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Article

Depth Profiling (ICP-MS) Study of Toxic Metal Buildup in Concrete Matrices: Potential Environmental Impact

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Abstract: This paper explores the potential of concrete material to accumulate toxic trace elements using ablative laser technology (ICP-MS). Concrete existing in offshore structures submerged in seawater acts as a sink for hazardous metals, which could be gradually released into the ocean creating pollution and anoxic conditions for marine life. Ablative laser technology is a valuable tool for depth profiling concrete to evaluate the distribution of toxic metals and locate internal areas where such metals accumulate. Upon rapid degradation of concrete these "hotspots" could be suddenly released, thus posing a distinct threat to aquatic life. Our work simulated offshore drilling conditions by immersing concrete blocks in seawater and investigating accumulated toxic trace metals (As, Be, Cd, Hg, Os, Pb) in cored samples by laser ablation. The experimental results showed distinct inhomogeneity in metal distribution. The data suggest that conditions within the concrete structure are favorable for random metal accumulation at certain points. The exact mechanism for this behavior is not clear at this stage and has considerable scope for extended research including modeling and remedial studies.

Keywords: concrete; seawater; toxic trace elements; laser ablation; environment; ICP-MS

1. Introduction

Concrete is a combination of gravel, sand, water and cement. It is usually earmarked for use in buildings and other structures. Parts of offshore concrete structures immersed in seawater form an excellent sump for toxic trace elements (such as beryllium, arsenic, cadmium, osmium, lead and mercury) [1]. Some of these toxic elements are present in seawater and also appear in cement at minor and trace levels (Table 1).

Table 1. Average trace element concentration and composition in typical seawater [2,3].

Element	Symbol	Approximate concentration (ppm) in sea water	Average concentration (ppm) in cement
Arsenic	As	1.8×10^{-3}	9
Cadmium	Cd	1.2×10^{-4}	1
Lead	Pb	3.6×10^{-5}	40
Mercury	Hg	2.0×10^{-6}	Not available

Therefore, the chief sources of residing toxic metals in submerged offshore concrete structures are seawater, cement and fine and coarse aggregate components used to make concrete. Constant accumulation of trace toxic elements in underwater concrete can pose a chronic threat to aquatic life. The mobility of such elements from concrete to the hydrosphere is a subject of progressive research, but it is known that this feature resembles the behavior in sediment. Gradual leaching and abrading of concrete by seawater slowly releases these metals, which are subsequently imbibed by marine organisms and plants. However, sudden degradation of submerged concrete could accelerate the release of these toxic metals into the ocean. We found that concrete has the capacity to concentrate toxic trace metals at multiple points in its microstructure. It is not clear at this stage why these toxic elements accumulate at these points, but such accumulation is of concern as rapid corrosion and erosion of immersed concrete could suddenly enrich the sea with these metals. Ablative laser technology has the capability of pinpointing these "hotspots" and revealing valuable information on toxic metal buildup in the internal structure of concrete. Sustainable development entails protection of natural resources by adoption of pre-emptive remedial measures to curb any threat of potential pollution. If we know beforehand the level of risk involved, the latent hazard can be conveniently assessed and averted. It is thus necessary to be able to predict the changes in natural systems resulting from such pollution. Our work therefore, represented a study to evaluate potential environmental effects by saturating concrete blocks in seawater to mimic offshore drilling conditions and assessing spasmodic accumulation of toxic trace metals (Be, As, Cd, Os, Pb, Hg) in cored samples using laser ablation ICP-MS (inductively coupled plasma-mass spectrometry).

