Development of CCB Fill Materials for Use as Mechanically Stabilized Marine Structures

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ABSTRACT

There are three kinds of FGD byproducts: refined FGD gypsum (93% $CaSO_4 \cdot 2H_2O$ and 7% $CaSO_3 \cdot 0.5H_2O$), FGD gypsum (70 - 93% $CaSO_4 \cdot 2H_2O$ and 7 - 30% $CaSO_3 \cdot 0.5H_2O$) and FGD sludge (60 - 70% $CaSO_4 \cdot 2H_2O$ and 30 – 40% $CaSO_3 \cdot 0.5H_2O$). The first two categories of FGD gypsum are used for wallboard and cement additives, and therefore have commercial value. The third category, FGD sludge, is a solid waste with no commercial value. The utility industry has to pay for its disposal. This research investigated the technical and economic feasibility of stabilizing waste FGD sludge for use as fill material in the construction of mechanically stabilized marine structures, including embankments, retaining walls and dikes. The development of such material addresses two important issues. First, the inventory of waste FGD sludge would be reduced via the development of a marketable product. Second, the development of lightweight briquettes that could compete economically with conventional structural fill material would provide agencies involved in coastal restoration efforts an alternative to the commonly utilized limestone. FGD sludge was stabilized using class C fly ash and Portland type II cement. Blocks of ten different composite combinations were fabricated and screened to select five ingredient for further testing. The selected stabilized FGD briquettes were subjected to dynamic leaching, specific gravity, compaction, porosity, surface hardness and field submergence tests. The dynamic leaching showed that 64%:35%:1%, 63%:35%:2% and 69%:30%:1% FGD: class C fly ash: Portland type II cement briquettes have low effective sulfur (sulfate and sulfite) diffusion coefficients ($m^2s^{-1}\times10^{-13}$) and lower values for 30 year effective diffusion depths (18-50 mm). The geotechnical tests conducted so far (Specific Gravity, Compaction and Sieve analysis) on the briquettes show all that all stabilized briquettes behave similar The field saltwater submergence experiment showed that these three stabilized FGD briquette can survive in the field for more than four months. The economic analysis showed that these briquettes can be manufactured at large scale at the cost of under $13/ton. These results imply the feasibility of using stabilized FGD briquettes as conventional structural fill material in the coastal protection projects.

BACKGROUND

Our nation's coastal regions are an invaluable source of natural resources, biological diversity and recreational pleasure. However, coastal erosion is claiming these valuable lands at an alarming yearly rate. The reasons for increased coastal erosion are many and range from increased population growth in the coastal areas to historic decisions to straighten rivers, which has resulted in the loss of alluvial sediment transport to sensitive areas. Additionally, as barrier islands erode away due to increased storm surges and natural erosion processes, the coastline itself has become more vulnerable.

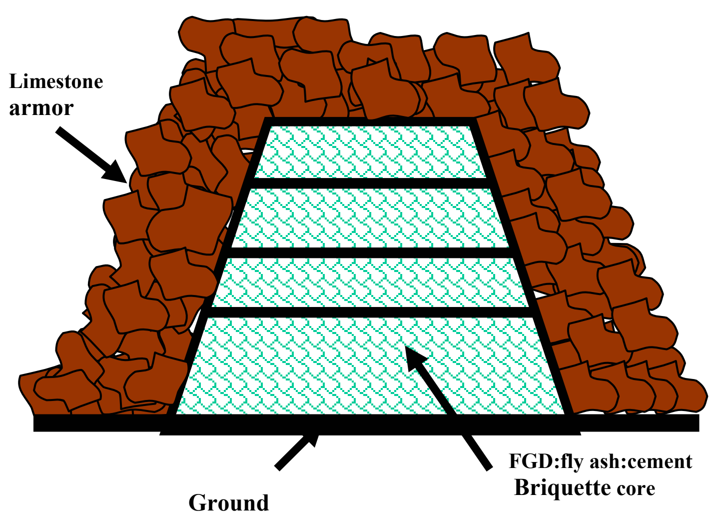
Coastal wetlands are being lost at a rate of 33.5 sq mi/year or one acre every 24 minutes (Louisiana Coastal Wetlands Conservation and Restoration Task Force and the Wetlands Conservation and Restoration Authority, 1998). The Gulf and southern Atlantic Coasts are seeing the greatest erosion problems. Louisiana, which contains approximately 42% of the nation's wetlands, is losing about 80% of the total area being lost yearly. If this trend continues, it could cost the US $33.6 billion from lost public use value over the next 50 years (National Coastal Wetlands Conservation Grant Program, 2000; Louisiana Coastal Wetlands Conservation and Restoration Task Force and the Wetlands Conservation and Restoration Authority, 1998). As important, the loss of coastal areas has started to threaten entire communities and cities. A good example of the seriousness of the issue was summarized in a recent Time magazine article titled "The Big Easy on the Brink". As stated in the article, "New Orleans will be the next lost city of Atlantis if measures are not taken to slow down and minimize the coastal erosion process" (Cohen, 2000). While New Orleans may be a special case, it serves as a global example of the ramifications of coastal erosion and lost wetlands.

Recognizing the national significance of lost wetlands, the US Congress passed the Coastal Wetlands Planning, Protection, and Restoration Act (CWPPRA, Breaux Act) (Public Law 101-646, Title III) to contribute federal monies yearly to wetland restoration projects. Additionally, since CWPPRA's inception in 1990, the U.S. Fish and Wildlife Service has been working with coastal states to acquire, restore, manage and enhance coastal wetlands through a matching grants program. To date, approximately $32 million dollars have been awarded to 23 coastal states and U.S. territories, with 40,000 acres of coastal wetlands being acquired, restored or enhanced (Louisiana Coastal Restoration, 2000).

The entire nation is experiencing wetland lost and coastal erosion problems. However, since Louisiana has the largest percentage of wetlands, much focus has been placed on this state. The State of Louisiana legislature passed the Louisiana State and Local Coastal Resources Management Act in 1978. In 1989, the Louisiana Legislature passed Act 6 of the second extraordinary session (R.S. 49:213-214) and a subsequent constitutional amendment that created the Coastal Restoration Division within the Louisiana Department of Natural Resources. Thus, Louisiana has a commitment to restore wetlands and decrease the amount of barrier island loss. Loss of these valuable entities has far-reaching implications that go beyond lost recreational lands. The barrier islands and wetlands also provide unique habitats for thousands of flora and fauna and provide protection from storm surges created by tropical storm and hurricane conditions. More globally, the wetlands and coastal areas associated with Louisiana serve as a nursery for many of the Gulf Coast aquatic organisms. Thus, loss of these areas will have a devastating impact on the entire Gulf region.

