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# Beneficial utilization of sewage sludge ash residues for the stabilization/solidification of As-, Cr-, and Cu-contaminated marine sediments

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**Abstract.** The management of incinerated sewage sludge ash (ISSA) residue after phosphorus recovery and dredged marine sediment contaminated with heavy metal(loid)s such as As(V), Cr(VI), and Cu(II) in coastal cities is a major concern due to the limited land space and stringent environmental regulations for solid wastes. This study proposes a novel recycling routine for the generated ISSA residue based on its high iron content. Briefly, the high iron ISSA residue was co-pyrolyzed with a biomass waste (peanut shell) at 1050 °C under N<sub>2</sub> atmosphere, yielding a composite material containing zero valent iron (ZVI). Due to the versatile applications of (ZVI) in environmental remediation, including the adsorption removal of heavy metal(loid)s, it could be an alternative low-cost candidate for the solidification/stabilization (S/S) treatment of contaminated marine sediments. The composite material was reused as a partial substitute of cement (at substitution rates of 20%) for the S/S treatment of contaminated marine sediments. The results showed that all the treatment groups could effectively reduce the leaching of As and Cu from contaminated sediments to a comparable level according to the toxicity characteristic leaching procedure (TCLP). CK (cement alone), SBC and BC groups showed a poor immobilization effect toward Cr(VI). Nevertheless, FBC, FSBC, and RBC significantly reduced the leaching of Cr(VI). Replacement of cement by these composite materials significantly reduced the mechanical strength of the S/S products compared to CK. Particularly, BC group demonstrated the lowest mechanical strength, which was 49% lower than that of CK. Even though the lowest mechanical strength was greater than 3 MPa, S/S products met the requirement for recycling as filling materials under local law. The results demonstrated the feasibility of producing ZVI containing biochar composites from ISSA residue and peanut shell, which could be further reused to substitute cement and enhance immobilization efficacy, particularly toward Cr(VI) for contaminated sediment.

## 1. Introduction

Routinely dredging of marine sediments is widely adopted in coastal cities with intense shipping activities, which ensures sufficient depth for navigation purposes [1]. The management of dredged marine sediment is challenging because of its huge amount [2]. Besides, sediments are often polluted by various heavy metal(loid)s such as cadmium, copper, lead, zinc, arsenic, and chromium worldwide due to natural and anthropogenic activities [3,4]. The disposal of the contaminated excavated sediments is of particular concern, and the disposal fee for these sediments is 50 times higher than the unpolluted sediments (92 HKD vs. 1.92 HKD/cubic meter sediment in 2019) in Hong Kong. On the other hand, with increasing awareness of circular economy, the beneficial reuse of solid waste, including excavated sediments, has gained global attention. Therefore, there is an urgent need to find



cost-effective disposal options for contaminated sediments, which not only achieves the immobilization of pollutants but also recycles the sediments into useful materials.

Various technologies such as biological, electrochemical, physical-chemical have been adopted to immobilize heavy metal(loid)s contaminated marine sediments [5]. Among these technologies, stabilization and solidification (S/S) technology with cement has been acknowledged as a low-cost and time-saving method for managing dredged sediments. S/S method can effectively immobilize heavy metals such as Cu, Zn, and Pb via physical encapsulation and chemical fixation [6]. Under an appropriate experimental design, the S/S treated sediment could have sufficient mechanical strength, which endows its application as various construction materials such as filling materials and paving blocks [1]. However, the immobilization of metal(loid)s such as As(V) and Cr(VI) by cement-based S/S technology remains questionable, particularly under a highly alkaline environment, which could be improved by the incorporation of metal(loid)s stabilizers [7]. What is more, the production of cement is associated with huge energy consumption and greenhouse gas (GHG) emissions [8]. Therefore, it is necessary to find/develop alternative substitution materials of cement, particularly those with multi-functionality towards inorganic metal(loid)s, which contribute to the management of solid wastes, energy reduction, GHG emissions, and enhanced performance for S/S of contaminated sediments [8].