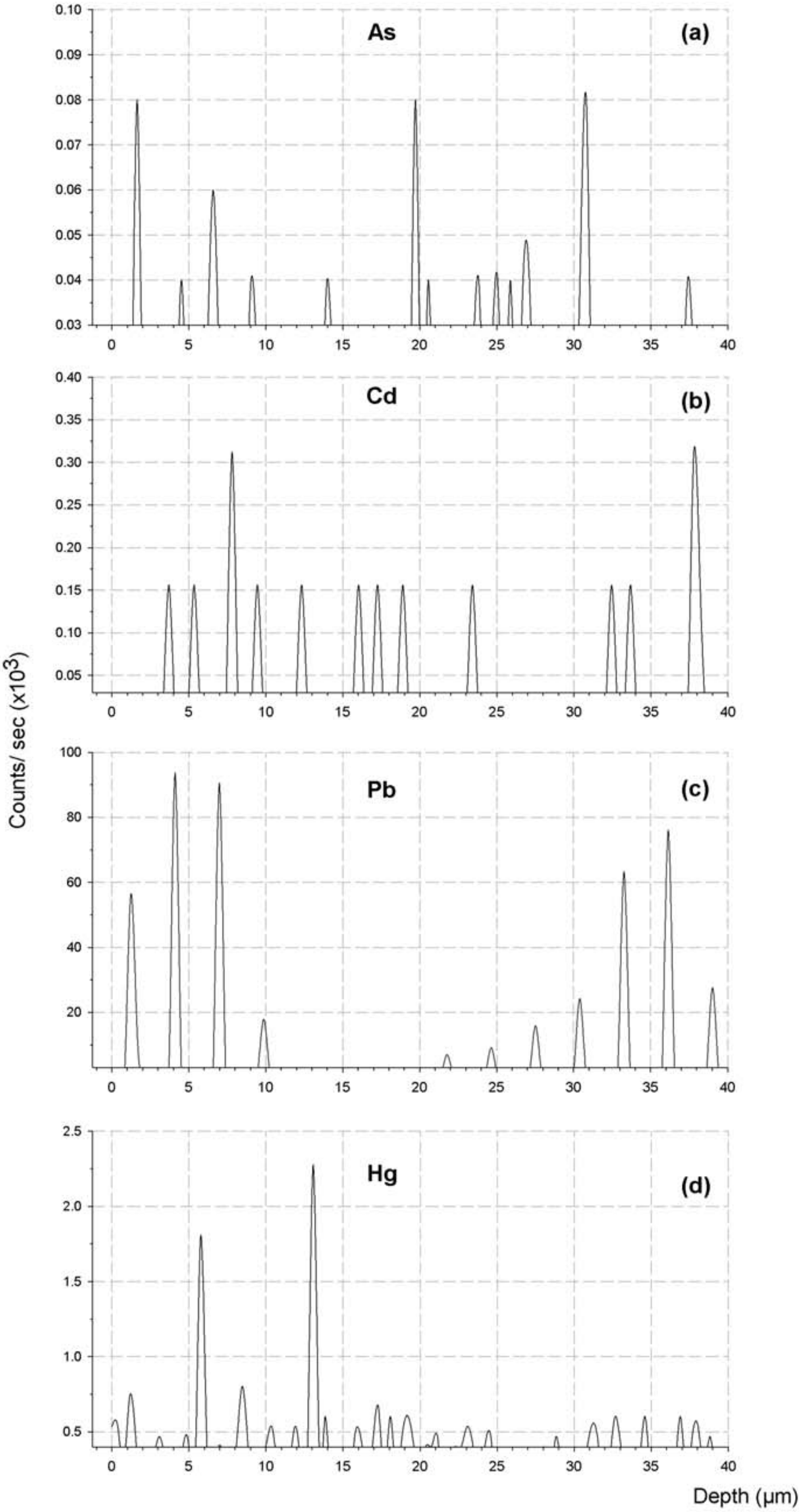
2. Results and Discussion

2.1. Trace Toxic Elemental Buildup in Concrete Matrices

The novelty of our work is attributed to the observation of toxic metal buildup at random points in the concrete matrix. This particular phenomenon of sporadic metal nucleation has not been previously documented in the area of cement and concrete research. Depth-profiling is an ultra-sensitive tool that has the capability of "drilling" through cored samples of concrete and obtaining relevant information on the distribution of toxic deposits. The laser itself is linked to a high performance ICP-MS instrument. The technique is semi-quantitative and capable of high resolution detection over a wide range of elemental levels. X-ray methods are useful, but lack the ability to control depth penetration. Nuclear particle irradiation is equally useful, but such techniques require nuclear accelerators, and tend to be limited to only a few microns below the surface. The competence, therefore, of the laser approach to delve deep below the surface of a sample is attractive for homogeneity studies of toxic elements in bulk materials. Of significance is that this investigation was conducted in the absence of reference standards, for the obvious reason that it was not possible to obtain suitable standards to match the highly inhomogeneous matrix of concrete.