Five federal partners (Natural Resources Conservation Service; National Marine Fisheries; USEPA; U.S. Fish and Wildlife Service and the U.S. Army Corps of Engineers) along with the State of Louisiana, develop, budget, and approve construction projects based on four basic engineering techniques. The structural techniques minimize erosion and soil breakdown caused by wave and tidal action. The sedimentary techniques create new wetlands or protect existing wetlands. The hydrologic technique controls water so that it benefits wetlands growth. And, the vegetative techniques reinforce existing wetlands and minimize soil erosion.

A number of engineering approaches have been used to counteract erosion along populated coastlines. Traditional protective measures have included structures such as seawalls, revetments, groins and detached breakwaters. These structures are made of stone, limestone, concrete and steel (Whiteneck and Lester, 1989), all of which are relatively expensive. Within Louisiana, the majority of material used as rip-rap and for dike construction is limestone mined and barged from Arkansas at a cost of $36 to $52 per ton of material (in place), with needed quantities in the tens of thousands of tons per project (LADNR, 2000). Construction of shoreline erosion dikes generally consists of a four feet wide crown with a 2 or 3 to 1 ratio back slope and a 3 or 4 to 1 ratio front slope (water side). Normally, the dikes are 2-3 feet are above the water line. The end result is the need for tremendous amounts of limestone. Besides cost, one of the problems with the use of limestone rip-rap is the excessive settlement of the embankment due to the consolidation of the underlying soils created by the limestone weight burden. Thus, the use of lightweight materials can potentially minimize this problem. Coal combustion byproduct (CCB) fill material could be used in conjunction with geogrid material as the core material, with limestone used as an armoring. This configuration would dramatically cut costs by reducing the amount of needed limestone and would reduce the overall weight burden. The development of economically competitive alternative fill materials using waste FGD sludge and class C fly ash would not only provide a use of these byproduct materials, but would also result in the establishment of a marketable industry. This research focused specifically on the use of waste FGD sludge and fly ash.



Of the more than 90 million tons of CCBs produced by the utility industry every year, greater than 20 million tons is FGD byproducts (ACAA, 1998). As the demand for cleaner burning increases, more utilities are using forced oxidation, resulting in more waste FGD sludge produced. There are three kinds of FGD byproducts: refined FGD gypsum (93% $CaSO_4 \cdot 2H_2O$ and 7% $CaSO_3 \cdot 0.5H_2O$), FGD gypsum (70 - 93% $CaSO_4 \cdot 2H_2O$ and 7 - 30% $CaSO_3 \cdot 0.5H_2O$) and FGD sludge (60 - 70% $CaSO_4 \cdot 2H_2O$ and 30 – 40% $CaSO_3 \cdot 0.5H_2O$). The first two kinds of FGD gypsum have been used for wallboard and cement additives, and therefore have commercial value. FGD sludge is a solid waste with no commercial value. The utility industry has to pay for its disposal. As of December 1994, there were at least 157 coal-fired boiler units at 92 power plants that had operating wet scrubbing systems. These plants are located in at least 32 states (USDOE, 1995). Although efforts have been focused on the reusage of FGD byproducts (mainly for terrestrial applications-road bases, bituminous mixtures, concrete admixtures, etc.), only small amounts are currently used. In 1998, 1.5 million tons of FGD byproduct was used to produce wallboard and 0.2 million tons of FGD byproduct was used to replace gypsum in the cement production. The other major uses included mining application (0.15 million tons), road base/sub base (0.08 million tons) and agriculture (0.05 million tons) (Robbins et al., 2000; ACAA, 1998; Smith, 1998; 1985;1982; Amaya et al., 1997; Prusinski et al., 1995; EPRI, 1995). The remainder of the material is disposed of in holding ponds or landfills. Stabilization or fixation and placement in landfills is the most common method of disposal (USDOTD, 2000).

The use of CCBs for aquatic applications has not been pursued as extensively as terrestrial applications. However, some early work done in the 1980s demonstrated the feasibility of using FGD: fly ash composites for artificial reef material (NYSEROA, 1985; Parker and Woodhead, 1983). Coal waste blocks were constructed using a fly ash to FGD ratio of 1:1 to 3:1, and resulting in a volume of 16,000 cm^3. The blocks were fabricated using conventional concrete block making equipment and cured, resulting in a cured strength of 2000 kPa. The blocks were placed in the sea near Long Island, New York to form an artificial reef. The reef had a relief of approximately 1 meter and a length of 70 meters, and covered 1,200 m^2. Following two years of monitoring, the reef had a well-established epifaunal community encrusting the blocks. No accumulation of trace metals was found in organisms associated with the reef, suggesting the compatibility of stabilized coal waste usage within the aquatic environment (Woodhead and Parker, 1983; George et al, 1983; Rose, 1983). While these results demonstrate the feasibility of using fly ash/waste FGD composites within the aquatic environment, they were not used in weight bearing situations.

Little literature is available on the use of waste FGD sludge and class C fly ash in mechanically stabilized marine structures. This use must not only consider the environmental suitability of placing this material in the environment, but also the structural/geotechnical properties to assure the material can provide strength to the structure. Portland type II cement was chosen as a binding agent with sulfate resistance. The Class C fly ash was chosen because it is a low cost binding agent. The Class C fly ash can also prevent the formation of ettringite that can cause rupture development of cement stabilized FGD briquettes. The selection of mixture ratios and compaction pressure is more critical for the fabrication of composites for marine use than for terrestrial use due to the highly soluble nature of gypsum ($CaSO_4$, approximately 4 g/l in full strength saltwater) (Jame, 1992), which is a major component of waste FGD sludge. Thus, development of waste FGD sludge briquettes for marine applications must consider not only the mechanical/physical properties of the composite, but must also utilize admixtures that encapsulates the material to prevent it from dissolving once submerged.

The overall goal of this research was to determine the feasibility of utilizing CCBs (waste FGD sludge and class C fly ash) as construction materials in coastal protection structures. The specific objectives of this research were to (1) refine the mixture composition for stabilized FGD sludge briquettes consisting of waste FGD sludge, class C fly ash and Portland type II cement, and (2) evaluate the pertinent environmental (long-term environmental impact from dynamic leaching, TCLP required by USEPA), geotechnical engineering properties (specific gravity, compaction and sieve analysis) and salt water survivability of the stabilized FGD sludge briquettes.

