

X Behavior of Blocks of Consolidated Spray Dryer
Flue Gas Desulfurization Wastes in the Sea

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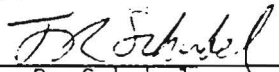
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ABSTRACT

Combustion of coal at electric power stations produces large quantities of fly ash and flue gas desulfurization wastes which must be disposed by environmentally acceptable means. Ocean disposal of these wastes is an attractive option for power stations with access to coastal waterways. For seven years, the Marine Sciences Research Center (MSRC), SUNY, has made very detailed studies on the interactions of a wide variety of coal combustion waste products in marine systems. A new FGD technology, Spray Drying Absorption, produces a dry end product composed of fly ash, desulfurization reaction products and excess reagent. With lime as the fixation reagent, the end products can be dampened and consolidated into self-hardening dense blocks. NIRO Atomizer, a manufacturer of spray drying systems has been investigating spray dryer FGD end product disposal and utilization for five years.

The MSRC has made an assessment of the feasibility of using solid blocks formed from dry FGD end products for ocean disposal reef construction. Several consolidated dry FGD end products from NIRO Atomizer's Riverside, Minn. dry FGD demonstration facility and Copenhagen dry FGD pilot plants were tested as solid proctor blocks. The wastes represent U.S. low sulfur western coal, high sulfur coal, and European coal applications. The waste blocks were exposed in seawater systems for up to a year. Block structural integrity was preserved during submersion, permeability was low and porosity remained virtually unchanged. The unconfined compressive strength was maintained and some proctors showed strength increases in seawater. Physical erosion in the sea was slight but some material (Dutch-2) was heavily eroded by boring clams, deterioration was rapid in this case. U.S. EPA tests for toxicity indicate that the wastes are non-toxic and, in the sea, the test proctors were colonized and overgrown by biological communities characteristic of the test sites. The results of the investigations so far, indicate that spray dryer FGD waste products in the sea behave like blocks of coal combustion waste mixtures of fly ash and "wet" FGD scrubber sludges, which we have studied in great detail. They were found to be without adverse effects in the marine environment.

FINAL REPORT TO NIRO

INTRODUCTION

POWER PLANT COMBUSTION WASTE DISPOSAL

Coal-fired electric power plants equipped with effective fly ash precipitators and flue gas desulfurization (FGD) scrubbers generate large amounts of solid wastes which must be removed from the plant site. A 500 MW plant operating at an average 65% load factor can consume 1.1 million tons of coal annually and generate 600,000 tons of ash and scrubber sludge. It is necessary to dispose of these wastes in a way which is environmentally acceptable and which imposes the lowest economic penalty on the utility company.

Disposal of such large volumes of coal combustion by-products is particularly difficult in the highly urbanized areas such as the industrial northeastern United States. Among the possible options which may meet the environmental standard are disposal in mine shafts or quarries, in land-fills, or in the ocean. Where land for disposal is not available nearby, the combustion waste products must be hauled to remote facilities at high costs. The coal fired power plants on Sjaelland, Denmark, especially in the Copenhagen area, are facing serious problems of disposal for combustion products. The need to protect the vital aquifers of Sjaelland against possible sources of contamination render land disposal very difficult and controversial. Precisely the same problems and concerns apply to combustion waste disposals from power plants on Long Island, New York. For coastal urban areas in general, the ability to dispose of the desulfurization wastes and the ash at sea would be an attractive option. However, ocean dumping of untreated loose fly ash, or wet FGD scrubber sludge, would be environmentally deleterious and is therefore unacceptable (Lunt et al., 1977).

THE COAL WASTE ARTIFICIAL REEF PROGRAM

The feasibility of a method for ocean disposal of large volume combustion waste from coal-fired power plants has been investigated by a multidisciplinary project team of oceanographers and engineers led by the Marine Sciences

Research Center (MSRC) and the Materials Science Laboratory of the State University of New York at Stony Brook, N.Y. The Coal-Waste Artificial Reef Program (C-WARP) has measured the performance of lime-fixated blocks of fly ash and FGD scrubber sludge mixtures submerged in the sea for prolonged exposures, and also measured the effects of the blocks in the marine environment.

Following extensive tests screening and characterizing candidate wastes, techniques were developed for high-speed, large volume processing of coal wastes into solid blocks which were rapidly cured to hardness in steam kilns. Using these new techniques, the program processed 500 tons of two fly ash and FGD scrubber sludge mixtures into more than 15,000 solid blocks (Parker et al., 1981).

In September 1980, the 500 tons of cured blocks were taken out to the Atlantic Ocean south of Long Island, N.Y. and used for the construction of a demonstration disposal artificial reef (Figures 1 and 2). The research program from 1980 to 1984 has principally focussed on serial measurements of the behavior of the new reef of blocks, its colonization by invertebrates and population of fishes, and also on possible effects of the reef upon the marine biota in the vicinity. The objective of this in situ research was to investigate the physio-chemical and biological interactions of the demonstration reef in the sea and to assess the acceptability of coal waste blocks in the marine environment as materials for construction of effective subsurface fishing reefs. This extended program of testing and oceanographic monitoring has found the blocks to be without adverse effects in the sea. Biological colonization and epifaunal settlement and growth are well established. Fishes inhabit the new reef in high population densities (Figure 3) and lobsters have immigrated, some fishes have been tagged and have shown quite high tag returns, -- most returns coming from sport fishermen (Parker et al., 1982; Woodhead et al., 1982).

Support for the C-WARP investigations was provided through joint sponsorship by the Electric Power Research Institute, U.S. Department of Energy, U.S. Environmental Protection Agency, New York State Energy Research and Development Authority, Power Authority of the State of New York, and the Long Island Lighting Company, Inc.

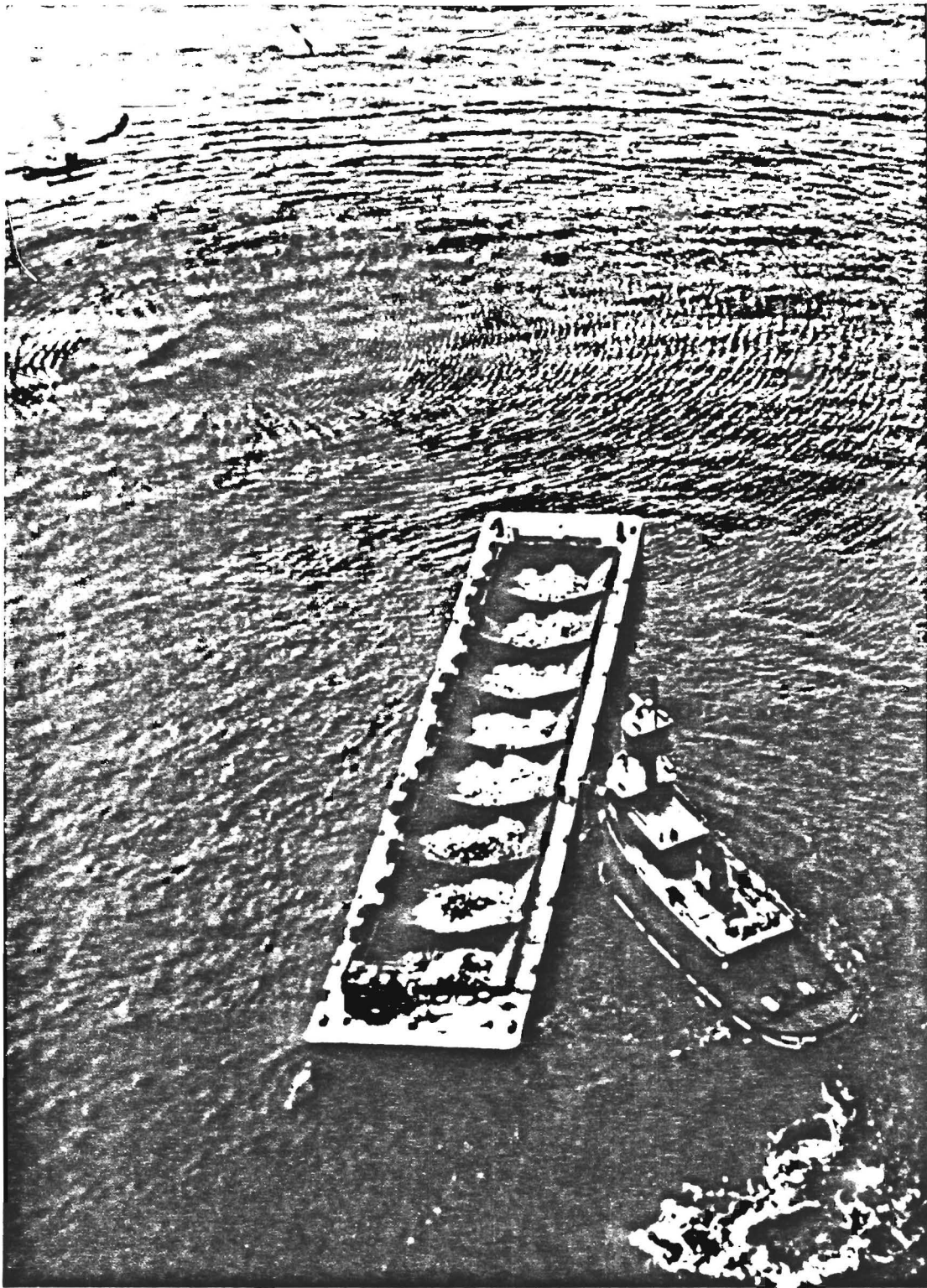


Figure 1. Barge with 15,000 coal waste blocks at project site in Atlantic Ocean.



Figure 2. Reef of blocks on seabed (21 m) after 8 months. Blocks are encrusted with worm tubes, mussels, etc.

