

The physical and chemical performance of artificial reef blocks made using quarry by-products

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The cost of construction materials is a major factor determining the economic viability of artificial reefs. The use of by-products is one method of reducing costs, but often, to comply with licensing conditions, chemical and physical stability have to be demonstrated before such materials may be employed. Granite quarrying produces a range of low-value by-products, including an aqueous granite powder suspension. When mixed with other by-products and consolidated using 5% (w/w) cement and 5% (w/w) coal fly-ash, this substance was used to produce concrete blocks with a compressive strength of approximately 14 N mm^{-2} after a standard 90-day curing period. The blocks exceeded the strength requirement of commercial building blocks (British Standard 6073) by five times, were cheaper to produce compared with standard construction-grade blocks, and permitted a range of design options to be considered through the inclusion of voids. The chemical stability of the proposed concrete and base granite material was tested, under conditions designed to maximize metal flux, and showed significant but very low leaching of iron, strontium, barium, rubidium, manganese, and uranium. Metal leaching was not necessarily in proportion to the metal concentration in the base material. Quarry by-products can be used in the manufacture of blocks that are physically robust and environmentally safe with a concomitant reduction in production costs.

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Introduction

Artificial reefs may be used for a variety of purposes, including coastal defence, fisheries protection through fishing effort exclusion, and environmental rehabilitation, and as a basis for fisheries enhancement (Jensen *et al.*, 2001). However, there are few published examples where artificial reefs have been used in conjunction with stock enhancement and proved to be financially viable (abalone representing a possible exception; Masuda and Tsukamoto, 1998). Where legislation permits, reefs made of decommissioned oil platforms or fishing vessels may offer a financially attractive solution to a disposal problem (Baine, 1995). In the case of coastal protection, considerable construction costs can be justified by the prevention of coastal erosion and/or flooding (Hamer *et al.*, 1998). However, in the case of aquaculture, and

where second-use materials are not available, construction costs have to be justified by benefits (Whitmarsh, 1997). Commercial potential is increased by minimizing construction costs through cheap material utilization and by scaling up production. Whitmarsh *et al.* (1995) predicted that in Northern Europe the minimum size of artificial reefs made from concrete blocks and/or quarried rock required for commercial lobster production is likely to be in the order of 5000 tonnes. Most European reef programmes are on a much smaller scale, and while such programmes have yielded important data on reef block performance (Hockley and Vandersloot, 1991; Sampaolo and Relini, 1994; Collins and Jensen, 1995; Leung *et al.*, 1997), the extrapolation of data from small- to commercial-scale reefs may be compromised by unforeseen scale effects relating to both performance and impacts. The construction of a 5000-tonne artificial

Table 1. Block constituents (all in kg m^{-3}) and subsequent mean strength development for six block design mixes (WPFC: washing plant filter cake; W/C: water:cement ratio; R^2 : proportion of total error explained by the linear regression of strength on time; C_o : regression coefficient; strength in N mm^{-2} after 90 days curing).

Mix	Dust	WPFC	Cement	Fly-ash	W/C ratio	R^2	C_o	Strength
1	80	Nil	4	16	0.49	0.99	0.17	16.7
2	79	Nil	4	17	0.35	0.89	0.21	22.0
4	37	48	5	10	1.70	0.95	0.09	10.3
5	90	Nil	5	5	0.78	0.97	0.15	20.9
7	92	Nil	4	4	0.86	0.99	0.14	17.0
8	68	22	5	5	0.97	0.97	0.15	16.8

reef, using commercially available concrete blocks, would incur considerable costs and be unlikely to demonstrate commercial viability. Obviously, complex and even more expensive non-standard shapes as used in some experimental reefs would only be justified on the basis of predicted increases in the rate of return. Little research has been conducted into the mass production of good-quality, low-cost construction materials that satisfy European legislative requirements for marine deployment.