METHODOLOGY

Raw Materials and Fabrication

Raw Materials: Raw flue gas desulfurization (FGD) sludge was obtained from Big Bend Electric Company, Tampa, Florida. The FGD was oven-dried at 45-50^oC for 6-12 hours, depending on moisture content. The oven temperature was checked twice a day and adjustments made if necessary. The dried FGD was crushed and passed through a 1.46-mm sieve. Type II Portland cement used was obtained from the River Cement Co., St. Louis, Missouri and class C fly ash from Bayou Ash Inc., Erwinville, Louisiana.

FGD Block Fabrication: Blocks of ten different composite combinations using FGD, class C fly ash, and Portland Type II cement were fabricated for screening purposes. The initial ten stabilized ingredient combinations (Table 1), which were selected using factorial design method. Fabrication of blocks was done in the LSU concrete lab. Dried, ground FGD passed through a 1.46 mm sieve, dried Portland type II cement and class C fly ash were combined according to the compositions in Table 1. The ingredients were homogenized and mixed with water equivalent to 8% of the dry mixture. Eighty-nine grams of the resulting mixture were poured into a 3.9 cm diameter steel mold and compacted to a 3.6 cm long cylinder under a pressure of 9.8×10^7 N/m^2 using a static press. The composites were allowed to cure at room temperature and 100% humidity for over two weeks before testing. The mean mass of all FGD blocks was 87.1 grams, with a solid density of 2.05 g/cm^3.

Briquette Fabrication: Stabilized FGD briquettes for investigating the feasibility of using FGD composites as coastal protection materials were fabricated by K.R. Komerack Briquetting and Research, Inc., Anniston, Alabama. The five best composite combinations from the screening phase were briquetted (Table 2). The FGD briquettes had an average biomass of 29.5 g and a solid density of 2.0 g/cm^3.

Table 1. Composition of the initial ten stabilized FGD Sludge: Class C fly ash: Portland type II cement combinations, which underwent a dynamic leaching, test for screening purposes.

FGD Sludge (%)	Class C fly ash (%)	Portland type II cement (%)
77	20	3
73	25	2
72	25	3
69	30	1
68	30	2
67	30	3
64	35	1
63	35	2
62	35	3
60	40	0

Table 2. Five composite combinations selected from the screening were briquetted for further testing.

FGD: Class C fly ash: Portland type II cement	Water (%)	Average Briquette Weight (g)	Amount (lb)
77%:20%:3%	5.0	29.91	69
64%:35%:1%	8.0	30.46	69
63%:35%:2%	8.0	29.98	69
69%:30%:1%	8.0	28.77	69
67%:30%:3%	8.0	28.52	69

Chemical Characterization

Dynamic Leaching Test: A dynamic leaching test was performed to evaluate the long-term environmental effects of the stabilized solid wastes. A variation of the dynamic leach test (ANS, 1986) was performed for both the screening and final evaluation studies. During the screening process, leachate from FGD blocks was collected and analyzed for calcium and sulfate, which is used as indicators of the dissolution potential of the block/ briquette. During final evaluation of the selected briquettes, leachate from the FGD briquettes was collected and analyzed for calcium and sulfate. The leachate volume to surface area ratio was 8:1. The composites were placed in 550 ml of 20 ppT artificial seawater (Instant Ocean™). The leachant was completely exchanged at intervals of 0.80, 0.29, 1, 2, 3, 4, 5, 8, 11, 14, 21 and 28 days. The experiments were performed in duplicate. The data from the leaching tests were used as the basis for the diffusion model.

Toxicity Characteristic Leaching Procedure (TCLP): The TCLP (USEPA, 1990c) test is designed to simulate the leaching a waste will undergo if disposed in an unlined sanitary landfill. The extraction fluid volume to crushed FGD briquette volume was 20:1. One hundred grams of the crushed briquette were agitated with 2000ml of extraction fluid (acetic acid solution having a pH of 2.88+/0.05) for 20 hours, and then the liquid was passed through 7 µm glass fiber filter to obtain the TCLP extract. The extract was digested with nitric acid using the USEPA 3015 method; the digested extract was analyzed for As, Cr, Cd, Pb, Se. If the TCLP extract contains any one of the 40 Toxicity Characteristics (TC) constituents in amounts equal to or greater than that specified in 40CFR 261.24(1992) than the waste will be declared a hazardous waste.

Sulfate, Calcium and Metal Concentration Measurements: Leachate from the dynamic leaching tests was analyzed for calcium, sulfate. The leachate was analyzed for alkalinity in accordance to <u>Standard Methods</u> (APHA, 1998). The extraction fluid from TCLP was The samples were analyzed for cadmium, chromium, lead, selenium and arsenic using ICP.

Physical Characterization

Surface Hardness: A cone penetrometer (Model No. WF 21510, Humboldt Mfg., Inc.) was used to measure the penetration depth of the dry, leached FGD briquettes following the British Standard methods of Testing Soils for Engineering Purposes (BS 1377:1977). The inverse of the penetration depth was used as a measurement of the surface hardness. Hardness at 6 different points was measured for the briquettes and its average value was used to calculate surface hardness of the briquettes.

Porosity Measurement: The porosity of the briquettes was measured by weight loss and effective diffusion coefficients. The FGD briquettes were immersed in tap water for 24 hours and then weighed (W_1). The briquettes were then dried in oven at 50°C for 24 hours and then weighed (W_2). The difference in the weights W_1 and W_2 is the weight of water filled by the pore spaces. The weight of water in the pores can be converted by divided by density of water. The porosities were calculated as pore water volume divided by composite volume.

Geotechnical Characterization

Compaction Characteristics: This test was carried out for briquettes as similar to that carried out for coarse aggregates (ASTM D698-00a). Raw FGD exhibits thixotropic properties hence compaction criteria are not specified in ASTM standards. The time interval between wetting and compaction in the laboratory was similar to that anticipated during construction to account for the influence of the rate of hydration on compaction characteristics (ASTM E 1861).

Sieve Analysis: The sieve analysis was conducted on the crushed materials obtained from the compaction tests giving the complete picture of physical degradation the briquettes will undergo when subject to the worst case loading.

Field Submergence: To study the survivability and dissolution potential for the FGD composites in the natural saltwater environment, five FGD briquettes of each selected combination were submerged in a bay located at Port Fourchon, Louisiana. The briquettes were tied with colored tags and placed in autoclaving baskets (Nalgene Brand) and suspended in the water column subjecting them to natural currents and tides and maximizing the interaction potential with various aquatic organisms. Monthly observations were made to determine deterioration of the briquettes.