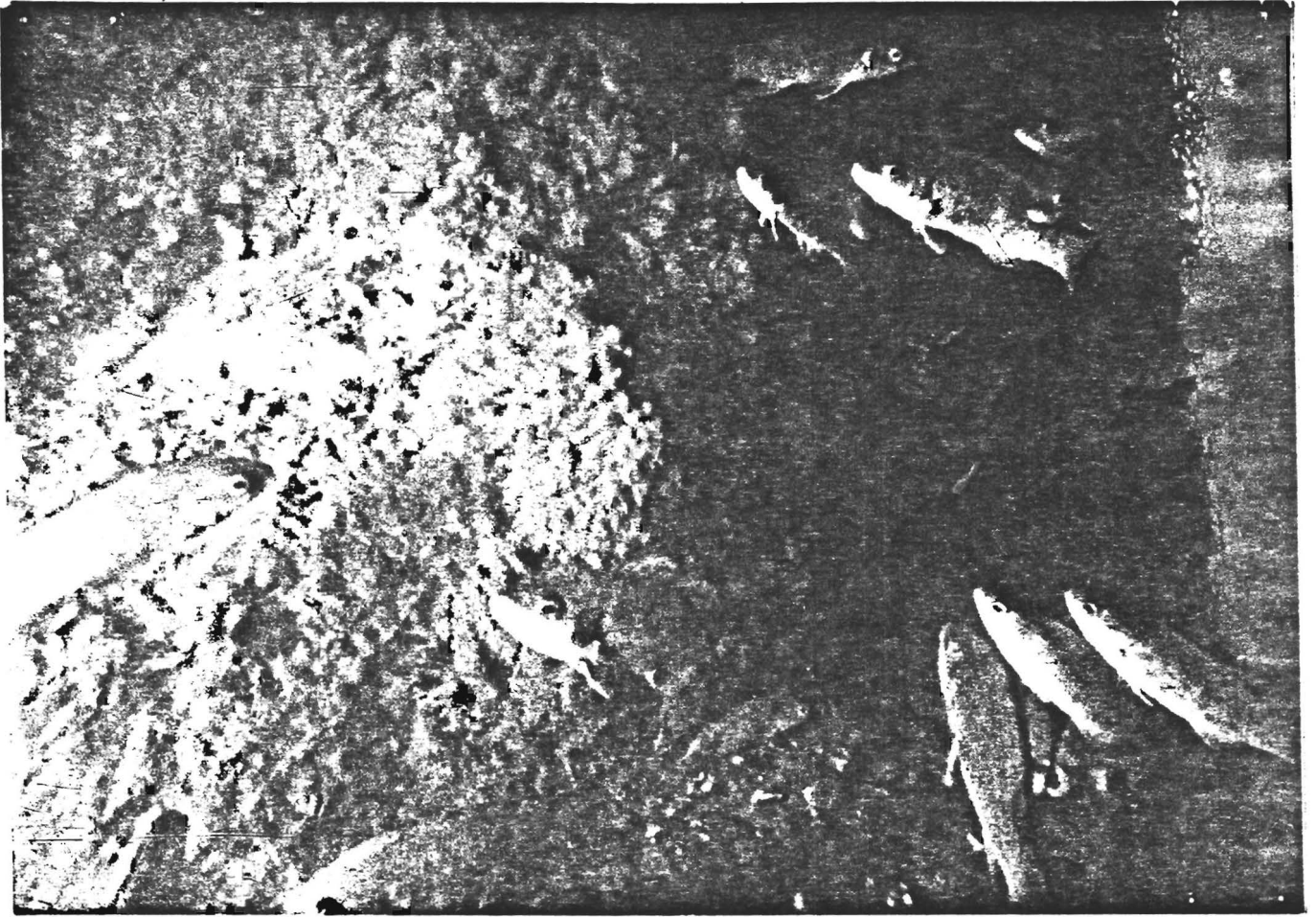


Figure 3. Heavily overgrown coal waste blocks at Conscience Bay site (7 m) after one year. Blocks are encrusted by bryozoan colonies (Bugula turrita), hydroids, and sponges. The fish are cunner, Tautoglabrus adspersus.

In associated investigations, the C-WARP scientists at MSRC have made extensive studies of the behavior and interactions of fixated coal waste blocks in freshwaters, including the N. American Great Lakes, as well as in estuarine environments, including Chesapeake Bay (Duedall and Humphries, 1982; Woodhead et al., 1984).

SPRAY DRYER FGD WASTE DISPOSAL

A new FGD technology, Spray Drying Absorption, was introduced about six years ago. This process produces a dry end product composed of fly ash, desulfurization reaction products and excess reagents. This waste material from dry SO₂ scrubbing is a new product and it is important to develop methods for environmentally acceptable disposal. A/S NIRO Atomizer has been investigating disposal and utilization options for these dry FGD end products over the past five years (Buschmann et al., 1980; Donnelly, 1981; Donnelly, et al., 1982).

PROGRAM OF MARINE INVESTIGATIONS ON SPRAY DRYER FGD WASTES

BACKGROUND

A/S NIRO Atomizer and their representatives made approaches to the MSRC at Stony Brook, N.Y. early in 1981 to consider the possibilities for a program of research to test the behavior of NIRO's FGD waste materials in marine systems, - along the lines of the successful C-WARP investigations being made by MSRC. Discussion of such investigations was developed at a meeting on April 5, 1981, it was then agreed to initiate marine studies on test blocks of spray dryer wastes which would be supplied to the MSRC by A/S NIRO, or their agents (W. Webster Associates, Pennsylvania).

The work required by NIRO consisted of the submersion in marine systems of cured test blocks of consolidated dry FGD wastes for extended periods. The submerged blocks were serially tested to measure changes in their physical properties. In the studies of blocks in the open sea, the biological colonization and overgrowth of the test materials were described in addition to physical testing.

The investigations were made in two phases. In the first phase during 1981, measurements were carried out on two series of proctor test blocks received by MSRC from W. Webster Associates on 1 July and 15 August respectively. Studies were made on the behavior of these proctors in marine systems until June 1982. Results from this collaborative work were presented in a joint paper "Ocean Disposal of Consolidated Spray Dryer Flue Gas Desulfurization Wastes" by Donnelly et al. (1983) at the International Conference on Coal Fired Power Plants and the Aquatic Environment in Copenhagen, 16 to 18 August 1982. A conclusion of that paper was that new investigations were required for three other types of dry FGD end products. The materials proposed for new investigations were:

- end product from high sulfur Illinois coal tests conducted at the Riverside dry FGD demonstration facility
- additional low sulfur blend product from Riverside in the form of briquettes
- end product from typical coals imported for European coastal applications

Immediately following the Copenhagen Int'l Conference the arrangements for this second phase of the work were agreed at NIRO in Soeborg. The second phase studies were made during 1983 on the proctors, and also on briquettes which were supplied directly by NIRO, Copenhagen. This report covers results and observations made by MSRC on the test proctors during both Phases 1 and 2 of the investigations of marine performance by the consolidated spray dryer FGD waste materials.

Over the past three years the MSRC, in conjunction with A/S NIRO Atomizer, has pursued this program of investigations to assess the feasibility of using solid blocks produced from dry FGD end products, for ocean disposal through fishing reef construction, or other underwater usage. Spray dryer waste products from the Riverside, Minn. demonstration dry FGD facility and from wastes representative of European coal-fired utilities have been compacted and cured into hard proctor blocks and supplied to MSRC for the marine testing program.

NIRO SPRAY DRYER FGD PROCESS AND WASTE PRODUCT

In the Spray Drying Absorption FGD process hot flue gas from the boiler is introduced to a spray dryer absorption chamber. In the chamber a liquid reagent, typically lime, is atomized into the boiler flue gas in which it simultaneously reacts with the sulfur dioxide and then dries to a powder. The dry powder is collected from the bottom of the chamber or downstream in a dust collector. A portion of the powder can be recycled to the feed system to improve system performance. When recycle is employed the end product is a homogenous mixture of fly ash, sulfur reaction products and excess reagent. Fly ash particulates are coated first with lime and then with the reaction products. These coatings are continuously stripped off in the particles and recoated during internal recycling. The end product typically contains less than two percent free moisture, it is a dry, free flowing powder. Typical end product compositions for both low and high sulfur coals are given in Table 1 (from Donnelly et al., 1982b).

The FGD end product from Spray Drying Absorption exhibits handling properties similar to dry fly ash. It is easily fluidized and can be transported either mechanically or pneumatically. The waste product typically exhibits pozzolanic properties related to the fly ash content and can be compacted into dense self-hardening bodies (Donnelly et al., 1982a and b). The excess lime present participates in the pozzolanic reactions and the presence of calcium sulfite and sulfate acts to retard the reaction rate (Buschmann et al., 1980; Donnelly, 1981). The intimate mixing of the fly ash, calcium sulfites and sulfates and excess lime in the individual particles achieves high dispersion to promote a uniform hardening of the stabilized product. These very desirable characteristics make dry FGD end products especially good candidate materials for large-scale, high speed, block production and ocean reef disposal.

The first full-size utility spray dryer FGD system in the U.S. started up in December, 1980 at the Northern States Power Company's Riverside Generating Station, Minn. The absorption system was designed and supplied by Niro Atomizer and Joy Manufacturing (Donnelly et al., 1982a; Kaplan et al., 1982).

Table 1. Typical spray dry FGD waste material composition
(from Donnelly, et al., 1982)

Component	Low Sulfur Coal (% wt)	High Sulfur Coal (% wt)
Fly ash	70	40
$\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$	16	38
^a $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$	8	12
$\text{Ca}(\text{OH})_2$	3	8
Moisture	2	2

^a $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$ - a mixture of hemi- and dihydrates.

WASTE MATERIALS TESTED

Phase 1 Material (1981-82)

Two sets of proctor test cylinders were produced by Webster Associates from spray dryer FGD end products collected from:

1. Riverside, Minn. spray dryer FGD plant from low-sulfur coal (termed Riverside-1)
2. A/S NIRO Copenhagen spray dryer FGD pilot plant (Copenhagen-1)

The first samples, identified as Riverside-1, were collected from the dry FGD system's waste disposal silo. The fuel burned in the boiler was a blend of low sulfur (~0.6%) Western sub-bituminous coal and a high sulfur petroleum coke. The equivalent sulfur content for coal is approximately 1.5 percent. The high loss on ignition can be attributed to the petroleum coke. The calcium oxide content is high reflecting the alkaline nature of the fly ash.

The second sample, identified as Copenhagen-1, was produced by NIRO Atomizer's pilot plant using a blend of German Ruhr and Aachen fly ashes. Sulfur dioxide and fly ash were injected in the pilot plant at a rate equivalent to approximately eight percent ash coal. The higher sulfur content of this end product reflects differences in ash contents for the coals.

The chemical composition and related properties to the two FGD end products used in Phase 1 investigations are compared in Table 2.

Webster & Associates made standard proctor cylinders (11.5 x 10 cm) from each sample. The test cylinders were prepared by mixing water and dry FGD end product, and following NIRO standard procedures, compacted the mixes. The cure hardening of sample Copenhagen-1 was supplemented by premixing 95% dry FGD end product with 5% Danish Portland cement.

Optimum moisture contents were determined for each sample, using a NIRO standard procedure. Optimum moisture content corresponds to the maximum dry density for the sample. Optimum moisture contents for dry FGD end products are

Table 2. Phase 1 spray dryer FGD end-products chemical and physical characteristics (from Donnelly, et al., 1982).

Sample ID	Riverside-1	Copenhagen-1
Type Fly Ash	Blend of 15% Petroleum Coke/Western Subbit.	Blend Ruhr/ Aachen Coal
Chemical Composition (All values in % weight)		
SiO ₂	24	29
Al ₂ O ₃	10	16
Fe ₂ O ₃	2.8	5.1
CaO	24	19
MgO	2.8	1.2
Na ₂ O	0.33	0.53
K ₂ O	0.25	2.1
SO ₃	14	19.9
Loss on ignition, %	21	-
Bulk density loose, g/cm ³	0.62	0.58

typically higher than for the corresponding fly ash and range from 25 to 40% added water. For these samples the optimum moisture contents are similar and yield almost the same dry densities. Compressive strength development after seven days cure reflect the differences in the pozzolanic activity of the fly ashes incorporated in the end product (Table 3). Based on the results of moisture density tests, series of proctor cylinders were prepared for each sample and cured for 30 days prior to initiation of studies of the behavior of the new materials in seawater.

Phase 2 Material (1983)

Two sets of proctor test cylinders were made by NIRO, in addition 50 kg of briquettes were also produced. These test materials were from:

1. Riverside Minn, spray dryer FGD plant, from high-sulfur coal (Riverside-2): 20 proctors
2. Dutch-type FGD waste (Dutch-2): 20 proctors
3. Riverside Minn. spray dryer FGD plant, from low-sulfur coal: 50 Kg of 1 in briquettes (Briquettes)

These FGD waste materials were received by MSRC as cured, hard test-blocks and briquettes. The details are not known about the production of FGD end products, their collection, or the chemical and physical characteristics of the three materials supplied for the Phase 2 tests in marine systems.

Test Sites

The cured FGD products were tested in three different marine environments in the vicinity of Long Island, N.Y. (Figure 4). All three test sites had previously been used extensively in the long series of the C-WARP investigations, and for each we had extensive information from those studies.

1. The C-WARP test site in the open Atlantic is 20 m deep on a quartz sand-covered seabed some 3 km south of Fire Island; details of seasonal changes in water quality parameters for the C-WARP test site have been described in Parker et al., (1981). Open frame-work test tables about 3 m long

Table 3. Phase 1 dry FGD end-products, moisture, density and strength results.

