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# VALORIZATION OF BASIC OXYGEN FURNACE SLAG IN THE MARINE ENVIRONMENT: STUDY OF POTENTIAL ENVIRONMENTAL IMPACTS

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# VALORIZATION OF BASIC OXYGEN FURNACE SLAG IN THE MARINE ENVIRONMENT: STUDY OF POTENTIAL ENVIRONMENTAL IMPACTS

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**ABSTRACT (in English)***: Increasing use and development of coastal areas leads to a growing demand for resources for construction of maritime infrastructures. Finding alternatives to energy-demanding concrete and quarried natural rocks is essential to mitigate overexploitation of natural resources and reduce $CO_2$ emission. This study aims to examine the potential of using a by-product of the iron and steel industry—Basic Oxygen Furnace Slag (BOF-Slag)—as a substitute for commonly-used materials, by evaluating the potential impact of this ready-to-use material as submerged structures in the marine environment. Physico-chemical analyses showed no negative impact of this material on sediment composition or seawater chemistry. Chemical composition of BOFS before and after immersion showed no differences over time, suggesting extremely low expected exposure levels in the environment. The study suggests that BOFS can be used for marine environment applications.*

**KEYWORDS**: Basic Oxygen Furnace Slag, Waste, Valorisation, Circular Economy, Marine, Offshore

## 1. INTRODUCTION

Coastal areas are increasingly impacted by recreation, tourism, maritime traffic, port development, among many other activities (Halpern et al., 2015). These human pressures also include more recently the exploitation of offshore resources (Le Berre, 2017). Coastal development leads to a concomitant increase in demands for resources needed for construction. Concrete is currently the most widely used material for construction of maritime infrastructure (e.g. port facilities, seawalls, breakwaters), coastal protection and defence structures (Guiraud, 2017), and artificial reefs (Souche et al., 2019), but other materials such as steel, natural stone and plastic are sometimes used.

The widespread use of concrete comes from its strong compatibility with the environment in which it is placed, as it is a durable, stable, and readily manufactured material. Nevertheless, this material presents several major inconveniences. For instance, its high weight requires heavy equipment to manipulate, both during the land transport phase and during loading and immersion in sea (Lukens & Selberg, 2004). Moreover, the main emissive component of concrete is cement, which is currently responsible for approximately 7% of global emissions and 4% of European $CO_2$ emissions (European Commission. Joint Research Centre., 2023). Thus, the carbon footprint of 1 $m^3$ of conventional concrete without reinforcement can be up to 197 kg $CO_2$eq (InfoCiments, 2022). Natural rocks can provide an alternative to concrete depending on the infrastructure considered, however, their use also presents various drawbacks, mainly related to their extraction, including irreversible soil degradation, modification of natural habitats, and impacts on biodiversity at quarry sites (Darwish et al., 2011). Transportation of natural rock also causes dust emissions, anthropogenic noise, and greenhouse gas emissions. Globally, these extractions also lead to the risk of depletion of deposits in cases of overexploitation.

Valorization of industrial by-products appears an interesting and valuable alternative, as it replaces the need for permanent storage or definitive disposal of these materials. The work presented in this article focuses on the valorization of aggregates derived from steel production processes: Basic Oxygen Furnace (BOF) Slag.

BOF-Slag is a by-product of the steelmaking industry, characterized by high alkalinity and significative density. Up to 80-130 kg of this by-product is generated per ton of steel, resulting in 2021 or annual production in France of approximately 1.1 million tons (CTPL, 2022).

This material is underutilized considering its availability, with current valorisation mainly in civil engineering uses (earthworks and embankments, port infrastructure) and in

agriculture as fertilizer (Malassingne & Coulon, 2012). In France, BOF-Slag is considered as inert and non-hazardous waste according with the European Waste Framework Directive (2008/98/EC). Its use is not permitted in marine environments according to the French Environmental Code (Article L218-43), which states that “The dumping of waste or other matter […] is prohibited.”. Nevertheless, BOF-Slag can be used in this environment in other countries, for example in the Netherlands for construction of dikes for maritime protection (Malassingne & Coulon, 2012).

Our study investigated the potential use of BOF-Slag as a substitute for concrete and natural rocks in the construction of marine infrastructures, according to the main requirements for selecting materials for this type of use, including: compatibility, duration over time, stability and functionality (Lukens & Selberg, 2004). The project focused particularly on studying the parameters of "compatibility" and "ecological functionality". The purpose of this project was to test whether BOF-Slag has any measurable impacts on marine ecosystem, through analysis of sediment, seawater, and BOF-Slag chemical composition following potential leaching. Physico-chemical and biological monitoring was conducted for two years at a study site in the north-western Mediterranean Sea, where 18 BOF-Slag modules were submerged from 2021 to 2023. This article presents the first physico-chemical results testing the "compatibility" parameter.

# 2. MATERIALS AND METHODS

## *2.1 Study material*

Eighteen 1 $m^3$ modules were submerged in the north-western Mediterranean Sea from April 2021 to July 2023. The modules were cubic in shape (Fig. 1) and consisted of a steel casing containing 1.5 tons of BOF-Slag.

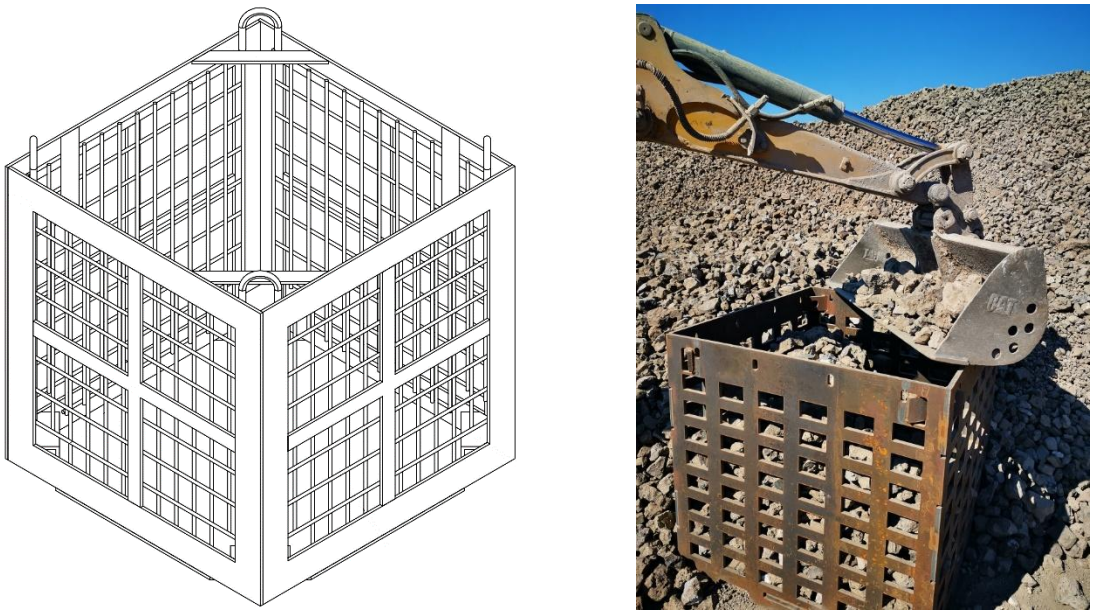

*Fig. 1.* ***At left****. Structure of the modules studied, without BOF-Slag.* ***At right****. Photography of one module filled with BOF-Slag.*