Market Analysis

The initial economic analysis performed at Louisiana State University for the PG briquetting process was used as a foundation of the economic analysis of the stabilized FGD sludge briquettes. The analysis assumes a 4,500,000 ton FGD sludge briquettes per year production facility located near Tampa, Florida. All cost figures are in the year of 2002.

Data Analysis

Diffusion of calcium and sulfur from the FGD blocks/briquettes is an indicator of dissolution rate. Determination of the effective diffusion coefficients is needed to predict the long-term stability of the briquettes in the marine environments. Duedall et al. (1983) developed a diffusion model based on Fick's second law of diffusion $\partial C/\partial t = D_e(\partial^2 C/\partial x^2)$, for $0<x<\infty$ and $0<t$, where C is the ion concentration with C_o being the initial concentration of the species, D_e is the effective diffusion coefficient of ions in the FGD briquette, x is the one-dimensional coordinate system for the briquette extended from the water interface at x=0 to the briquette center at $x=+\infty$, and t is time. This model is one-dimensional for ions in solidified briquettes and in well-stirred aqueous systems. It assumes a uniform distribution of diffused ions in the briquette and a flux of the ions across the water-water interface that is proportional to the concentration at the interface. The initial and boundary conditions for the one dimensional diffusion equation are:

Initial Condition: $C(x,0) = C_o$

Boundary Condition 1 (as x approached infinity):

$$De\left(\frac{\partial C}{\partial x}\right) = hC \qquad \text{for x=0 or} \qquad \lim \frac{1}{C}\frac{\partial C}{\partial x} \rightarrow \frac{h}{D_e}$$

where, h is the transfer coefficient

$\lim C(x,t) \rightarrow C_o$

Boundary Condition 2 (as x approaches infinity):

The solutions for the above equation where release of the parameter of interest is controlled by diffusion in the briquettes, $h \rightarrow \infty$, are

$$C(x,t) = C_o erf\left(\frac{x}{2\sqrt{D_e t}}\right)$$

$$J = C_o\sqrt{\frac{D_e}{\pi t}}$$

where, J is the daily flux of ions

The diffusion coefficient ($m^2 \cdot sec^{-1}$) can be obtained from the equation $D_e = \pi t (J/C_o)^2$. This model is widely applied for diffusion coefficient calculations (Edwards and Duedall, 1985; Cote, 1986; and Seveque et al., 1992) because it is simple, reliable, and self-verified. This diffusion model predicts a slope of 0.5 for a log-log plot of log(J) versus log(t), which can be used to verify the assumption of the model.

RESULTS AND DISCUSSION

Block Fabrication and Screening

The one-dimensional diffusion model in combination with the leaching data was used to calculate the effective diffusion coefficients (D_e) for calcium and sulfur (sulfate and sulfite). The diffusion coefficients were then used in conjunction with an economic analysis to select appropriate combinations for further testing.

Calcium Effective Diffusion Coefficients and Effective Diffusion Depths for FGD Blocks

Representative illustrations of logarithmic plots of J (Ca^{2+}, daily flux) vs. time are shown Figure 1. The slopes of the regression equations (Table 3) fell within the range of the theoretical values for diffusion (-0.5) and dissolution (-0.8). Effective diffusion coefficients for the ten composites ranged from $1.34 - 3.41 \times 10^{-13}$ $m^2 \cdot s^{-1}$, while effective diffusion depths ranged from 17.53 – 25.64 mm for 30 years submergence. These values are comparable to the values from previous research (10^{-13} – 10^{-14} $m^2 \cdot s^{-1}$) for Phosphogypsum: Class C fly ash: Portland type II cement composites (Guo et al, 2000, Rusch et al, 2001a).

Sulfur (sulfate + sulfite) Effective Diffusion Coefficients and Effective Diffusion Depths for FGD Blocks

Representative illustrations of logarithmic plots of J (S, daily flux) vs. time are shown in Figure 2. The slopes of the regression equations (Table 4) fell within the range of the theoretical values for diffusion (-0.5) and dissolution (-0.8). The effective diffusion coefficients for the ten composites ranged from 1.02 $m^2 \cdot s^{-1}$ to 2.45×10^{-13}-$m^2 \cdot s^{-1}$ while effective diffusion depths ranged from 13.89 – 36.53 mm for 30 years submergence (Table 4). These values are slightly higher than the calcium effective diffusion coefficients obtained in this study but are comparable to the values from previous research (10^{-13} – 10^{-14} $m^2 \cdot s^{-1}$) for Phosphogypsum: Class C fly ash: Portland type II cement composites (Rusch et al, 2001a). FGD dissolves to form Ca^{2+} ,SO_3^{2-} and SO_4^{2-}. SO_3^{2-} can be oxidized into SO_4^{2-}, which is still in the solution state. Ca^{2+}, on the other hand, may undergo minimal reactions to form calcite. Thus, sulfur may be considered a better indicator than calcium for the FGD sludge dissolution process.

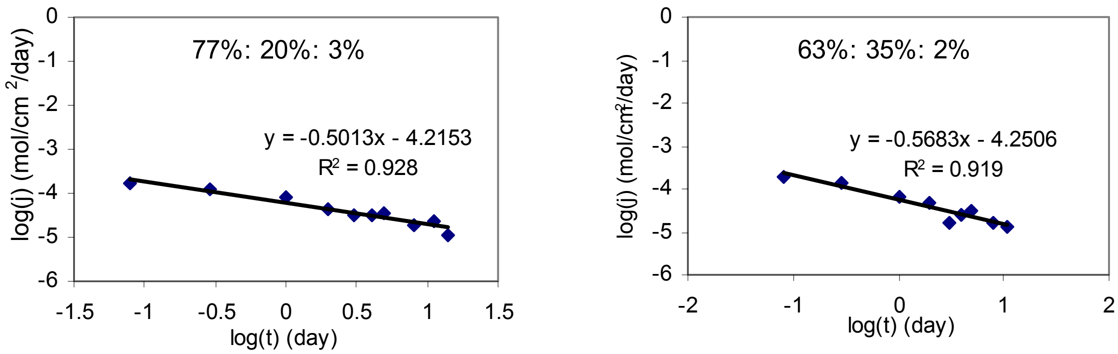


Figure 1. Calcium effective diffusion coefficients for 77%:20%:3% and 63%:35%:2% FGD:class C fly ash:Portland type II cement composite blocks was estimated by plots of log (J) Vs log (t).