Sample		Riverside-1			Copenhagen-1		
Cement added	%	0			5		
Water added	%	31	35	37	29	33	35
Density, g/ml							
	Wet	1.43	1.67	1.66	1.55	1.69	1.69
	Dry	1.10	1.24	1.21	1.20	1.27	1.25
Comprehensive Strength, psi							
	7 days @ 73°F	152	1370	1123	412	455	333

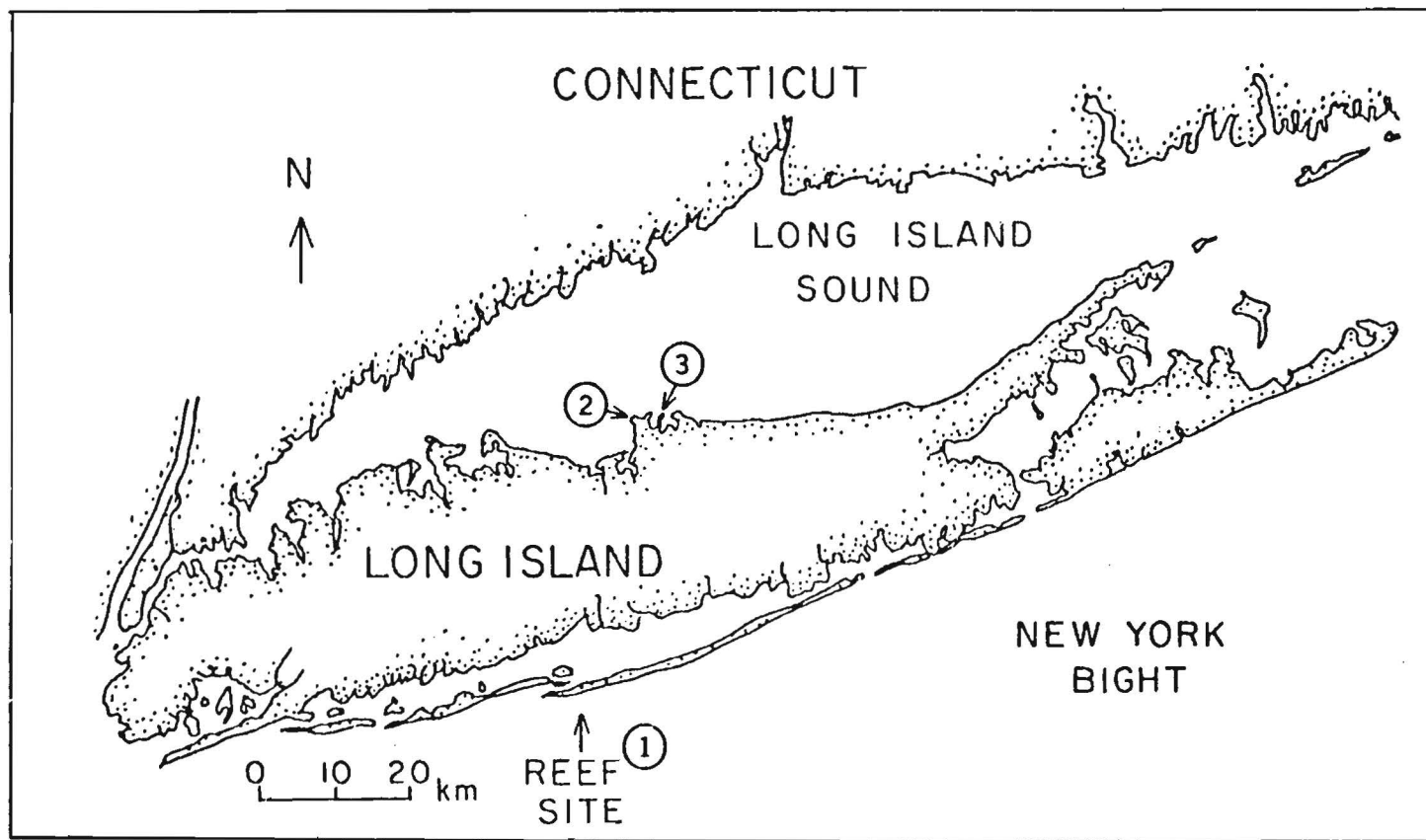


Figure 4. Project test sites: (1) Atlantic Ocean, (2) Flax Pond Sea Tables, (3) Conscience Bay (7 m).

have been placed on the seabed, the proctor test blocks were placed in plastic (PVC) racks which were set out on the table frames for tests of prolonged marine submergence on the behavior of the blocks of different coal waste materials (Parker et al., 1982a and b; Woodhead et al., 1982).

2. In Long Island Sound (north shore of Long Island) a tidally flushed sheltered embayment, Conscience Bay, has been used since 1977 as a test site for C-WARP. The site is about 6 m deep and the bottom is composed of poorly sorted gravel and sand. There are strong tidal currents in excess of 100 cm/sec. With such current speeds the waters are turbid. Salinities were between 25 ‰ and 30 ‰, water temperatures range seasonally between 0°C and 24°C and in harsh winters the site freezes over. Other details are described in Roethel et al. (1980; 1983).

3. Marine aquarium facilities at the MSRC's Flax Pond Laboratory were used to hold test blocks submerged 0.7 m deep for periods of up to a year. The aquaria were of the flow-through type, excess water running to waste pipes. The Flax Pond Laboratory is sited on the south shore of Long Island Sound, from which it pumps seawater. The Laboratory is about 4 km west of the Conscience Bay site and seasonal changes in water quality parameters were very similar for both the Conscience Bay site and for the waters flowing through the aquaria in the Flax Pond Laboratory (Parker et al., 1981).

In Phase 2 eight cured test proctors of each FGD waste plus about 25 kg of a sample of the briquettes were put in plastic racks on the seabed (7 m) at the Conscience Bay site. An additional eight proctors, of each FGD waste were placed in the flowing seawater tables at the Flax Pond Laboratory to allow more frequent visual inspection. Finally, four remaining proctors of each type were placed at the Atlantic Project site at a depth of 21 meters; two proctors of each types were tested after one month of exposure but the second pairs disappeared during a strong storm. The remaining pairs of proctors and the briquettes were retained for reference.

PHYSICAL PROPERTIES

Unconfined Compressive Strength and Density

Our previous experience with a wide range of power plant coal wastes has indicated that compressive strength provides a valuable indicator of probable block performance in the marine environment. Generally, cured strengths in excess of 300 psi for coal waste blocks have been found satisfactory for maintenance of integrity and strength when exposed in seawater for extended periods of at least several years.

The unconfined compressive strength of materials was tested following ASTM method C39-72, in which a load is applied until the sample fails. Each sample was placed in a Riehle universal testing apparatus with the axis of the proctor being aligned with the center of thrust of the pressure head. The load was applied steadily at a rate in the range of 20 to 50 psi per second, until the sample failed. The pressure (load/force) applied at failure of the test block provides a quantitative measure of integral strength of the sample. The maximum load carried during the test was recorded and this value was divided by the cross sectional area of the block to calculate the compressive strength, in psi.

Phase 1 results. The Copenhagen-1 proctors were placed in the sea tables at Flax Pond and tested after immersion periods of up to 1 year for changes in compressive strength. The Riverside-1 proctors were placed in flowing seawater tables at the Flax Pond Laboratory and also at the Atlantic C-WARP project site, at a depth of 2 meters. Other Riverside-1 proctors were retained in the lab for reference. Tables 4 and 5 present the results of testing the proctors for compressive strength after prolonged exposures in seawater.

The results for Copenhagen-1 proctors cover a year of immersion in flowing seawater in the Flax Pond aquaria. The cylinders show a wide variation in compressive strengths between samples, (Table 4). However, the compressive strengths are high and strength was maintained over the period of seawater exposure. The compressive strength measurements for proctor samples of Riverside-1 (Table 5) were consistently higher than for samples of Copenhagen-1

Table 4. Strength of consolidated Copenhagen-1 dry scrubber proctors.

Exposure (days)	Density (g/ml)		Test Site	Compressive Strength (psi)
	Dry	Wet		
0		1.68	MSRC	596
0		1.68	MSRC	648
	Avg 1.26	Avg 1.68 ± 0.0		Avg 622 ± 26
42		1.67	Flax Pond	808
42		1.67	Flax Pond	740
	Avg 1.27	Avg 1.67 ± 0.0		Avg 774 ± 34
78		1.71	Flax Pond	844
78		1.70	Flax Pond	741
	Avg 1.28	Avg 1.70 ± 0.0		Avg 792 ± 51
110		1.67	Flax Pond	729
110		1.67	Flax Pond	652
	Avg 1.27	Avg 1.67 ± 0.0		Avg 690 ± 38
160		1.68	Flax Pond	533
160		1.68	Flax Pond	536
160		1.68	Flax Pond	816
160		1.68	Flax Pond	806
	Avg 1.28	Avg 1.68 ± 0.0		Avg 672 ± 130
330			Flax Pond	828
			Flax Pond	692
			Flax Pond	623
	Avg 1.28	1.68		Avg 714 ± 76

Table 5. Strength of consolidated NIRO Riverside-1 dry scrubber proctors

Exposure (days)	Density (g/ml)		Site	Compressive Strength (psi)
	Dry	Wet		
0	1.23	1.66	MSRC	1325
0	1.21	1.64	MSRC	678
0	1.21	1.64	MSRC	941
0	1.22	1.65	MSRC	842
	Avg 1.22±0.03	Avg 1.65±0.01		Avg 946±189
30	1.22	1.65	Flax Pond	1092
30	1.24	1.67	Flax Pond	915
	Avg 1.23±0.01	Avg 1.66±0.01		Avg 1002±88
55			Atlantic	836
55			Atlantic	780
55			Atlantic	1130
	Avg 1.22±0.01	Avg 1.66±0.01		Avg 915±143
61	1.23	1.67	Flax Pond	1019
61	1.22	1.65	Flax Pond	835
	Avg 1.22±0.01	Avg 1.65±0.01		Avg 927±92
(90) ¹	1.21	1.64	MSRC ¹	1365
(90) ¹	1.21	1.64	MSRC	1341
(90) ¹	1.23	1.66	MSRC	1373
(90) ¹	1.23	1.66	MSRC	1281
	Avg 1.22±0.01	Avg 1.65±0.01		Avg 1340±29
90			Flax Pond	1345
90			Flax Pond	1015
	Avg 1.23±0.01	Avg 1.65±0.01		Avg 1180±35
98			Atlantic	934
98			Atlantic	974
98			Atlantic	812
	Avg 1.22±0.01 ²	Avg 1.65±0.01		Avg 906±63

- 1 Proctors stored dry at MSRC and tested after 90 days for changes in strength.
2 The results for 98 days exposure are composite results for Riverside-1 blocks tested; the block identification numbers washed off during exposure in seawater.

and reflect the greater pozzolanic nature of the fly ash component of the material.

As with samples of Copenhagen-1, individual Riverside cylinders exhibit a wide range of compressive strengths; there appears to be no real change in average cylinder strengths over the three month test period. Proctor cylinders exposed to the open seas in the Atlantic test site seem to show the lowest strengths, however there is no reason to believe that changes at the Atlantic site would have more effect than changes in the Flax Pond aquaria; these results were likely to be due to variation between individual cylinders. The compressive strengths were two to three times higher than 300 psi strengths considered a requirement for SSFA blocks in the sea.

The wet densities of the Copenhagen proctors were only slightly greater than those of Riverside end product. Neither set of proctors showed significant change in density during seawater exposure (Tables 4 and 5).

Phase 2 results. Compressive strengths of the Dutch-2 proctors were initially close to the minimum strength (300 psi) considered necessary for maintenance of physical integrity over the long-term in marine environments. Indeed during the in situ testing at sea the strengths of these proctors were generally below 300 psi, nevertheless block integrity was maintained. The Riverside-2 proctors had initial compressive strengths nearly twice the strengths of the Dutch-2 proctors, and well above the acceptable strength criterion of 300 psi.