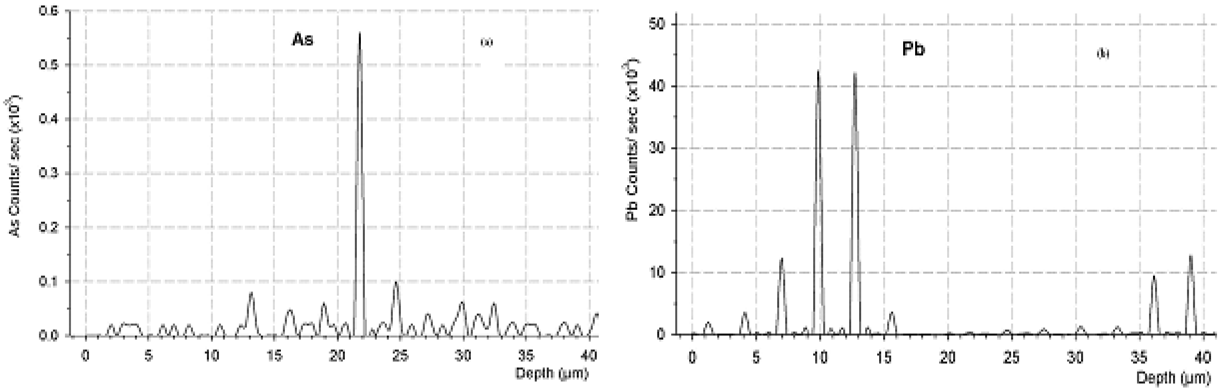
The results are therefore relative and compared in terms of intensities (counts/sec). Figure 1 represents typical depth profiling spectra of the selected elements (As, Cd, Pb, and Hg) from an unproofed sample. These spectra were accumulated from a single laser shot and each element was concomitantly recorded. Clearly, peaks are observed at random points in the bulk matrix. The mechanism of accumulation is not clear at this stage and warrants further investigation. The shape of the pores inside the matrix, the magnitude of the concrete sample porosity and its permeability to seawater are likely to be major factors in shaping mechanistic theories. Of interest are the intervals between peaks. We found that the gaps between peaks represent the major materials of concrete such as minerals and compounds containing sodium, magnesium, calcium (and silicon). The data suggest that compounds (or crystals) bearing toxic trace metals tend to ensconce themselves at "grain boundaries" or possibly contribute to epitaxial growth by accumulating on the surfaces of such particles where the physical and chemical conditions within the matrix are favorable for such buildup. It is difficult to say at this juncture where the pores are located without recording spectra of the complete range of major, minor and trace elements present in concrete. A point to bear in mind is that concrete is highly inhomogeneous. As previously stated, it is a *pot-pourri* of gravel, grit, sand, clinker, cement and water. The transport properties of the trace elements of interest would naturally be a function of the inhomogeneity of the bulk material. And the pattern of trace element buildup would therefore, vary considerably from one concrete block to another. The toxic elements considered here originated both from the mixture and the introduction of seawater. Saturation in seawater tends to create a more uneven and elevated distribution of these elements in comparison with the controls.

Figure 1. Depth profiling spectra of As, Cd, Hg and Pb.



We further observed that in some cases isolated peaks occurred as shown in Figure 2. Here again, the mechanism of these "hotspots" defy explanation and could possibly be attributed to encapsulation of these metals into the crystal lattices of the components of the bulk material. If this explanation is genuine, then intrusion of these metals into crystal lattices could provide clues to the stability of the bulk material and be of interest in modeling studies associated with concrete matrices. Of concern is the effect on the environment when these stored toxic trace elements are suddenly released to the hydrosphere through rapid disintegration of submerged concrete structures. We are interested in the threat posed to the ecosystem and the potential environmental impact.

Figure 2. Depth-profiling spectra of As and Pb showing "hotspots".