As a low-cost material, biochar particularly modified by low-cost iron bearing wastes demonstrates enhanced affinity towards metal(loid)s such as As and Cr compared with pristine biochar and has been widely used for the treatment of contaminated water and soil because of its excellent physico-chemical properties and easy availability of raw materials [9]. Concerning issues associated with limited land space and environmental consideration limited disposal of incinerated sewage sludge ash (ISSA) generated from the combustion of dewatered sewage sludge. ISSA showed an excellent possibility for phosphorus recovery due to global P scarcity. However, after P recovery from ISSA by the most feasible acid washing method [10], around 90% (by mass of) residue remained, which requires proper management. Given the rich iron content in ISSA residue after P recovery, it is of interest to produce a residue-modified biochar composite for partial substitution of cement for the S/S treatment of contaminated sediments, which can fulfill the multi-fold contribution.

This research produced the ISSA residue-modified biochar composite. Then the composite material was used together with cement for S/S of contaminated sediments. Finally, some important parameters were assessed, including the mechanical strength and leaching of heavy metal(loid)s from the S/S treated sediments.

## 2. Materials and methods

### 2.1 Binder materials and sediments

According to our previous studies [11], P-removed ISSA residue was washed and ground to pass a 75- $\mu\text{m}$  sieve. The chemical composition of the residue was determined using X-ray fluorescence (XRF, Rigaku Supermini 200), as shown in Table 1, which had a  $\text{Fe}_2\text{O}_3$  content of around 17.3%. The ISSA residue and peanut shell were thoroughly mixed by grinding; the mixtures were then pyrolyzed at 1050  $^\circ\text{C}$  (ramp: 10  $^\circ\text{C}/\text{min}$ ) for 1 h in a tube furnace (OTF-1200X) under  $\text{N}_2$  atmosphere to obtain the residue biochar composite (RBC) material. For comparison purposes,  $\text{Fe}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3/\text{SiO}_2$  modified biochar, and pristine biochar were produced under the same pyrolysis environment, and the corresponding modified biochar composite materials were named FBC, SBC, FSBC, and BC. These biochar composite materials were pulverized, stored in a desiccator, and used as a partial substitute for ordinary Portland cement (OPC) (shown in Table 1) for the S/S treatment in the subsequent experiments.

The dredged sediment (shown in Table 1) was collected locally in Hong Kong and was sieved through a 2.36 mm sieve before S/S treatment. The heavy metal(loid) contents were determined after digesting the pulverized (<75  $\mu\text{m}$ ) sediments by concentrated nitric and perchloric acid followed by ICP-OES (SPECTROBLUE) measurement, which had  $69.9 \pm 8.1$  mg/kg Cu exceeding the Lower Chemical Exceedance Level (LCEL) [12]. Hence, the collected sediment is classified as Category M, and it must

be properly disposed according to the local law. Since other metal(loid)s such as As(V) and Cr(VI) were also found in the local sediments with contents even exceeding the Upper Chemical Exceedance Level (UCEL), the collected sediments were further spiked by As(V) and Cr(VI) to over UCEL (As at  $68.9 \pm 6.6$  mg/kg, and Cr at  $233 \pm 16.1$  mg/kg) and stood for over 2 months before the S/S treatment.

**Table 1** Chemical composition of raw materials used in this study

Component (wt.%)	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	Cl	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Others
Sediment	2.45	0.881	17.1	66	0.131	1.3	2.26	4.57	3.17	0.197	1.6	0.341
ISSA residue	-	1.74	9.8	59.6	1.85	4.5	-	1.44	2.56	0.664	17.3	0.546
Cement	-	0.957	5.79	19.1	0.147	3.71	-	0.744	65.7	0.307	3.31	0.235

### 2.2 S/S sample preparation

The sediment mortar samples were prepared with pure cement as a control group (CK) and cement with a substitution of 20% by different composite materials (shown in Table 2) as different treatment groups. Specifically, the contaminated sediments with 20% water content (determined by preliminary experiment) were mixed with the binder for 2 min by a mechanical mixer to produce uniform mixtures. The fresh mixtures were then cast into 40 mm × 40 mm × 40 mm plastic mould and vibrated for 1 min to remove entrapped air bubbles. Afterwards, all the samples were packed with polyethylene sheets to avoid water loss and cured at room temperature for 28 days.