The changes in compressive strengths for the two types of Phase 2 proctors during extended submersion in marine systems are shown in Table 6 for proctors in the Flax Pond Laboratory, at 7 m in Conscience Bay and at 21 m in the Atlantic Ocean. The Riverside-2 proctors were always stronger than the Dutch-2 proctors and this difference in strength tended to increase from about 2x for initial strengths to 3x or more, over 6 months in the sea. The sets of Riverside-2 proctors in Conscience Bay and in the Flax Pond Lab showed considerable variations but tended to increase significantly in strength over exposures of 6 and 7 months. In the Atlantic at the C-WARP demonstration reef site only one set of proctors was retrieved, after one month, the remaining set being lost in a storm. However, during the 1 month exposure, these Riverside-2

blocks apparently increased in strength in the same way as the sets in Conscience Bay and in the Flax Pond Lab during the first month (Table 6).

The Dutch-2 materials varied considerably in strength between individual proctors. Unlike the Riverside-2 material, the strengths of Dutch-2 proctors did not increase during protracted submersion in seawater and may have diminished after 7 months in seatables at the Flax Pond Laboratory (although the variability shown between test blocks and the small numbers of samples tested may well account for these results). At the C-WARP reef site exposure was too short to draw significant conclusions although the results for the single test pair were of low strength, less than the 300 psi criterion. At the Conscience Bay site the Dutch-2 proctor sets maintained about the same strength as those in the laboratory seatables until the final pair was tested after 6 months. The 6 month proctors from Conscience Bay had very low strengths but they had been very extensively bored and eroded (Figure 5) by burrowing clams, Zirfaea crispata (see Biological Evaluation), causing the low strengths, which were therefore not comparable with the earlier measurements of proctor strength. This anomalous result will be discussed further in the biological section of the report. While the Dutch-2 proctors were always less strong than Riverside-2, they consistently yielded higher densities.

Porosity

The porosity of the two types of NIRO proctor samples was determined by the ASTM method C642-75. The test procedure required a series of progressive weighings after oven drying, saturation by immersion in seawater, immersed and boiled for 5 hours, and finally, suspended in water. The resulting weights were used to calculate specific gravity, the percent absorption, and the percent voids of the spray dryer FGD wastes. Porosities were not measured in Phase 1. Data on the measurements for calculation of porosity, as percent volume of permeable voids, is given in Table 7.

The Riverside proctors yielded higher porosities than Dutch-2 proctors, which is consistent with the density measurements (Table 6), the Riverside test materials being less dense than the Dutch-2 proctors.

Table 6. Compressive strength and density of dry scrubber proctors in seatables at Flax Pond Laboratory, in Conscience Bay test site, and in the Atlantic Ocean.

Sample	<u>Initial</u>		<u>1 Month</u>		<u>2 Months</u>		<u>7 Months</u>	
	Strength (psi)	Density (g/ml)	Strength (psi)	Density (g/ml)	Strength (psi)	Density (g/ml)	Strength (psi)	Density (g/ml)
Riverside-2	565	1.60	908	1.57	1326	1.70	1139	1.63
	665	1.71	883	1.61	1523	1.58	1057	1.62
Dutch-2	264	1.68	322	1.74	359	1.68	240	1.76
	372	1.70	352	1.70	316	1.68	208	1.73

Conscience Bay Test Site

Samples	<u>Initial</u>		<u>1 Month</u>		<u>2 Months</u>		<u>6 Months</u>	
	Strength (psi)	Density (g/ml)	Strength (psi)	Density (g/ml)	Strength (psi)	Density (g/ml)	Strength (psi)	Density (g/ml)
Riverside-2	565	1.60	521	1.68	850	1.64	958	1.64
	665	1.71	1072	1.71	1252	1.66	827	1.72
Dutch-2	264	1.68	268	1.75	271	1.74	67 ¹	1.78
	372	1.70	246	1.76	316	1.71	122 ¹	1.75

Atlantic Test Site

Sample	<u>Initial</u>		<u>1 Month</u>	
	Strength (psi)	Density (g/ml)	Strength (psi)	Density (g/ml)
Riverside-2	565	1.60	1031	1.68
	665	1.71	692	1.67
Dutch-2	264	1.68	226	1.76
	372	1.70	207	1.80

1 Blocks heavily bored and weakened by clams, the true strength of the unbored material could not be measured.

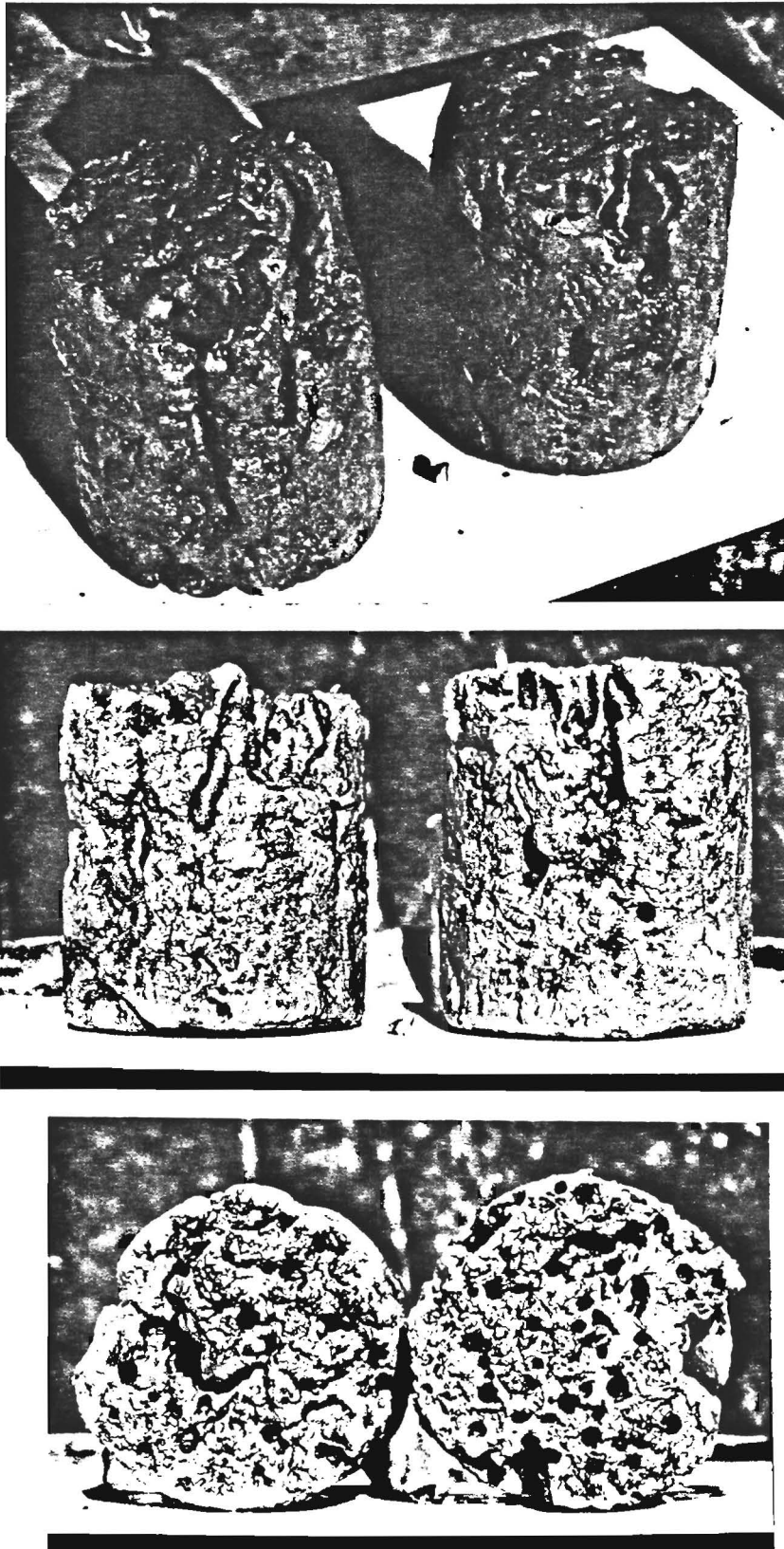


Figure 5. Test proctors of Dutch-2 material after 6 months at Conscience Bay test site.

Table 7. Porosity of test samples (using ASTM-C 642-75).

Specimen	Dry Weight (A)	Saturated Wt (B)	Sat. Wt After Boiling (C)	Suspended Wt (D)
<u>Riverside-2</u>				
-1	286.2g	447.7g	449.6g	168.6g
-2	301.7	460.9	463.3	192.3
-3	291.3	439.7	441.7	152.7
<u>Dutch-2</u>				
-1	337.4	462.5	465.7	188.4
-2	376.2	514.1	515.7	208.7
-3	365.2	491.8	494.9	203.6
-4	361.7	487.5	490.7	202.4

Calculations

- 1) Absorption after immersion, percent = $(B-A)/A \times 100$
- 2) Absorption after immersion & boiling, percent = $(C-A)/A \times 100$
- 3) Bulk specific gravity, dry = $g_1 = A/(C-D)$
- 4) Bulk sp. gr. after immersion = $B/(C-D)$
- 5) Bulk sp. gr. after immersion and boiling = $C/(C-D)$
- 6) Apparent sp. gr. = $g_2 = A/(A-D)$
- 7) Volume of permeable pore space (void), percent
 $= (C-A)/(C-D) \times 100$
or $= (g_2 - g_1)/g_2 \times 100$

Specimen	<u>Results</u>						Pore space %
	1	2	3	4	5	6	
<u>Riverside-2</u>							
-1	56.43	57.01	1.019	1.593	1.600	2.434	58.15
-2	52.77	53.56	1.113	1.701	1.710	2.758	59.63
-3	50.94	51.63	1.008	1.521	1.528	2.102	52.04
<u>Dutch-2</u>							
-1	37.08	38.03	1.217	1.668	1.679	2.264	46.27
-2	36.65	37.08	1.225	1.675	1.680	1.833	45.44
-3	34.67	35.51	1.254	1.688	1.699	2.260	44.52
-4	34.78	35.67	1.254	1.690	1.701	2.804	44.73

Permeability

Permeability coefficients were determined for the two types of test proctors using the Darcy falling head method as described in ASTM method D 2424.

Cross-section, cylindrical samples of test proctors, 4.2 cm thick, were epoxied into the bottom of PVC columns (21 cm long by 8 cm inner diameter). The 4.2 cm biscuit of sample was fitted into the bottom of the PVC column and epoxied in place with Foxy-Poxy[®]. A PVC end cap fitted with a nylon hose nipple was epoxied onto the bottom of the column. Permeability column elutriate passed through the nylon nipple into a covered plastic beaker which collected and measured the discharge water.

To begin the permeability test, the samples sealed in the columns were first saturated with seawater, then the columns were filled with seawater. Starting time and height were recorded and a plastic bag was attached to the top (open end) of the columns to prevent evaporation. Subsequent readings of time, water column height and volume of elutriate collected below the column were recorded and used to calculate the coefficient of permeability (K) by:

$$K = \frac{L}{A\Delta H} \frac{dq}{dt}$$

where L = proctor length (cm),

A = cross-sectional area of sample (cm²)

$\frac{dq}{dt}$ = rate of flow of water (cm³/sec), and

ΔH = change in water column height (cm).

Phase 1 results. Table 8 presents the results of the permeability determinations over time for the Copenhagen-1 samples. There is an initial rapid increase in permeability during the first two to three weeks of testing which results in a doubling of the permeability coefficient. This may be related to initial saturating of the samples. The permeabilities then level off to more or less steady values. The permeabilities are very low in the order of 10⁻⁸ cm/sec. The two curves in Figure 6 show variations in permeability between test-cylinder samples.

Table 8. Permeability of NIRO spray dryer product product, Phase 1.

