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CHEMICAL BEHAVIOUR OF CALCIUM IN STABILIZED OIL ASH REEF BLOCKS AFTER FIVE YEARS IN THE OCEAN

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Reef blocks made from stabilized oil ash were taken from the sea after five years in the ocean to examine the chemical behaviour of calcium. Experiments included (1) determination of the calcium leaching rate and a comparison with the rate for unexposed blocks to test the validity of a diffusion model for predicting long term (5 years) leaching rates, (2) determination of the effect of biological cover (shell) on the leaching rate, (3) determination of the leaching rate of the core of exposed reef blocks, (4) determination of the calcium content in 'ring areas' – regions of discoloration observed in sectioned exposed reef blocks, and (5) determination of the leachable fraction of the total calcium in exposed reef blocks. Results showed the presence of a pronounced calcium discontinuity zone located 3–7 cm from the outside surface of the reef blocks. Cumulated calcium release rates ranged from 2.81–3.14 $\mu\text{mol cm}^{-2} \text{day}^{-1}$ for original unexposed reef blocks and the core of exposed (in the ocean for five years) blocks, respectively, to 0.47–0.50 $\mu\text{mol cm}^{-2} \text{day}^{-1}$ for outside (facing sea water) surfaces of exposed reef blocks. Tank leaching studies also showed that the presence or absence of hard biological cover (shells) had little or no effect on the calcium release rate. The diffusion model normally used in modelling the chemical behaviour of calcium cannot be used to predict the long term (five years) leaching of calcium. The core of the exposed blocks released calcium at a rate similar to new, unexposed reef block material. Overall, it appears that the calcium discontinuity zone is probably responsible for restricting the release of calcium and hence the failure of the diffusion model.

KEY WORDS: oil ash, artificial reef, calcium diffusion model, leaching

INTRODUCTION

Background

Previous experiments have been conducted in which ash residue from the burning of oil, coal, and municipal solid wastes has been combined with Portland cement to form stabilized ash-concrete; this ash-concrete has been used in construction of artificial reefs such as in the Conscience Bay Study (Roethel, 1981), the Coal Waste Artificial Reef Program (C-WARP) in New York (Woodhead *et al.*, 1984), the Stabilized Oil Ash Reef Program (SOAR) in Florida (Metz and Trefry, 1988; Kalajian *et al.*, 1989; Duedall *et al.*, 1992) and the Poole Bay Coal Ash Reef in the United Kingdom (Collins *et al.*, 1990). Artificial reefs constructed with the oil or coal ash-concrete have been successful in enhancing the physical undersea environment with increase in the abundance of fishes and fouling organisms (Nelson *et al.*, 1988). The chemical behaviour of the stabilized ash-concrete blocks in sea water is usually

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investigated by determining the leaching behaviour of unexposed or 'new' block material in a controlled laboratory environment over short time periods, less than 200 days. Long term leaching behaviour of ash-concrete reef blocks *in situ* is predicted by a diffusion model developed by Duedall *et al.* (1983) based on extrapolations from short term laboratory studies. Actual long term chemical behaviour has been examined by investigating changes in chemical composition of reef units that have been retrieved from the sea-bed raised after several years exposure to the marine environment (Breslin and Roethel, 1993; Hockley and van der Sloot, 1991; Shieh *et al.*, 1989).

Until now no studies have been conducted to determine laboratory leaching rates from ash-concrete blocks in sea water after long term (several years) *in situ* exposure. It is generally thought, but never tested, that the over-growth of foulers living on artificial reefs may help to stabilize the block surface and reduce leaching by 'locking in' the elements or compounds behind the covered areas (Nelson and Vose, 1992).

Purpose of Research

The purpose of this work was to determine the leaching behaviour of calcium from stabilized oil ash-concrete in sea water and to examine the change in calcium content of the reef blocks after submersion in the marine environment for five years. Calcium was chosen because it is a major element in the mineral assemblages that provide structural integrity to the reef block; thus if relatively large amounts of calcium are lost due to leaching, block failure may result. The specific work involved two studies:

1. Calcium leaching
2. Block calcium composition.

Calcium Leaching Study: Laboratory tank leaching studies of calcium from stabilized oil-ash concrete blocks retrieved from the Vero Beach artificial reef site (off the coast of Florida) were made after five years of *in situ* exposure. The objectives of the tank leaching study were to determine: (1) the leaching behaviour of five year exposed oil ash-concrete and the extent to which the diffusion model predicts the leaching of calcium in the marine environment; (2) the effect of biological cover on the flux of calcium from oil ash-concrete at five years, exposure time; and (3) the extent to which calcium has been retained in the reef block by measuring the leaching behaviour of calcium from the core of a five year exposed block and comparison with leaching from an original unexposed block.

Block Calcium Composition Study: In this work the calcium content at depths and specific areas within the blocks was determined by examining changes in calcium concentration after five years' *in situ* exposure. The objectives of the block calcium study were to determine: (1) the changes in calcium content with depth in the block after five years' exposure and to compare the depth of leaching with that predicted from model; (2) the calcium content of the ring areas found in the reef blocks to determine if areas of different calcium concentration were specifically related to the rings; and (3) the differences in the calcium concentration at the blocks' surface which may result from the restriction of calcium diffusion due to biological cover.

The leaching behaviour of calcium from the stabilized ash-concrete blocks over time is normally described by a one-dimensional mathematical diffusion model developed by Duedall *et al.* (1983), refined by van der Sloot *et al.* (1985), and further investigated by Breslin (1986) and Breslin and Duedall (1988). In the model, the

rate of diffusion or flux of ions over time from an ash-concrete block in a well stirred aqueous system, assuming uniform distribution of elements within the block and a flux of ions across the block-water boundary that is proportional to the concentration at that boundary. The model allows for the calculation of the effective diffusion coefficient (D , $\text{cm}^2 \text{s}^{-1}$) for a leachable ion; D is given by:

$$D = \pi t(J/fS_0)^2 \quad (1)$$

where: t = time (day);

J = flux of the ion ($\mu\text{mol cm}^{-2} \text{day}^{-1}$);

S_0 = initial concentration ($\mu\text{mol cm}^{-3}$) of the ion in the block; and

f = leachable fraction of the ion in the block.

Determination of the short term laboratory leaching behaviour of unexposed block material is necessary for application of the diffusion model for long term predictions. D , S_0 , and f are considered constant. The effective diffusion coefficient is calculated, based on a determination of flux (J) from short term leaching studies ($t \approx 100$ days), the initial concentration (S_0) from acid digestion, and the leachable fraction (f).

Thus, the model predicts that flux (J) of calcium from the ash-concrete decreases in proportion to the square root of time:

$$J \approx t^{1/2} \quad (2).$$

Once the initial flux (J_i) at time (t_i) has been determined in a short term laboratory leaching experiment, the long term flux (J_t at time t_t) can be calculated.