**Table 2** Mixture design for S/S of sediment

Group	Binder (wt. %)						Sediment (wt. %)
	Cement	FBC	SBC	FSBC	RBC	BC	
CK	10						100
FBC	8	2					100
SBC	8		2				100
FSBC	8			2			100
RBC	8				2		100
BC	8					2	100

### 2.3 Testing programs

#### 1) Unconfined compressive strength

The unconfined compressive strength of the S/S samples was measured using a universal testing machine according to BS EN 12390-3 [13].

#### 2) Leaching characteristics

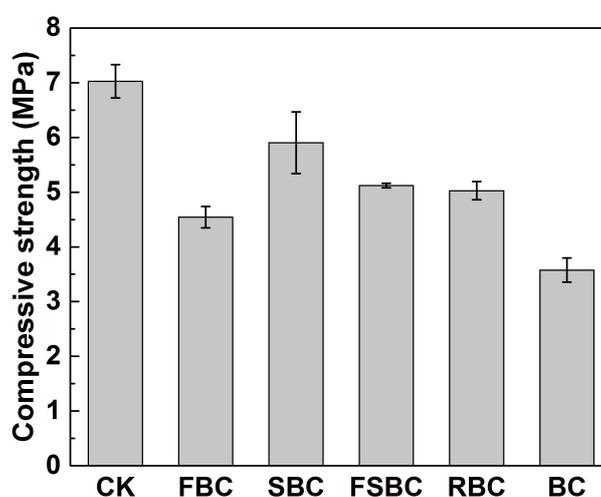
Toxicity characteristic leaching procedure (TCLP): The S/S products were leached with 0.1 M glacial acetic acid (pH  $2.88 \pm 0.05$ ) at a L/S ratio of 20 L/kg and rotated at 30 rpm for 18 h under ambient temperature [14].

A sequential extraction procedure (SEP) was adopted to assess the partition of targeted metal(loid)s in the S/S treated sediments. The extraction was carried out in 50 mL polyethylene centrifuged tubes with 1 g solid samples according to literatures with minor modifications [15][16]. The fractions determined were as follows: exchangeable (F1) (8 mL 1 M MgCl<sub>2</sub> at pH 7.0 for 1 h), carbonates (F2) (8 mL 1 M NaOAc at pH 5 for 5 h), reducible or Fe-Mn oxide bounded (F3) (20 mL 0.04 M NH<sub>2</sub>OH·HCl in 25% (V/V) HOAc at  $96 \pm 3$  °C for 6 h), oxidizable (F4) (3 mL 0.02 M HNO<sub>3</sub> + 5 mL 30% H<sub>2</sub>O<sub>2</sub> at pH 2 and  $85 \pm 2$  °C for 2 h, add 3 mL 30% H<sub>2</sub>O<sub>2</sub> for 3 h, cool down, add 5 mL 3.2 M NH<sub>4</sub>OAc in 20% (v/v) HNO<sub>3</sub> for 0.5 h), and residual fraction (F5) (HClO<sub>4</sub> and HNO<sub>3</sub> for total digestion).