Time t, days	Permeability coefficient $K \times 10^{-8}$ cm/sec		Water Volume Q, ml	
	Riverside-1	Copenhagen-1	Riverside-1	Copenhagen-1
2	4.33	2.14	5	3
4	5.59	3.66	13	10
7	6.64	3.54	25	20
10	6.45	4.61	37	31
24	7.45	5.05	93	80
31	6.68	5.05	113	103
35	6.86	5.26	130	120
51	8.96 ¹	4.56	182	144
60	6.54	4.79	205	181
66	6.64	4.85	227	200

1 Anomalous result

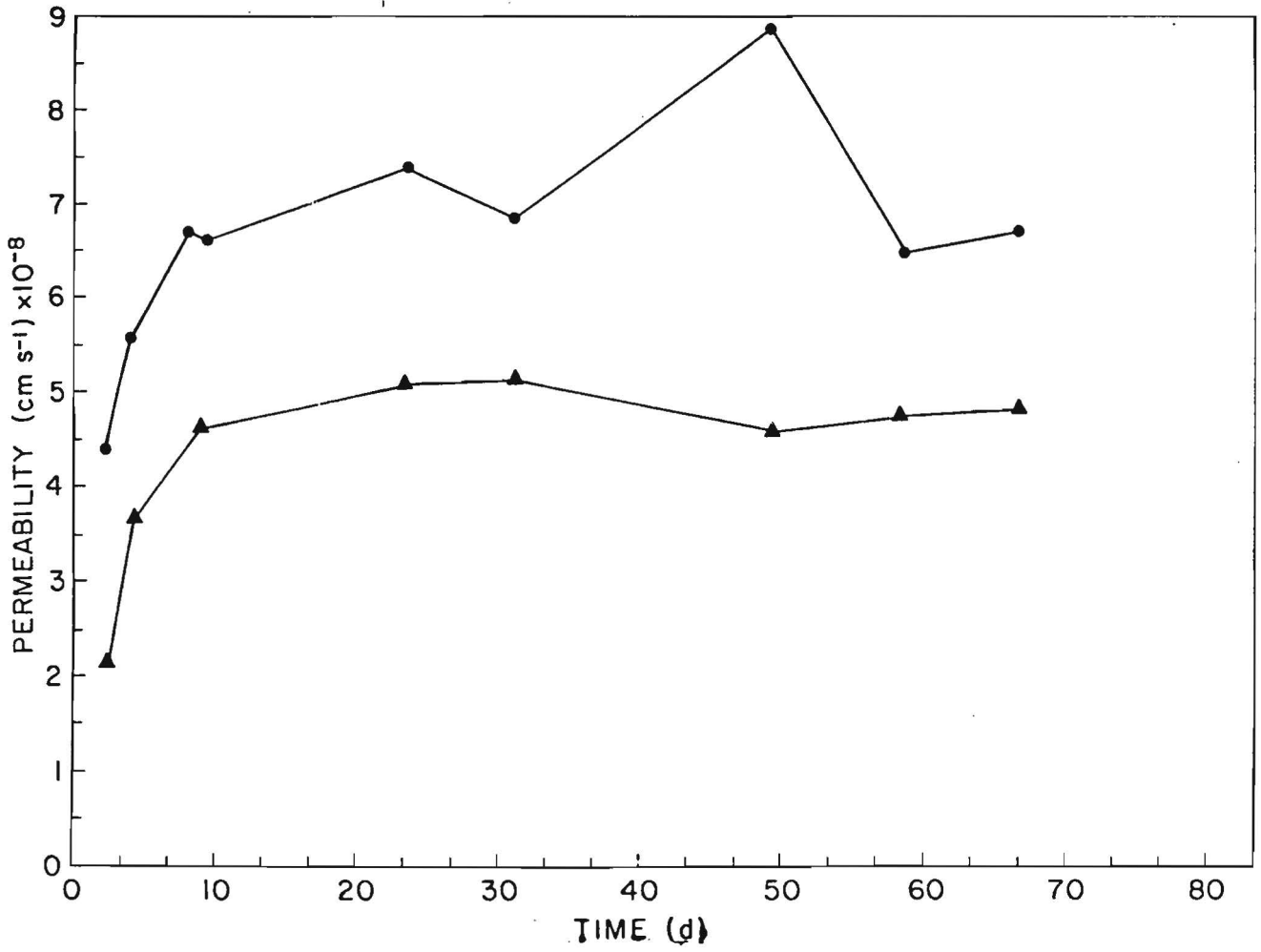


Figure 6. Permeability of test proctors: ● - Riverside-1, ▲ - Copenhagen-1.

Figure 7 shows weight increase versus time for samples of both Copenhagen-1 and Riverside-1 products due to water absorption by the proctor cylinders. The amount of water uptake by the cylinders is related to the porosity of the test materials.

Phase 2 results. The permeabilities are very low in the order of 10^{-8} cm/sec (Table 9). The Riverside-2 proctors yielded slightly higher permeability coefficients than the Dutch-2 samples. The difference between these results is consistent with the other physical properties determined for the proctors (in the preceding sub-sections), the Dutch-2 blocks were also found to be less porous and more dense than the Riverside-2 blocks. The permeability results for the cured blocks of both mixes are much lower than the permeability coefficients typical for untreated fly ashes and FGD sludges which are typically in the range of 10^{-4} to 10^{-5} cm/sec.

Behavior and Erosion of Blocks in the Sea

The Phase 1 test blocks, Riverside-1 and Copenhagen-1 were set out in plastic racks on the seabed at the C-WARP demonstration reef site in the New York Bight. After exposures of up to 14 weeks at the site blocks were retrieved for testing and the appearance of the blocks was noted, particular attention being given to evidence of physical erosion. Conditions at the site, 21 m deep, are relatively tranquil with tidal currents generally less than 20 cm/sec and only heavy seas causing stirring and resuspension of dense sandy sediments.

The Phase 1 proctors retrieved from the New York Bight showed no evidence of significant surface abrasion. The top and bottom edges were still rounding off due to physical erosion.

The Phase 2 test blocks Riverside-2, Dutch-2 and (Riverside) Briquettes were set out in the sea in open plastic trays on the seabed at Conscience Bay, Long Island Sound test site. The site is in the restricted "narrows" region near the entrance to the bay and tidal exchange currents run strongly at rates in excess of 100 cm/sec. At such current speeds coarser sediments carried in suspension may have considerable abrasive effects in the long term. However the bay itself is well protected from the surge and rush of storm seas.

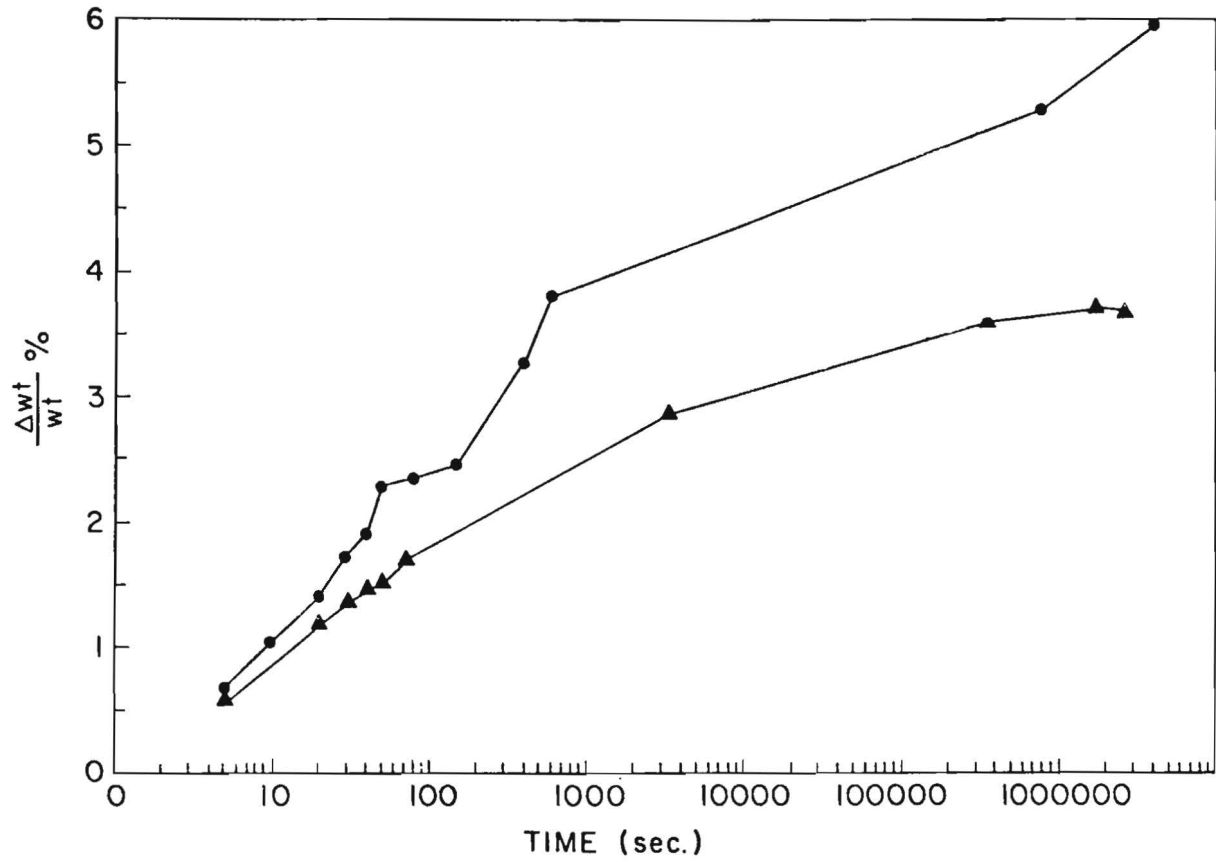


Figure 7. % water uptake by test proctors: ● - Riverside-1, ▲ Copenhagen-1.

Table 9. Permeability coefficients of samples tested in Phase 2.

<u>Riverside-2</u>				
Time (hrs)	<u>Proctor 1</u>		<u>Proctor 2</u>	
	Height (cm)	Coefficient (cm/sec)	Height (cm)	Coefficient (cm/sec)
0	18.25	0	19.28	0
6.2	16.19	1.44×10^{-4}	17.30	1.56×10^{-4}
10.8	16.11	3.22×10^{-6}	17.14	7.38×10^{-6}
23.3	15.55	1.08×10^{-5}	16.82	7.02×10^{-6}
31.9	15.23	4.47×10^{-6}	16.50	5.14×10^{-6}
48.5	14.76	4.32×10^{-6}	16.19	3.36×10^{-6}
55.2	14.28	3.68×10^{-6}	15.95	2.19×10^{-6}
147	10.95	7.61×10^{-6}	13.65	6.77×10^{-6}
170	10.15	1.49×10^{-6}	13.01	1.54×10^{-6}
176	9.84	5.61×10^{-7}	12.85	3.66×10^{-7}
196	9.36	7.33×10^{-7}	12.38	9.54×10^{-7}
223	8.33	1.32×10^{-6}	11.90	8.13×10^{-7}
248	7.69	7.05×10^{-7}	11.58	4.79×10^{-7}
319	5.63	1.60×10^{-6}	10.31	1.37×10^{-6}
366	4.04	9.94×10^{-7}	9.60	6.42×10^{-7}
414	3.01	5.47×10^{-7}	8.72	6.61×10^{-7}
486	1.26	7.35×10^{-7}	7.77	5.84×10^{-7}
533	-	-	7.14	3.44×10^{-7}
<u>Dutch-2</u>				
0	20.15	0	18.89	0
6.2	18.49	9.77×10^{-5}	17.15	1.18×10^{-4}
10.8	18.41	2.78×10^{-6}	17.15	0
23.3	18.25	2.73×10^{-6}	17.07	1.47×10^{-6}
31.9	18.01	3.13×10^{-6}	16.91	2.25×10^{-6}
48.5	17.93	6.94×10^{-7}	16.83	7.52×10^{-7}
55.2	17.77	1.24×10^{-6}	16.67	1.35×10^{-6}
147	16.74	2.99×10^{-6}	15.72	3.09×10^{-6}
170	16.50	5.88×10^{-7}	15.40	8.77×10^{-7}
176	16.34	3.73×10^{-7}	15.16	6.24×10^{-7}
196	16.10	4.95×10^{-7}	15.16	0
223	16.10	0	15.16	0
248	15.95	2.59×10^{-7}	15.08	1.48×10^{-7}
319	15.71	2.96×10^{-7}	15.08	0
366	15.23	4.97×10^{-7}	14.92	1.97×10^{-7}
414	15.15	7.28×10^{-8}	14.76	1.72×10^{-7}
486	15.00	1.22×10^{-7}	14.44	2.87×10^{-7}
533	14.76	1.65×10^{-8}	14.37	5.95×10^{-8}
702	14.28	2.01×10^{-8}	14.21	9.76×10^{-8}

The test-proctors retrieved from Conscience Bay were inspected for signs of physical breakdown or erosion of edges, etc. The Riverside-2 proctors were hard and exposed surfaces were smooth, slightly slick to the touch, they were not abraded, -- in fact they were protected from abrasion by the calcareous encrustations of epifaunal overgrowths which coated their surfaces (Figure 8) (see Biological Evaluation section). The briquettes also maintained surface integrity, showing little signs of erosion; the surfaces of many briquettes were also overgrown by an encrusting fauna.