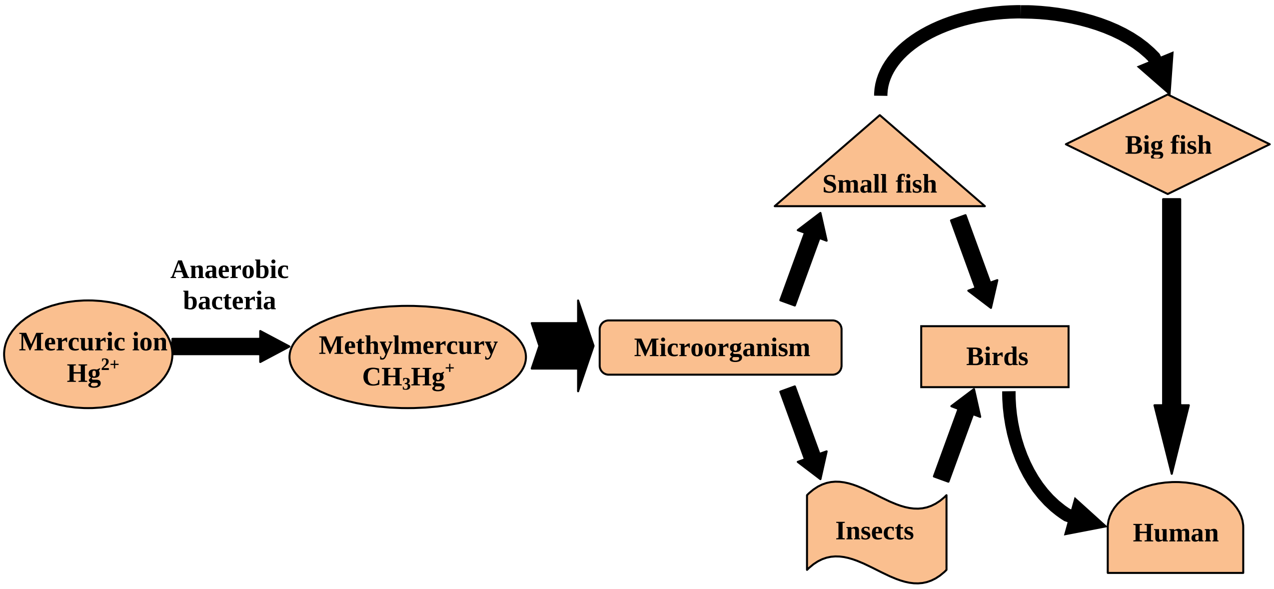


2.2. Potential Environmental Impact

The study is a definite source of interest because it can be linked to sustainable living. Environmental sustainability essentially seeks to improve human welfare by protecting resources used for human needs [4]. For example, concrete can undergo rapid degradation from mechanical stress, aggregate expansion, physical and chemical damage. Such damage could result in accelerated leaching of toxic trace metals creating increased pollution and anoxic conditions in the oceans. Hence, the general impact on the environment is a cause for concern, and our work could make a useful contribution to ongoing sustainable development. Essentially, the overall potential impact is primarily the deleterious effect on aquatic life and the indirect effect on public health via the food chain. It is known that dissolved toxic metals in seawater are linked to anoxic conditions (depletion of oxygen), which could lead to the mortality of marine organisms [5]. Studies of anoxia in oceans due to toxic metal enrichment are receiving worldwide attention. Protection of natural resources is part of a global effort and all sources of pollution have become the focus of intense environmental attention. It is therefore, vital to consider preemptive measures to minimize such pollution.

The resultant impact of elevated toxic metal bioaccumulation in the food chain is a secondary potential hazard and deserves further investigation [6]. Excess bioaccumulation of common trace toxic metals in the food chain could ultimately lead to serious disorders [7]. When released to ecosystems, these metals disrupt the existing biological balance [7]. The biochemical effects of such pollutants cannot be understated especially as new clinical evidence on their risks is constantly emerging. A brief discussion of the common biological effects of these metals and some recent information on their hazards to mankind is presented. Mercury is known to accumulate in aquatic food chains and fish [8,9]. It was originally thought that elemental mercury is relatively non-toxic, but it has been recently discovered that in addition to organomercurial compounds, small amounts of non-oxidized mercury can affect the central nervous system of humans [10-12]. The Minamata disaster is a prime example of mercury poisoning through contaminated fish. Methylmercury (CH_3Hg) is considered the most toxic form of mercury, and people are exposed to it by eating contaminated fish. It is generally produced by native bacteria primarily in rich marine environments that transform mercury into methylmercury [13], which enters the food chain through plankton (see Figure 3).

