

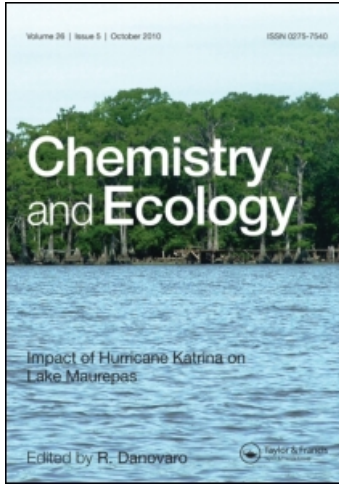
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STABILISED COAL ASH STUDIES IN ITALY

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The ENEL Ash Research Centre – (Brindisi, Italy) – has started a research programme on the use of coal ash derived from its thermoelectric power plants as a component of blocks for artificial habitats. After preliminary laboratory tests, systematic physical, chemical, and biological tests were carried out in an experimental installation constructed in the area of the Torrevaldaliga power plant (80 km NW of Rome).

Two reef models – each made by assembling pyramids of 225 20 × 20 × 20 cm blocks – were submerged in two tanks (10 × 2 × 1.5 m) with running sea water (water flow: 3–5 cm s⁻¹). The ash blocks were composed of fly ash (52.1%), bottom ash (26.1%), hydrated lime (5.2%) and water 16.6%, while concrete blocks were made of pozzolanic cement, sand and gravel. After two years, ash based blocks showed no weathering, volume variation or swelling; marked compressive strength and sonic velocity increases have, on the contrary, been recorded. No significant leaching of chemical elements of environmental concern was found. The biotic settlement on the ash blocks proved greater in quantity and better in quality than that on the concrete blocks; on ash blocks 62 species were found, compared to 54 on concrete. Ash-based materials seem to be more suitable for the settlement of the macrobenthos.

KEY WORDS: coal-ash, artificial reef, Mediterranean, macrobenthos

INTRODUCTION

The construction of artificial marine habitats is a modern technique for the protection, management and enhancement of marine coastal zones and in particular for fisheries. For such constructions, concrete materials are normally used in common with other maritime works. The utilization of cement-stabilised recycled waste material is increasing. There are several advantages, including reduced land disposal or dumping at sea and reduced land destruction by landfill and quarry extraction. In many countries the utilization of waste material, especially coal ash, is being investigated with positive results. Some coal-ash reefs have been tested successfully (Collins *et al.*, 1990, 1991, 1994a & b; Jensen *et al.*, 1994; Kuo *et al.*, 1994; Woodhead *et al.*, 1982, 1985). In Italy and in the Mediterranean Sea, however, there have been no such experiments.

In Italy, artificial reefs are multipurpose constructions in near-shore areas intended to prevent illegal trawling, to improve the restocking of fish populations by protecting eggs and juveniles, and to provide a refuge for the inshore fish community. The results obtained are promising (Bombace, 1989; Relini, 1991; Relini and Orsi Relini, 1990) and there have been numerous requests for artificial reefs coming from local fishermen.

The Italian Electricity Board (ENEL) has started a research programme with the aim of monitoring the use of coal ash derived from its thermoelectric power plants, at present 1.5 M tonnes per year, as a component of blocks for artificial habitats.

The general objective of the ENEL Ash Research Centre in Brindisi is to establish the most suitable methods for the exploitation, re-utilization or landfill of residues derived from combustion processes in thermoelectric power stations and to ascertain, in accordance with existing legislation, the compatibility of the blocks placed in the sea with the quality of the waters and the living organisms. The necessary information was obtained through laboratory tests, followed by confirmation in the open sea, as part of the research project named 'CENMARE Project'. This project is divided into three main stages:

STAGE 1 (1987–88) – Laboratory tests of a physical, mechanical and chemical nature in order to define the material to be used in the construction of artificial reefs and their compatibility with the marine environment.

STAGE 2 (1988–92) – Construction of an experimental plant at the Torrevaldaliga power station (Central Italy): production of model reefs with ash-based blocks; comparison with concrete blocks (reference blocks); experimental tests.

STAGE 3 (1992–95) – Planning and creation of demonstration habitats for fish repopulation in coastal sea waters, management and monitoring.

