

INVESTIGATION OF POTENTIAL LEACHABILITY OF ARSENIC AND HEAVY METALS FROM BLASTED COPPER SLAG AND CONTAMINATED MARINE SEDIMENTS BY SINGLE EXTRACTIONS IN SOUTH OF VAN PHONG BAY – VIETNAM

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Abstract: Copper slag is widely used as abrasive material for removing rust and marine deposits from ships to prepare the surface before painting. Development of shipping industry has raised an environmental concern related to the release of heavy metal from blasted copper slag in Vietnam. This study was conducted to investigate the characteristics of the blasted copper slag (BCS) and potentially contaminated sediment samples collected nearby the shipyard in south of Van Phong bay (south-central of Vietnam). Single extractions (with CaCl₂, (NH₄)₂EDTA, CH₃COOH and NaCl) were performed to examine under which conditions As and heavy metals (HMs) may leach from the BCS and sediment. The BCS samples were mainly composed of Fe, Ca, Al and Si (percentage levels). Furthermore, BCS contained significant amounts of Cu, Zn (8416 and 8439 mg/kg respectively) and Mo, Pb, As, Cr (2399, 853, 798 and 566mg/kg respectively). Results from the single extractions suggest that As and HMs in both sediments and BCS showed a low actual mobility and were not easily mobilized by sea water and/or organic complexation. Acidification had a more pronounced effect on As and HM release both in sediments and BCS.

Keywords: *Blasted copper slag; Leachability; Heavy metal; Sediment; Viet Nam.*

KHẢO NGHIỆM RÔ LỎI KIM LOẠI NẶNG VÀ TRẮNG TÍCH BIÊN ĐÔNG PHÍA NAM VÙNG VÂN PHONG – VIỆT NAM

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Tóm tắt: Nghiên cứu hàm lượng cao As và kim loại nặng (KLN) là tác nhân tiềm ẩn nguy hiểm trong việc lựa chọn các chất thiếc bám vào bề mặt tàu

tr c khi s n. Nghi n c u này kh o s t kh n ng r r As v KLN t x ng v tr m t c g n khu v c óng tàu t i v nh V n Phong. l nh ng th c v l nh ng ti m t ng c a As v KLN c kh o s t th ng qua ph ng ph p chi t n s d ng CaCl_2 , NaCl , EDTA v CH_3COOH . M u x ng ch a h m l ng ch y u l Fe, Ca, Al v Si (m c %), Cu, Zn (8416 and 8436mg/kg) v Mo, Pb, As, Cr (2399, 853, 798 v 566mg/kg). K t qu t ph ng ph p chi t n cho th y As v KLN trong x ng v tr m t c b i n u c l nh ng th c th p v l nh ng ti m t ng i v i t c nh n n c b i n v ch t h u c kh ng cao. Qu t tr nh axit h o a g y ra t c ng á ng k n s ph ng th c As v KLN trong tr m t c v x ng (ngo i tr Cd v Pb trong tr m t c).

T khóa: X ng, S r r ; Kim lo i n ng; Tr m t c; Vi t Nam.

I. INTRODUCTION

Copper slag is widely used as abrasive material for removing rust and marine deposits from ships to prepare the surface before painting. In recent years, shipping industrial activities developed in Vietnam, have raised an urgent environmental concern related to the use of copper slag as abrasive material for preparing the surface of the ships. The increasing of Cu and Zn concentrations in sediments collected near the shipyard factory in South of Van Phong bay has been noticed by some researches (Le Thi Vinh et al., 2006; Le Thi Vinh, 2012). It was documented that copper slag contains high amount of As and HMs which may be mobilized and introduced into environment (Vítková et al., 2011). With respect to the potential release of HMs from sediment/soil/waste materials, leaching /extraction tests are generally a better tool for environmental impact assessment than total elemental analysis (Van der Sloot & Dijkstra, 2004). According to Cappuyns (2012), single extractions represent a relatively fast, cheap, and simple way to assess HM mobility in contaminated soils and sediments. Furthermore, single extractions can give an indication of the “pools” or “sinks” of HMs that are potentially available under changing environmental conditions. This study was conducted to investigate the potential leachability of As and heavy metals (HMs) from blasted copper slag (BCS) and potentially contaminated sediments collected nearby the area of a shipping company in the south of Van Phong bay by using single extractions with CaCl_2 0.01M, $(\text{NH}_4)_2\text{EDTA}$ 0.05M, CH_3COOH 0.43M and NaCl 0.5M. Although a lot of controversy exists about the use of the term ‘heavy metals’ (Batley, 2012), this term is used in this study to indicate particularly the elements Cd, Cr, Co, Cu, Ni, Pb and Zn. Arsenic, which is actually a metalloid, will be mentioned separately. The use of the term ‘trace elements’ will not always be correct since the above mentioned elements sometimes occur in elevated concentrations in the investigated samples.