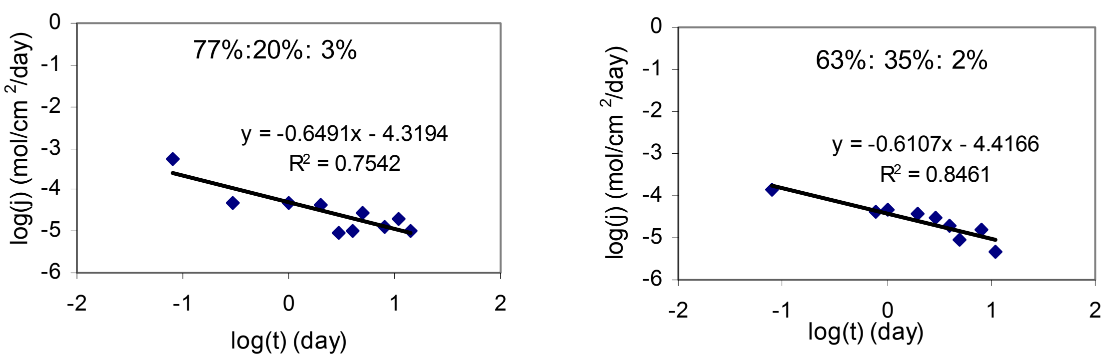


Figure 2. Sulfur effective diffusion coefficients for 77%:20%:3% and 63%:35%:2%FGD:class C fly ash:Portland type II cement composite blocks was estimated by plots of log (J) Vs log (t).

Selection of Best Composite for Further Testing

Effective diffusion coefficients (D_e) and economics were the two criteria used to determine which of the initial ten compositions were to be subjected to further testing. The lime stone used in Louisiana Coastal protection projects average cost of \$36 to \$52/ton. Thirty percent of the average limestone cost is chosen as economic criteria (\$13/ton). The composites must have met at least one of the D_e (calcium, or sulfur) and the target economic value (\$13/ton) to be included in the further experiments.

Based on saltwater submergence experiments from previous results, it was found that 63%:35%:2% phosphogypsum:class C fly ash: Portland type II cement composites can survive for more than two years (Guo et al., 2001). Thus, the Ca^{2+} and SO_4^{2-} effective diffusion coefficients for this composite were used as the maximum allowable levels for selecting FGD: Class C fly ash: Portland type II cement composites for further testing. The effective diffusion coefficients for Ca^{2+} and SO_4^{2-} are 1.51 $\times 10^{-13}$ and 1.63×10^{-13} $m^2 \cdot s^{-1}$, respectively (Rusch, 2001b). Considering the deviations, the maximum allowable values for Ca^{2+} and S (sulfate +sulfite) for FGD selection were selected to be 2.0×10^{-13} and 2.1×10^{-13} $m^2 \cdot s^{-1}$, respectively.

The economic analysis frame work developed for a phosphogypsum briquetting plant was expanded and updated for FGD (Rusch et al., 2001). The estimated costs of the ten stabilized FGD block combinations are listed in Table 5. The first five combinations (bold) met the criteria for selection for further testing

Table 3. The effective calcium diffusion coefficients and effective diffusion depths (t = 1 year and 30 years) were estimated for the FGD: Class C fly ash: Portland type II cement composite blocks subjected to the 28-day dynamic leaching study.

FGD Sludge (%)	Class C fly ash (%)	Portland type II cement (%)	D_e (m^2s^{-1} $\times 10^{-13}$)	Intercept	Slope	Mean D_e (m^2s^{-1} $\times 10^{-13}$)	Mean X_c (mm) (t=1 year)	Mean X_c (mm) (t=30 years)
77	20	3	1.579	-4.215	-0.501	2.068	3.58	19.64
77	20	3	2.556	-4.108	-0.581			
73	25	2	3.208	-4.084	-0.631	3.086	4.41	24.16
73	25	2	2.965	-4.108	-0.650			
72	25	3	3.672	-4.093	-0.624	3.393	4.71	25.84
72	25	3	3.114	-4.035	-0.664			
69	30	1	3.860	-4.069	-0.610	3.452	4.65	25.51
69	30	1	3.045	-4.120	-0.515			
68	30	2	1.867	-4.2329	-0.430	2.231	3.73	20.48
68	30	2	2.595	-4.1614	-0.725			
67	30	3	2.416	-4.1834	-0.649	2.486	3.96	21.69
67	30	3	2.555	-4.1721	-0.685			
64	35	1	1.933	-4.2517	-0.816	1.638	3.20	17.53
64	35	1	1.342	-4.3309	-0.774			
63	35	2	2.086	-4.242	-0.614	2.046	3.59	19.67
63	35	2	2.005	-4.250	-0.568			
62	35	3	2.986	-4.171	-0.624	3.079	4.40	24.14
62	35	3	3.173	-4.157	-0.606			
60	40	0	2.633	-4.212	-0.751	2.225	3.75	20.57
60	40	0	1.870	-4.286	-0.756			

Table 4. The effective sulfur diffusion coefficients and effective diffusion depths (t =1 year and 30 years) were estimated for the FGD: Class C fly ash: Portland type II cement composites subjected to the 28-day dynamic leaching study.

FGD Sludge (%)	Class C fly ash (%)	Portland typeII cement (%)	Inter-cept	Slope	D_e (m^2s^{-1} $\times10^{-13}$)	Mean D_e (m^2s^{-1} $\times10^{-13}$)	Mean X_c (mm) (t=1 year)	Mean X_c (mm) (t=30 years)
77	20	3	-4.319	-0.649	0.978	1.296	2.83	15.54
77	20	3	-4.210	-0.813	1.615			
73	25	2	-4.143	-0.692	2.447	2.348	3.84	21.08
73	25	2	-4.161	-0.727	2.250			
72	25	3	-4.273	-0.788	1.342	2.174	3.63	19.89
72	25	3	-4.097	-0.739	3.007			
69	30	1	-4.218	-0.638	1.941	2.143	3.67	20.13
69	30	1	-4.176	-0.564	2.350			
68	30	2	-4.146	-0.782	2.776	2.304	3.79	20.77
68	30	2	-4.236	-0.817	1.833			
67	30	3	-4.240	-0.956	1.854	1.643	3.21	17.59
67	30	3	-4.297	-0.768	1.432			
64	35	1	-4.140	-0.523	1.638	1.051	6.67	36.53
64	35	1	-4.193	-0.870	1.634			
63	35	2	-4.379	-0.706	1.107	1.022	2.53	13.89
63	35	2	-4.416	-0.610	0.936			
62	35	3	-4.287	-0.636	1.746	1.683	3.25	17.84
62	35	3	-4.303	-0.544	1.620			
60	40	0	-4.764	-0.543	3.290	2.451	3.87	21.21
60	40	0	-4.815	-0.505	1.612			

Table 5. The application of the D_e and economic criteria resulted in the selection of five FGD Sludge: Class C fly ash: Portland type II cement combinations for further testing.

