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以水泥窯協同處理再生重金屬污染土壤生產水泥之研究

Reutilization of Heavy Metal Contaminated Soils for Cement Production by Cement Kiln Co-processing

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本論文係張正欣君(學號R08541104)在國立臺灣大學環境工程學研究所完成之碩士學位論文，於民國110年6月30日承下列考試委員審查通過及口試及格，特此證明

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摘要

水泥窯協同處理(co-processing)利用廢棄物替代部分的製程燃料或水泥原料，可降低生產成本減少環境負荷並處理有害廢棄物。本研究添加兩種重金屬(場址 1 及場址 2)污染土壤，取代原料配比，以 0、3、7.6 和 10 wt.% 製作水泥，分析其工程特性，並利用事業廢棄物毒性特性溶出程序(TCLP)、合成降水溶出程序(SPLP)、EDTA 輔助 TCLP (EDTA-mediated TCLP)溶出程序以及再生粒料溶出程序(RALP)檢測重金屬趨勢。

經由成分分析，污染土壤可替代水泥原料中之黏土。特性分析結果顯示當添加土壤量愈多，礦物相 Ca_3SiO_5 (C_3S)之比例有下降的趨勢，Ca_2SiO_4 (C_2S)反之上升，使凝結時間延長且抗壓強度降低，尤其以添加高濃度之鉻污染土壤更為顯著。TCLP 試驗中，添加量超過 7.6%場址 1 的水泥粉之鉻溶出濃度超出事業廢棄物溶出標準，而添加量 10%的硬固水泥之鉻溶出濃度仍符合溶出標準，添加 10%場址 2 的水泥粉及硬固水泥之鉻溶出量皆符合標準。此外，EDTA 輔助 TCLP 相較於 TCLP 有更高的鉻溶出量。RALP 試驗結果顯示所有水泥皆可做為控制性低強度回填材料(CLSMs)。在本研究之添加比例下，以 3 wt.% 場址 1 及 10 wt.% 場址 2 污染土壤添加製作之水泥，可符合工程特性要求並兼具環境相容性。由經濟分析可知，水泥業者及污染行為人可藉由水泥窯協同處理獲得可觀的經濟效益。重金屬污染之土壤適合以水泥窯協同處理之方式進行循環利用，同時兼顧污染處理並降低傳統水泥生產之環境及經濟成本。

關鍵字:重金屬污染土壤、水泥窯協同處理、環境相容性、經濟分析

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Abstract

Co-processing is considered as an effective way to reduce the cost and environmental footprints for cement production by replacing fuel or raw materials with wastes. In this study, we investigated the influences of co-processing of two heavy metal-contaminated soils (Site 1 and Site 2) in cement kiln on the engineering integrity and heavy metal leachability of cement powders and cement mortars. The replacements of the contaminated soil were set at 0, 3, 7.6, and 10 wt.%. Engineering integrity of the cement products was verified using typical performance tests first, followed by three heavy metal leaching tests, namely Toxicity Characteristic Leaching Procedure (TCLP), EDTA-mediated TCLP and Synthetic Precipitation Leaching Procedure (SPLP). The results showed that in TCLP, only Cr was the concern, in which leachates of cement powders produced by co-processing with > 7.6% site 1 soils exceeded the TCLP Cr limit (5 mg/L), whereas all leachates of cement mortars met the regulations. EDTA-mediated TCLP could potentially release higher Cr concentrations, indicating that cautions were still needed when applying the cement products in harsh environments. It was determined that co-processing of 3 wt.%. site 1 and of 10 wt.%. site 2 soils could satisfy the engineering integrity and TCLP standards. Preliminary economic assessment indicated that using co-processing to treat heavy metal-contaminated soils can bring benefits for both cement industry and soil polluter and could be an attractive alternative for the remediation of heavy metal contaminated soil.

Keywords: heavy metal-contaminated soil, cement kiln, co-processing, environmental compatibility

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Chapter 1 Introduction

1.1 Background

The use of hazardous substances has been increasing with the increasing level of industrialization of human society. Illegal disposal of resulting hazardous wastes has caused pollutions in soil and groundwater, posing a potential risk to human beings and ecosystem (Nagajyoti et al., 2010; Durães et al., 2018). According to Taiwan Environmental Protection Administration (Taiwan EPA), over 95% of the registered illegal dumping sites are contaminated by heavy metals (Taiwan EPA, 2021b).