II. MATERIALS AND METHODS

1. Sampling and sample pretreatment

The studied area is located south of Van Phong bay, in Khanh Hoa province. A sampling campaign was undertaken in December 2010. Nineteen marine surface

sediment samples (uppermost 5cm and approximately 1kg each) were collected adjacent to the shipyard at 500m intervals (Fig. 1). The samples were taken from a boat by a grab and the exact coordinates of the sampling locations were recorded by GPS (Garmin – GPS12). Sampling sites are indicated in Figure 1. After collection, the samples were placed in sealed plastic bags, and transported to University of Science (Ho Chi Minh City, Vietnam). Here, the sediment samples were air dried, homogenized in a porcelain mortar and sieved over a 2 mm mesh sieve. Only the < 2 mm fraction in sediments was used for further analysis as suggested by UNEP/IOC/IAEA (1995). Three representative samples of BCS were collected in the dump sites. All BCS samples were air dried. Part of each BCS sample was crushed in a porcelain mortar for physico-chemical analysis whereas another part of each sample was used for extraction tests, without crushing.



Figure 1. Studied area and sampling sites

2. Characterization of samples

Immediately after sampling, pH and redox potential (Eh) of the sediments were measured at the sampling sites with a Hanah pH/Eh meter (HI 8424).

Air-dried sediment and BCS samples were transported to the Department of Earth and Environmental Sciences, University of Leuven (KU Leuven, Belgium) for further analysis. Total elemental concentration of samples (Al, Ca, Fe, K, Mg, P, S, As, Cd, Co, Cr, Cu, Mn, Ni and Zn) were determined based on ICP-OES (Varian 720ES, Varian Inc., Walnut Creek, CA, USA) analysis after being digested by the so-called 4 acid digestion method (concentrated (cc.) HNO₃ + cc. HClO₄ + cc. HF + 2.5M HCl) in a Teflon beaker on a hot plate. In order to evaluate the quality of the analytical method, two certified reference materials were also analyzed, namely GBW 07411 (soil, National Research Center for certified reference materials, China) and GBW 07311 (sediment, National Research Center for certified reference materials, China).

Grain size was determined by laser diffraction spectrophotometry (Malvern Mastersizer S long bed, Malvern, Worcestershire, UK) after removing carbonates (0.1M HCl), iron oxides (0.5% oxalic acid, boiling) and organic carbon (35%

H₂O₂) and applying a peptizing solution (10 g/l sodium polyphosphate, boiling) to sediments. Grain size of BCS was determined as received samples. The content of oxidizable substances (OS: organic matter + sulfides content) was determined by the Walkley and Black manual titration method. A mineralogical sample characterization was conducted by X-ray diffraction (Philips PW1830 diffractometer with Bragg/Brentano – 2 setup, CuK radiation, 45kV and 30mA, graphite monochromator). On selected surface marine sediment (high concentration of HMs) an XRD analysis was performed. The carbonate components in the sediment samples were removed by a HCl 1N treatment before XRD analysis.