BOF-Slag used in this study was sourced from the ArcelorMittal steel mill in Fos-sur-Mer (France). The initial chemical composition is presented in Table 1 (ArcelorMittal, 2019).

*Table 1. Typical chemical composition of converter slag from the Fos-sur-Mer factory.*

| CHEMICAL COMPOSITION | MEAN (%) |
|---|---|
| $AL_2O_3$ | 1,31 |
| CaO | 47,63 |
| Fe tot | 18,99 |
| $P_2O_5$ | 2,17 |
| $SiO_2$ | 13,07 |
| S tot | 0,05 |
| MgO | 6,39 |
| MnO | 3,74 |

## 2.2 Study sites

This study was conducted in the artificial reef concession of Leucate (site Z5, Fig. 2), located in the Natura 2000 area of the “Prolongement en mer des Cap et étang de Leucate” (FR9102012) and in the Marine Natural Park of the Gulf of Lions. This study area is characterized by a homogeneous environment mainly composed of sandy substrates, where modules were submerged between 15–18 m depth. The site included three stations, each equipped with six modules, and two control stations. Control Station 1 was located 350 m

southeast of the study stations, and Control Station 2 was located approximately 3 km north of the study stations.

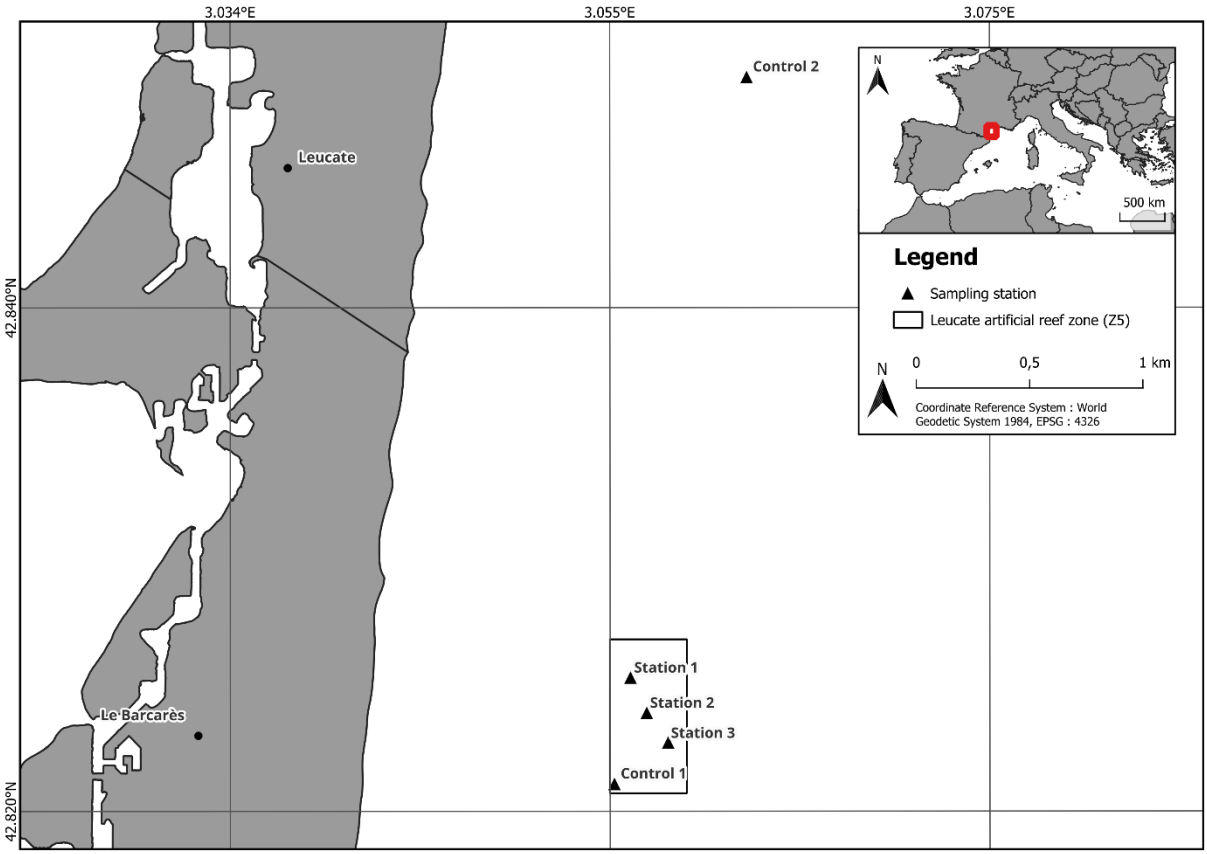


*Fig. 2. Location of study sites in the Mediterranean: off the coast of Leucate, within the Leucate artificial reef zone, and within the Gulf of Lions Natural Marine Park.*

## 2.3 Sampling and analysis protocols

*Evolution of sediment chemical composition*

Samples were collected manually using 40 cm diameter tube cores at the middle of the three stations before module immersion ($T_0$) and then in direct proximity to the modules 12 months after immersion ($T_1$). At each station, 3 different sediment samples were collected (0–2 cm, 2–5 cm and 5–10 cm) (following Egis Eau, 2016). Several replicates were taken per station: at $T_0$, two replicates in Station 1, three replicates in Station 2, and four replicates in Station 3. At $T_1$, three replicates in Stations 1 and 2 and four in Station 3. The samples were analysed in the laboratory using ICP-MS (Inductively Coupled Plasma Mass Spectrometry). The analyses focused on six major elements (Al, Ca, Fe, K, Mg, Na) and 18 trace elements (Ag, As, Ba,

Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Rb, Sb, Sr, Ti, U, V, Zn). A normalization of the elemental contents with respect to a reference element such as Al was applied to compensate for the grain size and mineralogical effects of the particulate material (Kerste & Smedes, 2002, Roussiez et al., 2005, Durrieu de Madron et al., 2020).