Foster Yeoman Ltd operates the Glensanda super-quarry on the Morvern Peninsula, Highland Region, Scotland, UK. To reduce visual impact, aggregates are transported from the quarry face to secondary processing facilities underground via a 300-m deep vertical shaft and a 1.2-km horizontal conveyor belt. One disadvantage of this method of transport is that the generation of scalpings (material passing a 40-mm sieve) increases from approximately 20% to 42% of total production. Following further processing, scalpings yield valuable sands and gravels with two products of negligible value remaining: granite dust (material passing a 4-mm sieve which has limited value) and washing plant filter-cake (dust washed off the aggregates). Artificial reefs were identified as having considerable potential on the west coast of Scotland (Wilding and Sayer, 1996), provided cost-effective construction materials could be locally sourced. Research was initiated into how Glensanda quarry by-products could be utilized in the production of suitable concrete blocks. The following factors were considered: (1) the costs of several low-value aggregate by-products available at Glensanda; (2) the relative costs (including transport) of cement and fly-ash; (3) the relatively high concentrations of heavy metals present in fly-ash and the requirement to demonstrate chemical integrity; (4) the requirement for extensive covered storage areas (to allow extended curing times); and (5) the compatibility of a range of block mixes with local block producing plants.

We investigate the potential for low-value quarry by-products in the development of environmentally safe,

robust, low-cost concrete blocks for use in artificial reef construction.

Methods

Concrete block manufacture

Concrete is a mixture of aggregate (generally crushed stone mixed with sand), one or more pozzolans (generally cement that is frequently pre-mixed with fly-ash) and water. The ratios of the various components and any admixtures used determine strength development and final strength of the concrete (Hughes and Amice, 1968). Test blocks were produced using ordinary Portland Cement (42.5 Blue Circle) and unprocessed, "run of station" fly-ash from Longannet Power Station (Clackmannanshire, Scotland), which were mixed with the other ingredients using a self-loading concrete mixer (Ultranz) providing highly accurate control over component quantities entering the mix. The compressive strengths of a range of mixes (Table 1) were tested by placing 10 cm^3 test blocks (in accordance with British Standard 1881 after curing for 7, 14, 28, or 90 days) in a pneumatic vice that gradually increased the force applied until the block cracked. At day 7 (with the exception of mix 5) and day 28, two blocks of each mix were tested; otherwise one block was tested. To ensure that the blocks would withstand onshore handling and deployment, a target strength of 10 N mm^{-2} was considered necessary.

Metal flux measurements

The metal flux protocol was designed to maximize leaching of trace metals. The material was ground to coarse powder, maintained at 16°C approximating the maximum expected in north temperate areas, and continually agitated without changing the water. Thus, the protocol represented the most extreme case of instantaneous catastrophic reef block disintegration.

Preliminary strength results and an appraisal of production costs indicated that block mix 8 (5% w/w fly-ash; Table 1) offered the optimum in terms of cost and strength gain. Therefore, metal flux analysis was conducted only on this mix. In addition, samples of granite scalplings were obtained from Glensanda Quarry by random sampling of the production pile and treated in the same way as the block samples.

Prior to use, all non-disposable glass and plastic wear was soaked in 1% hydrochloric acid (Fisher, Primar) for 2–3 days prior to use (to remove contaminating trace metals (Kammin *et al.*, 1995). All acid solutions were made up using high-performance liquid chromatography standard distilled water (Maxima, Elga). Block samples were obtained by knocking the corners off test blocks using a rounded acid-washed granite boulder. These pieces were placed inside a heavy-grade plastic bag and crushed into coarse fragments using the same boulder. Granite scalplings were treated similarly. All samples were dried at 80°C, in separate dishes, for 10–12 h. For each sample, the mixture of particle sizes was separated using nylon sieves (CISA, Cedaceria Industrial, Italy). Subsamples of the 500–1000 µm fraction (40 g each) of both concrete and granite were transferred to 1000 ml flasks and the remainder kept for total metal analysis. Artificial sea water (DeStefano *et al.*, 1998) was added (600 ml in each flask) and the suspension maintained on a cooled orbital shaker (Gallenkamp) at 16°C, set to 100 revolutions per minute and shaded from light. Polymer wool (Interpret, Surrey, England) was used to bung the flasks. The controls consisted of 600 ml artificial sea water. A total of 12 flasks were prepared consisting of four block samples, four granite scalplings, and four controls.