Heavy metal-contaminated soils can be remediated either by in-situ technologies such as surface capping, electrokinetics, soil flushing, bioremediation, and phytoremediation or by ex-situ treatments such as landfill, soil washing, solidification, and vitrification (Liu et al., 2018). As the necessity of circular economy prevails, recycling of waste resources via cement kiln co-processing has become the focus of recent research for hazardous waste management. Co-processing can use organic wastes as the fuel and inorganic wastes as the raw materials for cement kiln. The high temperature in the kiln can destroy organic pollutants and immobilize toxic compounds, which can be potentially employed for the ex-situ treatments of heavy metal-contaminated soil. The clinkers obtained can then possibly be used for various products used in civil engineering projects. Heavy metals in contaminated soils could

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persist after the high-temperature sintering and remain in clinkers. Evaluation of metal release into the environment, therefore, is required when the produced cement or concrete products are used.

Although the cement industry has embraced cement kiln co-processing for the production of cement, co-processing of heavy metal-contaminated soil is relatively rare. Furthermore, uncertainties associated with the amount of heavy metal-contaminated soils that can be used without compromising the engineering integrity and environmental compatibility of cement products still need to be resolved.

1.2 Research Objectives

The objectives of this study are

1. To investigate the maximum percentages of raw materials that can be replaced by heavy metal-contaminated soils in cement kiln co-processing for Portland Type-I cement production.
2. To evaluate the environmental compatibility of cement products by measuring the heavy metal leaching potentials in different leaching procedures.
3. To conduct an economic analysis to evaluate the benefits received by both cement industry and soil polluters.

Chapter 2 Literature Review

2.1 Heavy metal-contaminated soil

Heavy metals such as Cd, Cr, Cu, Pb, As, Hg, Ni and Zn generally refer to metalloids having a density greater than 5 g/cm^3. They can form different compounds and are persistent in the environment. Some heavy metals are carcinogenic and can be consumed by human beings via food chain when soil heavy metal pollution occurs (Tchounwou et al., 2012; Li et al., 2014). In soil environments, heavy metals exist in different forms including dissolved ions, organic complexes, exchangeable ions adsorbed on soil particles, and co-precipitates as shown in Figure 1 (Tabatabai et al., 2005). Currently in Taiwan, there are 7844 registered illegal dumping sites, in which 7593 sites, accounting 95% of the total registered sites, are contaminated by various heavy metals (Taiwan EPA, 2021b).

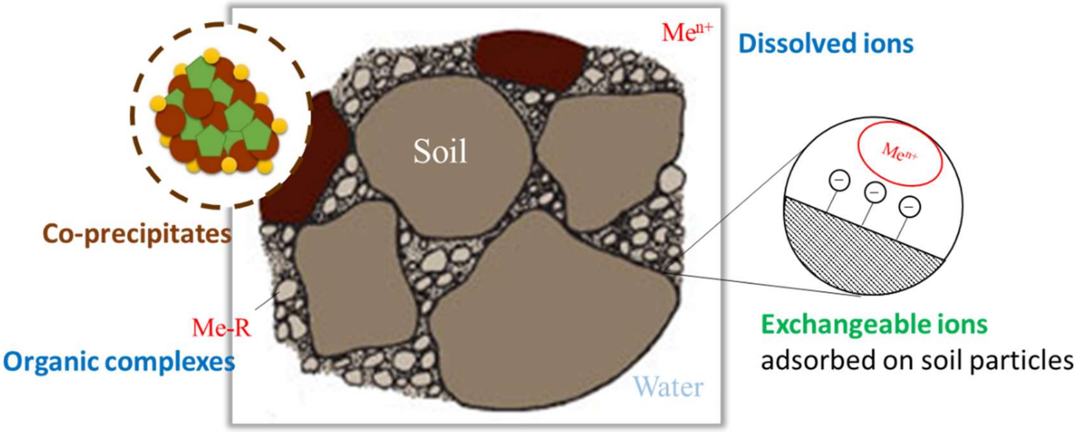

Figure 1. Different forms of heavy metals exist in the soil.