Formulation of Hypothesis and Design of Study

Figure 1 shows hypothetical flux versus time for the various scenarios of oil ash reef block leaching characteristics in sea water. The leaching behaviour of unexposed 'original block' material will be consistent with the diffusion model and provide data for prediction of long term leaching rates (Figure 1, case A). The hypothesis is that if the leaching rate of calcium over time from oil ash-concrete blocks is the result of simple diffusion and not affected by biological cover or chemical equilibrium or pore refinement processes (Hockley and van der Sloot, 1991) then the five year exposed blocks will leach at a rate predicted by the model. If the hard biological cover (shells) on the five year exposed blocks restricts diffusion of calcium below the covered surface area, then the rate of diffusion or flux would be lower than predicted by an amount proportional to the fraction of surface area covered (Figure 1, case B). In effect, the reduction in leaching rates as a result of biological cover would cause the block to leach at a rate consistent with that predicted for an older or longer-exposed block. By removing the hard biological cover, i.e. exposing areas where leaching has been restricted, we would expect the flux of calcium from the exposed and scraped block in the tank leaching studies to be similar to that of a 'younger' block (Figure 1, case C). If pore refinement occurs over a long term exposure to sea water and limits the effective depth of diffusion to 1–2 cm from the surface, then we would expect the rate of diffusion to decrease faster than predicted (Figure 1, case D). If the leachable contaminants of the oil ash-concrete have been 'locked in' by processes at the block surface, then we would expect a cut and exposed 'block core' to have a leaching rate similar to that of a new unexposed 'original block' (Figure 1, case E).

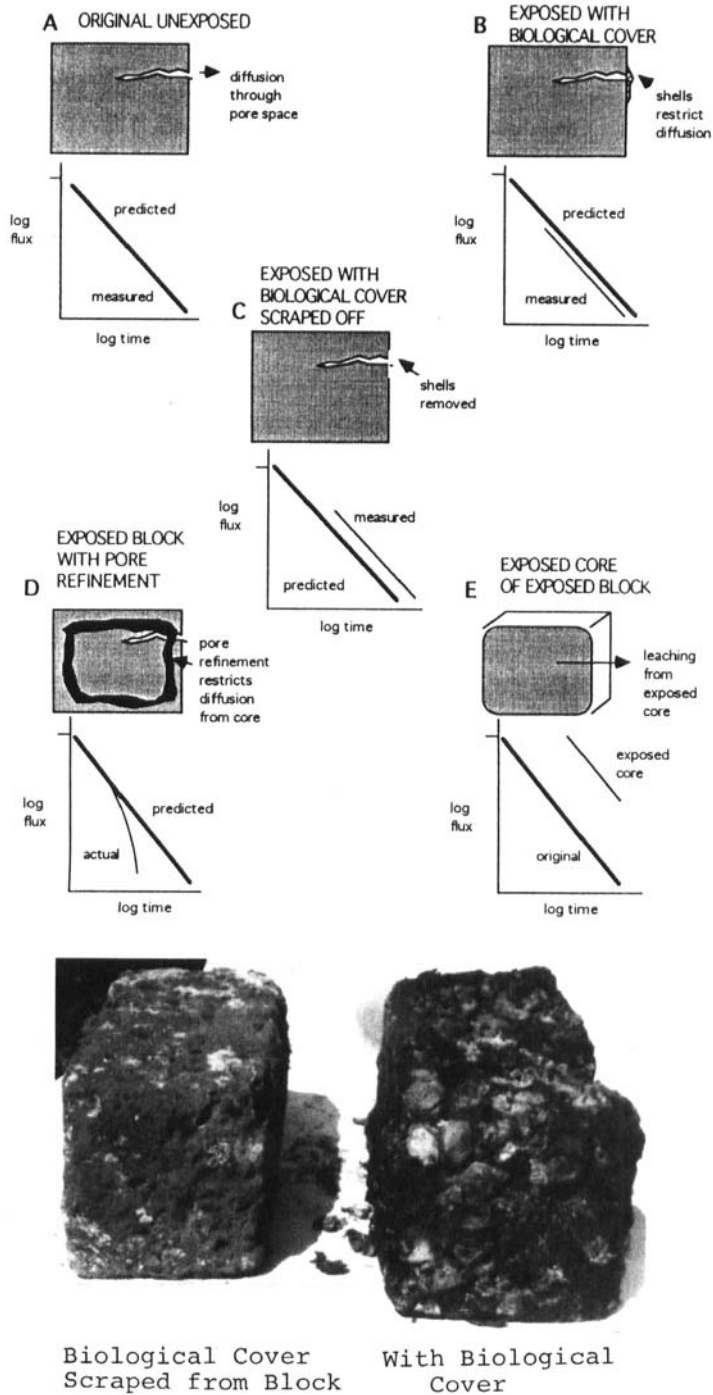


Figure 1 Hypothetical leaching rates of calcium from stabilized oil ash reef blocks for different conditions and processes and photograph of blocks, one with biological cover, the other with cover scraped off.

The design of the tank leaching study consisted of fourteen tanks with seven different conditions in replicates of two. There were four conditions of the oil ash reef blocks in eight tanks, and three controls in six tanks.

Experimental tanks:

- 1) 'Unexposed or original block': (Ob) – block fabricated at the same time as the other reef blocks with the same ingredients and stored in a laboratory; the cut side was covered with Plasti Dip® for consistency although not necessary.
- 2) 'Exposed with biological cover' (BCb) – exposed block with the soft biological cover removed and hard covering remaining; the cut side was covered with Plasti Dip® to prevent leaching from the exposed core.
- 3) 'Exposed and scraped' (Sb) – exposed block with all biological cover removed; the cut side covered with Plasti Dip®.
- 4) 'Core block' (Cb) – five year exposed block with the core exposed and the other five sides covered with Plasti Dip®.

Control tank:

- 1) 'Blank' – tanks that contained only sea water.
- 2) 'Surface covering control' – tanks that contained 20 × 20 cm piece of plastic covered with Plasti Dip® as a control for the covered sides of the blocks.
- 3) 'Shell control' – tanks contained shells with a total surface area similar to that of the shell covering on the exposed block with biological cover.

Determination of Calcium in the Block

The formation of ring areas of various shades of grey could be identified easily on all cross sectional exposed blocks. Figure 2 shows a cross sectioned block and ring areas visible which may be evidence of chemical equilibrium and pore refinement processes described by Hockley and van der Sloot (1991). There was also soft and hard biological cover on the surface of the oil ash reef block.

The block chemical composition was examined for both the total amount of calcium and the leachable fraction of the total calcium. The leachable fraction is defined as the fraction of the total amount of an element (calcium) capable of being leached from ash-concrete at high dilution. To investigate changes in the block calcium as a result of exposure, four different types of examination were made on the cross-sectioned blocks:

- 1) 'Depth Profile': The average calcium concentration with depth was determined to identify of areas of discontinuity, to examine the depth of leaching from within the block. Samples (Figure 2) were taken at 1 cm intervals around the block from the outside surface (exposed to sea water) of the block through to the centre of the core.
- 2) 'Ring Area Profile': Because the visible ring areas were irregular, a second chemical profile was made within the four areas of coloration, (Figure 2).
- 3) 'Biological Growth Profile': It has been found previously that inconsistencies in chemical profiles could be removed if profiles from the biologically encrusted surfaces were separated from those from the cleaner underside of the block (Hockley and van der Sloot, 1991). Thus, sampling was also done on the outer 1 cm of the block under an area covered by a shell and also under an adjacent area not covered by shells, to determine possible changes in the chemical