*Evolution of chemical contamination of water*

This evaluation was conducted according to the RINBIO protocol (Andral, 2002) based on the bioaccumulation properties of the Mediterranean mussel *Mytilus galloprovincialis*. Two calibrated packs of mussels were installed in each of the two control stations and in Stations 1 and 2. In Control Station 1, the packs were attached to components of the artificial reefs in the area, whereas in Control Station 2, the packs were weighted with 45 kg chain links. In the study stations, the packs were attached directly on the modules. Each pack was buoyed and positioned approximately 5 m below the sea surface for control stations and approximately 2 m above the module for study stations. The packs were submerged in April 2021, two weeks after module immersion, and retrieved two months later. Analyses, conducted on mussel tissue, focused on 13 elements (Al, As, Cr, Co, Mn, Hg, Mo, Ni, P, Pb, Se, Ti, V). Samples were prepared by microwave digestion. The elements were measured using the ICP-OES method defined by the NF EN ISO 11885 standard for Al and Ti, then by ICP-MS (internal laboratory method) for other elements.

*Evaluation of chemical composition of BOF-Slag*

Monitoring was conducted through leaching on samples before immersion ($T_0$) and after 1 year and 2 years of immersion ($T_1$ and $T_2$ respectively). The analyses focused on 20 chemical metrics (As, Ba, Cd, $Cl^-$, Cr, $Cr^{VI}$, Cu, $F^-$, Hg, Mo, Ni, $NO_3^-$, P, Pb, Sb, Se, Sn, $SO_4^{2-}$, V, and Zn). Two distinct analyses were performed on the samples: 1) standardized batch leaching test according to the German standard DIN 38414 S4 derived from the European Standard EN 12457-4 (with demineralized water as leachant); 2) experimental batch leaching test substituting the leaching agent used in standardized leaching test with seawater. This second

experimental protocol assessed the reaction of the substrate when in contact with the saline water while the modules were submerged. The seawater used for manipulation was collected by divers directly above the study sites, between 3–5 m below the surface.

## 2.4 Selection of studied elements

Among the 33 chemical metrics analyzed in this study, six were common to all three protocols, 11 were analyzed in only two of the three protocols, and 16 were typical of one protocol. To summarize and compare the results, this study presents the elements analysed in at least two protocols, as well as five of the elements analysed in only one protocol (Table 2). Their selection is based on the average chemical composition of the substrate studied (Table 1).

*Table 2. Chemical elements studied and their occurrence.*

| Analysis | Element | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Al | As | Ba | Ca | Cd | Co | Cr | Cu | Fe | Hg | K | Mg | Mn | Mo | Ni | P | Pb | Sb | Se | V | Zn |
| Sediment | | X | X | X | X | X | X | X | X | | X | X | X | X | X | | X | X | | X | X |
| Seawater | X | X | | | | X | X | | | X | | | X | X | X | X | X | | X | X | |
| Leaching | | X | X | | X | | X | X | | X | | | | X | X | X | X | X | X | X | X |

## 2.5 Statistical analyses

Statistical analyses were conducted using the software PAST (version 4.03). The significance level for the tests was set at $\alpha = 0.05$. Results with concentrations below the laboratory's quantification limit were replaced by half of the limit value, following the guidelines for water assessment. The data were $\log_{(x+1)}$ transformed and then normalized for sediments and mussels tissue analyses only. Normality and homoscedasticity of the data were tested using the Shapiro-Wilk test and Levene's test respectively.

For databases with two sets exhibiting a non-normal distribution, an ANOSIM (Analysis Of SIMilarity) was applied to detect potential statistical differences. P-values were

calculated using 9999 permutations. In case of significant differences, a SIMPER (SIMilarity PERcentage) analysis was conducted to determine the main parameters responsible for the observed dissimilarities, based on Euclidean distance matrix.

For data with three datasets exhibiting a non-normal distribution, a Kruskal-Wallis test was applied to detect potential statistical differences. In case of significant differences, a Dunn's post-hoc test was conducted to determine which samples significantly differed from each other.

Additionally, a Principal Component Analysis (PCA) was systematically conducted on the data that did not show significant differences to study the main parameters responsible for variabilities between measurement series, thereby reinforcing interpretations considering the limited size of the dataset.

# 3. RESULTS

## 3.1 Changes in the chemical composition of the sediment

The ANOSIM indicated a significant difference between $T_0$ and T1, with an R-value of 0.2197 associated with a p-value of 0.0001. The SIMPER analysis identified four parameters responsible for 28% of the observed dissimilarities: Cd, Ba, Mn and Co. For each of these elements, the mean concentration observed at $T_0$ was lower than that observed at $T_1$ (Table 3). Cd shows a particular change with a significantly higher concentration in sediments at $T_0$ than at $T_1$.

*Table 3. Average aluminium-normalised concentrations of chemical elements (µg.g-1) measured in sediments at T0 and T1.*

| | Mean ± SD | | Min-Max | |
|---|---|---|---|---|
| | $T_0$ (N=27) | $T_1$ (N=31) | $T_0$ (N=27) | $T_1$ (N=31) |
| As (µg.g$^{-1}$) | 0.265 ± 0.017 | 0.252 ± 0.027 | 0.232-0.306 | 0.196-0.294 |
| Ba (µg.g$^{-1}$) | 8.379 ± 0.483 | 7.688 ± 0.439 | 7.588-9.310 | 6.914-8.857 |
| Ca (µg.g$^{-1}$) | 0.585 ± 0.051 | 0.589 ± 0.293 | 0.479-0.694 | 0.413-2.103 |
| Cd (µg.g$^{-1}$) | 0.004 ± 0.000 | 0.002 ± 0.001 | 0.003-0.005 | 0.001-0.004 |
| Co (µg.g$^{-1}$) | 0.123 ± 0.007 | 0.113 ± 0.010 | 0.112-0.135 | 0.094-0.139 |