3. Single extractions

The composition of a CaCl₂ 0.01M extract can be considered representative for pore water composition (Sahuquillo et al., 2003). From an environmental point of view, the pore water composition gives an indication of the actual mobility which is considered as the “mobile fraction” (Cappuyns, 2012). The CaCl₂ extraction was based on protocol of the SMT (Standards Measurement and Testing, Quevauviller, 1998) program, but in the present study, the extraction procedure was repeated 4 times, resulting in four different liquid/solid (L/S) ratios (10, 20 30, and 40L/kg, 16h for each extraction step). For the ammonium-EDTA extraction, the protocol of the European Standards, Measurements and Testing program (SMT) was followed, using ammonium-EDTA 0.05M at L/S 10 (1h of extraction) to evaluate the metal–chelate complexation fraction. The acid extractable fraction (consisting of exchangeable metals and metals bound to carbonates) was also based on the procedure described by the SMT program, using an extraction with acetic acid (0,43 M). However, the extraction was repeated 3 times, resulting in three different L/S ratios (40, 80, 120 L/kg, 16h for each extraction step). To evaluate the effect of seawater on the mobility of As and HMs in sediments and BCS, an extraction with a 30g/l NaCl solution was used at four consecutive extractions resulting in four different L/S ratios (10, 20 30, and 40 L/kg, 24h for each extraction). Metal concentrations in the leachates were measured by ICP-OES.

III. RESULTS - DISCUSSION

1.Characterization of BCS and sediment

1.1. BCS

XRD analysis of BCS samples revealed the dominance of amorphous phases (> 90%) and the occurrence of fayalite, magnetite, maghemite and elemental copper. Average chemical composition, fine fraction (< 63µm) and pH of the BCS are given in Table 1. The pH value of BCS (8.13) indicates a weak alkalinity. The BCS samples were mainly composed of Fe, Ca, Al and Si (percentage levels). Furthermore, BCS contained significant amounts of Cu, Zn (8419 and 8436 mg/kg respectively), and Mo, Pb, As, Cr (2399, 853, 798 and 566 mg/kg respectively). According to Gorai et al. (2003), typical copper slag is usually found in an impure iron silicate glass with small inclusions of copper and copper sulphide. Moreover, the variation in chemical properties of copper slag depends

on the types of furnace or process used for treatment of the slag. The result of XRD analysis suggest that fayalite and sulphide phases exist in the present BCS but are not the major phases because of the low content of SiO₂ and S found in the samples.

1.2. Sediment

XRD results indicated that the main components in the analyzed sediments after carbonate removal were quartz, albite, oligoclase, orthoclase, muscovite and some amorphous phases. The mean and range (minimum-maximum) of the fine fraction (< 63µm, silt & clay), OS, pH, elemental concentrations and detection limit (DL) of As and HMs are summarized in Tab. 1.

Table 1. Mean and range of the fine fraction, OS, pH and elemental concentrations.

	Unit	Sediment		BCS		Sample 16	Sample 19	DL
		Mean	Range	Mean	Range			
Al	%	1.01	0.12 - 3.28	2.00	1.89 - 2.09	1.19	1.33	-
Ca	%	21.99	10.82 - 27.65	2.16	2.00 - 2.41	17.42	18.76	-
Fe	%	1.30	0.06 - 9.14	41.02	39.40 - 43.01	8.6	9.14	-
K	%	0.54	0.06 - 1.44	0.32	0.22 - 0.58	0.56	0.62	-
Mg	%	0.94	0.58 - 1.74	0.82	0.77 - 0.92	0.64	1.4	-
P	%	0.02	0.02 - 0.03	0.5	0.04 - 0.05	0.03	0.03	-
S	%	0.19	0.16 - 0.3	0.21	0.16 - 0.28	0.26	0.3	-
As	mg/kg	19	1 - 168	798	698 - 893	131	168	2
Cd	mg/kg	-	-	23	22 - 24	5	6	0.1
Co	mg/kg	-	-	228	218 - 345	43	44	0.1
Cr	mg/kg	35	8 - 135	566	482 - 657	117	135	0.5
Cu	mg/kg	332	1 - 3321	8419	8051 - 8953	2882	3321	0.5
Mn	mg/kg	148	34 - 365	1331	1120 - 1469	268	291	0.1
Ni	mg/kg	11	3 - 35	113	58 - 139	32	35	0.5
Pb	mg/kg	22	1 - 170	853	801 - 939	158	170	1
Zn	mg/kg	187	3 - 1733	8436	5714 - 9520	1585	1733	0.5
OS	%	0.34	0.18 - 0.7	1.98	1.51 - 2.21	0.65	0.7	-
pH		9.88	7.78 - 11.77	8.17	8.06 - 8.17	9.02	8.5	-
<63µm	%	33.73	1.59 - 93.37	6.61	3.19 - 14.09	24.03	15.14	-

The results show that the fine-grained fraction strongly varied between the sediments, ranging from 1.6 to 93.4%. Generally the fine-grained fraction shows higher values in the quite areas which are far from the harbour (i.e. samples 1, 3, 6, 8, 9, 18). The contents of OS as well as total S content in surface sediments were low (mean: 0.34 and 0.19% respectively). As and HMs show high concentrations in samples which contain high Al concentrations (samples 1, 2, 3, 12, 13, 14 and 18) or samples collected near the harbour (samples 16, 19). Cadmium and Co were only detected in sample 16 (5 and 44mg/kg respectively) and sample 19(6 and 43 mg/kg respectively).