At 1, 2, 4, 8, 17, 32, 50, and 104 days after the initiation of the experiment, 6 ml of the suspension was removed from each flask using a syringe (Discardit, Becton Dickinson) attached to a small length (10 cm) of acid-cleaned plastic tubing. The suspension was forced through a 5.0 µm filter followed by a 0.2 µm filter (both Sartorius, Minisart), acidified using 600 µl of concentrated nitric acid (Fisher, Primar). All samples were stored at 4°C in plastic vials. After each sample was taken, syringe, tube, and filters were discarded and 6 ml of the previously prepared artificial sea water was added, using a new syringe, to the experimental flasks (thus maintaining the suspension volume).

Total metal concentration

Approximately 20 g of each of the 500–1000 µm sieved granite and concrete samples was comminuted using an agate ball and mill grinder (Christison Scientific, Pulverisette 5). Aliquots of powder were transferred to Teflon boiling tubes and the mass determined. Concentrated hydrochloric, nitric, and hydrofluoric acid

(3, 5, and 3 ml, respectively; all Fisher, Primar; Wu *et al.*, 1996) were added. Total dissolution was accomplished by microwave high-pressure closed digestion in a microwave accelerated reaction system (MARS 5, CEM Corp.) at maximum power (1200 W). A process blank (acid mix with no sediment) was included to verify no crossover contamination and satisfactory digestion. The resultant solution was then evaporated to dryness (120°C, 12 h), re-dissolved in 2% nitric acid, made up to 100 ml using 2% nitric acid and transferred to plastic vials. The solution was then stored at 4°C until analysis.

Induced coupled plasma mass spectrometry (ICP-MS)

Metal concentrations in the digested granite and concrete and the artificial sea water (leachates) were determined according to Bettinelli *et al.* (1998) using fully quantitative ICP-MS (PlasmaQuad PQ3 Turbo-plus, VG Elemental, Cheshire, England). The standard instrument conditions used were:

Lens	Volts	Gas	Flows (l min ⁻¹)	Misc. settings
Lens 4	-90.0	Cool gas	12.50	Pole Bias 7.0V
Lens 3	5.0	Aux gas	0.60	Radio freq. Power 1350W
Lens 2	0.5	Neb gas	0.78	Peri speed 53%
Lens 1	0.0			
Collector	-4.0			
Extraction	-320.0			

Sample aliquots (0.3 ml) were added to 9.6 ml 2% nitric acid and 0.1 ml of a 1000 ppb bismuth/indium internal standard (SPEX, CertiPrep). Calibration curves for 27 metals and metalloids were produced using 0, 1, 5, 10, 15, 30, 50, and 75 ppb standards (multi-elemental solutions 1, 2A, 3, and 4; Claritas ppt, SPEX CertiPrep, Inc).

Metal concentrations in blanks consisting of 2% nitric acid and the internal standard were determined and subtracted from the results of the concrete, granite, and control samples (blank subtracted). Where adsorption of metals had occurred, negative concentration values were generated (where the sample mean was lower than the blank). The replacement of the 6-ml aliquots, taken at each sampling date, with artificial sea water resulted in a minor dilution of the remaining suspension. The results from the ICP-MS analyses were corrected to allow for this dilution.

Statistical analyses

Development of strength over time in the concrete blocks was examined using regression analysis. Unplanned comparisons between the estimated mean

strengths (at 90 days) of different block mixes were made by analysis of covariance (least-squares means; [Littel et al., 1991](#)) with a Bonferroni correction for type I error ([Sokal and Rohlf, 1995](#)).