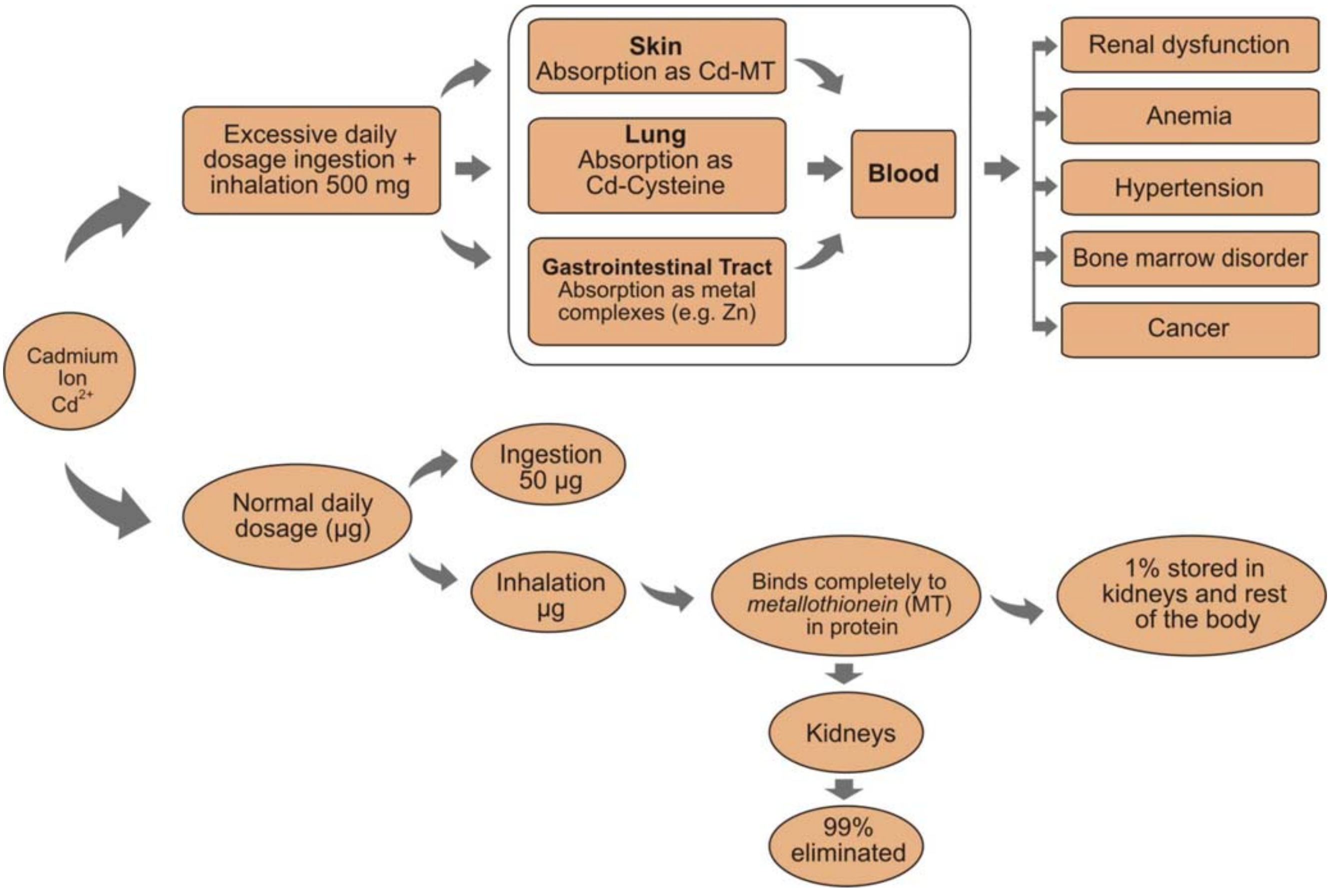
Figure 3. Propagation of mercury in food chain.