FGD (%)	Class C fly ash (%)	Portland type II cement (%)	Selected by Ca^{2+}	Selected by Sulfur	Estimated Cost ($/ton)
77	**20**	**3**	**Yes**	**Yes**	**10.15**
64	**35**	**1**	**Yes**	**Yes**	**12.26**
63	**35**	**2**	**Yes**	**Yes**	**12.94**
69	**30**	**1**	**No**	**Yes**	**11.10**
67	**30**	**3**	**No**	**Yes**	**12.46**
68	30	2	No	Yes	11.78
73	25	3	No	No	10.62
72	25	3	No	No	11.30
62	35	3	No	No	13.62
60	40	0	No	No	12.73

Briquette Fabrication and Testing – Final Analysis

Briquetting solid wastes has advantages of low production cost and easy handling. Therefore, the commercial application of solid wastes has to be in the form of briquettes.

Sulfur (sulfate + sulfite) Effective Diffusion Coefficients and Effective Diffusion Depths of the Stabilized FGD Briquettes

The logarithmic plots of J (S, flux) vs. time are shown in Figure 3. The effective diffusion coefficients of sulfur for the five selected FGD briquettes ranged from 2.63 $m^2.s^{-1}$ to $4.16\times10^{-13} m^2.s^{-1}$, while effective diffusion depths ranged from 11.8 – 25.1 mm for 30 years submergence (Table 6). These values are 1.3- 4 times higher than the sulfur effective diffusion coefficients of the FGD blocks obtained in this study but are comparable to the values from previous research (10^{-13} – 10^{-14} $m^2 \cdot s^{-1}$) for Phosphogypsum: Class C fly ash: Portland type II cement composites (Rusch et al, 2001a) and other research (10^{-13} – 10^{-14} $m^2 \cdot s^{-1}$) from Duedall (1983). The leachate was not analyzed for calcium due to limited funding hence the effective diffusion coefficients for calcium are not available.

TCLP Test: The ICP analysis results of the TCLP leachate solution are shown in Table 7. The Cd, Pb, Cr, Se and As concentrations in the leachate are far below the maximum concentration of these metals that can be classified as hazardous materials.

Surface Hardness: The surface hardness is estimated for the dried FGD: class C fly ash: Portland type II cement briquettes subjected to the 28-day dynamic leaching study are listed in Table 8. When binding agent content is high the surface hardness is high. These readings imply that the surface hardness may be used as an indicator for surface dissolution potential for the FGD briquettes.

Comparison of the Porosities from Weight and Effective Diffusion Coefficient: The porosities can be obtained by many ways. The porosity obtained during this study were calculated from weight and effective diffusion coefficient measurements. There is a relationship between effective diffusion coefficient and porosity: $D_e=D_o\phi^2$ (Ullman and Aller 1982). Where D_e is the ion effective diffusion coefficient in the porous media; D_o is the ion diffusion coefficient in the saltwater; ϕ is the porosity. The sulfate ion diffusion coefficients in salt water is $9.8\times10^{-10}(m^2.s^{-1})$ (Li and Gregory, 1974). The comparison of the porosities from weight and effective diffusion coefficient measurements (Table 9) show about 36% (from Sulfate) of porosities is effective porosities.