Elemental concentration data were heteroscedastic (even after \log_{10} transformation). In the case of the digests where there were two treatments (granite and concrete), the concentrations were compared using the Kruskal–Wallis test ([Sokal and Rohlf, 1995](#)). In the case of the metal flux study, the comparison of all three means (control, granite, and concrete) after 104 days was achieved using a Satterthwaite correction for degrees of freedom where the correction is proportional to the heteroscedasticity of the data ([Wesfall et al., 1999](#)). While multiple comparisons between each day pair for each element could have been conducted, the family-wise error rate for this number of comparisons would have been considerable and therefore the trends in metal flux over time (leaching kinetics) are shown graphically for treatments that show significant differences in leaching after 104 days.

The concentrations of 27 elements were measured both in the digest experiments and in the leaching experiments. The elements reported here were selected on the basis of environmental concern, relevance to previous literature and concentration. Those trace metals that showed significant differences in concentration between concrete and granite are included in the metal flux analysis (even where there is no significant treatment affect) to allow a comparison between leaching rate and concentration in the base material.

All statistical analyses were conducted using SAS[®] software (SAS Institute Inc., Carry, NC, USA).

Results

All concrete mixes showed a significant increase in strength over time (linear regression, $p > 0.001$, $n = 6$, except mix number 5, where $n = 5$). The mixes were divided into three groups on the basis of increasing final strength ([Table 1](#)): (1) mix 4; (2) mixes 1, 7, and 8; and (3) mixes 2 and 5. The reduction in the water to cement ratio (mixes 1 and 2) resulted in a significant increase in strength development ($p < 0.001$, $n = 6$). The inclusion of 25% washing plant filter-cake in mix 8 did not have a significant effect when compared with mix 7. However, strength development in mix 4, containing 56% washing plant filter cake, was significantly less compared to mix 8 ($p < 0.02$, $n = 6$). A reduction of approximately 2% in the total pozzolanic content (fly-ash and cement; mixes 5 and 7) also reduced strength development significantly ($p < 0.05$, $n = 5$ and 6, respectively).

The major trace metals (nominally above 10 ppm) in both the granite and concrete samples were (in descending order) iron, barium, strontium, manganese,

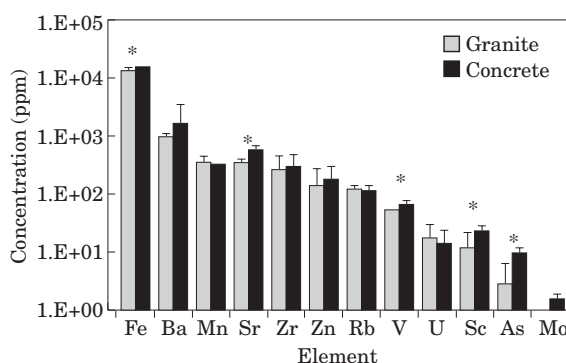


Figure 1. Mean concentration and upper 95% confidence limits ($n = 4$) of major trace elements found in granite (grey bars) and concrete of mix 8 (black bars). Significant differences (Kruskal–Wallis test; $p < 0.05$) are indicated by an asterisk.

zirconium, zinc, rubidium, vanadium, scandium, and uranium ([Figure 1](#)). Granite and concrete also contained measurable (but low) concentrations of arsenic (2.67 and 9.25 ppm, respectively), while concrete contained molybdenum in very low concentrations (1.45 ppm). Concrete contained significantly more iron, strontium, scandium, vanadium, and arsenic compared with granite ($p < 0.05$, $n = 4$).

Barium, iron, manganese, molybdenum, rubidium, strontium, and uranium leached in significant amounts from both the concrete and granite treatments when compared with the controls ([Figure 2](#)). Conversely cadmium, lead, and zinc concentrations were lower or equivalent in both the treatments compared with the control ([Table 2](#)). In addition, the granite treatment also resulted in lower concentrations of arsenic and vanadium compared with the control. Significant differences in leaching of iron, manganese, molybdenum, rubidium, strontium, and uranium between the granite and concrete treatments were also shown ([Figure 2](#), [Table 2](#)).