| | | | | |
|---|---|---|---|---|
| Cr (µg.g$^{-1}$) | 0.774 ± 0.063 | 0.744 ± 0.074 | 0.660-0.925 | 0.612-0.908 |
| Cu (µg.g$^{-1}$) | 0.149 ± 0.021 | 0.139 ± 0.017 | 0.121-0.215 | 0.106-0.199 |
| Fe (µg.g$^{-1}$) | 0.407 ± 0.024 | 0.390 ± 0.033 | 0.372-0.459 | 0.336-0.458 |
| K (µg.g$^{-1}$) | 0.429 ± 0.015 | 0.442 ± 0.022 | 0.393-0.449 | 0.410-0.482 |
| Mg (µg.g$^{-1}$) | 0.133 ± 0.007 | 0.128 ± 0.013 | 0.118-0.150 | 0.105-0.155 |
| Mn (µg.g$^{-1}$) | 5.517 ± 0.670 | 4.635 ± 0.725 | 4.441-7.170 | 3.425-6.297 |
| Mo (µg.g$^{-1}$) | 0.010 ± 0.002 | 0.009 ± 0.003 | 0.008-0.013 | 0.006-0.026 |
| Ni (µg.g$^{-1}$) | 0.299 ± 0.029 | 0.280 ± 0.024 | 0.250-0.358 | 0.229-0.329 |
| Pb (µg.g$^{-1}$) | 0.362 ± 0.021 | 0.350 ± 0.021 | 0.333-0.420 | 0.317-0.415 |
| Sb (µg.g$^{-1}$) | 0.014 ± 0.004 | 0.012 ± 0.004 | 0.010-0.029 | 0.009-0.028 |
| V (µg.g$^{-1}$) | 0.999 ± 0.054 | 0.970 ± 0.073 | 0.912-1.125 | 0.848-1.143 |
| Zn (µg.g$^{-1}$) | 1.205 ± 0.100 | 1.211 ± 0.228 | 0.992-1.398 | 0.897-1.742 |

For each chemical element, the mean concentration observed at $T_1$ is lower than that observed at $T_1$, except for Ca, K and Zn. An increase in Zn is observed in the sediments of Station 1 at $T_1$.

## *3.2 Changes in the chemical contamination of water*

The ANOSIM showed no differences between the measured concentrations for the two control sites and the two stations, with an R-value of 0 associated with a p-value of 0.667.

According to the PCA (Fig. 3), 89% of the total variance of the data is explained by PC1, 9% by PC2, and 2% by PC3. From this projection, it appears that the variability between the two controls is mainly due to Al in PC1. This parameter is also primarily responsible for the observed variabilities on PC2 between the two test stations, followed by P, As and Se.

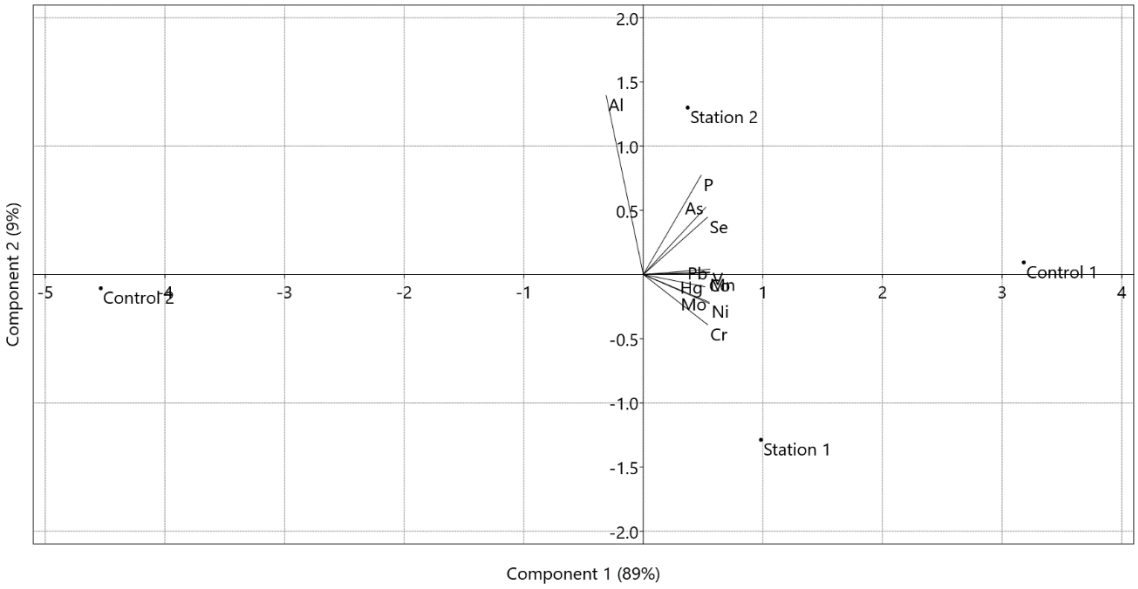


*Fig. 3. Principal Component Analysis (PCA) performed using the concentration data of chemical elements in mussel tissue for both control and test stations.*

Further analysis of the results showed higher concentrations for most elements in Control 2 compared to the test stations and Control 1. However, the mean concentrations in the control sites are higher than the mean concentrations in the tested samples for the elements As, Co, Cr, Mo, Ni, P, Pb, Se, and V (Table 4).

*Table 4. Average concentrations of chemical elements (mg.kg-1) measured in mussel tissue at T0 and T1.*

| | Mean ± SD | | Min-Max | |
|---|---|---|---|---|
| | Control | Test | Control | Test |
| Al (mg.kg$^{-1}$) | 695 ± 176 | 620 ± 296 | 570-820 | 410-830 |
| As (mg.kg$^{-1}$) | 3.085 ± 1.534 | 3.675 ± 0.474 | 2.00-4.17 | 3.340-4.010 |
| Co (mg.kg$^{-1}$) | 0.168 ± 0.230 | 0.200 ± 0.014 | 0.005-0.330 | 0.190-0.210 |
| Cr (mg.kg$^{-1}$) | 0.813 ± 1.142 | 1.150 ± 0.467 | 0.005-1.620 | 0.820-1.480 |
| Hg (mg.kg$^{-1}$) | 0.006 ± 0.005 | 0.006 ± 0.001 | 0.003-0.0100 | 0.005-0.006 |
| Mn (mg.kg$^{-1}$) | 7.440 ± 6.732 | 7.275 ± 0.502 | 2.680-12.200 | 6.920-7.630 |
| Mo (mg.kg$^{-1}$) | 1.055 ± 0.884 | 1.235 ± 0.219 | 0.430-1.680 | 1.080-1.390 |
| Ni (mg.kg$^{-1}$) | 0.500 ± 0.636 | 0.650 ± 0.156 | 0.050-0.950 | 0.540-0.760 |
| P (mg.kg$^{-1}$) | 433 ± 176 | 514.5 ± 99.7 | 309-558 | 444-585 |
| Pb (mg.kg$^{-1}$) | 0.575 ± 0.672 | 0.615 ± 0.049 | 0.100-1.050 | 0.580-0.650 |
| Se (mg.kg$^{-1}$) | 0.295 ± 0.276 | 0.350 ± 0.057 | 0.100-0.490 | 0.310-0.390 |
| V (mg.kg$^{-1}$) | 1.495 ± 1.803 | 1.620 ± 0.113 | 0.220-2.770 | 1.540-1.700 |

## 3.3 Changes in the chemical composition of BOF-Slag

*Standardized batch leaching test*

The results of the Kruskal-Wallis test do not indicate a significant difference between the datasets ($H_{(2)}$=1.589, p=0.445).