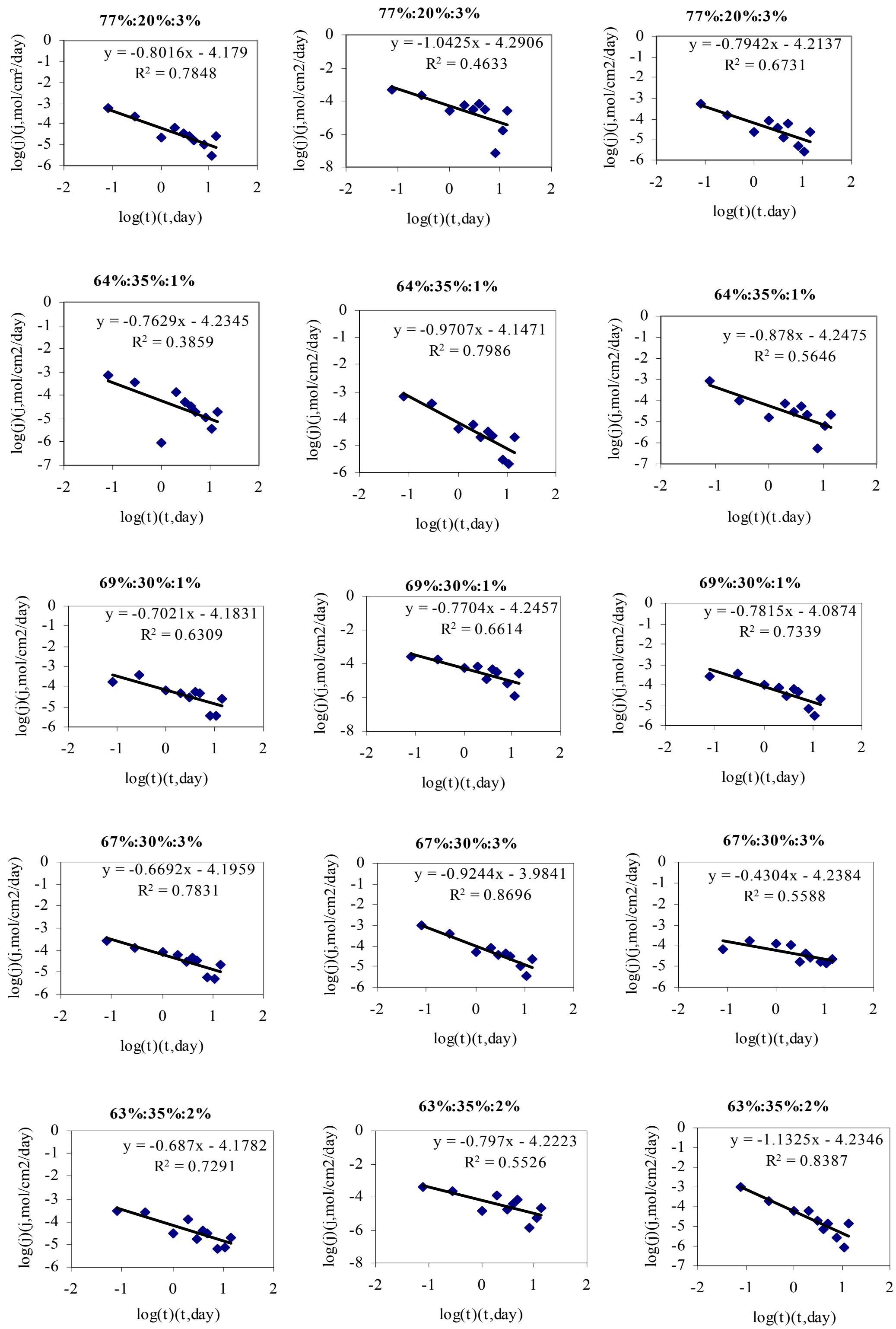


Figure 3. Sulfate effective diffusion coefficients for five FGD:class C fly ash:Portland type II cement briquettes were estimated by plots of log (J) vs log (t).

Table 6. The effective sulfate, (SO_4^{2-}) diffusion coefficients and effective diffusion depths (t = 1 year and 30 years) were estimated for the FGD: class C fly ash: Portland type II cement composite briquettes subjected to the 28-day dynamic leaching study.

FGD (%)	Class C fly ash (%)	Portland type II cement (%)	D_e ($m^2s^{-1}\times10^{-13}$)	Average ($m^2s^{-1}\times10^{-13}$)	X_c (mm) (t=1 year)	X_c (mm) (t=30 years)
77	20	3	6.57	3.22	4.22	23.13
77	20	3	1.31			
77	20	3	1.78			
64	35	1	2.19	4.16	4.97	27.23
64	35	1	7.01			
64	35	1	3.27			
63	35	2	2.46	2.63	4.06	22.28
63	35	2	2.42			
63	35	2	3.00			
69	30	1	1.98	2.87	4.21	23.10
69	30	1	4.03			
69	30	1	2.62			
67	30	3	2.32	3.38	4.45	24.37
67	30	3	5.98			
67	30	3	1.84			

Table 7. Analysis of TCLP extracts of FGD: class C fly ash: Portland type II cement

Briquettes for presence of various metals by ICP

Elements	77%:20% :3% (ppm)	64%:35% :1% (ppm)	63%:35% :2% (ppm)	69%:35% :1% (ppm)	67%:30% :3% (ppm)	Maximum Conc. USEPA (ppm)
Arsenic	<0.05	<0.05	<0.05	<0.05	<0.05	5.0
Cadmium	<0.05	<0.05	<0.05	<0.05	<0.05	1.0
Chromium	0.08	0.076	0.083	0.07	0.076	5.0
Lead	<0.05	<0.05	<0.05	<0.05	<0.05	5.0
Selenium	<0.05	<0.05	<0.05	<0.05	<0.05	1.0

Table 8. The Surface hardness which was measured at six different points on the leached briquettes showed that surface hardness is approximately proportional to the amount of binding agents

FGD (%)	Class C fly ash (%)	Portland type II cement (%)	Surface Hardness (mm^{-1}) Average of Six points (mm^{-1})	Overall Average (mm^{-1})
77	20	3	75.4	81.9
77	20	3	84	
77	20	3	81.9	
64	35	1	64.9	67.7
64	35	1	65.3	
64	35	1	67.7	
63	35	2	69.8	98.8
63	35	2	89.1	
63	35	2	98.8	
69	30	3	89.3	97.3
69	30	3	98.8	
69	30	3	97.3	
67	30	1	96.2	79.2
67	30	1	82.1	
67	30	1	79.2	

Specific Gravity Test: This test was performed to relate gravimetric and volumetric quantities of the mechanically stabilized fill material. Specific gravity of the briquettes which, are to be used as fill materials in the coastal relief construction works was calculated according to the test method for Specific Gravity of Coarse Aggregate (ASTM C127). The results for the test conducted on the five composite combinations are listed in Table 10. The results showed that all ingredient combinations behave similar.

Sieve Analysis: The crushed materials obtained from the FGD briquette compaction tests were subjected to the sieve analysis, giving the complete picture of physical degradation the briquettes will undergo when subject to the worst case loading. The results of sieve analysis are listed in Figure 4. The percentage change of the D_{10} ($\Delta D_{10} = (D_{10}i - D_{10})/D_{10}i$) and D_{50} ($\Delta D_{50} = (D_{50}i - D_{50})/D_{50}i$) are listed in Table 11, where subscript i represents the original briquettes before compaction test. The results show that all ingredient combination behave similar

Table 9 . The comparison of the porosities from different sources showed that about, 36% (from Sulfate) of porosities is effective porosities.

FGD	Class C	Portland type II	Porosity (%)	
(%)	Fly ash (%)	Cement (%)	From $D_e(SO_4^{2-})$	Weight measurement
77	20	3	2.59	5.24
77	20	3	1.16	4.34
77	20	3	1.35	4.64
64	35	1	1.50	4.77
64	35	1	2.67	4.96
64	35	1	1.83	4.97
63	35	2	1.59	4.47
63	35	2	1.57	5.27
63	35	2	1.75	4.86
69	30	1	1.42	4.59
69	30	1	2.03	5.04
69	30	1	1.63	4.73
67	30	3	1.54	4.44
67	30	3	2.47	4.71
67	30	3	1.37	5.24

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Table10. Calculation of Specific Gravity of briquettes for use as fill materials.