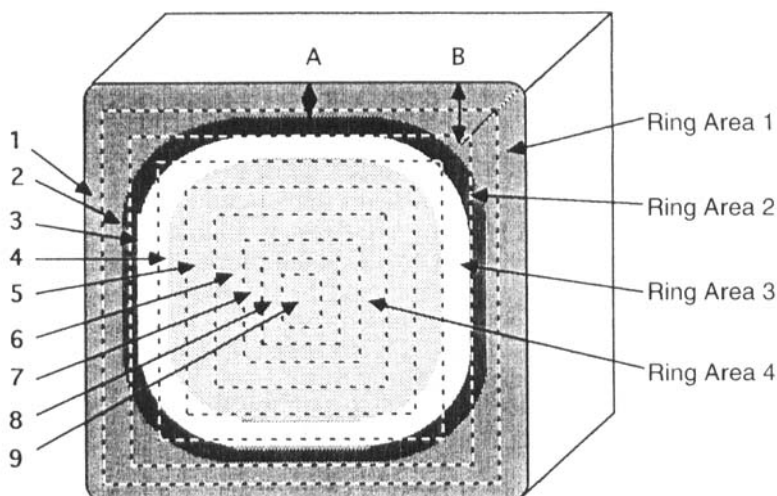


Figure 2 Pictorial view of section exposed oil ash reef block showing the four ring areas as visible shades of coloration. Figure drawn to scale based on measurements given in Table II. Also shown are the nine areas sampled to developed a profile of calcium concentration for the exposed oil ash reef block.

composition due to biological cover (Figure 3). First, the block was broken through an area covered by a large shell. Then, the remaining shell was chipped away and a 1 cm³ sample was taken below the shell covered area along with another sample taken just outside the area covered by the shell.

- 4) 'Unexposed Sample': A fourth sample was taken from all areas of an unexposed block or 'original' block, including surface and core samples.

MATERIALS AND METHODS

All glassware used in the experiments was cleaned carefully with soapy water, soaked in a 10% H₂SO₄-10% HCl acid bath for at least one day and then rinsed at least three times with distilled-deionized water. Plastiware, including the 5 gallon tanks for the leaching study, was treated in a similar manner except that nitric acid was used in place of sulphuric acid in the acid bath. All apparatus was stored under a plastic cover or in plastic bags until use.

Block Samples and Preparation

The Stabilized Oil Ash Reef (SOAR) was constructed on April 7, 1987, 2 km off Vero Beach, Florida. Some of the original SOAR reefs blocks, retained and stored in a laboratory for future reference, were used in this work. The blocks were fabricated originally in 1987, using oil ash stabilized within a fly ash matrix by the addition of cement and lime to form 20 cm × 20 cm × 40 cm blocks. The mix design used to manufacture the stabilized oil ash blocks was (dry composition) 39.7% oil ash, 39.7% fly ash, 15.9% cement, and 4.7% lime (Kalajian *et al.*, 1989). The initial water content of the mix was 25%.

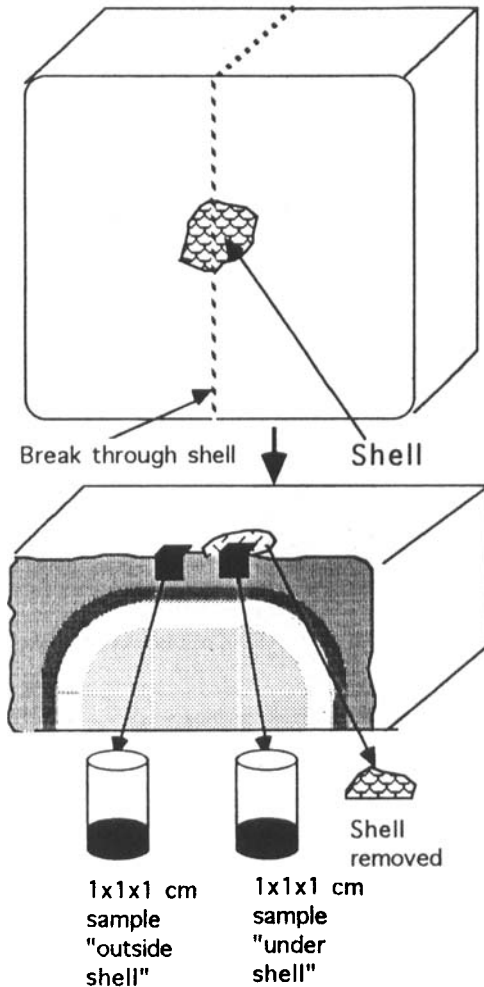


Figure 3 Sampling method under a shell covering and in area adjacent to shell covering.

On April 7, 1992, exactly five years after the SOAR reef construction, divers retrieved several block samples from the reef site. The exposed blocks and one stored block were cut into approximate thirds (Figure 4) with the middle portion being used to test compressive strength in another study; the remaining ends were used in the tank leaching studies.

Table I shows the dimensions of the block samples used in the leaching tank experiment. The table also gives the surface area of the blocks and the area covered by the hard biological material (shells) which was 16–24% of the total surface area. Cross sections of the exposed blocks revealed the visible ring areas of various shades of grey as previously mentioned (Figure 2). Table II shows the dimensions of the four ring areas and Figure 2 shows an average block cross section drawn to scale based on the measurements in Table II as well as the similar coloration of the ring areas. Patterns of the ring areas were not as regular as those shown in

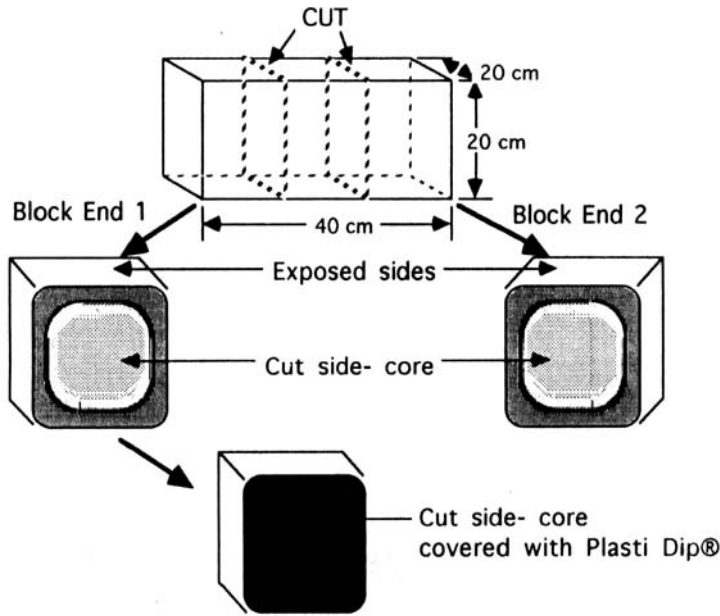


Figure 4 Schematic view of the preparation of oil ash reef blocks for tank leaching experiment.

Table I Characteristic of blocks used in the tank leaching study

Block 1		Dimensions (cm)			Surface Area (cm ²) ^a	Biological Covering (cm ²) ^b	Percent Biological %	Block Weight (g) ^c
Original 1	Ob1	19.3	18.7	9.8	1106	N/A	–	4702
Original 2	Ob2	19.3	18.6	9.0	1041	N/A	–	4258
Scraped 1	Sb1	19.3	18.5	9.4	1068	N/A	–	5485
Scraped 2	Sb2	19.0	18.1	9.7	1064	N/A	–	5223
Biological cover 1	BCb1	19.3	18.3	9.6	1075	182	16.9	6217
Biological cover 2	BCb2	19.2	18.5	9.5	1072	253	23.6	5887
Core 1	Cb1	19.2	18.5	9.7	355	N/A	–	5689
Core 2	Cb2	19.3	18.5	9.6	357	N/A	–	5660

^a The Plasti Dip® coated side is not included.