This paper deals mainly with data collected during the 24 months in the experimental plant at Torrevaldaliga. The results of the physical-mechanical and chemical tests carried out in the laboratory are summarized since they are referred to in previous published papers (Sampaolo and Relini, 1991). The tests were carried out on the basis of joint collaboration between ENEL CRC, ISMES, CISE and the Institute of Zoology of Genova University.

MATERIALS AND METHODS

Physical-mechanical Tests

Six mixtures were studied (Table I) which involve mainly the use of fly-ash and bottom-ash with the slight addition of a hydraulic binder (Portland cement and/or lime).

The following characteristics were established for the mixture to be used in block construction for artificial reefs: a) compressive strength > 5 Mpa, and b) tensile strength > 0.5 Mpa, necessary to give the mass good cohesion and reduced effective porosity. The following laboratory tests were carried out:

on the mixtures, maximum density and optimum moisture content (ASTM D1557.91)

on the samples, after a curing time of 28 days (Italian regulation UNI, 6127), uniaxial compressive strength (ASTM C39.86), uniaxial tensile strength (ASTM

Table I Composition of the six mixtures tested.

Mixture n.		1	2	3	4	5	6
Fly ash (C.L.)	%	61.0	49.4	69.2	69.1	73.1	71.1
Bottom ash (C.P.)	%	9.7	24.7	–	–	–	–
Portland Cement 325	%	1.9	–	6.3	3.1	–	2.1
Hydrated lime	%	4.8	4.9	3.1	6.3	5.3	5.3
Water	%	22.6	21.0	21.4	21.5	21.6	21.5

C496.90), sonic velocity (ASTM D2845.90), permeability (by flow pump method, currently used in geotechnics, not normalized, Olsen *et al.*, 1985).

During two years of experimentation at the plant, 44 ash-based blocks and 44 concrete blocks were also subjected to nondestructive tests (geometry, swelling, density, sonic velocity). For each block, 12 sonic velocity measurements in two orthogonal directions were made at 3 month intervals from 0 to 24 months of immersion. Tests showed that there were no distortions and no appreciable variations in density either in the ash or in the concrete samples; there were no external signs of weathering, such as fissures or the flaking-off of pieces of material.

Chemical Tests

Preliminary leaching tests were carried out in the laboratory on 3 blocks (of 20 cm side) immersed in a volume of sea water equal to 20 litres (solid/liquid ratio 1:2.5) held in a polyethylene container and maintained in continual agitation over a 90-day period. The water was sampled and analyzed periodically (0, 1, 2, 5, 15, 30, 45, 60 and 90 days). At the end of this first 90 day period the sea water was replaced with fresh sea water of the same origin to allow for a second 90 day trial cycle.

Conductivity, redox potential, pH, dissolved oxygen and temperature were tested and the presence of the following elements was also checked: Ca, Mg, Al, Na, Si, K, Cu, Mn, Zn, Fe, Cd, Pb, Hg, As, Be, Cr, Se, Te, Tl, Sb (for methodology see Sampaolo and Relini, 1991)

Solids blocks were also sampled by core boring with a diamond – tip rotary bit (20 mm I.D.) and then divided into sections with a diamond – blade cutting machine. Deionized distilled water was used throughout as the cooling fluid. Sections were 4 mm thick and they were cut from the surface (i.e. 0 to 4 mm depth), and at 5 mm, 20 mm, and 50 mm depth. Finally they were ground in a tungsten carbide jar mill for subsequent analyses.

Mineralogical determinations were carried out by X-Ray Fluorescence Spectrometry (XRF) after fusion into a glass bead with lithium tetra-borate. All the remaining elements were measured by a combination of ICP-OES and GF-AAS after dissolution with a nitric/hydrochloric/perchloric acid mixture in a microwave oven. The same chemical determinations were carried out at the plant.

Interest was focused in particular on the control of:

Cu, Mn, Zn, Fe, Cd, Pb, As, Tl, Cr, Se, Sb, with experiments to determine leaching in sea water

the above elements and in addition Al, Si, Mg, Ca, Na and K relative to the analyses of concrete blocks and ash-based blocks.

A preliminary characterization of the sea water was from samples taken at the entrance to the power plant, analyzing for the basic content of metallic elements, dissolved in the water and present in the 'particulate' phases near the water-intake and at the discharge from the tanks.