## 3. Results and discussion

### 3.1 Compressive strength

The compressive strength of the S/S treated sediments is one of the most crucial parameters determining the potential applications. For instance, the S/S products with compressive strength over 0.35 MPa according to US EPA, and can be reused as filling material in Hong Kong when the compressive strength is greater than 1 MPa [17]. As shown in Figure 1, all the groups showed a compressive strength greater than 3.5 MPa, following the order of CK > SBC > FSBC  $\approx$  RBC > FBC > BC. CK group had the highest mechanical strength of around 7 MPa, whereas BC group exhibited the lowest mechanical strength of around 3.6 MPa. 20% substitution of cement by BC caused an almost 49% reduction on mechanical strength which revealed the detrimental effect of BC substitution on the mechanical strength of the produced S/S products. On the other hand, the mechanical strength of FBC, SBC, FSBC and RBC groups were all significantly higher than that of BC, demonstrating that mineral biochar composites showed better performance for mechanical strength development than the pristine BC.



**Figure 1** Compressive strength of 28-day S/S products.

### 3.2 TCLP leaching of S/S treated sediments

TCLP was adopted to assess the S/S efficacy of contaminated sediments (as shown in Figure 2). pH is acknowledged as one of the most crucial parameters influencing the leaching behaviors of metal(loid)s from solids. The contaminated sediment had a pH of  $8.01 \pm 0.39$ . All the treatment groups increased the soil pH to a similar level at around 12.20. The leached As, Cr, and Cu concentrations from raw sediment were around  $0.38 \pm 0.08$  mg/L,  $6.81 \pm 0.50$  mg/L, and  $1.32 \pm 0.05$  mg/L. All the S/S treatment groups significantly reduced the leached concentrations of As, Cr, and Cu. Specifically, the leached As concentrations in the TCLP leachate of different S/S groups were close to each other ( $0.11 \pm 0.01$  mg/L  $\sim$   $0.13 \pm 0.03$  mg/L) but significantly lower than that of raw sediments ( $0.38 \pm 0.08$  mg/L). Similarly, all treatment groups significantly reduced the Cu concentration in the TCLP leachate from  $1.32 \pm 0.05$  mg/L to a range of  $0.03 \pm 0.001$  mg/L to  $0.07 \pm 0.002$  mg/L. Nevertheless, no significant differences were observed within different treatment groups. The leaching of Cr however was quite different from As and Cu. Specifically, CK, FBC, and BC groups achieved a similar reduction on Cr concentration in the TCLP leachate ( $3.21 \pm 0.24 \sim 3.72 \pm 0.67$  mg/L), which were significantly lower than that of the raw sediment ( $6.81 \pm 0.50$  mg/L). RBC further reduced the Cr concentration to a considerably lower level than CK, FBC, and BC groups. However, the Cr immobilization by RBC was inferior to those of FBC and FSBC, as these two groups reduced the Cr concentration in TCLP leachate to an even significantly lower level than RBC. These results demonstrated that all the treatment groups were comparable regarding immobilization of As and Cu. While, the immobilization efficacy toward Cr follows the order of CK  $\approx$  SBC  $\approx$  BC < RBC < FSBC  $\approx$  FBC.