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According to Soil and Groundwater Pollution Remediation Act in Taiwan, heavy metal contaminated soil is determined as S-grade waste and has to be treated. Currently, heavy metal contaminated soils were increasingly treated ex-situ in Taiwan, using technologies such as S/S, landfill, brick kiln co-processing, cement kiln co-processing, and reuse as alternative raw materials of silica in the steel industry. According to the statistics published by the Taiwan EPA, the percentage of treatment capacity shows the following order: cement kiln co-processing (38%) > landfill (35%) > S/S (23%) > reuse as alternative raw materials of silica (4%) (Taiwan EPA, 2021a). Brick kiln co-processing is less popular because the sintering temperature is only around 1000ºC which is ineffective to trap heavy metals. On the other hand, cement kiln co-processing can better fix heavy metals due to the higher temperature employed in the kiln (1400-1600ºC).

The cement produced by cement kiln co-processing is typically used as building materials. Therefore, the leaching of heavy metals from cement needs to be evaluated. It is necessary to consider the rainfall characteristics, geo-environmental background of building, or even the content of metals in the contaminated soils (Taiwan Industry Technology Research Institute, 2016).

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2.2 Co-processing of cement industry

Portland cement is a complex solid solution composing of CaO, SiO_2, Al_2O_3, Fe_2O_3, MgO, and trace elements. Through solid-liquid phase reactions at high temperature in the rotary kiln, the raw materials are transformed to clinker, and then mixed with gypsum to form cement. When the cement reacts with water, the hydration process will occur immediately and hydrated products will be generated (Taylor, 1997).

The major mineral phases in the clinkers include alite (C_3S), belite (C_2S), tricalcium aluminate (C_3A), and ferrite (C_4AF). The proportions of mineral phases can be calculated by Bogue's calculation (Equations (1)-(4)) (Bogue, 1929).

$$C_3S\ (\%) = 4.071(CaO) - 7.602(SiO_2) - 6.718(Al_2O_3) - 1.430\ (Fe_2O_3) \tag{1}$$

$$C_2S\ (\%) = 2.867(SiO_2) - 0.754(C_3S) \tag{2}$$

$$C_3A\ (\%) = 2.605(Al_2O_3) - 1.692(Fe_2O_3) \tag{3}$$

$$C_4AF\ (\%) = 3.043(Fe_2O_3) \tag{4}$$

Based on the proportions of mineral phases in the clinker, the engineering characteristics such as hydration rate, setting time, compressive strength, and corrosion resistance can be estimated. In general, C_3S and C_2S control the compressive strength in early and end ages, while C_3A and C_4AF affect the hydration rate and setting time (Shetty, 2008).

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In the hydration reactions, C_3S and C_2S react with water to form calcium silicate hydrate gel (C-S-H gel) and lime ($Ca(OH)_2$) (Equations (5)-(6)). C-S-H gel is the main hydration product in Portland cement, and is primarily responsible for the strength in cement-based materials. C_3A and C_4AF become needle-like ettringite, a prototype of Aft (tricalcium aluminate or ferrite tri-substituted hydrates) (Equations (7)-(8)) (Allen et al., 2007).

$$2C_3S + 7H \rightarrow C_3S_2H_4 \text{ (C-S-H gel)} + 3CH \tag{5}$$

$$2C_2S + 5H \rightarrow C_3S_2H_4 \text{ (C-S-H gel)} + 1CH \tag{6}$$

$$1C_3A+3C\bar{s}H_2+26H \rightarrow C_3A\cdot 3C\bar{s}\cdot H_{32} \text{ (ettringite)} \tag{7}$$

$$3C_4AF+12C\bar{s}H_2+110H \rightarrow 4[C_6(A,F)\bar{s}_3H_{32}]+2(A,F)H_3 \text{ (AFt)} \tag{8}$$