The Experimental Plant

The plant was constructed in the area of the Torrevaldaliga South ENEL power station situated 80 km NW of Rome. The plant was designed to feed two trial

tanks. Each tank, made of zinc-plated steel and lined with fibre glass, was 2.00×10.00 m in size and 1.50 m in depth. The water supply was obtained by means of a pumping station at sea, made up of two pipes in VTR DN 300 about 200 metres in length, each fitted with a submerged 100 l s^{-1} pump, from which the water was conveyed to the sedimentation tank (surface 45 m^2 , 3 m high). Six pumps were installed in this tank, 3 for each pipe, capacity 33 l s^{-1} each, which sent the fluid on through two pipes in VTR DN 300 until it reached the two trial tanks after about 400 m.

Considering the high quality required in the chemical tests, materials were chosen for all components of the plant so as to avoid the release of chemical elements, particularly heavy metals, in analytically determinable quantities.

Models of underwater reefs, made up of 225 blocks ($20 \times 20 \times 20$ cm) were set up in the trial tanks using the pyramid configuration (Figure 1). Coal-ash blocks were immersed in one trial tank while concrete blocks made of pozzolanic cement, sand and gravel, were placed in the other tank, which was used as a reference. The blocks were prepared in a rigid chamber of known volume by compressing a known quantity of mixture whose optimal values of density and humidity had been established by the Proctor test. All the blocks were cured in a climatic cell for 28 days.

Biological Tests

In order to study the biological associations which formed on the ash and cement blocks, the work schedule involved quarterly checks of the blocks immersed for three, six, nine, twelve, fifteen, eighteen, twenty-one and twenty-four months from April 1990 to March 1992.

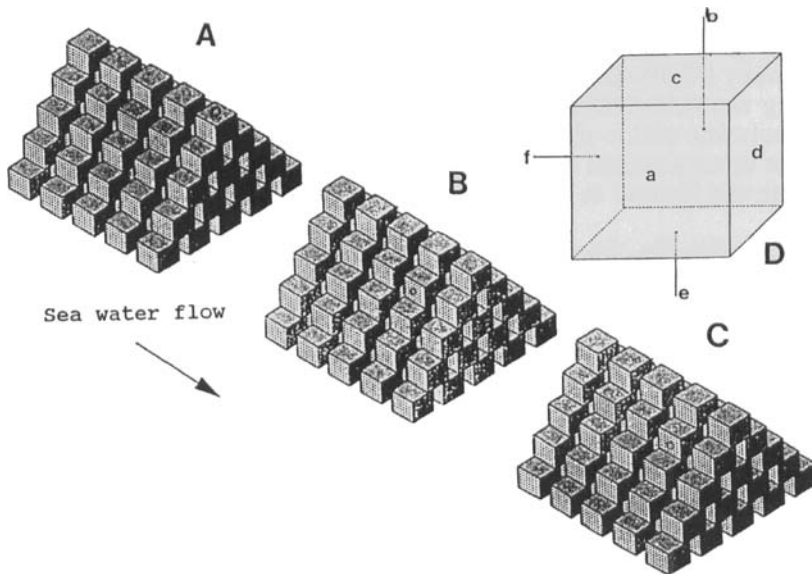


Figure 1 Arrangement of the three pyramids (A,B,C) in each tank in relation to the flow of sea water and identification of the faces of a individual cube (D).

The six sides of each block were photographed and the macrobenthos described using a microscope. The settlements were assessed according to the following characteristics:

- the species richness (number of species per unit surface)
- the density (number of individuals per dm^2)
- the covering indices (surface occupied by each taxon).

Thus each systematic group was assigned a value which takes account of the percentage of the surface covered by the same group according to the following scheme: + = negligible presence, 1 = <5%, 2 = 5–25%, 3 = 25–50%, 4 = 50–75%, 5 = > 75%.

The biomass of the settled association was evaluated through measurement of wet weight, dry weight at 100°C. and of ash at 500°C.

Bioaccumulation

For bioaccumulation control, the bivalve *Ostrea edulis*, the gastropod *Bittium reticulatum* and some macroalgae settled on the blocks were used. Also some mussels (*Mytilus galloprovincialis*) were put on the experimental blocks and examined after 3 and 6 month exposure. The molluscs were left for 18 h in filtered water to eliminate ingested and non-ingested particles. Samples were stored at -20°C. After lyophilizing, a quantity of 2–5 g was taken and subjected to incineration at a low temperature in oxygen in a radio frequency generated plasma, with the aim of destroying the organic matrix. The samples were dissolved in a microwave oven using a mixture of acids in closed teflon containers. The elements considered are: aluminium, arsenic, cadmium, copper, chrome, iron, lead, selenium and zinc.