^b It was only possible to measure the biological cover on the cut ends of one block as others had already been scraped of biological cover for other studies.

^c The weight was measured after the blocks had air dried for several days.

Figure 2; the rings follow the block surface but were rounded at the corners as shown.

Tank Leaching Methods

To investigate the leaching of the stabilized oil-ash concrete blocks the tank leaching method was used (Duedall *et al.*, 1983; Breslin, 1986; Edwards and Duedall, 1985;

Table II Measurements of ring area dimensions on cross sectioned five year submerged blocks^a

Ring Area	Coloration	Average Ring Area Width (cm)	Standard Deviation (cm) ^d	Maximum Ring Area Width (cm)	Minimum Ring Area Width (cm)
1A ^b		1.5	0.8	2.5	0.7
1B ^b	grey-brownish	2.9	1.4	6.0	2.5
2	dark grey	1.0	0.6	2.0	0.5
3	very light grey	1.3	0.5	2.0	0.5
4 ^c	light grey	n/a	n/a	n/a	n/a

^a See Figure 2.

^b Because the rings do not parallel the surface of the block the measurements of 'Ring Area 1' were taken both along the edges (shown by A in Figure 2) and at the corners (shown by B in Figure 2).

^c No measurements were made on 'Ring Area 4' because this area exists from 'Ring Area 3' to the centre of core of the block.

^d Measurements were made on all four edges and corners of three replicate blocks (n=12).

van der Sloot and Groot, 1989). The ratio of block surface area (not including the Plasti Dip covered side) to litre of sea water in this study was 113 cm²:1 litre. The tank water was replaced with decreasing frequency from 3 days to five week intervals. 20 ml samples were collected from all tanks at times corresponding to the frequency of sea water changes. At each sampling the weight of each tank was measured to determine the volume of sea water; volume changes due to evaporation were found to be insignificant. pH was also measured during the leaching study.

Plasti Dip[®] was applied to the surface of the test samples to prevent leaching from the 'freshly' cut side of the block where the core had been exposed. The coating prevented leaching but did not alter the tank water calcium content either by leaching or absorption/adsorption. As necessary for the tank leaching experimental design, involving blocks with and without the hard biological covering, the remaining hard biological covering was removed by prizing off or scraping it away while taking care to minimize any damage to the block surface.

The samples were filtered through a 0.40 μm Nucleopore polycarbonate filter, acidified with Ultrex[®] nitric acid to a pH of 1–2, and stored in sealed 30 ml polypropylene bottles at 4°C until analysis. The samples were analyzed for calcium using a Perkin-Elmer 5100 atomic absorption spectrometer (AAS). The results of the tank leaching study were used to calculate the release of calcium over time (B) in order to determine the flux (J) of calcium from the blocks to the sea water. The calcium released was normalized to the surface area of the block:

$$B = [(C_t - C_o) \times V_t] / A \quad (3)$$

where: B = Ca²⁺ released (μmol cm⁻²) from the last sea water change to the time of sampling;

C_t = Ca²⁺ concentration (μmol l⁻¹) in the test tank at time t;

C_o = Ca²⁺ concentration (μmol l⁻¹) in the control tank at time t;

V_t = volume of water in the test tank at time t;

A = geometric surface area (cm²) of the block.

To obtain the calcium released between sampling times within the same water change, the following formula was used:

$$B'_i = B_i - B_{(i-1)} \quad (4)$$

where: i = sample number since the last sea water change;

B_i = calcium released ($\mu\text{mol cm}^{-2}$) from the time of the last sea water change to the i th sampling time;

$B_{(i-1)}$ = calcium released ($\mu\text{mol cm}^{-2}$) from the time of the last sea water change to the $i-1$ sampling time; and

B'_i = calcium released ($\mu\text{mol cm}^{-2}$) from the $i-1$ sampling time to the i th sampling time since the last sea water change.

The flux of calcium from the block at each sampling time is:

$$J = B'_i [t_j - t_{(j-1)}] \quad (5)$$

where: J = Ca^{2+} flux ($\mu\text{mol cm}^{-2} \text{ day}^{-1}$);

j = sample number;

B'_i = calcium released ($\mu\text{mol cm}^{-2}$) between sampling time as calculated above;

and

t = time of exposure (days).

The calculated fluxes are not instantaneous rates but are averaged over a finite period of time. The results of the tank leaching study were plotted as the cumulated amount of calcium released over time ($\sum_0^1 (B'_i)$).

Analysis of Calcium Content in the Block

Sampling of the block material was accomplished using a silicone carbide grinding stone to obtain precise samples from specific areas on or in the block. This method is similar to that used by Hockley and van der Sloot (1991). Triplicate samplings were made from three separate blocks. This technique was used to grind specific areas of the blocks to obtain a fine powder easily passable through a 0.5 mm sieve. Each powder sample was shaken vigorously to ensure homogeneity. Approximately 1.5 g was obtained so that both the acid digestions and the leachable fraction determinations could be made.

Bulk chemical analysis of the various stabilized oil ash-concrete samples was performed using the $\text{HF}-\text{H}_3\text{BO}_3$ digestion technique (Breslin, 1986). National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1633a fly ash was digested to determine the completeness of the digestion. A 95% recovery of calcium has been reported and was also found in this study (Shieh and Duedall, 1992; Becker, 1990; Breslin, 1986).

Leachable Fraction Determination

The leachable fraction of calcium was determined on specially prepared samples using the methods of Breslin (1986). The samples were oven-dried at 103°C prior to weighing. Approximately 0.63 g of each sample was weighed accurately and placed in a 125 ml polyethylene bottle to which 125 ml of filtered sea water was added (200-fold dilution). The bottles were shaken mechanically for 72 hours. The samples were then filtered through a $0.40 \mu\text{m}$ Nucleopore polycarbonate filter, acidified with Ultrex[®] nitric acid to a pH of 1-2, and stored at 4°C until analysis. The samples were analyzed for calcium using the Perkin-Elmer 5100 atomic absorption spectrometer (flame method).

Determining Calcium Content Change

The variation in calcium content with respect to both total calcium and the leachable fraction was examined by comparing five year exposed blocks with unexposed original block material. The percent change was determined as:

$$100 \times (C_e - C_o)/C_o$$

where: C_e is the percent content of calcium or percent leachable fraction in the exposed block; and

C_o is the percent content of calcium or percent leachable fraction in the unexposed original block.

A positive value for the percent change means there had been an increase or enrichment of calcium; if the percent change was negative, a decrease or depletion of calcium had occurred (Shieh *et al.*, 1989).

Sea Water Collection and Ca/Cl Determination

The sea water used in the study was collected at the Florida Institute of Technology Indian River Marine Science Research Centre, Vero Beach, Florida. The sea water was pumped directly from the ocean to the laboratory through a submerged pipe located about 5 m below the sand, approximately at the shore line. After obtaining the sea water, it was filtered in the laboratory through a 0.45 μm Gelman polycarbonate filter to remove particulate and larger colloidal matter. Titration (Mohr method) was used to determine chlorinity. From chlorinity and published values for the Ca/Cl content, the initial calcium in the sea water was calculated.

Calcium Analysis

The concentration of calcium in leachate samples was measured using AAS; three absorbance measurements were made on each diluted sample. The dilution was made with 1.0% La^{3+} (w/v) solution. Accuracy of the analysis was ensured by measuring a reference standard of known concentration periodically during the analysis.

