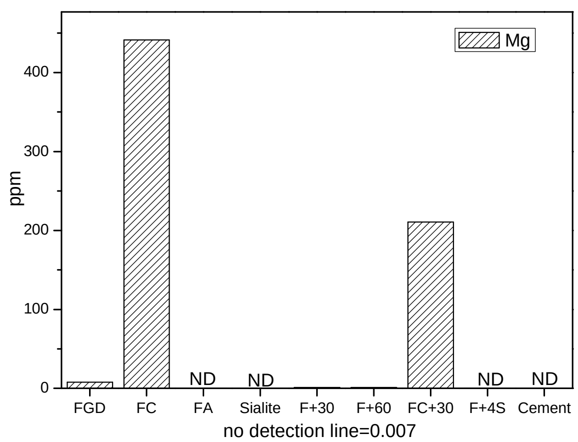
Only boron exceeded the regulation limits. The level for K, Na, Ca and Mg are below the regulation limits. Boron level in FGD filter cake is four times as much as the regulation limit.



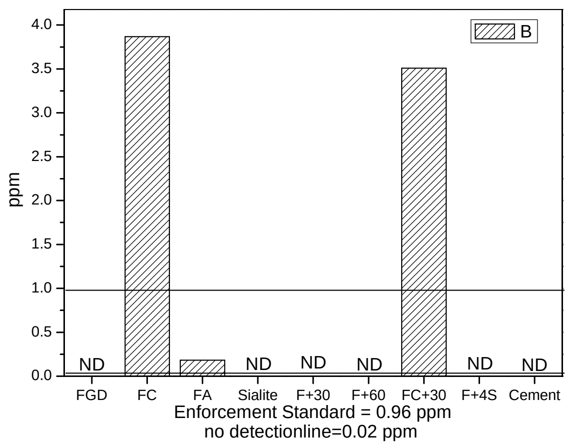
(a) K content



(b) Na content



(c) Mg content



(d) B content

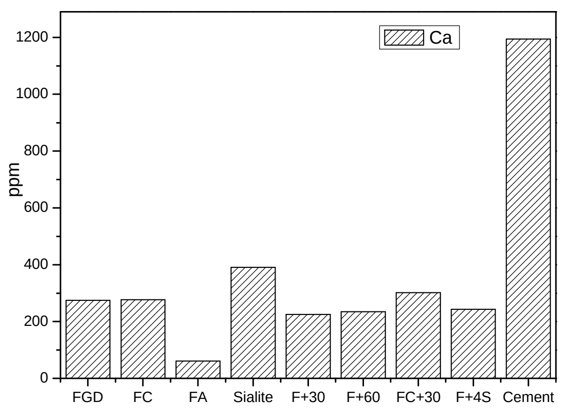
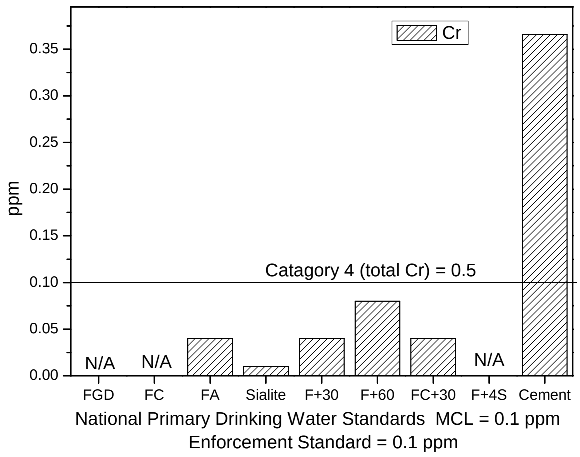
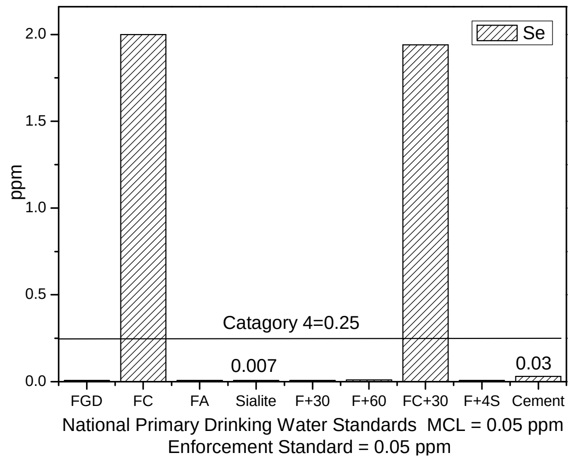