The Dutch-2 proctors set out at the Conscience Bay site did not fare well. They were rather less hard than the Riverside-2 blocks and also were more slick to the touch, almost "greasy". Effects of physical abrasion were seen in some blunting, or rounding, of top and bottom edges, although such effects were not pronounced. However the Dutch-2 blocks were severely eroded by boring clams, Zirfaea crispata. The boring clams went on to expand the size of their burrows as they grew in size within the blocks, until sections of the tops of blocks fell away or were eroded further physically (Figure 5). Small crabs used the holes in the blocks as refuges and they also worked on the material, eroding it to extend their holes. These proctors were also colonized and overgrown by a calcareous encrusting community of the same invertebrates that grew on the Riverside-2 blocks but in places large plaques of encrustations had fallen away from the Dutch-2 proctor surfaces and the epifaunal community obviously did not provide a protective coating from the intrusive activities of Z. crispata.

Mineralogy

X-ray diffraction. Samples of Riverside-2 and Dutch-2 proctors which had been exposed in seawater for 6 months were analyzed by x-ray diffraction to determine possible changes in the minerals of major and minor phases in the cured FGD materials. Samples of the Riverside Briquettes that had been submerged at 7 m deep in Conscience Bay were also analyzed and compared with fresh (unreacted) Briquette samples. The dry FGD samples were ground to pass through a 500 μm sieve. The powdered samples were mounted in the hole of an aluminum test slide. The prepared samples were analyzed on a General Electric Model 5 diffractometer using $\text{CuK}\alpha$ radiation at 30 Ku and 15 ma; the samples

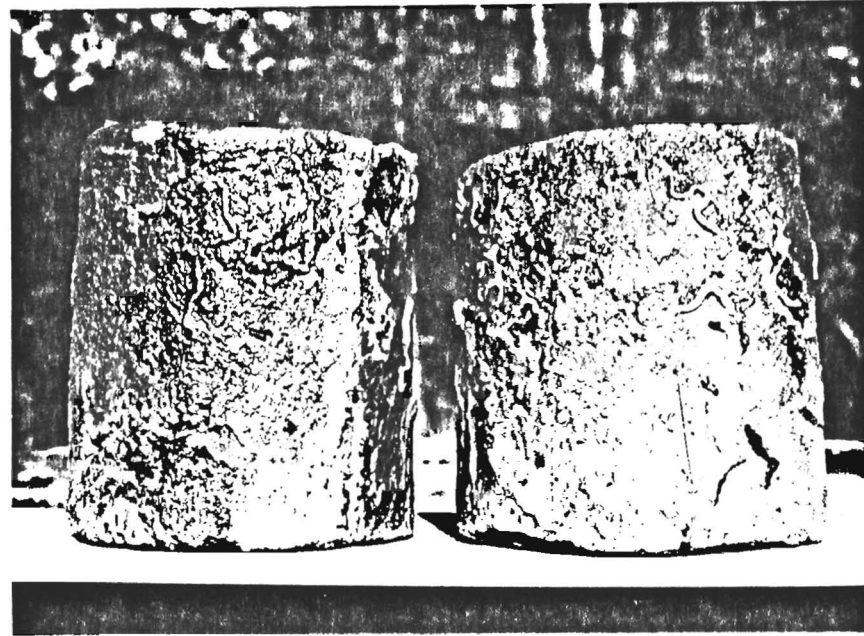
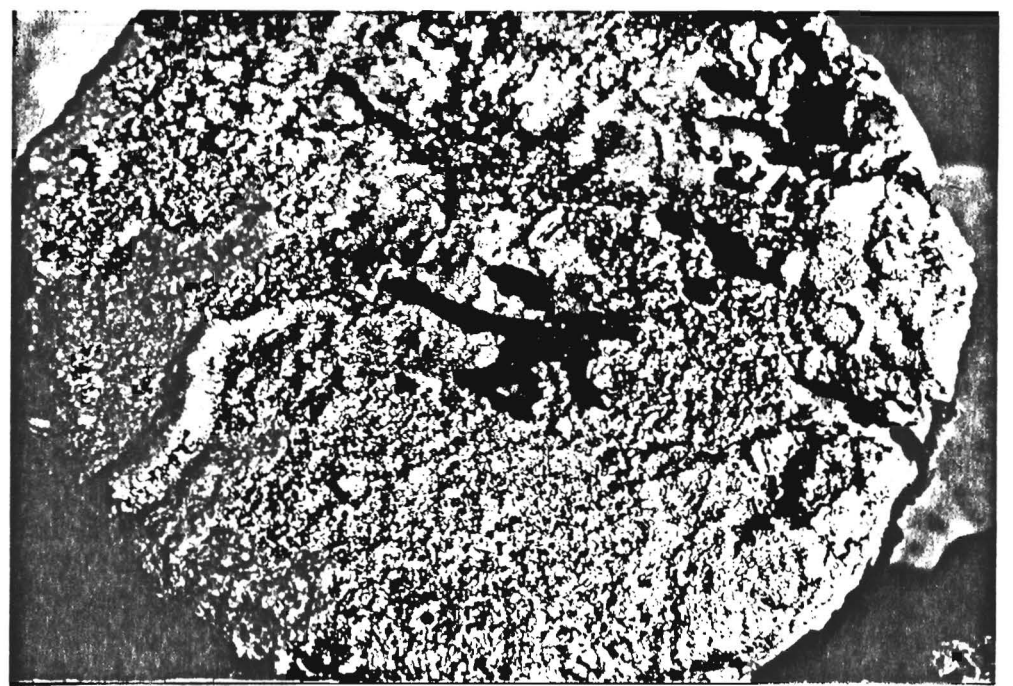


Figure 8. Test proctors of Riverside-2 material after 6 months at the Conscience Bay site.

were scanned from $5^{\circ}2\theta$ to $60^{\circ}2\theta$. Phases were identified from the pattern of peaks and classified as major or minor based on relative peak heights.

Table 10 presents the x-ray diffraction results for the NIRO FGD dry samples. Only small differences can be seen between the mineralogy of Riverside-2 and Dutch-2 proctors. The significant changes occur in the briquettes exposed to seawater, the calcite (CaCO_3) is depleted and tobermorite ($\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$) seemed to have been enriched.

Some Mg-enriched minerals, as epsomite and periclase, may have increased slightly in the marine reacted briquettes. The changes in Mg-enriched compounds are of interest because our earlier investigations in the C-WARP and related programs, have shown that coal waste blocks (in this case mixes of "wet" FGD sludge and fly ash fixated with lime) exposed in the sea for extended periods, tend to slowly leach calcium. The calcium is replaced by magnesium-based compounds through an ion-exchange system (Parker et al., 1984, Woodhead et al., 1984).

Scanning electron microscopy (SEM). SEM was used to examine the fine morphology and size of particles of the cured Riverside Briquettes both before and after exposure to seawater. Grain mounts of the samples were glued to SEM studs and coated with gold before being examined over a range of magnifications under a Joel Model 35C scanning electron microscope operated at 25 KV.

The large pore spaces seen in the photomicrographs (Figure 9) of the unreacted briquettes are not evident in the pictures of the briquettes exposed in the sea for 6 months. The fine particles filling the SEM photograph and the absence of large pores seem to indicate that recrystallization and mineral formation was occurring during reaction submerged in seawater.

Conclusions on Physical and Chemical Behavior of Spray Dryer FGD Wastes

Reacting NIRO Spray Dryer FGD products with lime and consolidating this material into cured solid blocks markedly improves the physical properties of the FGD products for disposal in the sea. Untreated, low density FGD sludges and fly ash would be dispersed widely throughout the water column and would

Table 10. Mineralogy of test samples exposed in seawater for 6 months.

Mix	Riverside-1	Riverside-2	Copenhagen-1	Copenhagen-2	Briquette-1*	Briquette-2*	Briquette-1	Briquette-2
Gypsum (CaSO ₄)	m	m	m	m	m	m	m	m
Calcium Sulfite Hemihydrate (CaSO ₃)	M	M	M	m	M	M	M	M
Quartz (SiO ₂)	M	M	m	M	M	M	M	M
Calcite (CaCO ₃)	m	-	m	M	m	m	-	-
Ettringite Ca ₆ Al ₂ (SO ₄) ₃	m	m	m	M	-	m	m	m
Epsomite (MgSO ₄)	m	m	m	-	-	-	m	-
Hematite (Fe ₂ O ₃)	m	m	-	-	m	m	m	m
Magnetite (Fe ₃ O ₄)	m	m	m	M	m	m	m	m
Mullite (2AlO ₃ .2SiO ₂)	m	m	m	M	m	m	m	m
Magnesite (MgCO ₃)	-	-	-	-	-	-	-	-
Percilase (MgO)	m	-	m	m	-	m	m	m
Tobemmorite (CaO.SiO ₂)	M	M	m	M	m	m	M	M
Portlandite [Ca(OH) ₂]	M	M	M	M	M	M	M	M