The leaching kinetics of trace metals differed among elements and among treatments (control, granite, and concrete). For example, leaching of barium reached a maximum concentration of between 2 and 4 ppb immediately after the granite or concrete was immersed in sea water ([Figure 2a](#)), while the concentration of iron leaching from the concrete increased until day 50 and then declined ([Figure 2b](#)). Granite did not leach any iron (no significant difference between granite and the control at day 104; [Table 2](#)) even though it was present in high concentrations ($> 10\,000$ ppm) in the base material. Leaching of manganese from granite showed a clear increasing trend over time and had not reached an equilibrium concentration after 104 days ([Figure 2c](#)). Manganese leached significantly more from granite compared with concrete ([Table 2](#)) yet is present in similar concentrations in the respective base materials ([Figure 1](#)). Concentrations of rubidium, strontium, and

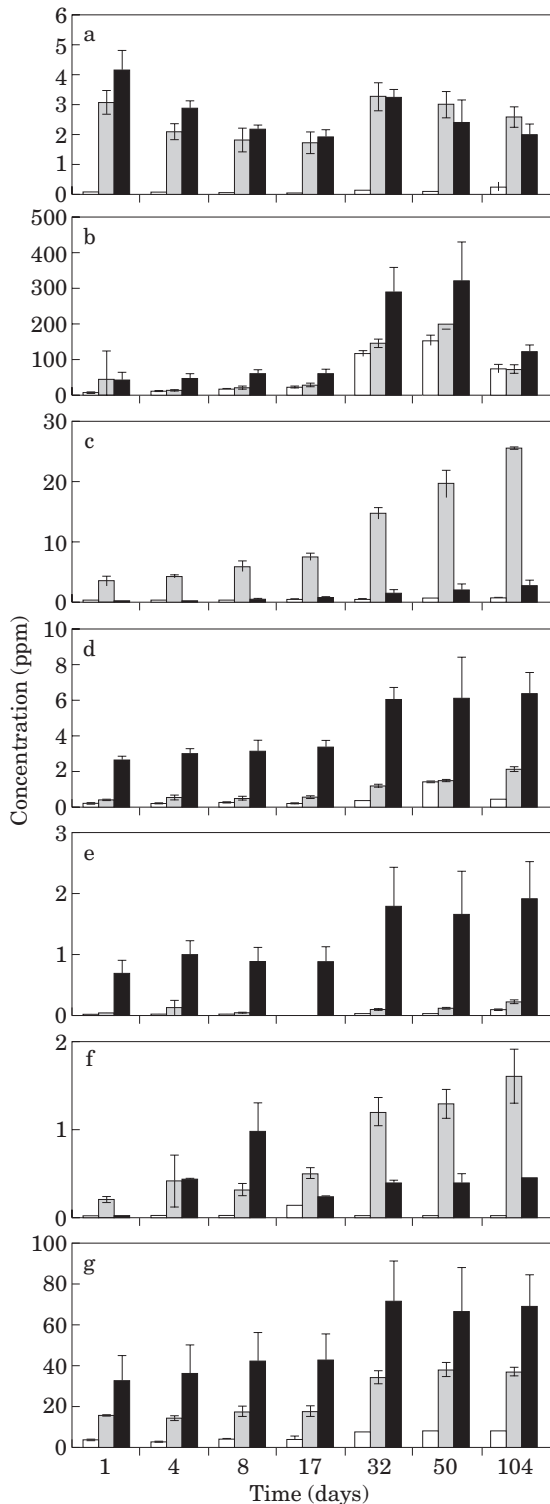


Figure 2. Concentration and 95% confidence limits ($n=4$) of seven elements in leachates from granite (grey bars), concrete (black bars), and controls (open bars) over time: a. Barium; b. Iron; c. Manganese; d. Rubidium; e. Molybdenum; f. Strontium; g. Uranium.

molybdenum leachates from concrete reached equilibrium after 32 days at approximately 6, 70, and 1.75 ppb, respectively (Figure 2d, g, e respectively). After 104 days, uranium leachate concentrations from concrete had stabilized, but from granite they had continued to increase (Figure 2f).