Cadmium on the other hand accumulates largely in shellfish and scallops [14]. This could result in significant human exposure to cadmium through the ingestion of contaminated foodstuffs. When excessive amounts of Cd^{2+} are ingested, it replaces Zn^{2+} at key enzymatic sites causing metabolic disorders [15-17]. This effect tends to be irreversible, and recent research suggests that the risk exists at lower levels of exposure than previously thought [11] as shown in Figure 4.

Lead poisoning through the food chain is well known. Lead has been the intense focus of environmental health research for decades. Depending on the dose, lead poisoning in children and adults can cause a wide spectrum of health problems, ranging from convulsions to coma and renal failure. Research in lead poisoning is ongoing and recently, a John Hopkin's report provided new information on the neurotoxicity of lead and its effect on brain receptors [18]. Uptake of arsenic in fish and marine life is also well documented. In a recent discovery [2], relatively low levels of arsenic were found to inhibit activation receptors that affect many genes that suppress cancer and regulate blood sugar and, at higher levels, is known to trigger diabetes as well as cancer [11].

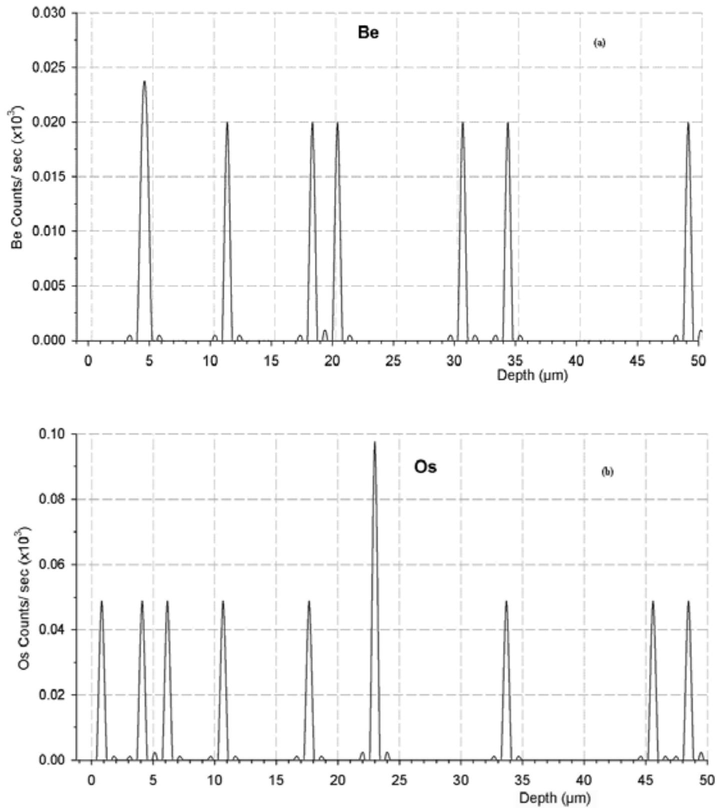
Figure 4. Metabolism of cadmium.



2.3. Detection of Beryllium and Osmium in Concrete

The occurrence of beryllium (Be) and osmium (Os) in concrete matrices is not widely known and our technique was adequately sensitive to detect them. Figure 5 presents spectra showing the accumulation of Be and Os at exclusive spots in concrete matrices. This is a novel discovery and here again the mechanisms surrounding the sporadic, intermittent appearances of these metals in the microstructure of concrete is unclear, and a more detailed study is necessary for further elucidation on this behavior. Clearly, constant leaching and corrosion of offshore concrete structures could discharge elevated amounts of Be and Os in seawater to be imbibed by marine organisms. It is known that plankton bio-accumulates Be [19] and since plankton is the food source of other marine organisms there is the risk of Be entering the food chain. Osmium on the other hand is linked to phytoplankton, which in turn is consumed by aquatic organisms [20]. The clinical effects and toxicity of Be and Os are cloudy and are currently the subject of rigorous medical research. Exact clinical evidence of the detrimental impact of these toxic metals on humans is yet to be forthcoming.