C-CaO; S-SiO_2; A-Al_2O_3; F-Fe_2O_3; H-H_2O; $\bar{s}$-S

Due to the shortage of natural minerals, there is a need for the cement industry to find a new technique to reduce consumption of natural resources (Lamas et al., 2013). Therefore, cement kiln co-processing, which can not only use solid waste as a substitute for raw materials to reduce the demand of natural minerals but also use high calorific wastes as fuels to minimize consumption of non-renewable fossil fuels, attracts international interests in recent years (Aranda-Usón et al., 2013). The solid wastes that have been used in the co-processing include contaminated soil (Yang et al., 2010; Yang et al., 2012; Yan et al., 2018), metal slag (Alp et al., 2008; Wu et al., 2018), sewage sludge (Chen et al., 2010; Shen et al., 2017), and municipal solid waste (MSW) (Shih et al., 2003; Krammart and Tangtermsirikul, 2004; Pan et al., 2008; Lam et al., 2011). This technique transforms wastes into the resources, solving the problems of overloaded landfills (Choy et al., 2004). Ideally, co-processing is capable of enveloping hazardous substances by cement products to reduce their mobilities because of the high temperature, long residence time, and high level of turbulence employed in the rotary kiln.

Table 1 displays the current status of co-processing in different countries or regions. For example, in Japan, the solid wastes used as raw materials increased from 23% in 1990 to 47% in 2013 and maintained at a constant level in recent years (Japan Cement Association, 2020). In Taiwan, only a few cases use inorganic sludge, slag, or bottom ash as raw materials to produce cement products (Taiwan Ministry of Economic Affairs, 2017).

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Table 1. The status of international countries that uses the wastes for cement production by co-processing.

Country	Status	Reference
EU	The European Union cement industry uses pozzolan, slag, foundry sand, end-of-life tire, and agricultural wastes as alternative fuels for cement production and has substituted 43% fossil fuels for supplying the thermal energy to the clinker making process.	(ECOFYS, 2019; LafargeHolcim, 2021; Titan Cement, 2021)
Japan	The ratio of alternative thermal energy used in the burning process in Japan had risen from 5.4% in 2000 to 18.9% in 2018, and the solid wastes used as raw materials increased from 23% in 1990 to 47% in 2013 and maintained at a constant level in recent years.	(Japan Cement Association, 2020)
USA	In America and Mexico, nutshell, industrial waste, and plastics were used as alternative fuels to substitute 10.9% of fossil fuels in 2012.	(Ali Hasanbeigi, 2012)
New Zealand	New Zealand has substituted 83% of fossil fuels in cement production with waste oil and solvent, and has almost replaced the use of coal.	(Concrete NZ, 2020)

Cement produced by co-processing must meet the engineering requirements including chemical composition, chloride ion content, setting time, compressive strength, etc. In addition, cement products must be environmentally compatible. In Australia, China, Switzerland and EU, the allowable contaminant limits for heavy metals, sulfur, chlorine, and persistent organic pollutants (POPs) in wastes feeding to the cement kiln have been developed. In Sweden and China, upper limits of total content of heavy metals in clinkers and cement products have been set. In Taiwan, the

Ministry of Economic Affairs regulates the types and amounts of wastes that can be reused in cement industry in order to meet the engineering requirements of final products. Specifically for the cement products, only China GB/T 30810 and the United Kingdom BS 6920 limit the leaching of heavy metals from cement products to meet drinking water standards.

2.3 Mechanism of metal immobilization by co-processing

The immobilization of heavy metals in cement kiln co-processing involves two processes. One is calcination (Equations (9)), a thermal treatment to make heavy metals coalesce and fixed into a solid or porous mass via high temperature. The other is hydration (Equations (10)), in which heavy metals can be trapped in the hydrated compounds during the formation of mortar or concrete (Zhang et al., 2009).

Calcination process: $\mathrm{A + B(M) \rightarrow AB(M)}$ (9)

Hydration process: $\mathrm{AB(M) + H_2O \rightarrow H(M)OH_2}$ (10)

where A represents raw material for clinker production, B(M) represents waste containing heavy metals, AB(M) represents the clinker containing heavy metals, and $\mathrm{H(M)OH_2}$ represents hydrated compound containing heavy metals.