Fig. 11 ICP results for several basic cation content

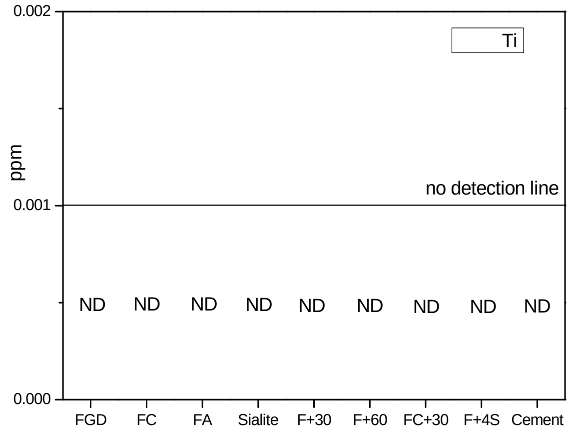
3.5.5 Heavy metals



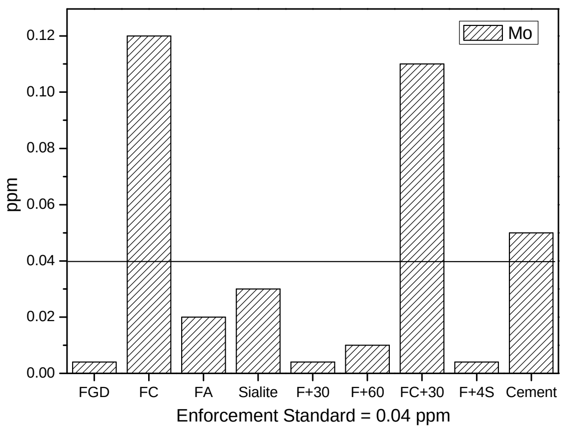
(a) Cr content



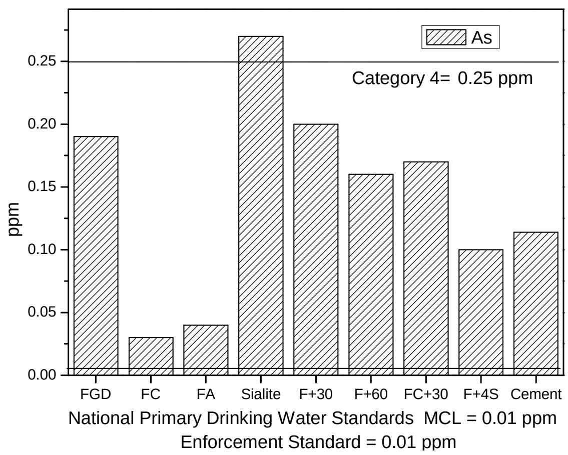
(b) Se content



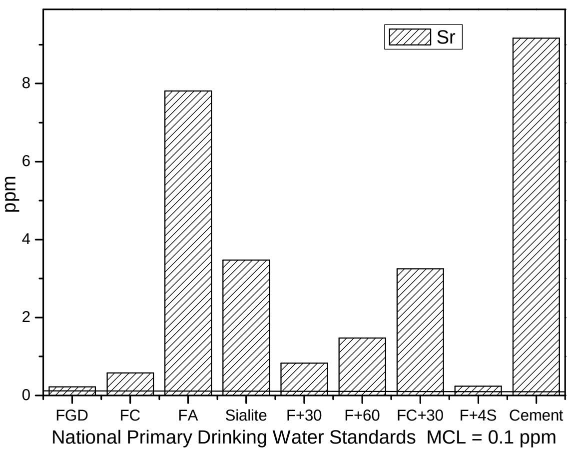
(c) Mg content



(d) B content



(e) As content



(f) Sr content

Fig. 12 ICP results for Heavy metals content

Fig.12 indicates that the strontium and arsenic content of FGD gypsum are higher than national primary drinking water standard, but it lower than the category 4, which means it can be used in confined geotechnical fill and encapsulated transportation facility embankment.

FGD filter cake is rich in chloride, sulfate, boron, selenium, strontium and arsenic, which exceeded the drinking water standard.

Cement contains much more chromium, molybdenum and strontium than sialite. However, considering these additives are cementitious materials, most of heavy metals could be stabilized after hydration. This needs to be verified by field demonstration.

4. Conclusions

The following conclusions can be made, based on the laboratory tests:

(1) Adding fly ash increased the maximum dry density and CBR values of FGD gypsum and filter cake.

(2) Unconfined compression strength of FGD gypsum and filter cake increased with the increase of fly ash contents. The maximum of UCS of FGD gypsum mixed with 60 percent fly ash reached 1.3 Mpa. The maximum of UCS of filter cake mixed with 30 percent fly ash wass slightly greater than 0.55 Mpa. Adding more fly ash also can improve the Young's modulus and E 50 of FGD gypsum and FGD filter cake.

(3) Leaching results showed that the strontium and arsenic contents in FGD gypsum are higher than national drinking water standard, but it lower than the category 4 of NR518, which means it can be used in confined geotechnical fill and encapsulated transportation facility embankment

(4) FGD filter cake is rich in chloride, sulfate, boron, selenium, strontium and arsenic, which exceeded the drinking water standard and can not be used in pavements without stabilization.

Acknowledgements

The FGD materials used in this study was provided by We Energies. The authors wish to thank Mr. Bruce Ramme of We Energies for his support and help.

Reference

1. American Coal Ash Association (ACAA). 2006 coal combustion product (CCP) production and use. American Coal Ash Association; Aurora, CO, 2007.

2. Bigham JM, Kost DA, Stehouwer RC, Beeghly JH, Fowler R, Traina SJ, Wolfe WE, Dick WA. Mineralogical and engineering characteristics of dry flue gas desulfurization products. Fuel 2005;84:1839-48.

3. Electric Power Research Institute (EPRI). Flue gas desulfurization by-products: Composition, storage, use, and health and environmental information. EPRI, Inc; Palo Alto, CA: 1999.

4. Prusinski JR, Cleveland MW, Saylak D. Development and construction of road bases from flue gas desulfurization material blends. In: Proceedings of the eleventh international ash utilization symposium. Electric Power Research Institute; Palo Alto, CA: 1995.

5. Saylak D, Estakhri CK. Stabilization of road bases containing coal combustion by-products sulfates and sulfites using high volume fly ash cement. In: 1999 international ash utilization symposium, Center for applied energy research. University of Kentucky; 1999.

6. Butalia TS, Wolfe WE, Zana B, Lee JW. Flowable fill using flue gas desulfurization material. Journal of ASTM International 2004;1(9):1-12.

7. Butalia TS, Wolfe WE, Lee JW. Evaluation of a dry FGD material as a flowable fill. Fuel 2001;80:845-50.