RESULTS

Tank Leaching Study

Figure 5 shows the cumulated amount (expressed as $\mu\text{mol cm}^{-2}$) of calcium released over time (days) for the SOAR 'original' unexposed blocks (Ob). Ob1 and Ob2 (duplicate blocks) released 414 $\mu\text{mol cm}^{-2}$ and 443 $\mu\text{mol cm}^{-2}$ of calcium in 149 days. The release of calcium persisted throughout the entire sampling period for both unexposed blocks. Figures 6 and 7 show the cumulated calcium released from exposed blocks 'scraped' of biological cover (Sb) and from exposed blocks with biological cover (BCb). Sb1 and Sb2 released 96 $\mu\text{mol cm}^{-2}$ and 80 $\mu\text{mol cm}^{-2}$ to the tank waters in 149 days. BCb1 and BCb2 released 75 $\mu\text{mol cm}^{-2}$ and 87 $\mu\text{mol cm}^{-2}$ in 149 days. Figure 8 shows the cumulated calcium release over time for the core of an exposed block (Cb). Cb1 and Cb2 released 336 $\mu\text{mol cm}^{-2}$ and 279 $\mu\text{mol cm}^{-2}$ of calcium in 91 days.

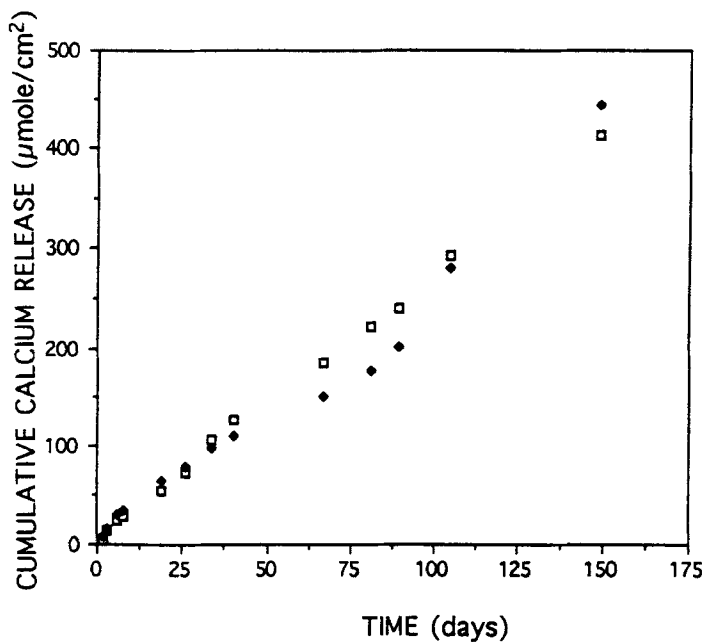


Figure 5 Cumulated release of calcium in tank leaching experiment for unexposed original oil ash reef block: \blacklozenge original reef block 1 (Ob1); \square original reef block (Ob2).

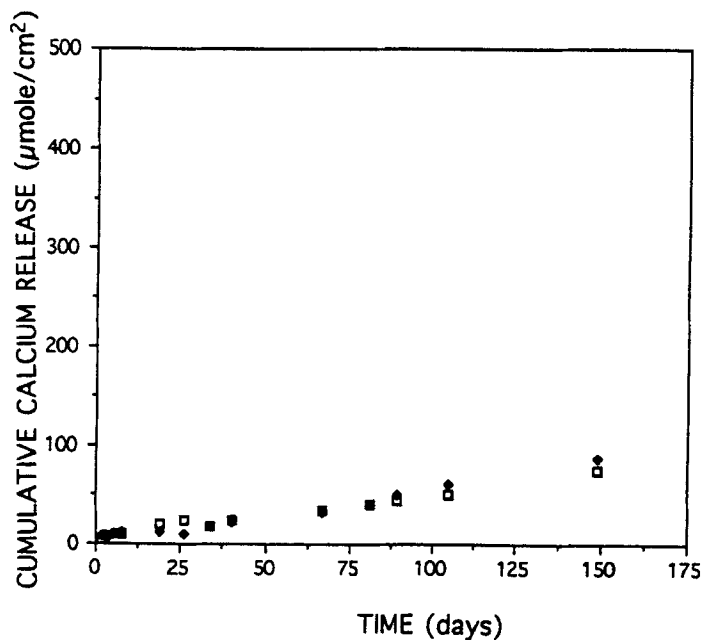


Figure 6 Cumulated release of calcium in tank leaching experiment for exposed (in the ocean for 5 years) oil ash reef block scraped of biological cover. \blacklozenge scraped block 1 (Sb1); \square scraped block (Sb2).

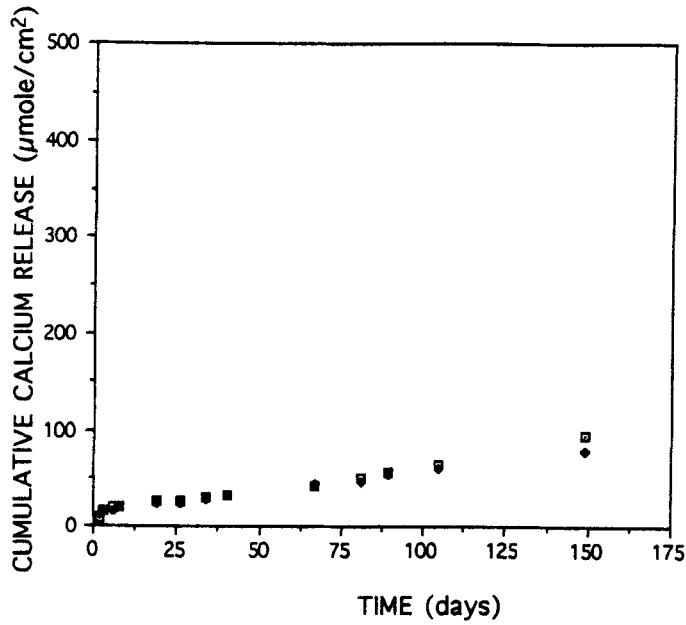


Figure 7 Cumulated release of calcium in tank leaching experiment for exposed (in the ocean for 5 years) oil ash reef blocks with biological cover. □ biological cover block 1 (BCb1); ♦ biological cover block 2 (BCb2).

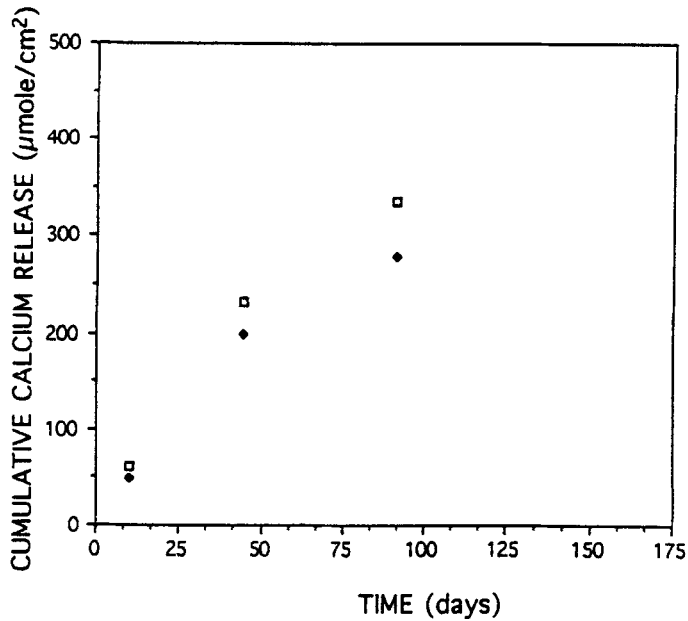


Figure 8 Cumulated release of calcium in tank leaching experiment for exposed (in the ocean for 5 years) oil ash reef block with core exposed. □ core block 1 (Cb1); ♦ core block 2 (Cb2).