According to the PCA, 98.7% of the total variance of the data can be explained by the first axis PC1 while the other 1.3% can be explained by the second axis of the PCA. It appears that the variability between $T_0$, $T_1$, and $T_2$ is mainly due to variations in Ba concentrations (Fig. 4). However, the variability between $T_0$ and the other two sampling periods is primarily attributable to fluctuations in Cu, V, and Se concentrations.

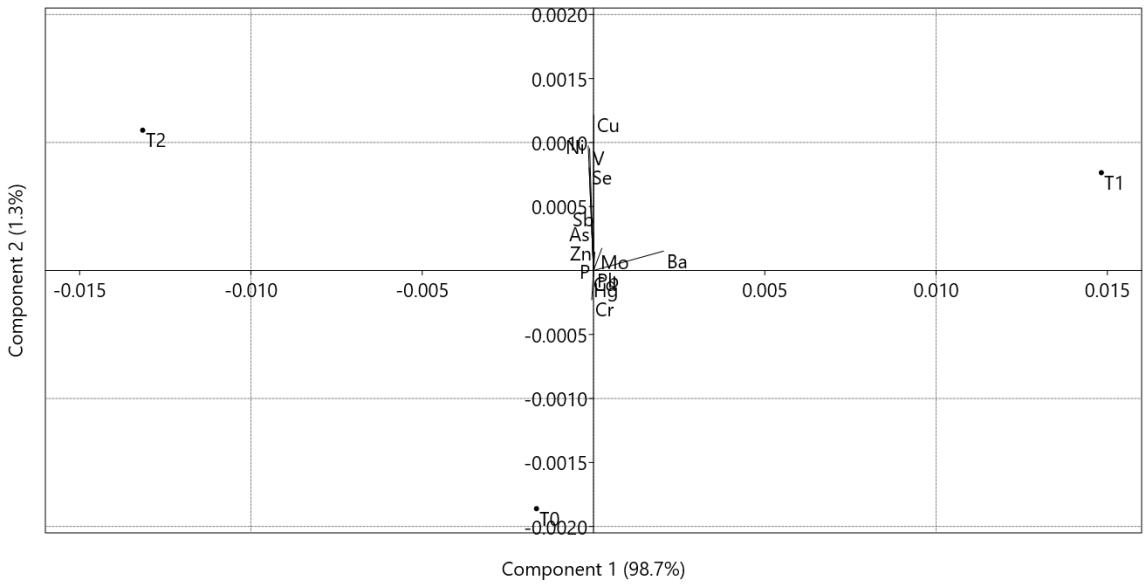


*Fig. 4. Principal Component Analysis (PCA) performed using the results from the series of analyses conducted at T0, T1, and T2 by normalized leaching on immersed and non-immersed BOF-Slag samples.*

*Experimental batch leaching test (seawater leachant)*

The results of the Kruskal-Wallis test indicated no significant difference between the sample series ($H_{(2)}$=0.1832, p=0.9114).

According to the PCA, the primary axis explained 97.5% of the total variance of the data, with the remaining 2.5% explained by the secondary axis. The variability between $T_2$ and the other two sampling periods seems mainly due to variations in P concentrations, whereas the variability among the three sampling periods can be explained by variations in

Se, Ba, V and Mo concentrations (Fig. 5). It is worth noting that the variation observed for P might be attributed to a change in the laboratory's quantification limit, which shifted from a value <0.1 mg.l$^{-1}$ to <1 mg.l$^{-1}$, leading to a large variation in measurement since values below the quantification limits were replaced by half of that limit. Nevertheless, P is an element that has consistently been measured lower than the laboratory's quantification limit.

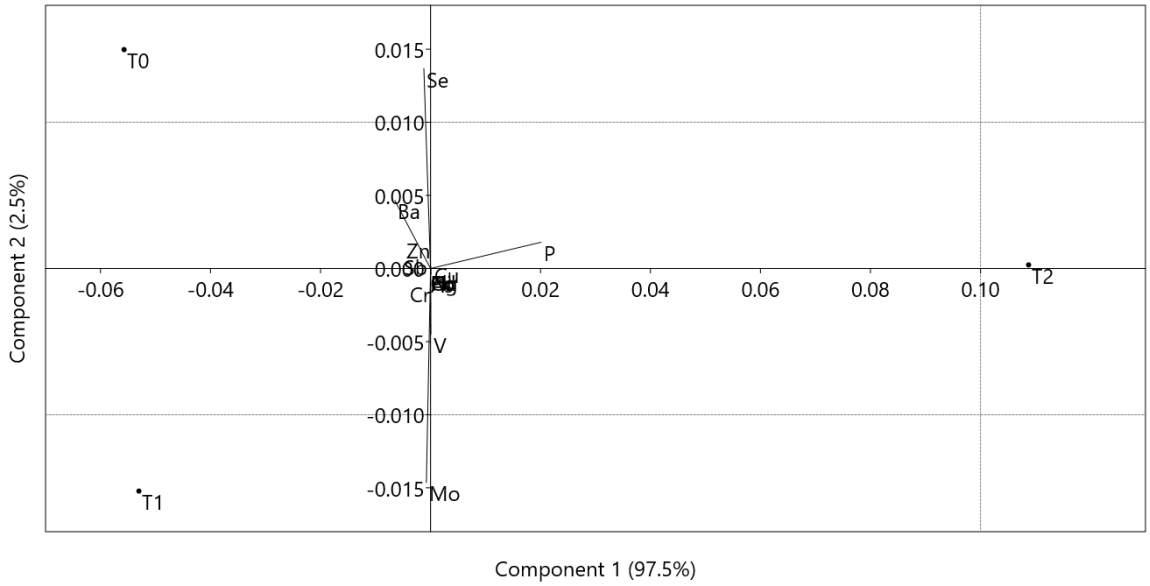


*Fig. 5. Principal Component Analysis (PCA) performed using the results from the series of analyses conducted at T0, T1, and T2 by experimental leaching on immersed and non-immersed BOF-Slag samples.*

*Analysis of elements responsible for observed variabilities*

Trends in the main parameters highlighted by the PCA and responsible for the variabilities between the three sampling periods were explored individually (Fig. 6).