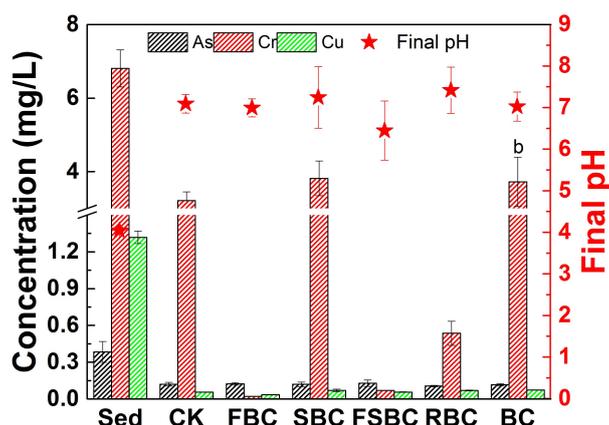


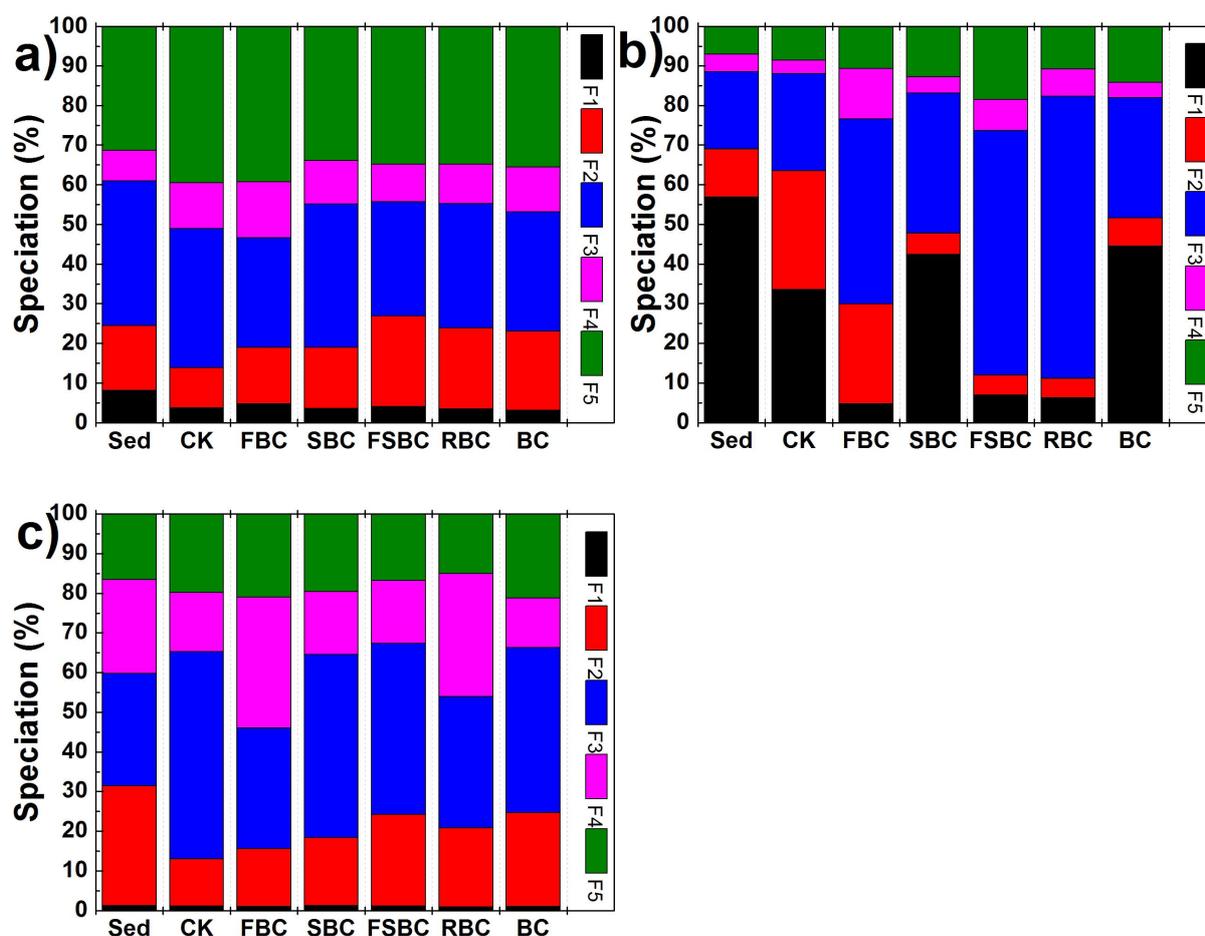
Figure 2 TCLP of S/S sediment.