In the results shown in Figures 6 and 8 a more rapid release of calcium from the exposed blocks (Sb and BCb series of blocks) is evident during the first 6–8 days of the experiment as these blocks became re-equilibrated with the sea water, but after the eighth day the rate of release was constant for both the Sb and the BCb blocks. This phenomenon (more rapid release of calcium initially) was most likely due to residual sea salt calcium present in the pores of the blocks; calculations show that 80% of the calcium released from the exposed blocks during the initial 6–8 days of the experiment could have come from sea salt. After the 6–8th day of the experiment this effect becomes negligible.

Table III shows the cumulated calcium release and the average flux for each tank condition over the sampling period. The cumulated release of calcium starting from the 8th day and continuing to the end of the sampling period averaged between replicate tanks is also shown. The flux (J_t) is represented as a finite rate determined from the change in calcium released over the corresponding period of time:

$$J_t = \Delta C / \Delta t$$

To determine J_t , the cumulated calcium released must be measured over a specific period of time. In the experiments conducted, because the release of calcium showed no tendency to level off for the exposed blocks, the flux of calcium was averaged over the sampling period beginning at the eighth day of sampling. J_t values for the unexposed original blocks and the exposed core blocks were also calculated in the same manner.

Values for J_t for all block conditions, as well as results from Breslin (1986), are shown in Figure 9. Mean fluxes of calcium for the exposed core of the five-year exposed block are shown at times corresponding to the time frame of the present tank leaching study, rather than beginning at a time of 1825 days (5 years), for comparison with the results for original unexposed SOAR reef block. The J_t value of the exposed block with biological cover and the J_t for exposed block scraped of

Table III Cumulated calcium release and flux^a

Block	Cumulated Calcium Released ($\mu\text{mol cm}^{-2}$) ^b	Average Cum. Calcium ($\mu\text{mol cm}^{-2}$)	Std.Dev. Cum. Calcium ($\mu\text{mol cm}^{-2}$)	Flux of Calcium ($\mu\text{mol cm}^{-2} \text{ day}^{-1}$) ^c	Average Flux ($\mu\text{mol cm}^{-2} \text{ day}^{-1}$)	Std.Dev. Flux ($\mu\text{mol cm}^{-2} \text{ day}^{-1}$)
Original 1	384	397	18	2.72	2.81	0.13
Original 2	409			2.9		
Scraped 1	75	67	11	0.53	0.47	0.08
Scraped 2	59			0.42		
Biological cover 1	66	71	8	0.47	0.5	0.05
Biological cover 2	76			0.54		
Core 1	312	284	40	3.43	3.12	0.44
Core 2	256			2.81		

^a See Figure 5–8.

^b Cumulated calcium released over 141 days starting at day 7 of the tank leaching experiment. 'Core' blocks cumulated calcium released for 91 days.

^c Flux of calcium is averaged over entire sampling period.

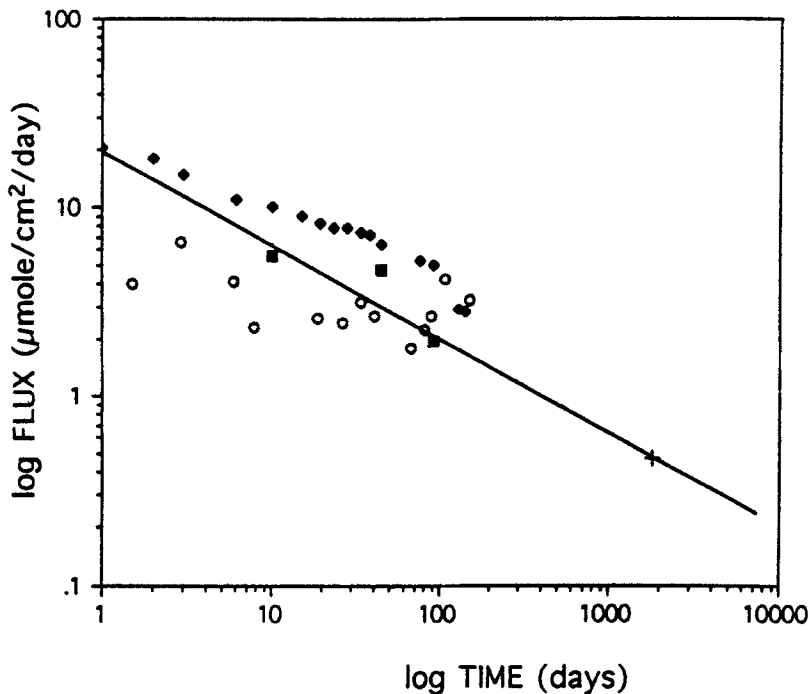


Figure 9 Calcium flux versus time. ◆ short term leaching data from Breslin (1986); ○ short term tank leaching unexposed reef block, current study; ■ exposed core (five year reef block); + exposed surface (five year reef block). The solid line drawn through the point for the exposed surface five year block has a slope of $-1/2$ in accordance with the diffusion model.

biological cover at a time of 1825 days (5 years) have been averaged (Table III) to give the single value shown on Figure 9. A solid line is drawn through the average five year flux with a slope of $-1/2$ to demonstrate the predicted flux, both backwards and forwards in time, from the diffusion model.

Block Calcium Analysis and Leachable Fraction

The calcium content of the single unexposed block was determined to be 12.5% (SD 0.4%). It was determined previously that the unexposed blocks contained 11.0% calcium (SD 0.3%) (Shieh *et al.*, 1989). The calcium content determined from the single available unexposed block is within the accepted published 15% block-to-block variation (Shieh *et al.*, 1989), consistent with that found at the core of the exposed blocks.

The leachable fraction had not been determined previously for the SOAR reef blocks. The leachable fraction of total calcium in the single unexposed block was found to be 5.3% (SD 2.8%). The relatively high standard deviation demonstrates that there is high variability in leachable calcium in the block.

The residual calcium, from sea water present in the pore space due to the drying of the blocks after retrieval from the ocean, can be shown to be an insignificant contribution to the total calcium content. For example, assuming a porosity of 40%, the residual calcium would account for less than 0.2% of the total calcium content

in the exposed blocks. It is also assumed that the residual calcium from sea salt is soluble and thus would make a 0.2% contribution to the measured percent leachable fraction.

Calcium Profile

The calcium profile (with depth into the block), based on analysis of 1 cm wide areas around the block from the surface to the core, is shown in Figures 10 and 11 with corresponding data in Table IV. These results show that at a depth of 9 cm, which is at the central core of the exposed block, the average total calcium content and the leachable fraction are consistent with values found for an original unexposed SOAR reef block, 12.6% and 5.3%, respectively; the variability with respect to each is also consistent with the original unexposed block, 0.6% and 2.4% respectively.