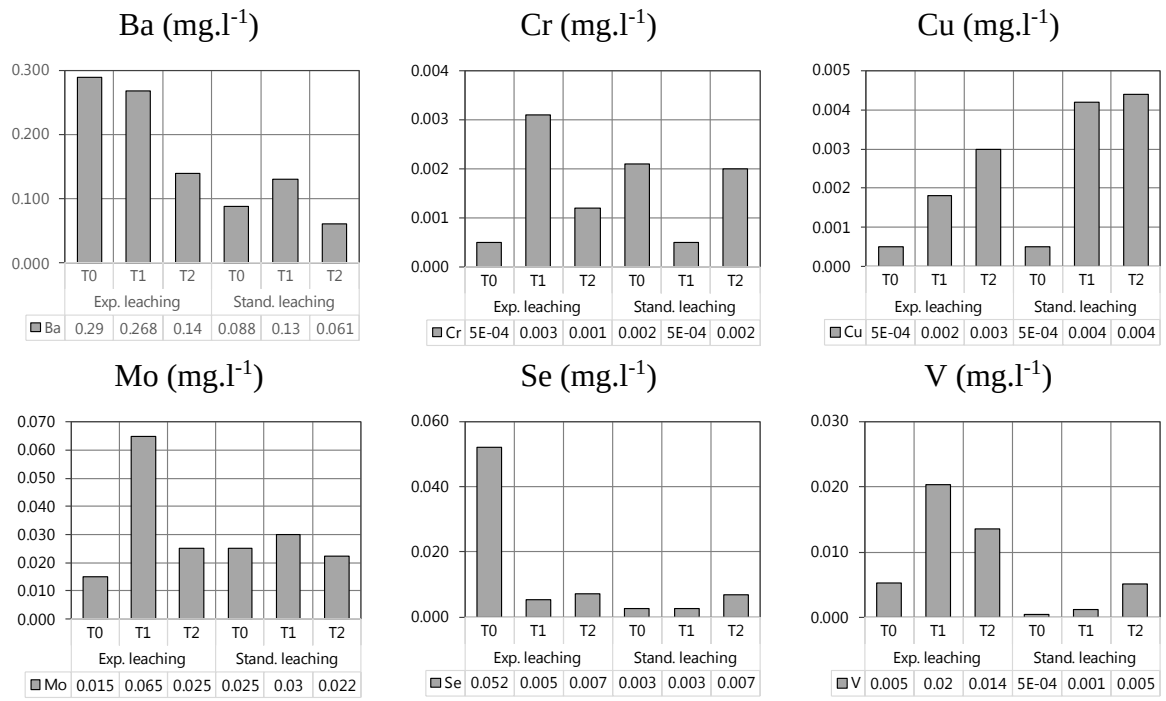


*Fig. 6. Comparisons of chemical element concentrations highlighted by PCA for each leaching (standardized and experimental).*

For experimental batch leaching test, the concentrations of Cr, Mo and V showed a similar pattern, with an increase at $T_1$ compared to $T_0$ followed by a decrease at $T_2$. This trend is also observed in the case of standardized leaching for Ba and Mo. Only Ba showed a consistent decrease with each sampling period ($T_0$, $T_1$ and $T_2$), while Cu showed a continuous increase.

For standardized batch leaching test, the concentration of Cr showed the opposite pattern compared to experimental leaching test, with a lower concentration at $T_1$ (<0.001 mg.l$^{-1}$) compared to $T_0$ (0.0021 mg.l$^{-1}$) and $T_2$ (0.002 mg.l$^{-1}$). Similarly, the Se concentration was significantly higher at $T_0$ (0.052 mg.l$^{-1}$) compared to $T_1$ (0.0054 mg.l$^{-1}$) and $T_2$ (0.0071 mg.l$^{-1}$). In the case of standardized leaching, however, the concentration of Se in the eluate is below the laboratory's quantification limits at $T_0$ and $T_1$ (0.0068 mg.l$^{-1}$ at $T_2$).

## 4. DISCUSSION

The objective of this study was to evaluate the compatibility of BOF-Slag in the marine environment, potentially to use it as a substitute for concrete or natural rocks in the construction of maritime infrastructure.

The analyses aimed to verify the absence of any adverse impact of BOF-Slag on the environment through the study of changes in the chemical composition of sediment, water chemistry as seen in bioaccumulators (Mediterranean mussels), and the overall composition of the material. These results were examined in relation to control concentrations and initial concentrations, as well as various quality thresholds, geochemical backgrounds, and ecotoxicological threshold values for the compartments studied.

## 4.1 Changes in the chemical composition of the sediment

The concentrations measured in the sediments at $T_1$ were compared to those measured at $T_0$, and to the background levels of heavy metals in surficial sediments of the Gulf of Lions (Roussiez et al., 2005) for the following elements: Co, Cr, Cu, Ni, Zn and Pb. Overall, most elements showed a concentration at $T_1$ lower than at $T_0$, except for Ca, K and Zn. Also, most elements showed a concentration lower than the background level, except for Zn. The increase in Ca concentration at $T_1$ can be explained by a sample containing numerous shells. Except for Ca, the trace elements analyzed exhibit a more pronounced variability than the major elements. The increase in Zn may be explained by the metal structure containing the BOF-Slag. These three elements (Ca, K and Zn) were not highlighted by the SIMPER analysis as responsible for the observed dissimilarities.

## 4.2 Changes in the chemical contamination of water

The concentrations measured in the mussel tissue do not seem to indicate any adverse impact from the BOF-Slag.

The concentrations of Pb, Hg, Ni, As and Cr are lower than the "baseline level" of the RINBIO program grid from 2015 (Witkowski et al., 2017), and the concentrations of Pb, Hg and Ni are lower than the Mediterranean median concentrations from the results of the ROCCH surveillance network points (IFREMER's Réseau d'Observation de la Contamination

CHimique du littoral) (IFREMER, 2006). Only Cr showed a value higher than the Mediterranean median concentration. However, since the concentration of Cr is higher in the mussel tissue from Control 1 than in the mussel tissue from Station 1, this increase may not be attributable to any potential leaching from the BOF-Slag. Finally, there was significant variability observed for Al among the samples, particularly between the control sites. This variability could be explained by the clay content in the sediments, which are mainly composed of hydrated aluminum.