It can be inferred from this result that, sample 16 and 19 can be considered as two hot spots of HM contamination in the studied area. This finding could be explained by the location of the sampling sites. Sample 19 has the shortest distance from the harbour (119m) compared to other samples. The fine blasted copper slag from ship repairing activity could be scattered and settled down to the sea and sediment nearby.

2. Actual mobility and potential mobility of As and HMs based on single extractions

Total concentrations of As and HMs in sediments can provide information on the current pollution status but do not allow to assess the actual and long-term release of heavy metals into the environment. Single extractions may give some information about the potential release of heavy metals under changing environmental conditions. As discussed above, sediment samples 16 and 19 possessed extremely high total concentrations of all heavy metals. Therefore, they were selected together with the BCS samples to perform the above mentioned single extractions.

2.1. Actual mobility

In this study, the extraction with CaCl_2 did not show a high efficiency neither in sediment samples nor in BCS samples, Arsenic and most HMs were below detection limit (DL), except Zn which was released in very low concentrations (< 1% of total concentration). These results are quite similar to Sahuquillo et al. (2003) who found a low extraction yield of HMs (below 1% of the total content) with mild extractants (CaCl_2 and NaNO_3) in soil and sediments. It can be concluded that the sediments and BCS are characterized by a low actual mobility of the studied metals.

2.2. Potential mobility

Influence of high chloride concentrations

To investigate the mobility of As and HMs under the influence of high chloride concentrations like in seawater, a NaCl 0.5M solution (equivalent salinity to 32‰) was used. Concentrations of As and most HMs (Cd, Co, Pb and Zn) in the NaCl-extracts of the sediments were below DL. Although Cd is known to have a high affinity to form complexes with chlorides (Du Laing et al 2008), this was not observed in this study. Only low percentages of As and Cr were extracted by NaCl (< 0.5% of the total content in the sediment). It indicated that sediment have a poor leachability of As, Cd, Co, Pb and Zn under sea water condition.

A similar metal extractability for BCS can be inferred from the results. Most HMs (Cd, Co, Cu, Pb and Zn) in the NaCl extracts were below DL. Arsenic, Cr and Ni were found in very low concentrations (<1% of total concentration).

Influence of complexation and acidification

Arsenic and HM extractabilities (as % of total concentration) in the sediment samples with EDTA increased in the following order: Cd > Zn > Pb > Cu > Ni > Co > As > Cr. As and HM extractabilities by EDTA are given in Fig. 2. It can be

seen from the results that Cd, Zn, Cu and Pb showed a high release from the sediment if compared to other metals. These findings are comparable to the results described in Wu et al. (2011) and Sahuquillo et al. (2003) who reported a high release of Cd, Zn, Cu and Pb from sediment samples by EDTA extraction.