In Figure 10, profiles of total calcium content are given for three replicate exposed blocks and an average value for the original unexposed block. In each exposed block replicate, there was a distinct depth of discontinuity, or minimum calcium concentration, in the chemical profile. However, the depth at which the discontinuity occurred was quite variable, 2, 3, and 5 cm into the block as shown in Figure 10. From the region of discontinuity, moving towards the core of the block, total calcium content increased to values consistent with those found in the unexposed block.

The percentage of the total calcium capable of leaching, i.e. the leachable fraction, is shown in Figure 11. At the surface of the block, the leachable portion of total

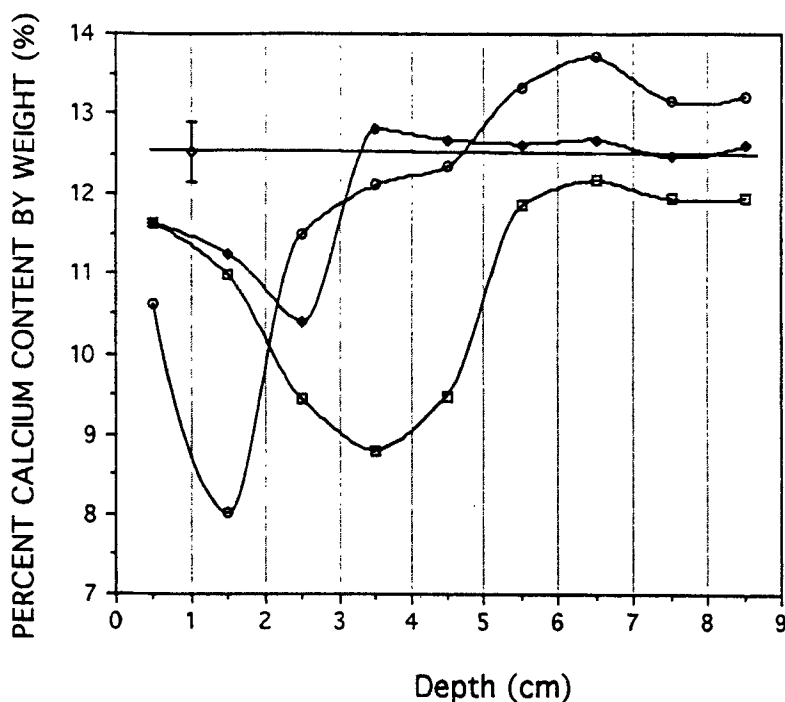


Figure 10 Depth profile of calcium concentration. □ exposed block 1; ♦ exposed block 2; ○ exposed block 3; and ◇ mean value for unexposed blocks.

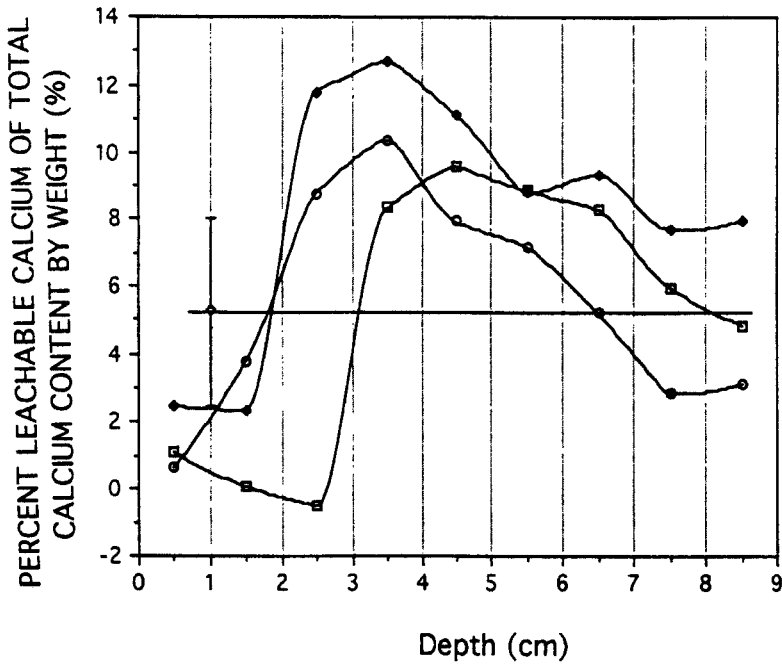


Figure 11 Depth profile of leachable fraction of total calcium. ■ exposed block 4; ○ exposed block 5; □ exposed block 6; ◇ mean value (n = 3) for original unexposed blocks.

Table IV Calcium depth profile^a

		Depth (cm) ^b									
		1	2	3	4	5	6	7	8	9	Ave
Block 1	Total Ca (%)	11.6	11.0	9.5	8.8	9.5	11.8	12.2	11.9	11.9	10.9
	Leachable Fraction (%)	1.1	0.1	-10.5	8.3	9.6	8.8	8.3	6.0	4.9	5.2
Block 2	Total Ca (%)	11.6	11.3	10.4	12.8	12.7	12.6	12.7	12.5	12.6	12.1
	Leachable Fraction (%)	2.5	2.4	11.8	12.7	11.1	8.8	9.3	7.7	8.0	8.3
Block 3	Total Ca (%)	10.6	8.0	11.5	12.1	12.3	13.3	13.7	13.2	13.2	12.0
	Leachable Fraction (%)	0.7	3.8	8.8	10.4	7.9	7.7	5.2	2.9	3.2	5.5
Average	Total Ca (%)	11.3	10.1	10.4	11.2	11.5	12.6	12.9	12.5	12.6	11.7
	Leachable Fraction (%)	1.4	2.1	6.7	10.5	9.5	8.3	7.6	5.5	5.3	6.3
Std.Dev.	Total Ca (%)	0.6	1.8	1.0	2.1	1.8	0.7	0.8	0.6	0.6	0.7
	Leachable Fraction (%)	1.0	1.9	6.4	2.2	1.6	0.9	2.2	2.5	2.4	1.7
Percent change ^c											
Block 1	Total Ca (%)	-7.1	-12	-25	-30	-24	-5.4	-2.9	-4.7	-4.7	-6.8
	Leachable Fraction (%)	-79	-98	-110	+57	+81	+67	+57	+13	-7.7	+20
Block 2	Total Ca (%)	-17.2	-110	-117	+2.2	+1.2	+0.7	+1.2	-0.6	+0.5	
	Leachable Fraction (%)	-5.3	-5.5	+124	+144	+111	+66	+77	+46	+51	
Block 3	Total Ca (%)	-15	-36	-18.2	-13.3	-11.5	-6.4	+9.4	+5.0	+5.4	
	Leachable Fraction (%)	-88	-28	+66	+96	+50	+36	-1.5	-45	-40	

^a See Figure 10 and 11.

^b Sample number and depth refer to Table II.

^c Percent change from original ash-concrete where total calcium is 12.5% and leachable fraction is 5.3%.

calcium in the exposed block had decreased by a factor of 2–3 from the corresponding value for the unexposed block. Surprisingly, there was a sharp increase in the calcium leachable fraction at depths of 3–7 cm, where the leachable fraction increased to greater than the measured leachable fraction in the original unexposed block. The leachable fraction values then decreased moving towards the block core where the values were similar to that measured for the unexposed block.