FGD (%)	Class C Fly ash (%)	Portland type II Cement (%)	Specific Gravity	Average
77	20	3	2.040	
77	20	3	2.020	
77	20	3	2.006	2.033
64	35	1	2.007	
64	35	1	2.034	
64	35	1	2.016	2.019
63	35	2	2.030	
63	35	2	1.906	
63	35	2	2.004	1.980
69	30	1	2.022	
69	30	1	2.032	
69	30	1	2.009	2.031
67	30	3	2.050	
67	30	3	2.086	
67	30	3	2.066	2.066

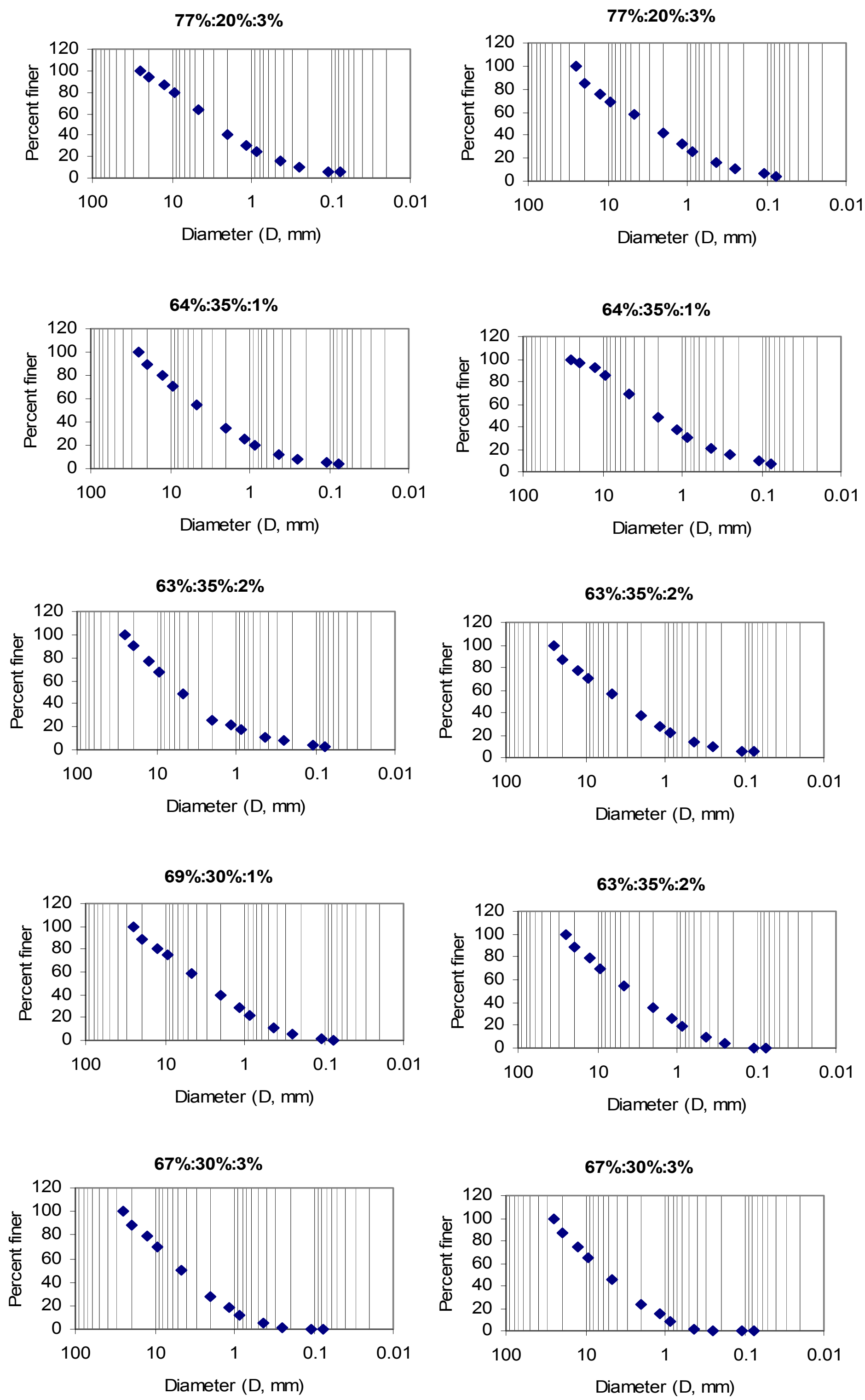

Figure4. Plots of particle gradation obtained from sieve analysis.

Table 11. Δ D50 and Δ D10 were calculated from sieve analysis

Composite Combination	Δ D50 (%)	Average Δ D50 (%)	Δ D10 (%)	Average ΔD10 (%)
77%:20%3%	0.843	0.843	0.992	0.993
77%:20%3%	0.843		0.995	
64%:35%:1%	0.843	0.869	0.987	0.988
64%:35%:1%	0.895		0.990	
63%:35%:2%	0.738	0.791	0.984	0.986
63%:35%:2%	0.843		0.987	
69%:35%:1%	0.843	0.817	0.987	0.983
69%:35%:1%	0.791		0.979	
67%:30%:3%	0.791	0.791	0.953	0.953
67%:30%:3%	0.791		0.953	

Field Submergence: The briquettes were submerged in a bay located at Port Fourchon, Louisiana. The summary of the observations from a four-month submergence study is given in Table 12. The long term submergence results are not available. The FGD composite briquettes designated with 'poor' status showed significant degradation by size and came out of the tied tags. Briquettes designated as 'good' showed only slight degradation; whereas the 'excellent' briquettes are staying firmly with the tags with very little sign of decrease in dimensions.

Table 12. Status of FGD briquettes after four months of field saltwater submergence experiment has shown that three ingredient combinations with low cost survive.

FGD (%)	Class C fly ash (%)	Portland type II cement (%)	Status	Cost ($/ton)
77	20	3	Good	10.15
64	35	1	Excellent	12.26
63	35	2	Excellent	12.94
69	30	1	Excellent	11.10
67	30	3	Poor	12.46

CONCLUSIONS

(1) The effective sulfur (Sulfate + Sulfite) diffusion coefficients of the stabilized FGD: class C fly ash : Portland type II cement blocks is 1.02 – 2.14 ($m^2s^{-1}\times10^{-13}$) while the effective sulfur diffusion coefficient of the stabilized FGD: class C fly ash : Portland type II cement briquettes is 1.34 – 3.96 ($m^2s^{-1}\times10^{-13}$) the higher effective diffusion coefficient for the briquettes indicate that the fabrication conditions for the FGD briquettes is not optimal.

(2) The field salt water submergence experiment shows that 64%:35%:1%, 63%:35%:2% and 69%:30%:1% FGD: class C fly ash: Portland type II cement briquettes have survived for more than 4.5 months.
(3) TCLP test shows that the content of Cr, Cd, As, Pb and Se in the TCLP extraction fluid is far below the maximum concentration limits set by USEPA for declaring a waste to be hazardous .
(4) The geotechnical tests conducted so far on the briquettes show all that all stabilized briquettes behave similar.
(5) The economic analysis shows that 64%:35%:1%, 63%:35%:2% and 69%:30%:1% FGD: class C fly ash: Portland type II cement briquettes can be manufactured at large scale under cost of $13/ton.
These results indicate the feasibility of using light weight stabilized FGD briquettes as conventional structural fill material in the coastal protection projects.

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