* unexposed to seawater

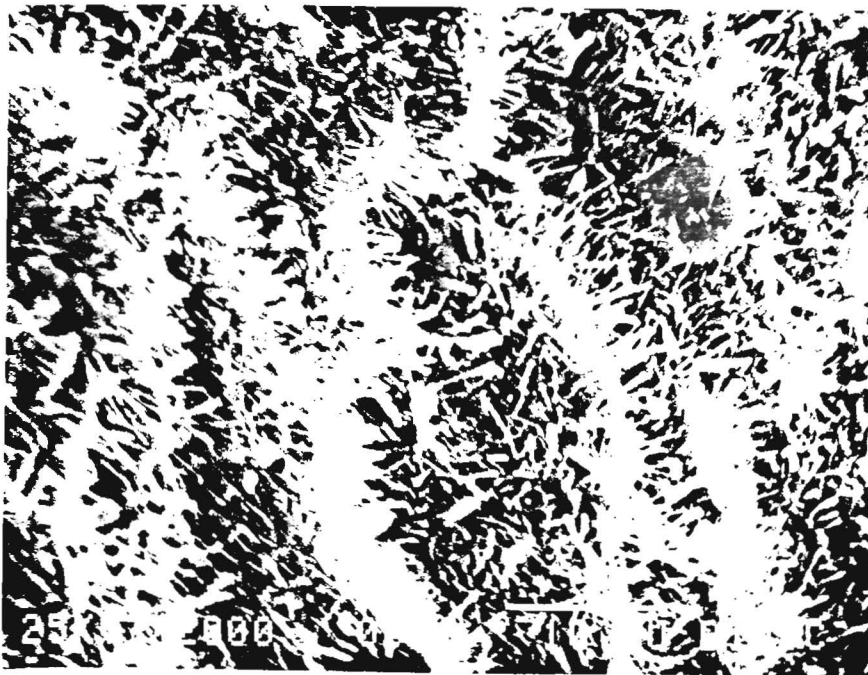
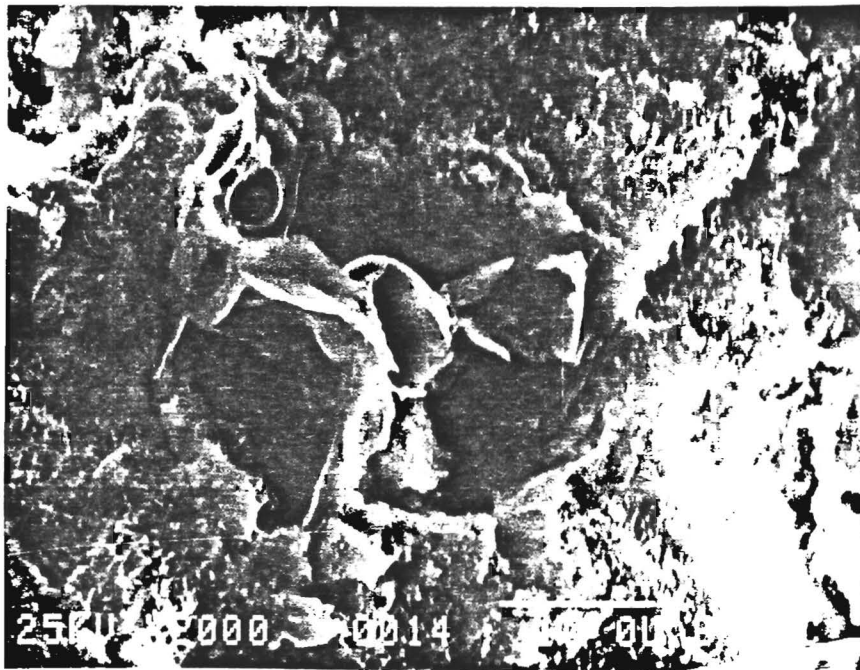


Figure 9. Photomicrographs of Riverside Briquettes (a) before and (b) after 6 months at the Conscience Bay site.

pave the seabed over as they settled. As fixated blocks, bulk densities are considerably greater and exposed surface areas of the wastes reduced by many orders of magnitude. At the same time, the blocks of fixated waste materials are 100 to 1,000 times less permeable than either untreated FGD product or fly ash. The blocks of fixated wastes maintained their structural integrity during prolonged submersion in marine environments, and, in the case of the Riverside-2 blocks (made from U.S. high sulfur coal wastes), strength increased with duration of exposure.

The spray dryer FGD blocks are rich in calcium (Tables 1 and 2) and from our experiences with several types of FGD wastes in the sea we expect that loss of calcium would be an important aspect of leaching. This seems to be confirmed by the high calcium content of leachates found in the U.S. EPA Extraction Procedure (Donnelly *et al.*, 1982). We also expect that calcium lost from blocks in seawater would be slowly replaced by magnesium in an ion-exchange system (Parker *et al.*, 1984, Woodhead *et al.*, 1984a and b). It is of interest therefore that x-ray diffraction analyses indicated that calcium (as calcite, CaCO_3) was depleted in the blocks in the sea, but that the magnesium-enriched minerals epsomite and periclase in the blocks, may have increased at the same time. Following 6 months submersion, considerable deposition of crystalline structure was found to have occurred filling pores within the material of the test blocks.

BIOLOGICAL EVALUATION

The suitability of the dry FGD end-products as materials for the settlement and growth of communities of marine organisms was assessed by noting the species of animals and seaweeds which were found in living association with the various test blocks in the sea, when they were retrieved from the test sites.

Biological Community on Phase 1 blocks

During Phase 1 investigations the tests in the sea were made at the C-WARP site in the open Atlantic Ocean. Although it was the aim of the Phase 1 studies to assess only physical behavior of waste blocks in the sea, it was found that several species of marine invertebrate animals were growing attached to the

test-proctors. No seaweeds were found during the period of exposure because the seabed (at 21 m deep) was below the depth of light penetration sufficient for photosynthesis in the relatively turbid waters of the nearshore, inner continental shelf.

The blocks were exposed on the seabed at 21 m for up to 98 days in the fall season of 1981. Several invertebrates settled on the block surfaces but the dominant organisms was the branching colonial bryozoan, Bugula turrita. B. turrita has been commonly found to be a dominant sessile organism growing on the C-WARP reef blocks (formed from mixtures of fly ash and "wet" FGD scrubber sludge) in the autumn at this site; this bryozoan is also a dominant organism settling annually at the same time on the rocks and rubble of the nearby Fire Island artificial reef which was built in the 1960s. Other organisms found on the Phase 1 waste blocks following retrieval from the sea are listed in Table 11. The number of species, 7, is relatively small because blocks of coal waste materials at this site and depth are found to be colonized rather slowly; our earlier C-WARP investigations had found the same low rates of biological colonization on both coal wastes and on test blocks of concrete placed at the site (Parker et al., 1982a; Woodhead et al., 1984a; Woodhead and Jacobson, in press). Those C-WARP studies found average numbers of only 7 to 10 species of invertebrates on the coal waste test blocks after 6 months exposure at the same site. All of the species growing on the NIRO proctors are typical of the communities previously found on C-WARP coal waste reef blocks.

Biological Community on Phase 2 Blocks

The NIRO product proctors used in Phase 2 were tested in the sea at the Conscience Bay site on Long Island Sound (Figure 4). Although the marine exposures in situ were only up to 7 months, the surfaces of the blocks were more extensively colonized than had been found on the Phase 1 proctors in the Atlantic Ocean. The differences between the two sets of blocks are probably principally due to the differences between the environments at the test sites, rather than the differences in the properties of the blocks themselves. The Conscience Bay site is only about 7 m deep and although the water is turbid, sunlight penetration is sufficient for photosynthesis by seaweeds and other algae. Seaweeds attached and grew readily on the tops of proctors, thereby

Table 11. Animals found growing on the Phase 1 NIRO test proctors following exposure in the sea at the Atlantic test site 21 m deep, during the fall season, 1981.

Branching bryozoan	<u>Bugula turrita</u>
Encrusting bryozoan	<u>Schizoporella</u> sp.
Barnacles	<u>Balanus crenatus</u>
Tube worms	<u>Polydora socialis</u> <u>Sabellaria vulgaris</u>
Rock crab, juv.	<u>Cancer irroratus</u>
Starfish	<u>Asterias forbesi</u>

rapidly increasing the biomass in the colonizing community. A consequence of this early biomass production was that although the seaweeds had mainly died back to small fragments by the end of the year when the NIRO proctors were retrieved in December 1983, the community remaining was richer in numbers of species both of animals and plants and it overgrew block surfaces much more extensively than had been found on the (Phase 1) blocks from the C-WARP site at 21 m depth (below the photic zone).

Photographs of samples of the Riverside-2 proctor test blocks and of the Riverside Briquettes retrieved at the end of December 1983, after 6 months marine exposure at the Conscience Bay site, are shown in Figures 8 and 10. The proctors were covered over most of their surfaces with encrustations of calcareous bryozoans and included calcified tubes of polychaete worms, mainly Hydroides dianthus. On the top of blocks there were short attachments and fragments of red and green seaweeds but the growths had by then died-back for the winter. One or two holes had been cut into one of the Riverside-2 proctors by boring clams, Zirfaea crispata, causing minor damage. The Briquettes were colonized by the same fauna as the proctor cylinders, some were entirely covered by sheets of calcareous bryozoan colonies, but other briquettes had no bryozoans producing dramatic differences in appearance (Figure 10), although tube worms, limpets, crabs, etc. lived on or amongst all of the briquettes (Table 12).

The Dutch-2 proctors retrieved from Conscience Bay had deteriorated badly from biological erosion, principally by the boring of clams, Z. crispata followed by secondary working by small crabs and other organisms. The proctors of Dutch-2 FGD waste were softer than the Riverside-2 material and biological erosion was accompanied by some physical erosion, leading to rounded contours of eroded areas (Figure 5). The Dutch-2 proctors were much less overgrown by biological communities and it was apparent that, although these blocks had been successfully settled by an epifauna, plaques of the encrusting organisms had subsequently fallen off or been washed away from the relatively soft surfaces of these blocks. This same surficial softening was also responsible for the successful settlement and rapid boring of the blocks by the clam, for which the Dutch-2 blocks provided an ideal environment.

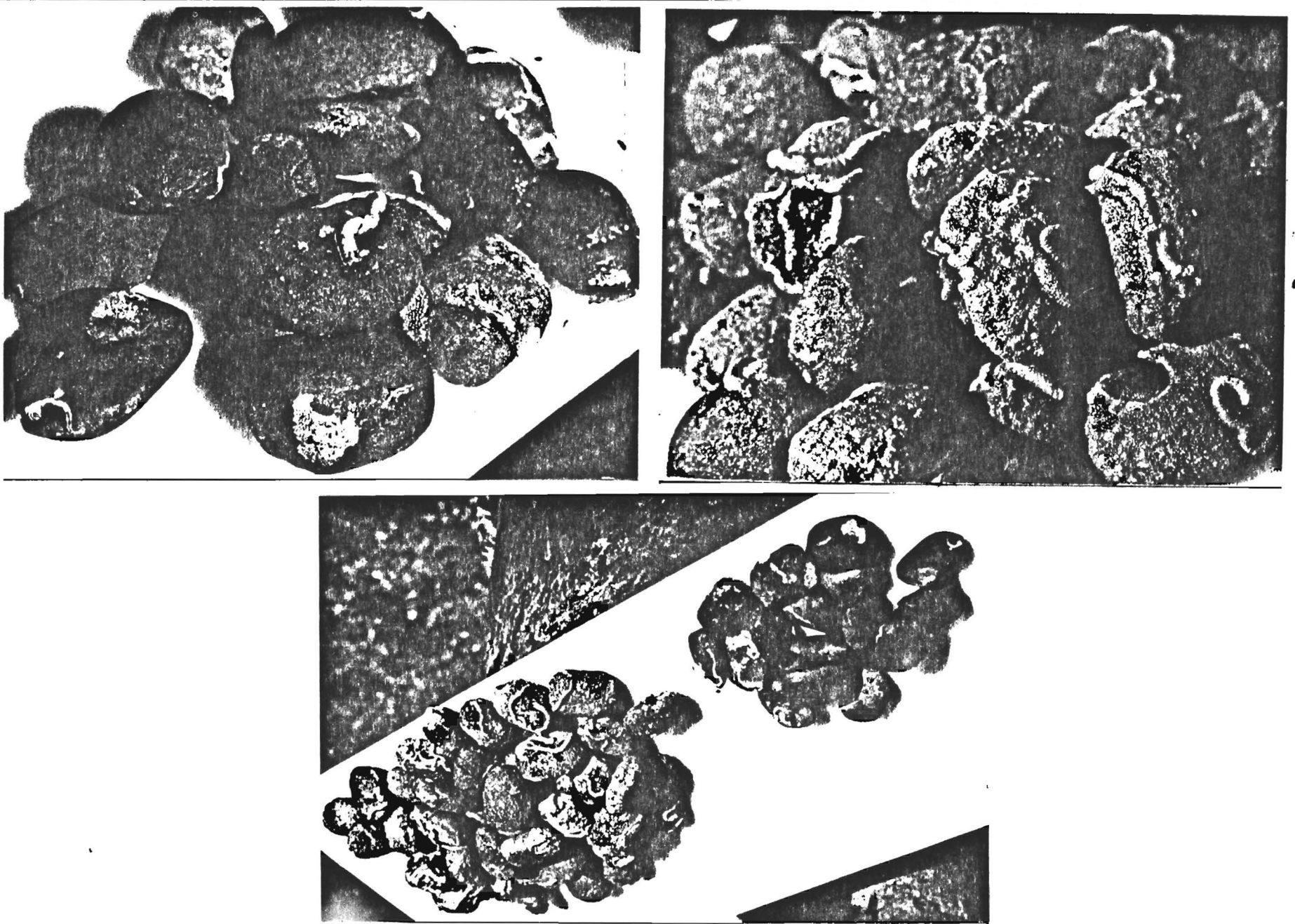


Figure 10. Riverside Briquettes after 6 months at the Conscience Bay site.