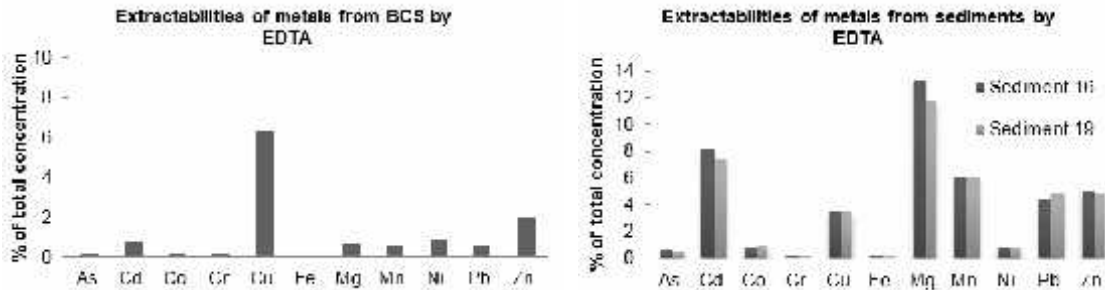


Figure 2. Metal extractabilities by EDTA

Sahuquillo et al. (2003) pointed out that complexation agents are assumed to extract both the carbonate and organic bound fractions of heavy metals in soil and sediments. Therefore, the percentage extracted by EDTA sometimes is higher than the percentage extracted by CH_3COOH , depending on sediment composition (Quevauviller et al., 1997). However, this was not observed in the present study. In general, less than 10% of heavy metals were extracted from the sediments by both reagents (Fig. 2).

Among the HMs, Cu, Zn and Cd displayed a high absolute release from the BCS samples. The absolute release of As and HMs by EDTA was in the following order: $\text{Cu} > \text{Zn} > \text{Pb} > \text{Ni} > \text{As} > \text{Cr} > \text{Co} > \text{Cd}$. However, relative to the total concentration, the released fraction was limited ($< 10\%$ of total concentration) and the order was: $\text{Cu} > \text{Zn} > \text{Ni} > \text{Pb} > \text{Cd} > \text{Co} > \text{Cr} > \text{As}$. There was no significant correlation between total concentration and the extractabilities of metals by EDTA in both sediment and BCS (average R was 0.03 and 0.19 respectively). The amount of As and HMs extracted by EDTA in sediment samples were higher than in BCS. It thus can be assumed that As and HMs in sediment are more sensitive to complexation than in the BCS. The limited release of Arsenic and most HMs by EDTA ($< 10\%$ of total concentration) both in sediments and BCS, indicate that As and HMs in the sediments and the BCS samples in this study will not mobilized easily by an organic complexation agent.

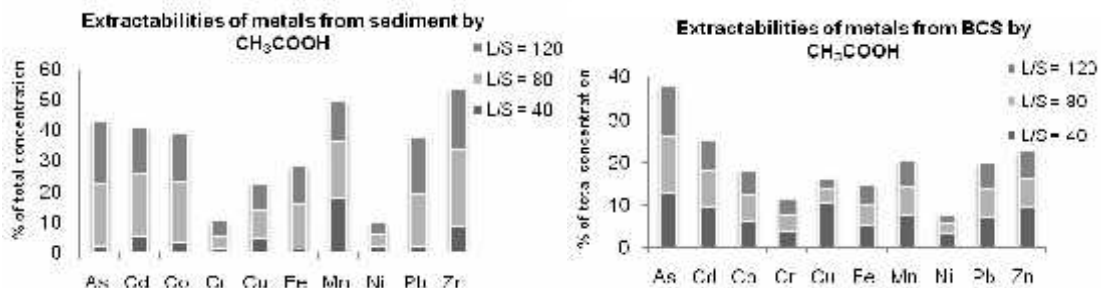


Figure 3. Metal extractability of sediment and BCS during CH_3COOH extraction.

Extractabilities of elements by CH_3COOH in sediment (sample 16) and BCS are illustrated in Fig. 3. In sediments, extractability (as % of total concentration) with CH_3COOH increased in the following order: $\text{Zn} > \text{As} > \text{Cd} > \text{Co} > \text{Pb} > \text{Cu} > \text{Cr} > \text{Ni}$ (Fig. 3).

Extractabilities of As, Zn and changes of pH value during three consecutive extractions in sediment are given in Fig. 4. The release of Zn and As was especially important in the second (L/S 80) and third extraction (L/S 120).

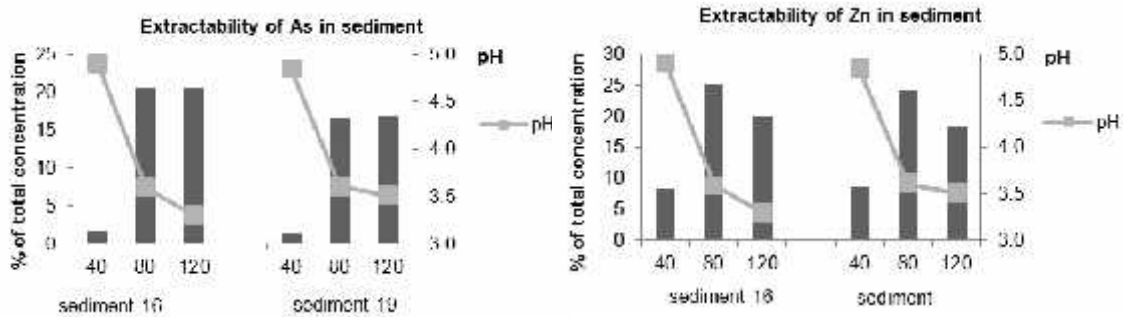


Figure 4. Extractabilities of As, Zn during CH_3COOH extraction in sediments.