Discussion

Our results indicate that granitic by-products are ideal materials for producing blocks that achieve high strength gain with relatively low amounts of cement and fly-ash. The utilization of these by-products and the use of standard concrete producing plant has resulted in the production of a block that is between 25% and 40% cheaper than similar commercially available blocks.

The development of strength in concrete has been the subject of considerable research by the marine construction industry (Mackechnie and Alexander, 1997). The inclusion of up to 10% "dust" (equivalent to washing plant filter-cake) has been reported to increase strength and decrease slump in some mixes, especially in those with relatively low water to cement ratios (Celik and Marar, 1995; Hughes and Amice, 1968). The inclusion of 22% washing plant filter-cake (mix 8) did not have an affect on strength compared with a similar mix containing no washing plant filter cake (mix 7), while the inclusion of a higher proportion of fine material (mix 4) did significantly reduce strength gain over time. However, the reduction observed in mix 4 may be explained by the concomitant increase in the water to cement ratio that is required to maintain workability and ensure good dispersion of ingredients in a mixture containing a high proportion of washing plant filter cake. Poor dispersal may result in the development of planes of weakness that cause block breakage and may have contributed to the relatively low ($<2 \text{ N mm}^{-2}$) pre-deployment block strength reported for other artificial reef blocks (Collins *et al.*, 1992). Mix 8 resulted in block strength development similar to concrete blocks used in a 220 tonnes artificial reef based in Hong Kong ($16\text{--}38 \text{ N mm}^{-2}$, ca. 7% fly-ash; Leung *et al.*, 1997) and exceeded our pre-set objective of 10 N mm^{-2} set after a 90-day curing period. This mix also contained a relatively high proportion of fine material with a concomitant reduction in production costs, and therefore satisfied both strength and cost criteria.

Concrete (mix 8) and granite ballast are similar in chemical composition and the addition of the pozzolans (5% cement and 5% fly-ash) only resulted in significant increases in the concentrations of iron, strontium, scandium, vanadium, and arsenic. Of these metals, iron and strontium showed significantly higher leaching from concrete when compared with granite. This conflicts with the findings of Sampaolo and Relini (1994), who recorded no trace metal leaching from concrete blocks

Table 2. Metal element (E) leachate concentrations (m: mean; s.d.: standard deviation; n=4) from concrete (C), granite (G), and control (co) treatments after 104 days constant agitation and pairwise comparisons of means (d.f.: Satherwaite approximation of degrees of freedom; *p<0.05; **p<0.01, ***p<0.001).

E	C		G		co		C vs. co		C vs. G		G vs. co	
	m	s.d.	m	s.d.	m	s.d.	d.f.	p	d.f.	p	d.f.	p
As	1.27	0.14	1.10	0.05	1.26	0.08	4.8	—	3.7	—	4.9	*
Ba	2.02	0.28	2.59	0.30	0.23	0.14	4.5	***	5.9	—	4.2	***
Cd	-0.055	0.087	0.073	0.011	0.117	0.019	3.3	*	3.1	—	5.0	*
Cr	0.38	0.67	-0.14	0.20	0.10	0.09	3.1	—	3.6	—	4.0	—
Cu	0.15	0.07	0.16	0.04	0.20	0.06	5.9	—	5.1	—	5.5	—
Fe	115.8	16.9	70.4	9.6	72.1	7.8	4.2	**	4.7	**	5.8	—
Mn	2.49	0.80	25.24	0.22	0.45	0.02	3.0	*	3.4	***	3.1	***
Mo	1.89	0.55	0.23	0.03	0.11	0.01	3.0	**	3.0	*	4.6	**
Pb	0.005	0.036	0.029	0.019	0.189	0.092	3.9	*	4.6	—	3.3	—
Rb	6.32	0.99	2.04	0.09	0.36	0.01	3.0	**	3.1	**	3.2	***
Sr	67.9	13.1	36.3	2.0	7.4	0.2	3.0	**	3.1	*	3.1	***
U	0.42	0.02	1.59	0.25	0.01	0.01	4.8	***	3.0	**	3.0	**
V	2.02	0.28	1.76	0.05	1.90	0.06	3.2	—	3.2	—	6.0	*
Zn	0.21	0.37	0.30	0.20	0.97	0.06	3.2	*	4.6	—	3.5	**