Ring Area Calcium Content

Table V shows the total calcium content and leachable fraction specific to the ring areas associated with coloration described in Table II. The results of the chemical investigation of ring areas are consistent with the results of the chemical profile (see Table V and Figures 10 and 11). In ring area 1, total calcium was much higher than expected in the exposed block where leaching of calcium over time should have resulted in the greatest depletion of calcium. Total calcium in ring area 1 was depleted by only 1.7%, on average (Table V), even though the leachable fraction was reduced by almost 80% on average. At the dark ring area, ring area 2, total calcium was depleted by 28.4% on average with greater than 82% decrease in the value of the leachable fraction. Ring area 3, the white ring area, showed further decreases in total calcium, averaging 36% less than the original calcium content, while in the same area the leachable fraction abruptly increased. In ring area 4, total calcium approached the value for unexposed block; however, in this ring area the leachable fraction of calcium increased by almost 80% over the value for the unexposed block.

Calcium Content Immediately Under Biological Cover

The calcium content in the reef block under an area covered by hard biological cover, thought to restrict diffusion (see Figure 1), was measured on three blocks. Under the shell-covered area the average total calcium was 11.4% (SD 1.0%) and the average leachable fraction was 2.2% (SD 0.8%). Just adjacent to the shell covered

Table V Total calcium content^a and leachable fraction specific to the ring area associated with coloration described in Table II.

		Ring Area			
		1	2	3	4
Block 4	Total Ca (%)	11.3	8.6	8.1	11.9
	Leachable Fraction (%)	1.3	-0.4	7.0	9.4
Block 5	Total Ca (%)	11.0	8.7	7.5	11.8
	Leachable Fraction (%)	1.4	1.0	4.2	8.8
Block 6	Total Ca (%)	14.7	9.6	8.4	13.0
	Leachable Fraction (%)	0.6	2.0	8.5	9.9
Average	Total Ca (%)	12.3	9.0	8.0	12.2
	Leachable Fraction (%)	1.1	0.9	6.6	9.4
Std.Dev.	Total Ca (%)	2.1	0.5	0.5	0.7
	Leachable Fraction (%)	0.4	1.2	2.2	0.6
Percent change ^b	Total Ca (%)	-1.7	-28.4	-36.1	-2.6
	Leachable Fraction (%)	-79.4	-82.8	+24.4	+77.9

^a See Figure 2 and Table II for ring area dimensions

^b Percent change from original oil ash-concrete where total calcium was 12.5% and the leachable fraction was 5.3%.

area, mean total calcium was 11.7% (SD 0.3%) and the mean leachable fraction was 3.0% (SD 0.4%). Thus, the presence of shells on the block appeared to have no significant effect on the calcium content at the surface of the five year exposed blocks.

DISCUSSION AND CONCLUSIONS

The relationships between the flux of calcium leaving the reef block surfaces, the characteristics of the leachable fraction, the appearance and concentration of calcium in the ring areas, the depth of diffusion, and the role of fouling on diffusion are not well understood even after this study. At best we can only integrate or correlate a few of these processes or characteristics to each other.

For fluxes we have found that after five years' *in situ* exposure, the flux of calcium from the exposed oil ash-concrete blocks, determined from the tank leaching study, was $0.49 \mu\text{mol cm}^{-2} \text{ day}^{-1}$ on average (Table III). Neither the original flux values reported by Breslin (1986), nor the values of J_t for the unexposed blocks determined in this work, would have predicted the relatively low value of J_t of $0.49 \mu\text{mol cm}^{-2} \text{ day}^{-1}$ for the 1825 day (5 years) exposed reef block. Basically, the values of J_t obtained during a tank leaching study, when plotted against time, fall above the line of slope ($= -1/2$, Figure 9) and thus the diffusion model (equation 1), if used as a predictive tool, will overestimate the flux of calcium at some future time.

The failure of the model to predict fluxes is related probably to the calcium profiles (and rings) (i.e. S_0 in equation 1 is not constant) from the block surface through to the central core (see Figures 10 and 11) and the large changes in the leachable fraction (i.e. f in equation 1 is not constant). The first area is the outer 1–3 cm corresponding to a visible ring area 1. In ring 1, it was expected that calcium would show the greatest depletion due to leaching of calcium with time. However, in this ring total calcium was depleted by only 9.8%, compared to the original unexposed SOAR block, with less than 1% capable of being leached determined by the leachable fraction analysis. This suggests that over five years of exposure either leaching is very slow or that the once calcium depleted block surface later began to accumulate calcium possibly by the precipitation of a non-leachable mineral in the pore space of the block. The *in situ* precipitation of calcium carbonate at the block surface has been reported in previous studies (Roethel and Oakley, 1985; Labotka *et al.*, 1985; Hockley and van der Sloot, 1985). The calcium ions on their diffusion path out of the block or the re-entry of calcium and/or carbonate ion from sea water may create conditions of supersaturation with respect to calcium carbonate. It seems likely that calcium carbonate supersaturation conditions could be enhanced by the presence of biological cover composed of calcium carbonate shell; we did observe a relatively large cover of 'hard' biological growth beneath the soft cover.

Ring area 2 was found at a depth of 1.5–3.5 cm from the surface; here there was an unexpectedly large depletion (28%) of total calcium. Also, surprisingly, in this second area there was a minimum leachable fraction of calcium (Table V).

The third area occurred at depths of 2–5 cm and is referred to as ring area 3. In this ring, total calcium was depleted by more than 36% on average (Table V). At the same depth a discontinuity appears in total calcium; this occurred at 0.5–2 cm within or below the discontinuity in the leachable fraction.

The fourth ring area is found 3–5 cm from the surface and extends to the core. In this ring total calcium content was similar to that of the unexposed SOAR original

block. However, in this ring the leachable calcium had increased and was highest at the outer boundary of ring 4, then decreased towards the central core. Only at the very centre are both leachable fraction and total calcium consistent with values for the unexposed SOAR original reef block.

The original hypothesis that the calcium content of an exposed block core would be more or less unchanged within the zone of diffusion as a result of exposure appears to hold true. A possible explanation is that the core of the exposed reef blocks over the five years was, in effect, isolated from the diffusion/discontinuity zones described earlier. As a result, the J_t values for the cores of the exposed and unexposed blocks are similar (Table III). How long such isolation would exist would be difficult to determine because so little is known about the mechanisms associated with the diffusion/discontinuity zones.

Finally, on the role of biological cover in restricting diffusion of calcium (Figure 1), Nelson and Vose (1992) suggested that over-growth of foulers in artificial reefs may help to stabilize the block surface and reduce leaching of block contaminants by 'locking in' metals behind the covered areas. In the present work we found that the presence of hard biological material covered approximately 15–20% the surface of the five year oil ash-concrete block samples. Because the values of J_t for both the scraped exposed blocks and the biologically covered blocks were nearly the same, we conclude that a 20% biological cover has no measurable effect on the calcium flux over five years.

In conclusion, our work showed that:

- (1) the diffusion model based on short term laboratory leaching behaviour cannot be used to predict long term fluxes;
- (2) the flux of calcium from oil ash-concrete reef blocks is reduced by more than 80% after five years' *in situ* exposure.
- (3) after five years' exposure total calcium remain unchanged in the central core of the oil ash reef block; and
- (4) biological cover on the reef blocks tested had no significant effect on the flux of calcium from the oil ash reef blocks.

We suggest that future studies dealing with composition of reef blocks should examine the mineralogy of the ring areas to identify non-leachable and leachable forms of calcium to identify the process by which the leachable fraction increases as a result of long term exposure.

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