Furthermore, the significant change in pH (from L/S = 40 to L/S = 80) with dramatical release of elements illustrate the dependence of element release and pH. The low extractability during the first extraction with CH_3COOH (L/S = 40) might be explained by the acid neutralizing capacity (ANC) of the sediment, keeping the pH of the extract relatively high and preventing the mobilization of HMs.

Extractabilities of As and Zn from BCS during three consecutive extractions with CH_3COOH are illustrated in Fig. 5.

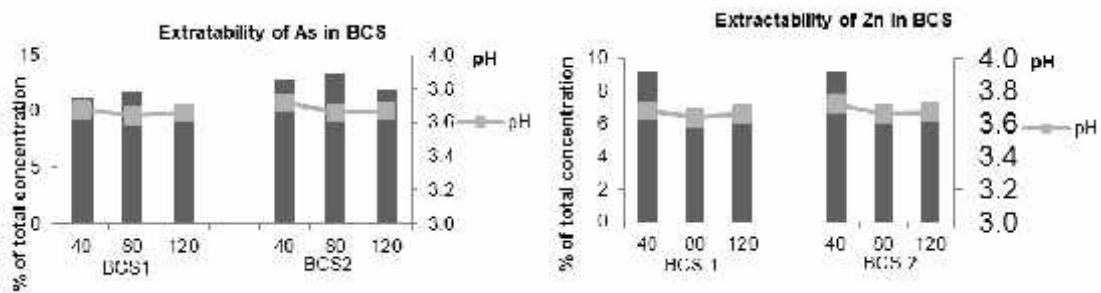


Figure 5. Extractabilities of As and Cu during CH_3COOH extraction in BCS

For the BCS sample, the order of extractabilities was as follows: $\text{As} > \text{Cu} > \text{Zn} > \text{Cd} > \text{Pb} > \text{Cr} > \text{Ni}$ (Fig. 3). Arsenic and most HMs were released in similar amounts in the three consecutive extraction steps. However, for Zn and Cu, the highest concentrations were released during the first extraction (L/S = 40: 897 and 882 mg/kg for Cu and Zn respectively). It can be seen from Figure 5 that there was no significant variation in pH during consecutive CH_3COOH extractions. This observation indicates a low ANC of BCS. No significant correlation was found between total concentration of metals and the percentage

extracted by CH₃COOH (average, for all metals, correlation coefficient $R < 0.4$). It therefore can be concluded that there is likely no significant relationship between the total concentration and the leachability of metal in the BCS.

Comparison of acidification and complexation

The predominant process affecting the release of heavy metals and As was assessed by using the ratios of elements extracted by EDTA and CH₃COOH. This ratio was calculated for each element.

Ratio = extractability by EDTA (% as total concentration) / extractability by CH₃COOH (% as total concentration, L/S = 40). These ratios are given in Tab. 2.

Table 2. Ratios of extractability by EDTA and CH₃COOH (L/S = 40) in sediment

Sediment	As	Cd	Co	Cr	Cu	Ni	Pb	Zn
16	0.3	1.7	0.3	0.1	0.9	0.5	2.3	0.6
19	0.4	1.3	0.3	0.1	0.8	0.5	2.1	0.6

It was found from the results that Pb, Cd and Cu have highest ratios, suggesting that acidification had a more pronounced effect on As and HM release in sediments, except for Cd and Pb. This might be explained by the fact that Cu and Pb have high complexation constants ($\log K = 18.8$ and 18.0 , respectively) (Perez et al., 2008) which indicates a high affinity of these elements to ammonium-EDTA. Arsenic and HMs in BCS were found to have ratios below 1, which indicates that BCS was more sensitive to acidification than to complexation processes. According to the results of the single extractions, even though BCS particles were recorded in the surface sediment, the risk for environmental release of As and most HMs from the sediment was relatively low under changing of environmental conditions (resuspension, complexation and acidification). However, acidification has a more pronounced effect on As and HM release both in sediments and BCS suggested a pH_{stat} leaching test to examine the influence of acidification to As and HM release for long term monitoring.