RESULTS

Physical-mechanical Determinations

Of the six mixtures (Table I) tested, those which provided the best characterization for economic reasons were the following:

- #2–49.5% fly ash + 24.7% bottom ash + 4.9% hydrated lime + 21% water
- #5–73.1% fly ash + 5.3% hydrated lime + 21.6 water.

For both mixtures the compressive strength values at 28 days of curing always gave results higher than 5 Mpa.

Of the two mixtures, the one chosen to make the blocks to be used in the experimental plant was #2 because both types of ash produced by coal thermoelectric power stations could be used in this way. The compressive strength value after 28 days of curing reached 10 Mpa, while the compressive strength values measured on reference samples of concrete exceeded 50 Mpa. Optimum dry density was $1,415 \text{ g cm}^{-3}$ (wet density = $1,730 \text{ g cm}^{-3}$).

The volume values showed no change. The values recorded for sonic velocity on the ash-based blocks show a consistent increase with time (from 2200 m s^{-1} to

3300 m s⁻¹ after 6 months). Comparison with non-immersed blocks did not show appreciable differences. The values for concrete showed an increase from 0 to 6 months of immersion, after which a practically constant VL value of around 5000 m s⁻¹ was recorded.

The following compressive strength values were obtained: 10, 25.8, 29.4, 31.0 and 31.4 Mpa (average of 3 samples), respectively at 0, 3, 6, 9 and 12 months of immersion for ash-based blocks; for concrete blocks average strengths were 51.7, 71.1 and 72.0 Mpa, respectively at 0, 6 and 12 months of immersion.

The ash-based samples immersed in water for the 6-month period show a permeability value of $K = 10^{-7} - 10^{-8}$ cm s⁻¹.

Chemical Determinations

During laboratory submersion tests, pH values did not change during time, and with regard to the macro constituents of the ash-made blocks, aluminium and silicon were the elements that showed a clear leaching tendency: about 140 mg of silicon and 7 mg of aluminium in 180 days. Of the trace elements, arsenic, chromium, selenium and tellurium can be solubilised. The release rate proved to be fairly constant over time. The maximum concentrations in solution were, however, in the order of tens of $\mu\text{g l}^{-1}$ for arsenic, chromium, selenium and less for tellurium. For the remaining elements tested (Na, K, Cu, Zn, Fe, Cd, Pb, Hg, Be, Sb, Te) no leaching was found.

Interest was focused especially on the monitoring of some elements of environmental concern (Italian regulations) (Cu, Mn, Zn, Fe, Cd, Pb, As, Tl, Cr, Se, Sb, Be) regarding the leaching in sea water. (Beryllium was only investigated as suspended solid sampled with sea water.)

Before the start of the experiment, mineralogical analyses were carried out on 12 cores (20 mm in diameter, 50 mm in height) taken from the blocks (from 1 to 3 months of curing). The following crystalline forms were recognised: quartz (SiO₂), mullite (3 AlO₃·2 SiO₂) and calcite (CaCO₃). Mullite and quartz are normal components present in ash and calcite originates from the setting and hardening process of the hydraulic binder.

In general, ash blocks present a higher level of trace metals in comparison with concrete (Table II). From the results of overall chemical analysis, only a few phenomena regarding the blocks sampled are clearly demonstrated:

- 1) There is a clear increase in the concentration of sodium, depending on time, as an effect of the continual immersion in sea water.
- 2) An increase, although moderate, in the magnesium level is noted, as expected following the process of dolomitisation, previously determined in laboratory tests.
- 3) An increase in the manganese level is noted, depending on time; there is no obvious explanation for this phenomenon.
- 4) No differences in chemical composition were observed between block sides.

For all the other elements studied, no variations were measured in concentrations that would differentiate from the normal variability due to the non-homogeneity of the samples and the analytical techniques used.

Table II Chemical characterization of concrete and ash blocks showing the mean and standard deviation of 6 samples.