The mechanisms involved in the two heavy metal immobilization include sintering, precipitation, adsorption, inclusion, and substitution (Figure 2). In the calcination process, the high temperature of sintering reconfigures heavy metals to replace other elements with a similar size and charge to form a solid solution (Liao et al., 2016; Guo et al., 2017). For example, Cr^{3+} (0.62 Å) can replace Al^{3+} (0.54 Å), Pb^{2+} (1.19 Å) or Cd^{2+} (1.09 Å) can replace Ca^{2+}(1.00 Å), and CrO_4^{2-} (0.44 Å) can replace SiO_4^{4-} (0.40 Å). Heavy metals can also form a new crystal phase. For instance, minerals with spinel structures such as $ZnAl_2O_4$ and $NiAl_2O_4$ can accommodate heavy metal in available cation sites. It has been indicated that spinel structure can resist an acidic environment and reduce the leachability of heavy metals (Lu and Shih, 2015; Su et al., 2015; Tang and Shih, 2015).

In the hydration process, the formation of C-S-H gel and ettringite is accompanied by the generation of calcium hydroxide (Equations (5)-(6)), which causes a high alkaline environment to allow heavy metal precipitating as hydroxide compounds or other salts. Metal ions may adsorb on the surfaces of cement particle and hydration products or even be encapsulated by these products. C-S-H gel can fix heavy metals by providing a chain of silicate tetrahedra for bonding or accommodating heavy metals into the interlayer space. Heavy metals with similar size and charge can also replace other elements in C-S-H gel and ettringite (Gougar et al., 1996; Hong and Glasser, 2002; Guo et al., 2017). It has been found that the adsorption of heavy metals on the surfaces of C-S-H gel is the first step prior to their incorporation into the structure. Similarly, Ca^{2+} and Al^{3+} in the channels of ettringite can be replaced by divalent and trivalent metals with similar radius, respectively. Previous research indicates that oxyanion-substituted monosulfate (Afm) possesses a better immobilization effect on oxyanions than the oxyanion-substituted ettringite (Chrysochoou and Dermatas, 2006).

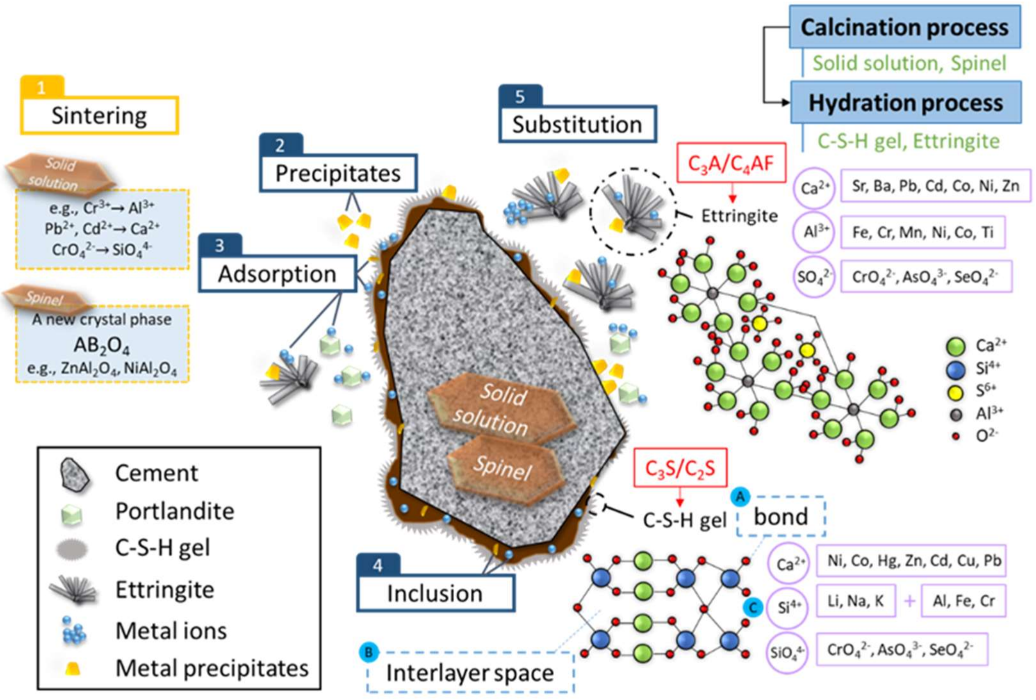

Figure 2. The scheme of metal immobilization mechanism by co-processing.