IV. CONCLUSION

Results from the single extractions suggest that As and HMs in both sediments and BCS showed a low actual mobility (according to CaCl₂ extraction) and were not easily mobilized by sea water (extractability < 1% of total concentration by NaCl extraction) and organic complexation (extractability < 10% of total concentration by EDTA extraction). Extraction with CH₃COOH indicated that acidification has a more pronounced effect on heavy metal release both in sediments and BCS (except for Cd and Pb in sediments).

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REFERENCES

1. Batley, G. E., 2012. ‘‘Heavy Metal’’-A Useful Term. *Integr. Environ. Assess. Manag.* 8(2), 215.
2. Cappuyns, V., 2012. A Critical Evaluation of Single Extractions from the SMT Program to Determine Trace Element Mobility in Sediments. *Applied and Environ Soil Sci* 2012: 1–15.
3. Du Laing, G., De Vos, R., Vandecasteele, B., Lesage, E., Tack, F.M.G., Verloo, M.G., 2008. Effect of salinity on heavy metal mobility and availability in intertidal sediments of the Scheldt estuary. *Est. Coast. Shelf Sci.* 77, 589 - 602.
4. UNEP/IOC/IAEA. ,1995. Manual for the geochemical analyses of marine sediment and suspended particular matter. Reference methods for marine pollution studies.
5. Le Thi Vinh, Pham Van Thom, Nguyen Hong Thu, Duong Trong Kiem, Pham Huu Tam, 2006. The impacts of Zn and Cu in NIX grains from the Hyundai - Vinashin Shipyard (HVS) upon the environmental quality of Mygiang, Van Phong bay. *Collection of Marine Research Works. Vol XV*: 81-91.
6. Le Thi Vinh, 2012. Heavy metals in the environment of Van Phong-Ben Goi bay in Khanh Hoa province. *Journal of Marine science and Technology. Vol XII (3)* : 12-13.
7. Gorai, B., Jana, R. K & Premchand., 2003. Characteristics and utilisation of copper slag—a review. *Resour. Conserv. Recycl.* 39, 299–313.
8. Perez, G., Lopez-Mesas, M & Valiente, M., 2008. Assessment of heavy metals remobilization by fractionation: Comparison of leaching tests applied to roadside sediments. *Environ. Sci. Tech.* 42, 2309–2315.
9. Quevauviller, P., Rauret, G., Rubio, R., Lopez-Sanchez, J.F., Ure, A., Bacon, J., Muntau, H., 1997. Certified reference materials for the quality control of EDTA- and acetic acid-extractable contents of trace elements in sewage sludge amended soils (CRMs 483 and 484). *J. Anal. Chem.* 357, 611 – 618.
10. Quevauviller, P., 1998. Operationally defined extraction procedures for soil and sediment analysis I. Standardization. *TrAC.* 17(5), 289–298.
11. Sahuquillo, A., Rigol, A. & Rauret, G., 2003. Overview of the use of leaching/extraction tests for risk assessment of trace metals in contaminated soils and sediments. *Trends Anal. Chem.* 22, 152–159.
12. Vítková, M., Ettler, V., Mihaljevi , M & Sebek, O., 2011. Effect of sample preparation on contaminant leaching from copper smelting slag. *J. Hazard Mater.* 197, 417–23.
13. Van der Sloot, H. & Dijkstra, J., 2004. Development of horizontally standardized leaching tests for constructions materials: a material based or release based approach? Identical leaching mechanisms for different materials (p. 56). Dutch Ministry of Housing, Spatial Planning and the Environment (VROM), Soil, Water and Rural Environment Directorate (project nr. 2003.06.089).
14. Wu, G.H., Cao, S.S., Chen, S.R., Cao, F.T., 2011. Accumulation and remobilization of metals in superficial sediments in Tianjin, China. *Environ. Monit. Assess.* 173, 917–928.