	Al %	As $\mu\text{g g}^{-1}$	Be $\mu\text{g g}^{-1}$	Ca %	Cd $\mu\text{g g}^{-1}$	Cr $\mu\text{g g}^{-1}$	Cu $\mu\text{g g}^{-1}$	Fe %	K %	Mg %	Mn $\mu\text{g g}^{-1}$	Na $\mu\text{g g}^{-1}$	Pb $\mu\text{g g}^{-1}$	Sb $\mu\text{g g}^{-1}$	Se $\mu\text{g g}^{-1}$	Si %	Tl $\mu\text{g g}^{-1}$	Zn $\mu\text{g g}^{-1}$
concrete	0.66	3.48	0.48	27.58	0.16	17.83	6.16	0.38	0.14	5.88	234.16	1.32	5.50	<0.30	<0.40	1.45	<0.40	18.00
std.dev	0.29	0.26	0.09	1.06	0.17	1.34	0.68	0.03	0.02	0.67	29.10	0.12	0.95	-	-	0.09	-	8.08
ash blocks	12.23	3.60	3.93	11.58	3.29	108.33	74.16	2.53	0.38	1.15	281.16	1.44	55.66	1.11	8.05	16.41	<0.40	51.83
std.dev	0.29	0.20	0.53	0.42	3.64	4.18	17.65	0.14	0.01	0.01	10.22	0.05	1.49	0.17	0.26	0.62	-	6.22

The data relating to the water phase do not show any appreciable leaching phenomena compared to the intrinsic variability of the analytical methods used for the elements As, Cd, Cr, Fe, Mn, Sb, Se, and Tl. The moderate variations which were found (of the order of ppb) are of no environmental interest and can be seen as associated with the coastal origin (urban and industrial waste) of the water supplying the tanks.

After two years' investigation, it can be stated that none of the analytical checks show any significant leaching of metal elements, in particular for the ash blocks.

Biological Determinations

In spite of the selection of settlers for the different components (pumps, pipe, sedimentation basin, etc.) of the plant (see Sampaolo and Relini, 1991), good settlement occurred on the blocks, and after just three months it was possible to find differences between colonisation on ash blocks and concrete ones (Tables III, IV).

After two years' observation on ash blocks, 62 species were found, compared with 54 on concrete (Table V), while during the first year 50 and 39 were found. A larger number of species was found on concrete test panels exposed in the sea and along the pipes feeding the experimental tanks. The main groups and species recorded were the following: algae (macro and microalgae, Corallinaceae), serpulids (in particular *Pomatoceros triqueter*, *Protula* sp., *Hydroides elegans*, *Filograna* sp., *Josephella marenzelleri*), spirorbids (*Pileolaria militaris*, *P. pseudomilitaris* and *Janua pseudocorrugata*), encrusting Bryozoa (mainly *Schizoporella* species), solitary and compound ascidians. Few hydroids, barnacles or bivalves (mainly *Ostrea edulis* and *Anomia ephippium*) were found.

In particular, on the ash blocks, algae together with serpulids are dominant components during the whole cycle of observations; on the other hand Corallinaceae and spirorbids reach a maximum in 9-month associations, and then fall in the 12-month association. Sponges, gastropods and bivalves are always represented in low numbers, while ascidians, which show a reasonable settlement on substrata immersed for 3 months, decrease to the level of sporadic presence as the length of the period of immersion increases. Always present, however, are the colonies of encrusting bryozoans with less marked seasonal fluctuations than the non-encrusting bryozoans.

On the concrete blocks, the associations are reduced and algae, Corallinaceae, serpulids and spirorbids are the dominant components; sponges are less represented than on the ash blocks; gastropods and bivalves settle in small quantities, while the settlement of encrusting bryozoans is greater, especially on the half-year blocks. The colonies of the non-encrusting bryozoans are particularly evident on the three-month blocks where ascidians are missing, although they are abundant on the corresponding ash substrata.