### 3.3 Speciation of metal(loid)s in S/S products

Sequential extraction was further employed to investigate the speciation of As, Cr and Cu before and after S/S treatment of the sediment. It is widely known that the exchangeable (F1) and residual (F5) fraction is the most labile and stable species, respectively. While the carbonates (F2) and Fe/Mn oxide bounded (F3) fractions are susceptible to the surrounding environment, such as the pH and redox potentials. As shown in Figure 3, the As species in the contaminated sediment followed the order of F3 (36.6%) > F5 (31.3%) > F2 (16.3%) > F4 (7.7%) > F1 (8.1%), demonstrating that the sediment had quite a strong leaching potential of As because F1 to F3 fractions accounted for around 61% of the total As. After the S/S treatment, all the treatment groups reduced the F1 fraction from 8.1% to the range of 3.1% ~ 4.7% and increased the F5 fraction from 31.3% to the range of 34.8% ~ 39.6%. And F1 to F3 fractions in different treatment groups followed the order of FBC (46.6%) < CK (49.0%) < BC (53.2%) < SBC (55.2%)  $\approx$  RBC (55.3%)  $\approx$  FSBC (55.7%), all lowering than the raw sediment. This result indicated that all the treatment groups effectively stabilized As in contaminated sediment.

As for Cr, the F1 fraction was 56.9% and the F5 was only 7.0%, indicating that the raw sediment had a very high leaching potential of Cr. CK, SBC, and BC achieved a slight reduction of F1 to 33.5%, 42.4% and 44.5%. While FBC, FSBC, and RBC significantly reduced F1 to 4.8%, 6.9% and 6.3%, and increased F3 in contaminated sediment from 19.5% to 46.7%, 61.7% and 71.1%. This was due to the presence of ZVI in FBC, FSBC, and RBC, which had a strong affinity to Cr and resulted in an increase of F3 fraction. The F1 to F3 fractions in contaminated sediment was 88.5%. Those fractions in CK, SBC, and BC were similar or slightly lower than the contaminated sediment, indicating these groups were ineffective for S/S of Cr. The replacement of cement by other iron biochar composites FBC, FSBC, and RBC however reduced these fractions to 76.6%, 73.7%, and 82.3%, demonstrating the important role of ZVI in the immobilization of Cr in contaminated sediment.

For Cu, the contaminated sediment had a very low F1 fraction of around 1.2%. The F2 fraction (30.2%) was relatively high. All the S/S treatment groups showed similar F1 fractions in the range of (0.9% to 1.2%). CK achieved the highest reduction on F2 from 30.2% to 11.8% and increased the F3 fraction from 28.3% to 52.3%. Other treatment groups also achieved a similar reduction on F2 and increased F3 fraction.



**Figure 3** Speciation of a) As, b) Cr, and c) Cu in sediment before and after S/S treatment of sediment.

#### 4. Conclusions

This study investigated the feasibility of co-valorisation of Fe-bearing ISSA residue and peanut shell via pyrolysis to produce low-cost iron biochar composites, which were used to partially substitute cement during the S/S treatment of As-, Cr-, and Cu-contaminated marine sediments. 20% substitution of cement during the S/S treatment caused significant reductions on the mechanical strength of the S/S products compared with CK. BC group had the most detrimental effect on mechanical strength compared with other treatment groups. All S/S treatment groups observed a significant reduction on the leaching of As and Cu compared with raw sediments. Compared with CK, cement substituted by all the other amendments in this study resulted in similar leaching levels of As and Cu as assessed by TCLP. For Cr, CK, SBC, and BC groups, negligible immobilization effects were showed compared to the raw sediment. Nevertheless, the substitution of cement by RBC, FBC, and FSBC demonstrated a notable S/S efficacy for Cr, which was attributed to the transformation of mobile Cr in contaminated sediment to stable fractions. Overall, this study suggests that the phosphorus recovered ISSA residue rich in iron could be co-pyrolyzed with peanut shell to produce a low carbon and low energy-consumption composite material that could be reused as a partial substitute of cement in S/S of contaminated sediment and demonstrated significantly improved remediation performance for Cr.

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