Figure 5. Depth profiling spectra of beryllium (top panel) and osmium (bottom).



2.4. Suggested Remedial Measures

Clearly, implementation of appropriate pre-emptive remedial measures to restrict any such hazard to the hydrosphere is necessary. It is important to bear in mind that natural conservation is attracting universal interest and potential contamination of this nature can pose a significant threat. These particular problems can be curbed by searching for solutions to limit pollution in the ocean. To facilitate the task of remediation, it would be useful to monitor toxic metal levels in seawater at different depths in areas surrounding offshore oil rigs to obtain some insight of the function of metal toxicity levels with depth. This could provide information on the origin of the toxicity and some method could be devised to inhibit it. An optional remediation procedure would be to ensure that concrete coatings are relatively impervious to seawater. This will limit the threat from potential pollution through physical and chemical damage of submerged concrete. Alternatively, chemical additives could be added to concrete to create a more uniform distribution of toxic trace metals by improving their transport properties through the bulk material. The use of finely crushed concrete with consummate mixing for special application to offshore oil rigs could also contribute to homogeneous distribution of trace toxic metals in the bulk material. These exercises could help control any potential threat to the environment and ensure sustainable living.

3. Materials and Methods

3.1. Sample Preparation/Sample Handling

The cement material (Portland cement, Type 1) originated from the Ras Al Khaimah cement plant in the United Arab Emirates (UAE). The concrete mix was designed using fine and coarse aggregates from the UAE. The maximum aggregate size was 10 mm. The concrete mix preparation was based on the British Method Design (BRE 106). Two lots of concrete mixes were prepared to meet minimum target strengths of 20 N/mm^2 and 40 N/mm^2 (labeled Grade 20 and Grade 40 respectively). For Grade 20 the water/cement ratio was 0.54:1 and the aggregate/cement ratio was 5.98:1; and for Grade 40 these respective ratios were 0.41:1 and 4.68:1. Slump tests were conducted to ensure the practical workability of the concrete mixtures. Bricks were cast from the two lots of concrete mixture. After casting, the bricks were cured under wet hessian blankets and polyethylene film. Compressive strength tests were performed on three concrete cubes (150 × 150 × 150 mm) from each lot of concrete mix after seven days to establish if the samples had attained the appropriate strengths. For Grade 20, the average measured compressive strength was 37.5 N/mm^2 and for Grade 40 the value was 50.0 N/mm^2 [21].