The biomass measurements confirm the qualitative and quantitative differences expressed in the cover indices between the associations which settle on the ash blocks and those on the concrete (Figure 2). Moreover, the increase in colonisation with the increased length of the period of immersion is much more evident and gradual for the ash blocks than for concrete, at least up to 15 months of immersion (Figure 2). During the 24 months' observation, it was found that the accumulation of fouling (total wet weight) was greater on the ash-based substrata for the whole period of immersion except for blocks exposed for 21 months. Furthermore, still considering

Table IV Coverage indices of epibiota on different sides of concrete blocks (a-f, shown in Figure1.) after 3, 6, 9, 12, 15, 18, 21 and 24 months immersion. (Key: 1 = < 5%, 2 = 5-25%, 3 = 25-50%, 4 = 50-75%, 5 = > 75%)

	3M JUNE 1990		6M SEPT. 1990		9M DEC. 1990		12M MAR. 1991		15M JUNE 1991		18M SEPT. 1991		21M DEC. 1991		24M MAR. 1992			
	a	b	c	d	e	f	a	b	c	d	e	f	a	b	c	d	e	f
Microalgae	3	4	4	2	4	3	1	4	3	1	3	3	2	1	3	3	3	1
Macroalgae	1	1	1	1	2	2	1	3	2	1	4	3	2	4	3	2	4	4
Corallinaceae	+	+	+	1			+	+	+									
Protozoa																		
Pontifera																		
Hydroidea	1	3	2	2	3	1	3	2	3	2	2	2	2	2	2	2	2	2
Serpulidae	+	+	1	2	3	1	3	2	3	3	3	2	3	3	3	3	3	3
Spirorbidae	+	+	1	2	3	1	2	2	1	1	1	1	1	1	1	1	1	1
Polychaeta errantia																		
Bivalvia																		
Gastropoda																		
Cirripedia																		
Amphipoda	1	1	2	1	2	2	4	+	3	1	2	4	3	3	1	2	4	3
Bryozoa (incr.)	2	3	2		1				+	1	3	2	3	1	3	+	+	+
Bryozoa (not incr.)	+	+	+	1					1	+	+	+	1	+	+	+	+	+
Ascidacea																		

Table V List of taxa found on the blocks of ash, concrete and on panels.

	ASH	CONCRETE	PANELS
Algae	+	+	+
Corallinaceae	+	+	+
Foraminifera	+	+	+
Folliculinidae	+	+	+
<i>Sycon</i> sp.	+	+	+
<i>Leucosolenia</i> sp.	+	+	+
<i>Leuconia</i> sp.			+
<i>Clathrina coriacea</i>			+
<i>Halocordyle disticha</i>			+
<i>Bougainvillia ramosa</i>			+
<i>Halecium</i> sp.			+
<i>Tubularia crocea</i>			+
<i>Eudendrium</i> sp.			+
<i>Clytia hemisphaerica</i>			+
<i>Clytia gravieri</i>			+
<i>Obelia dichotoma</i>			+
<i>Obelia geniculata</i>			+
<i>Laomedea angulata</i>			+
<i>Laomedea calceolifera</i>	+	+	+
<i>Sertularella gaudichaudi</i>			+
Actinaria			+
Platyhelmintha	+		
<i>Serpula concharum</i>	+	+	+
<i>Serpula vermicularis</i>	+	+	+
<i>Hydroides elegans</i>	+	+	+
<i>Hydroides dianthus</i>			+
<i>Hydroides</i> sp.	+	+	+
<i>Vermiliopsis striaticeps</i>	+	+	+
<i>Pomatoceros triqueter</i>	+	+	+
<i>Pomatoceros lamarkii</i>	+	+	+
<i>Spirobranchus polytrema</i>	+	+	
<i>Protula</i> sp.	+	+	+
<i>Josephella marenzelleri</i>	+	+	+
<i>Filograna</i> sp.	+	+	+
<i>Pileolaria militaris</i>	+	+	+
<i>Pileolaria pseudomilitaris</i>	+	+	+
<i>Janua pseudocorrugata</i>	+	+	+
Polychaeta errantia	+	+	+
<i>Vermetus triqueter</i>	+	+	+
<i>Monodonta turbinata</i>	+	+	
<i>Bittium reticulatum</i>	+	+	
<i>Fissurella nubecula</i>	+	+	+
<i>Diodora graeca</i>			+
<i>Patella aspera</i>	+	+	
Nudibranchia			+
<i>Mytilus galloprovincialis</i>	+	+	+
<i>Mytilaster minimus</i>			+
<i>Ostrea edulis</i>	+	+	+
<i>Anomia ephippium</i>	+	+	+
<i>Acanthocardia tuberculata</i>			+
<i>Musculus subpictus</i>	+		+
<i>Hiatella</i> sp.	+	+	+
<i>Chama gripoides</i>	+	+	
<i>Clamys varia</i>	+		+
<i>Balanus perforatus</i>	+	+	+
<i>Balanus amphitrite</i>			+