## *4.3 Changes in the chemical composition of BOF-slag*

The standardized batch leaching tests reflected a stable chemical composition of the BOF-Slag. The concentrations measured in the eluate were consistently lower than the values from the quality reference level of the SETRA guidelines applied to the leaching analysis results, based on the thresholds for Type 3 road uses (the most restrictive type) (SETRA, 2012) or even lower than the limit values defined by French regulation for inert (non-hazardous) waste landfilling. These comparative references are provided for indicative purposes since no reference framework currently exists in France for leaching analysis results of BOF-Slag intended for use in the marine environment. The variations identified for some variables by PCA or visual analysis of the results (for example higher concentration of Se at $T_0$: 0.052 $mg.l^{-1}$) may be explained by the effect of immersion or by the intrinsic variability of the material and samples tested.

The experimental batch leaching tests performed also showed a stable chemical composition of the BOF-Slag, except for some elements such as Ba, Mo, V and Se. In the absence of a reference framework for this type of analysis, the concentrations of elements highlighted by PCA or visual analysis of the results (Ba, Mo, V and Se) were compared to the ecotoxicological reference values available in the database of the European Chemicals Agency (ECHA) and defined according to the REACH (Registration, Evaluation,

Authorization and Restriction of Chemicals) regulation. When available, the results were compared to the Predicted No Effect Concentration (PNEC) as well as the No Observed Effect Concentration (NOEC). The PNEC is the concentration of a chemical substance in a specific environment below which it is unlikely that unacceptable effects on the aquatic ecosystem and the organisms living in it will occur during long-term or short-term exposure. The NOEC is defined as the highest tested concentration of a substance for which no statistically significant effect ($p<0.05$) is observed compared to the control, within a specified exposure period (ECHA, 2008)

Regarding Ba, no pertinent PNEC for the marine environment can be determined according to the ECHA guidelines for several reasons. Firstly, Ba levels in seawater are subject to significant variability, ranging from 2 to 60 $\mu g.l^{-1}$ with an average concentration of about 13 $\mu g.l^{-1}$ (Bowen, 1979). Referring to the guidelines of the European Chemicals Agency, the marine PNEC derived from 12.4 $\mu g.l^{-1}$ obtained from the freshwater PNEC is therefore comparable with the typical seawater levels for barium. Secondly, seawater contains approximately 2,700 $mg.l^{-1}$ of sulfate, and Ba combines with sulfate ions to form barium sulfate, or barite. Barite is a highly insoluble compound [$Ksp = 1.08 \times 10^{-8}$ (Lide, 2004)], which precipitates in marine sediments. In summary, due to the high levels of sulfate in the marine environment and the low solubility of barium sulfate, dissolved barium levels will remain constant in seawater regardless of the amount of Ba introduced into the system.

Regarding Mo, a pertinent PNEC for the marine environment can be obtained from reliable values identified for 12 marine aquatic species representing nine different taxonomic groups (Heijerick et al., 2012). Thus, the PNEC retained by the ECHA for Mo in the marine environment is 2.28 $mg.l^{-1}$. However, the concentration values of Mo measured in the eluates have never exceeded this value.

Regarding V, a relevant PNEC for the marine environment can be obtained from reliable values identified for larvae of several marine species (Fichet & Miramand, 1998), following the ECHA guidelines. This PNEC, calculated with a safety factor of 10 from the No Observed Effect Concentration (NOEC) of 25 µg $V.l^{-1}$, stands at 2.5 $\mu g.l^{-1}$. However, this value of 2.5 $\mu g.l^{-1}$ is relatively close to the typical geochemical range of V in seawater, typically observed between 1.5 and 1.8 $\mu g.l^{-1}$ (Donat & Bruland, 1995; Bruland & Lohan, 2003). In the context of this study, the concentration values of V measured in the eluates, under extremely concentrated conditions, exceed the PNEC but remain below the NOEC.

Regarding Se, a relevant PNEC for the marine environment can be obtained from reliable values identified for the effect of $Na_2SeO_3$ on the growth of the fish *Pagrus major* (Kim & Kang, 2014) and the reproduction of the invertebrate *Allorchestes compressa* (Ahsanullah & Brand, 1985). This PNEC, calculated with statistical extrapolation approach from the No Observed Effect Concentration (NOEC) of 25 µg $Se.l^{-1}$, stands at 2 $\mu g.l^{-1}$. In the context of this study, the concentration values measured of Se in the eluates, under extremely concentrated conditions, exceed the PNEC but remain below the NOEC for the measurements made at $T_1$ and $T_2$. However, a value higher than the NOEC is observed at $T_0$ (non-immersed samples) from experimental batch leaching test (52 $\mu g.l^{-1}$). This variation can be attributed to the high concentration level of Se in the seawater used for this test (41 $\mu g.l^{-1}$).

## 5. CONCLUSIONS

According to the REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) regulation, the different steps of chemical safety assessment consist of: 1) compiling and evaluating all relevant available information about the substance under study; 2) assessing the hazard (including establishing Predicted No Effect Concentrations (PNECs)); 3) assessing exposure and risks, through an exposure scenario associated with an exposure estimate; and 4) reaching a decision for refining the assessment through iteration (ECHA,

2011).

In this study, no parameter appears to be of concern in the considered compartments, either through intrinsic comparison or comparison to existing thresholds (geochemical background, quality standards, or ecotoxicological values). Indeed, the few elements whose variability was highlighted either by statistical analysis or visual analysis were mostly lower than the values at the initial state (Cd, Ba, Mn and Co in sediments), lower than the values in the control sample (Cr in bioaccumulators), or below the considered thresholds (geochemical background, quality reference, or ecotoxicological values). Only Zn showed an increase in sediment between $T_0$ and $T_1$, possibly related to the metallic structure of the modules. However, the impact of this metal structure is not the subject of this study. Among the ecotoxicological reference values, V and Se may have concentrations in the eluate exceeding the Predicted No Effect Concentration (PNEC) but are lower or equal to the No Observed Effect Concentration (NOEC). In the context of this study, and considering the concentrations measured in the eluate compared to the PNEC of the studied substances, it appears that the expected exposure levels in the environment are significantly lower than the no-effect doses as well as the geochemical background.

In contrast, monitoring across various biological compartments (fish, benthic fauna, attached fauna and flora, acoustic landscape; Ecocean pers. comm.) reflects an ecological attractivity in BOF-Slag similar to natural rocks or concrete. Colonization by marine fauna is rapid, and species assemblages, abundance, and richness are similar between BOF-Slag and natural rocks or concrete modules.

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## DECLARATION OF INTEREST

The authors declare the following financial interests which may be considered as potential competing interests: Marc Fixaris and Jérémie Domas report financial support was provided by ArcelorMittal.

The other authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author, JL, upon request.