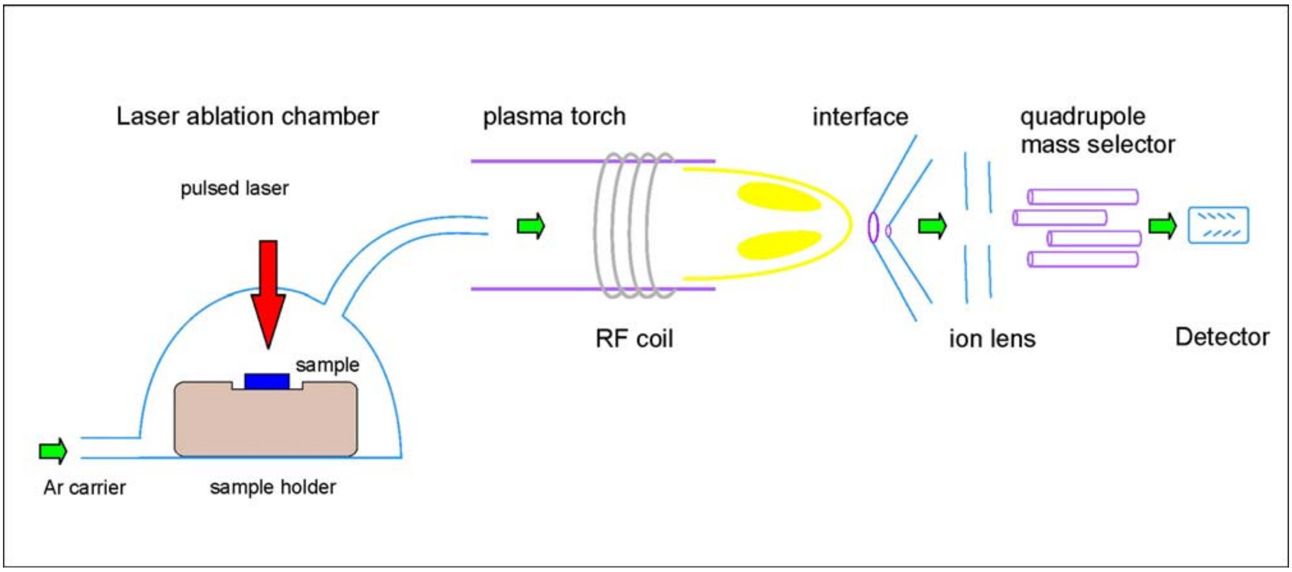
The cured bricks in each lot were further separated into two batches. Solvent free 100% epoxy resin (waterproof, chloride and carbonation resistant coating for protection of concrete) was applied to the bricks in one batch. The coating generally has excellent resistance to chemicals and UV exposure (*i.e.*, suitable for offshore oil rigs) with an expected life span of about ten years. No coating treatment was applied to the bricks in the other batch. The two batches of coated and uncoated bricks in each lot were immersed in a pond of sea water. After several months, all the bricks were removed from the pond and samples were cored (discs of 5 mm diameter by 2 mm thick) from the bulk material using a standard coring tool [Makita TB131, Taiwan]. Laser experiments were conducted on coated and uncoated samples (right and left, Figure 6, respectively).

Figure 6. Proofed (right panel) and unproofed (left) cored discs.

3.2. Instrumentation/Spectral Characteristics

Samples were investigated with a Perkin Elmer SCIEX DRC-e ICP-MS (Connecticut, U.S.) fitted with a New Wave UP-213 laser ablation system (Figure 7). The core-sections were placed in a special sample holder with dimensions 5 cm × 5 cm. Samples were subjected to 213-nm laser irradiation; the level of the beam energy was 60%, with a beam diameter of 100 µm. The laser was programmed to continuously ablate successive depths of 5 µm at each point and "drilled" through the sample to a depth of 50 μm. Depth-profiling spectra were recorded for each measurement. Characteristic intensities originating from the metals of interest were measured; and valid considerations were given to potential interferences and matrix effects. Prior to each run, the instrument underwent appropriate calibration and correction for background. The study was largely semi-quantitative in the absence of standardization, and for the purposes of comparison, all measurements were conducted under identical experimental conditions. Signal intensities were compared with surface metals and those occurring in the bulk of the sample; and appropriate spectra were produced to observe fluctuations in characteristic metal intensity spatially and with penetration depth. Spatial studies can reveal irregularities by measuring the elemental composition at different points on the surface. Depth profiling has the potential of providing information on the homogeneity of distributions below the surface. Thus detailed analysis of different spots on the sample could provide a valuable insight into the elemental distribution.

Figure 7. Schematic diagram of the LA-ICP-MS system.



3.3. Validation of the Technique

Solid standards of matching matrix are generally not available, and the only recourse to validating the analytical performance of the laser technique was to examine an available certified standard, which in our case was a glass bead (NIST, Certificate 613). Replicate measurements (n = 10) for equivalent counting times were conducted at random points, and relative standard deviations of less than 5% were attained indicating that the operational performance of the facility was acceptable.

4. Conclusions

Our study demonstrated that concrete matrices are complex and possess the capacity to store trace toxic metals at particular points in their structures. This phenomenon is relatively novel and deserves further study specifically in the area of concrete and cement research targeted for offshore oil rigs. The potential environmental impact and biochemical implications of the sudden discharge of these metals into seawater were discussed and possible remedial measures were suggested. Of considerable interest was the detection of beryllium and osmium in concrete. This aspect is unexplored and could be the subject of future study. Our work could provide useful information for modeling and simulation studies (linked to concrete) and also has scope for epitaxial research.

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