Table V Continued

	ASH	CONCRETE	PANELS
<i>Balanus trigonus</i>	+		+
Pantopoda	+		+
Caprellidae			+
Other Amphipoda	+		+
Isopoda	+		+
<i>Walkeria uva</i>		+	+
<i>Zoobothryon verticillatum</i>			+
<i>Bowerbankia gracilis</i>	+	+	+
<i>Notella</i> sp.			+
<i>Aetea</i> sp.	+	+	+
<i>Callopora dumerillii</i>			+
<i>Caberea boryi</i>	+	+	+
<i>Beania mirabilis</i>			+
<i>Bugula neritina</i>		+	+
<i>Bugula stolonifera</i>	+		+
<i>Watersipora subovoidea</i>	+	+	+
<i>Watersipora complanata</i>	+	+	
<i>Schizobrachiella sanguinea</i>	+	+	+
<i>Schizoporella errata</i>	+	+	+
<i>Schizoporella longirostris</i>	+	+	+
<i>Schizoporella unicornis</i>	+		+
<i>Schizoporella mutabilis</i>	+	+	+
<i>Schizoporella</i> sp.	+		+
<i>Microporella marsupiata</i>		+	+
<i>Disporella hispida</i>			+
<i>Chorizopora brogniartii</i>	+	+	
<i>Celleporina</i> sp.	+	+	
<i>Cellepora</i> sp.	+	+	
<i>Turbicellepora magnicostata</i>	+		+
<i>Turbicellepora crenulata</i>	+	+	
<i>Crisia</i> sp.	+	+	+
<i>Tubulipora</i> sp.			+
Echinodermata		+	
<i>Clavelina lepadiformis</i>			+
<i>Didemnum maculosum</i>			+
<i>Didemnum granulatum</i>	+		+
<i>Diplosoma listerianum</i>			+
<i>Ciona intestinalis</i>	+	+	+
<i>Asciidiella aspersa</i>	+		+
<i>Molgula manhattensis</i>			+
<i>Styela plicata</i>			+
<i>Polycarpa gracilis</i>			
<i>Botryllus schlosseri</i>	+	+	+
Piuridae	+		+
Total	62	54	88

the average wet weight values of all the blocks under examination, an increase in the accumulation of biomass was found up to 15 months and then a considerable reduction at 21 months. An explanation for this was due more to environmental factors than to the materials under examination.

On substrata immersed for 24 months, there is a definite recovery in the biomass values; these reach values close to those obtained after the first year of study.