2.4 Assessment of environmental compatibility

The environmental compatibility of cement products produced from co-processing needs to be ensured before their applications. Table 2 summarizes the leaching methods that have been used to assess the environmental compatibility of materials or wastes. Toxicity Characteristic Leaching Procedure (TCLP) developed by the United States Environmental Protection Agency (USEPA) is the most commonly used protocols (US EPA, 1992). In the test, the waste is mixed with acetic acid solution for 18 h to simulate the leachability of hazardous elements in landfill conditions. Nevertheless, it has been indicated that the TCLP protocol could underestimate heavy metal leachability of co-processing cement products or other alkaline materials because the acetate solution employed in the test could not provide sufficient buffer capacity to maintain the acidic pH (Halim et al., 2004b; Shi and Kan, 2009; Lu et al., 2019). EDTA-mediated TCLP, which could leach comparable levels of metals (especially copper and lead) to those in Multi-final pH Leaching Test (US EPA, 2012) with a final pH of 4-5, has been developed to assess the environmental compatibility of alkaline materials (Lu et al., 2019). Another leaching methods using different leaching solutions or apparatuses have also been developed to simulate the heavy metal leachability under different circumstances. Synthetic Precipitation Leaching Procedure (SPLP) which immerses the waste into sulfuric acid/nitric acid solution before agitation for 18 h, is used to simulate

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the heavy metal mobility in rainwater (US EPA, 1994). Recycled Aggregates Leaching Procedure (RALP), implemented at the beginning of 2021 in Taiwan, is specifically used to simulate the leaching of heavy metals when recycled aggregates produced from incineration plants are reused (Taiwan EPA, 2019). In the test, the aggregates are immersed in deionized water stirring for 6 h. Table 3 shows the regulatory limits in Taiwan based on TCLP and RALP, respectively.

Table 2. The comparison of leaching methods mentioned in this study.

Method name	TCLP	SPLP	EDTA-mediated TCLP	RALP
Appropriate scenarios	Waste in landfill leachate	Waste in rainwater	Waste in a durably acidic environment	Classification of recycled aggregates
Extraction fluid	pH=2.88 or 4.93 $CH_3COOH_{(aq)}$	pH=4.20 or 5.20 H_2SO_4/HNO_3	pH=2.88 or 4.93 $CH_3COOH_{(aq)}$ with addition of 7 mM EDTA	pH=5.8~6.3 deionized water
Liquid/Solid ratio (L/S)	20			10
Operating manner	Tumbling for 18 hours at 30 ± 2 rpm			Stirring for 6 hours at 200 rpm
Reference	EPA Method 1311	EPA Method 1312	Lu et al., 2019	NIEA R222.10C

Table 3. The comparison of regulatory limits based on TCLP and RALP.

TCLP

Metal	Hg	Cd	Se	Cr^{6+}	Cr	Pb	As	Ag	Cu	Ba
Level (mg/L)	0.2	1.0	1.0	2.5	5.0	5.0	5.0	5.0	15.0	100.0

RALP

Metal	Pb	Cd	Cr	Cu	As	Hg	Ni	Zn
Primary level (mg/L)	0.01	0.005	0.05	1.0	0.05	0.002	0.1	5.0
Secondary level (mg/L)	0.1	0.05	0.5	10.0	0.5	0.02	1.0	50.0