The list of animal and plant species associated with the Phase 2 test proctors and the NIRO Briquettes at the test site in Conscience Bay is given in Table 12. A total of 20 species of invertebrates and 4 species of seaweeds together with a number of unidentified microscopic benthic diatoms, were found associated with the NIRO spray dryer FGD test materials. The number of seaweeds would probably have been larger if the test proctors had been retrieved during the autumn, before the winter die-off of algae had taken place. These figures for the species richness of the colonizing communities growing on the blocks of NIRO FGD waste products are very similar to the communities reported growing on coal waste blocks placed at the Conscience Bay test site in 1977 (Roethel, Duedall and Woodhead, 1983). In those investigations, 19 invertebrate species and 5 species of seaweeds were recorded during the first year at the same site. Many of the species recorded on the coal waste blocks in the 1977 surveys at the site (Table 13) were also found on the NIRO blocks and briquettes in 1983.

Discussion of Biological Colonization

There have been few reports concerning the biological communities inhabiting coal combustion waste materials. Exceptions, which are of particular interest to our study, are the investigation of coal waste blocks in Conscience Bay in 1977-78 (Roethel et al., 1980; 1983), the investigation of coal waste blocks in the Atlantic Ocean (Woodhead et al., 1984; Woodhead and Jacobson, in press), and the report of Bamber (1983) on the fauna inhabiting aggregates formed on the seabed from fly ash dumped in the North Sea, off Northumberland, U. K.

The earlier studies on blocks of coal wastes in Conscience Bay (by Roethel et al., 1983) are closest to the Phase 2 studies reported here, of course. Many of the same species found in the communities associated with the NIRO test blocks were found in the investigations in 1977 and 1978 as can be seen from comparisons between Tables 12 and 13. The rather limited observations of colonization occurring on Phase 1 NIRO blocks, in the Atlantic Ocean, found virtually the same communities and similar low rates of colonization as had been found during the first 6 months of submergence at the site (and at the same time of year) on C-WARP test blocks and on concrete. The North Sea fauna on fly ash aggregates reported by Bamber (1983) consisted of 28 species living

Table 12. Organisms associated with the NIRO test blocks and briquettes in Conscience Bay, Long Island.

Seaweeds

Enteromorpha compressa
Callithamnion seirospermum
Chaetomorpha sp.
 Unidentified benthic diatoms

Porifera (sponges)

Haliclona loosanoffi
Halichondria sp.

Coelenterata (hydroids)

Obelia geniculata
Sertularia sp.
Halecium sp.

Annelida (segmented worms)

Hydroides dianthus
Lepidonotus squamatus
Serpula vermicularis

Anthropoda (crabs, shrimps)

Palaemonetes vulgaris
Neomysis americana
Panopeus herbsti
Carcinus maenas
 Unidentified harpacticoid copepods

Mollusca (mussels, limpets)

Acmaea testudinalis
Zirfaea crispata
Mytilus edulis

Echinodermata (sea stars)

Asterias forbesi

Bryozoa

Schizoporella unicornis
Microporella ciliata
Cryptosula pallasiana
Bugula turrita

Fishes

Blackfish, juv. Tautoga onitis
 Cunner, juv. Tautoglabrus adspersus

Table 13. Organisms observed on the surfaces of fly ash/"wet"FGD sludge blocks during 1977 the first year of submersion in Conscience Bay (from Roethel et al., 1983).

Seaweeds

Codium fragile
Bryopsis plumosa
Grinellia americana
Dasia dicellata
Antithamnion cruciatum

Coelenterata (hydroids and anemones)

Tubularia crocea
Obelia dichotoma
Sertularia sp.
Metridium dianthus

Annelida (segmented worms)

Serpula vermicularis
Nereis arenaceodonta

Mollusca (snails and bivalves)

Busycon canaliculatum
Lunatia heros
Zirfaea crispata
Crepidula fornicata
Urosalpinx cinerea

Bryozoa

Schizoporella unicornis
Membranipora pilosa
Bugula turrita

Echinodermata (sea stars and urchins)

Arbacia punctulata
Asterias forbesi

Arthropoda (crabs, shrimps and barnacles)

Pagurus longicarpus
Libinia emarginata
Balanus balanoides

Fishes

Blackfish Tautoga onitis
 Cunner Tautoglabrus adpersus
 Silversides Menidia menidia
 Toadfish Opsanus tau
 Killifish Fundulus heteroclitus
 Winter flounder Pseudopleuronectes americanus

on, or within the fly ash. The North Sea fauna contains 5 species which are common in the fauna associated with C-WARP coal waste test bricks, and 9 genera of closely related invertebrates occur in the two faunal assemblages. From these several similarities between the marine epifaunal communities commonly growing on the NIRO dry FGD materials, on the C-WARP coal wastes, and on fly ash aggregates in the North Sea, it is concluded that the NIRO blocks provide a substrate for the settlement and growth of marine invertebrate larvae having qualities resembling the fixated mixtures of "wet" FGD sludge and fly ash used for the C-WARP reef blocks.

Boring pholad clams, Zirfaea crispata, were very characteristic of all three community assemblages associated with coal waste blocks and aggregates, but not with concrete. The NIRO test blocks were in the sea for only 6 months and Dutch-2 blocks were heavily bored by the clam, Z. crispata. We have found specimens of this pholad clam at least 3 years old in other coal waste blocks. Bamber (1983) reported clams of this species which were 7 years old in North Sea aggregates. Bamber suggests that such long residence within the coal wastes indicates that the material is not toxic. This conclusion received support from elemental analyses of the tissues of Z. crispata taken from within coal waste blocks (Roethel et al., 1980; 1983), which showed no accumulation of potentially toxic trace elements. In related analyses made on acid digests of epifaunal biomass collected from the surfaces of coal waste blocks and from natural rocks at the Conscience Bay site, Roethel et al. (1983) found no evidence of elevated levels of potentially toxic trace elements (Cd, Pb, Cu, Se, Hg, As, Zn) in the biomass from the epifaunal community growing on the coal waste materials. Blocks of coal wastes do not appear to threaten negative impacts to the benthic faunas in the sea.

In the North Sea, Bamber (1983) noted some selective settlement on fly ash by cyphonautes larvae of bryozoans. We have also found selective settlement on blocks of coal wastes by some invertebrate larvae (for example, the clam, Zirphaea crispata, and the polychaete worm, Polydora socialis) when provided a choice between coal waste or concrete substrates. Similarly, in freshwaters amphipods are found to have strong selection for coal waste substrates (Woodhead et al., 1984b). Nevertheless, a majority of organisms colonizing coal wastes in the sea, including the NIRO FGD materials, are common to the communities colonizing concrete substrates.

The similarities between the epifaunas growing on coal combustion waste derivatives in the three different marine environments suggests that during prolonged submersion in the ocean, stabilized blocks of NIRO FGD residues would probably be colonized and overgrown by encrusting epifaunal communities in ways similar to the growth of the communities examined quantitatively in the C-WARP investigations (Woodhead et al., 1984a; Woodhead and Jacobson, in press). It is concluded that fixated, consolidated NIRO FGD product cured to hard solid blocks provide an acceptable substrate for settlement and growth by communities of encrusting invertebrates which are characteristic of other solid coal waste and of concrete substrates, and which are characteristic of epifaunal communities on artificial fishing reefs in the New York Bight.

EVALUATION OF SPRAY DRYER FGD PRODUCTS FOR MARINE DISPOSAL

Dry scrubbing waste products contain fly ash, desulfurization reaction products, excess reagents and products of side reactions. For lime-based dry scrubbing FGD systems, all components except the fly ash are calcium compounds that have relatively low solubility in water. Although there is wide variability between the products from coal-fired plants in different regions, the waste products from lime-based dry FGD systems are generally similar in chemical composition to fixated mixtures of fly ash with FGD sludges from wet scrubbing systems using lime or limestone (Thompson et al., 1982). We found the FGD products supplied by NIRO for marine testing to resemble blocks of wet scrubber waste with fly ash mixtures, both mineralogically and in their physical properties in our marine testing systems. It is with our wide experience investigating a variety of coal combustion waste products in the sea that we have assessed the behavior of the blocks of NIRO dry scrubber products and their potential acceptability for ocean disposal.

Fixation of FGD wastes, consolidation and curing to hard solid blocks, is central to aquatic disposal systems and the NIRO wastes are very suitable for such processing. The dry FGD product is ideal for handling and feeding by automated high-speed block production machines and cured block strengths are satisfactory for factory handling, stacking, and disposal. Such blocks of FGD waste product are more dense than the unprocessed product, surface areas

exposed to the environment are reduced by several orders of magnitude and permeabilities of the block materials are low, about 10^{-7} cm/sec. Leaching from the blocks in aquatic systems is slow and, in accordance with the U.S. Environmental Protection Agency's "Extraction Procedure", the blocks would be classified as non-toxic, non-hazardous (Donnelly, et al., 1982; Thompson, et al., 1982).

In the sea, blocks of all of the dry FGD products tested maintained structural integrity and compressive strength over submersion periods from 3 months to 1 year. In the case of the Riverside-2 blocks, there was a significant increase in strength during marine exposure and we have previously found similar strengthening by blocks of related coal waste mixtures during protracted submersion in the sea. The blocks therefore provide a potentially stable base for biological colonization. The settlement and growth of characteristic marine organisms on the test proctors closely resembled the colonization processes which we have previously measured in detail on other coal waste blocks and on concrete. These similarities in colonization were found on proctors set out at both the Conscience Bay, Long Island Sound, and the Atlantic test-sites.

Although physical erosion of blocks was slight, biological erosion of the less strong Dutch-2 blocks caused considerable deterioration. The damage was due to extensive boring by pholad clams, Z. crispata which normally inhabit soft rock substrates of slate/clay types of texture; the Dutch-2 blocks provided an ideal substrate for these clams. Only one or two clams succeeded in boring into the harder Riverside blocks, otherwise the Riverside blocks were overgrown by epifaunal communities with calcified skeletons, which probably provide some "protection" of the blocks from marine environment.

The problem of boring by the clams is clearly a potentially serious one but it is our experience that clams bore into the less strong, softer block materials. The hardness and strength of coal waste materials can be modified very significantly in accordance with the pozzolanic properties of the fly ash, the ratio of wastes in the mix, the types of reaction additives and their dispersion, and the curing regime employed. Until these factors which contribute importantly to development of block strength have been explored, the

fitness of particular FGD wastes to resist bioerosion in the marine environment will remain uncertain. However, from our experience, it seems very likely that the strength of such materials of Dutch-2 may be improved considerably by relatively simple changes in the processing and curing methods.

These investigations have been limited in their scope and duration, and clearly important questions remain regarding behavior and the compatibility of dry FGD waste blocks in the sea. The results reported here suggest that consolidated blocks of the NIRO FGD residues may have little or no adverse impact in the sea; ocean disposal may be a viable option. We make such tentative initial assessments from our extensive experience assessing other coal combustion wastes in the sea and their similarities in behavior with the dry FGD materials. Investigations of longer duration must be made in the sea with a range of dry FGD materials from coal-fired power plants. Future plans for marine investigations should consider a larger scale of field operations to approach industrial disposal conditions. We have much experience in such large-scale marine investigations and we have real interests in continuing and expanding our collaborative work with NIRO Atomizer.

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