(some containing >70% coal ash), but this may be explained by the heterogeneous nature of the blocks and variations in the circulating sea water. Leaching of molybdenum from fly-ash has been previously documented (Duchesne and Reardon, 1999) and our results concur with those findings as there was significantly higher leaching of molybdenum from concrete when compared with granite. While concrete contained significantly more arsenic and vanadium compared with granite, these elements did not leach more from the concrete treatment compared to the granite. The leaching kinetics of trace metals such as arsenic, molybdenum, and vanadium thus appear complex. This concurs with Hower *et al.* (1996), who reported that arsenic concentrations in the base material and subsequent levels of leaching are not directly related. A more important factor may be that trace metals such as arsenic, molybdenum, and vanadium are bound through chemical reactions occurring during the hardening of concrete (Lecuyer *et al.*, 1996). This binding process may also account for the lower leaching of uranium from concrete compared with granite even though uranium was present in approximately equal concentrations in both base materials. Cadmium was reported to be lost (or remobilized) from the concrete blocks making up the Poole Bay artificial reef (Jensen *et al.*, 1994). In contrast, our results indicate that, while cadmium was present at very low (and similar) concentrations in both base materials, it was absorbed in both treatments (granite and concrete). The attraction of metals to particulates is well documented. Fly-ash itself has been used to remove copper and lead from waste water (Gupta and Torres, 1998), while Hall *et al.* (1996) reported that lead is attracted to the particulate phase. This could account for the lower concentration of lead in the treatments, but not zinc, as

it is found preferentially in the dissolved phase (Hall *et al.*, 1996).

Marine sediments are likely to be enriched in trace metals as a consequence of land-based dissolution, transport to the oceans, and subsequent precipitation, particularly in nearshore sediments (Chester, 1990; Shimmiel, 1993). Any assessment of chemical impact of artificial reefs can only be based on the background trace metal concentrations in the receiving environment. On the west coast of Scotland, Shimmiel (1993) observed background solid phase (sediment) concentrations of iron, manganese, zirconium, vanadium, zinc, chrome, and scandium that were higher than those present in the concrete mix proposed here. In addition, the pore water concentrations of barium, iron, manganese, molybdenum, rubidium, strontium, and uranium naturally occurring in sediments from Scottish west coast sea lochs as reported by Shimmiel (1993) exceeded those that leached from the finely-ground concrete in our experiment after 104 days of continuous agitation at elevated temperatures. The leaching of these elements in the field would therefore require the mobilization of the respective elements against their concentration gradients. Our analysis of metal fluxes was designed to represent the maximum potential for leaching. For the estimated metal flux levels to be replicated in the field, an entire reef would have to instantaneously disintegrate into a limited volume of sea water. The extremely low levels of leaching observed combined with relatively high and variable (both temporally and spatially; Morrisey *et al.*, 1994a, b) background concentrations of trace metals indicates that the chances of being able to detect significant reef-derived trace metals in the environment around the reef is extremely small.

Our study has demonstrated that granite dust and granite washing plant filter-cake can be consolidated using relatively low levels of cement and fly-ash to produce a cost-effective robust concrete block suitable for mass production. The inclusion of 5% (w/w) fly-ash does not result in high levels of leaching and is essential for the production of a physically resilient block that is environmentally safe. As the technology for measuring ever-lower concentrations of trace metals develops, regulations governing reef deployment need to change and should specify allowable concentrations of trace metals that are inevitable components of even the most inert of construction materials.

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