## REFERENCES

Ahsanullah, M., & Brand, G. W. (1985). Effect of selenite and seleniferous fly-ash leachate on growth and viability of the marine amphipod Allorchestes compressa. *Marine Biology*, *89*(3), 245‑ 248. https://doi.org/10.1007/BF00393657

Andral, B. (2002). *Le réseau intégrateurs biologiques (RINBIO) en Méditerranée—Evaluation de la contamination chimique basée sur l'utilisation de stations artificielles de moules* [Guide méthodologique]. AERMC, IFREMER.

ArcelorMittal. (2019). *Fiche Commerciale—Laitiers d'Aciérie de Conversion Fos-sur-Mer*.

Bowen, H. J. (1979). *Environmental chemistry of the elements*. Academic Press.

Bruland, K. W., & Lohan, M. C. (2003). Controls of Trace Metals in Seawater. *Treatise on Geochemistry*, *6*, 625. https://doi.org/10.1016/B0-08-043751-6/06105-3

CTPL. (2022). *Flux de laitiers d'Aciérie (France)*. Enquête nationale.

Darwish, T., Khater, C., Jomaa, I., Stehouwer, R., Shaban, A., & Hamzé, M. (2011). Environmental impact of quarries on natural resources in Lebanon. *Land Degradation & Development*, *22*, 345‑ 358. https://doi.org/10.1002/ldr.1011

Donat, J. R., & Bruland, K. W. (1995). Trace Elements in the Oceans. In *Trace Elements in Natural Waters* (p. 223‑ 252). John Wiley & Sons, Ltd. https://doi.org/10.1002/9781118349083.ch11

Durrieu de Madron, X., Stabholz, M., Heimbürger-Boavida, L.-E., Voutquenne-Nazabadioko, L., Kerhervé, P., & Ludwig, W. (2020). Approaches to evaluate spatial and temporal variability of deep marine sediment characteristics under the impact of dense water formation events. *Mediterranean Marine Science*. https://doi.org/10.12681/mms.22581

ECHA. (2008). *Guidance on information requirements and chemical safety assessment Chapter R.10 : Characterisation of dose [concentration]-response for environment.*

ECHA. (2011). *Guidance on information requirements and chemical safety assessment. Part A: Introduction to the Guidance document* (Version 1.1).

Egis Eau. (2016). *Bonnes pratiques pour la caractérisation des matériaux en vue d'une opération de dragage et d'immersion en milieu marin et estuarien.* (GEODE).

European Commission. Joint Research Centre. (2023). *Decarbonisation options for the cement industry.* Publications Office. https://data.europa.eu/doi/10.2760/174037

Fichet, D., & Miramand, P. (1998). Vanadium toxicity to three marine invertebrates larvae : *Crassostrea gigas, Paracentrotus lividus* and *Artemia salina*. *Chemosphere*, *37*(7), 1363‑ 1368. https://doi.org/10.1016/S0045-6535(98)00118-0

Guiraud, P. (2017). *Les ouvrages en béton en site maritime*. Solutions béton, Infociments. https://www.infociments.fr/sites/default/files/article/fichier/SB-OA-2016-2.pdf

Halpern, B. S., Frazier, M., Potapenko, J., Casey, K. S., Koenig, K., Longo, C., Lowndes, J. S., Rockwood, R. C., Selig, E. R., Selkoe, K. A., & Walbridge, S. (2015). Spatial and temporal changes in cumulative human impacts on the world's ocean. *Nature Communications*, *6*(1), 7615. https://doi.org/10.1038/ncomms8615

Heijerick, D., Regoli, L., & Stubblefield, W. (2012). The chronic toxicity of molybdate to marine organisms. I. Generating reliable effects data. *Science of The Total Environment*, *430*, 260‑ 269. https://doi.org/10.1016/j.scitotenv.2012.03.045

IFREMER. (2006). *RNO. Surveillance du Milieu Marin. Travaux du Réseau National d'Observation de la qualité du milieu marin.* Edition 2006.

InfoCiments. (2022). *L'empreinte carbone du béton*.

Kerste, M., & Smedes, F. (2002). Normalization procedures for sediment contaminants in spatial and temporal trend monitoring. *Journal of environmental monitoring : JEM*, *4*, 109‑ 115. https://doi.org/10.1039/B108102K

Kim, J.-H., & Kang, J.-C. (2014). The selenium accumulation and its effect on growth, and haematological parameters in red sea bream, Pagrus major, exposed to waterborne selenium. *Ecotoxicology and Environmental Safety*, *104*, 96‑ 102. https://doi.org/10.1016/j.ecoenv.2014.02.010

Le Berre, I. (2017). L'artificialisation des littoraux : Déterminants et impacts. In B. B, L. B. Y, & R. A (Éds.), *Sols Artificialisés et Processus d'artificialisation Des Sols : Déterminants, Impacts et Leviers d'action* (p. 234‑ 254). Expertise Scientifique Collective (ESCo). IFSTTAR, INRA. https://hal.science/hal-01764526

Lide, D. R. (2004). *CRC Handbook of Chemistry and Physics, 85th Edition*. CRC Press.

Lukens, R. R., & Selberg, C. (2004). Guidelines For Marine Artificial Reef Materials—Second Edition. *Artificial Reef Subcommittees of the Atlantic and Gulf States Marine Fisheries Commissions*, *121*, 205.

Malassingne, O., & Coulon, H. (2012). *Utilisation des laitiers sidérurgiques dans les ouvrages maritimes et fluviaux* (CETMEF). CEREMA.

Roussiez, V., Ludwig, W., Probst, J.-L., & Monaco, A. (2005). Background levels of heavy metals in surficial sediments of the Gulf of Lions (NW Mediterranean) : An approach based on 133Cs normalization and lead isotope measurements. *Environmental Pollution (Barking, Essex: 1987)*, *138*(1), 167‑ 177. https://doi.org/10.1016/j.envpol.2005.02.004

SETRA. (2012). *Acceptabilité environnementale de matériaux alternatifs en technique routière—Les laitiers sidérurgiques* (Cerema (ex-Setra)).

Souche, J.-C., Pioch, S., Salgues, M., De Weerdt, K., Agostini, A., & Hayek, M. (2019). De la conception à l'éco-conception des ouvrages maritimes : Intégrer la nature au projet d'aménagement maritime. *Revue Paralia*, *12*, n01.1-n01.26. https://doi.org/10.5150/revue-paralia.2019.n01

Witkowski, F., Andral, B., & Tomasino, C. (2017). *Campagne RINBIO 2015. Surveillance des niveaux de contamination chimique pour biomonitoring actif*. https://archimer.ifremer.fr/doc/00419/53043/