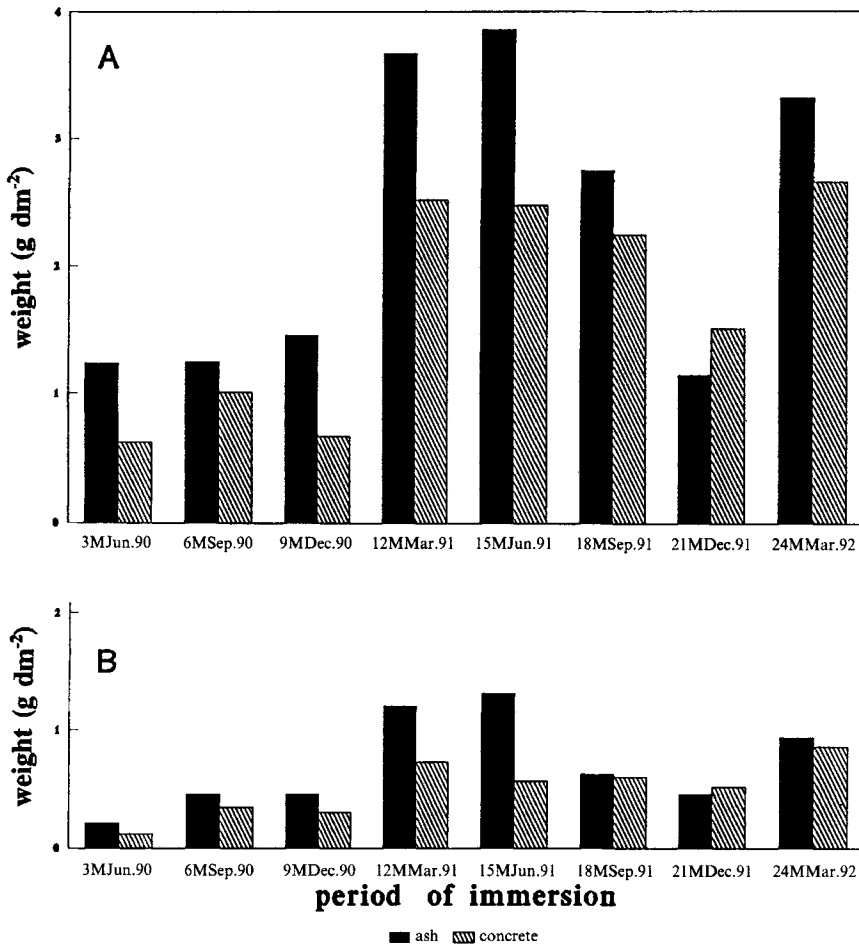


Figure 2 The average total weight (g dm^{-2}) of colonising organisms on the ash and concrete blocks, A = wet weight, B = dry weight.

Bioaccumulation

As far as bioaccumulation is concerned no significant differences were found in the contents of elements examined between the samples taken on the concrete blocks and those with ash (see Table VI).

CONCLUSIONS

The results obtained after two years at the experimental plant are encouraging. They show that coal-ash may be used advantageously for artificial reef materials without giving rise to any specific technical or environmental problems. The physical-mechanical results, in particular, demonstrate that neither distortions in form, nor swelling or even deterioration, which could be caused by prolonged contact with sea water,

Table VI Metals concentrations ($\mu\text{g g}^{-1}$ dry weight) in algae, mussels, gastropod (*Bititium reticulatum*) and oysters after different periods of exposure.

		Al	As	Cd	Cr	Cu	Fe	Pb	Se	Zn	
ALGAE	15 months	11600	30	0.3	28.3	22	11300	3.9	0.4	251	
		12100	26	0.3	24.1	15	9700	3.3	0.5	356	
	18 months	2400	21	0.2	10.4	18	3900	18	0.9	312	
		2500	31	0.2	8.5	17	3400	15	0.9	300	
	21 months	24730	43	0.2	40	19	14660	30	<1.0	275	
		23750	59	0.2	30	24	14530	21	<0.6	232	
MUSSEL	24 months	12750	26	0.2	20	25	14550	38	0.7	110	
		9050	18	0.2	14	22	11450	26	0.9	170	
	3 months	21	33	0.9	20.1	58	325	3.1	3.8	178	
		33	36	0.9	19.1	56	314	3.6	5	220	
	6 months	65	13	0.4	4.9	18	206	1.3	2.4	309	
		75	16	0.4	5.4	21	226	2.2	3.7	363	
BITTIUM	6 months	89	17	0.9	5	20	171	0.6	3	246	
		42	19	0.8	3	16	116	0.2	3	216	
	15 months	110	4.5	0.03	1.8	16	131	1.2	0.9	137	
		180	3.7	0.03	2.5	17	155	1.5	0.8	138	
	OYSTER	15 months	283	30	2.1	0.8	292	463	5.3	2.9	3500
			398	26	3.1	1.3	315	457	3.5	4.2	3000

were noted. The chemical tests (in the laboratory) showed there was a limited leaching of some macro elements such as aluminium, calcium, silicon and a negligible leaching (several ppb) of elements of environmental interest (As, Cr, Se, Tl). In the conditions of water flow in the tanks, the periodic sampling of some chemical elements did not show any appreciable leaching. No bioaccumulation was found.

Considering epibenthic organisms the data collected thus far show a greater degree of settlement on the ash blocks compared to those made only of concrete. The ash-based material neither selects nor hinders settlement but even proves to be more suitable (we do not know why) than concrete for the settlement of benthic organisms, both qualitatively and quantitatively. In fact, the species diversity on the ash-based blocks is higher than that on concrete blocks (Table V), with 62 species on the former material as against 54 on the latter. Biomass expressed in wet, dry and ash weight is always higher on the blocks made of ash than that found on those made of concrete.

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