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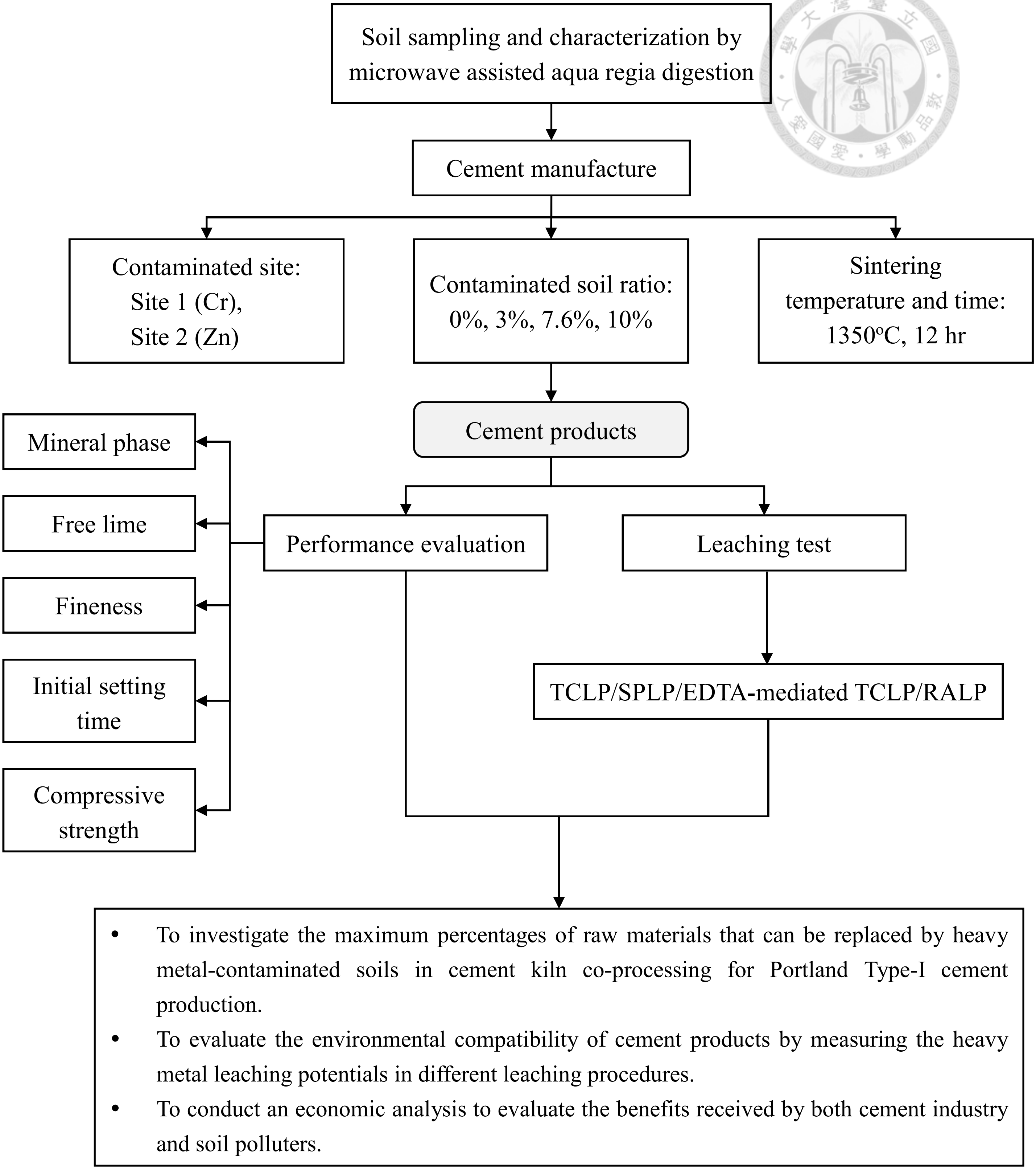
Chapter 3 Materials and Methods

3.1 Experimental design

The overall experimental design of this study is shown in Figure 3. The main objectives of this study are to: 1. investigate the maximum percentages of raw materials that can be replaced by heavy metal-contaminated soils in cement kiln co-processing for Portland Type-I cement production, 2. evaluate the environmental compatibility of cement products by measuring the heavy metal leaching potentials using different leaching procedures, and 3. conduct an economic analysis to evaluate the benefits received by both cement industry and soil polluters.. Two heavy metal-contaminated soils having distinct heavy metals obtained from two registered contaminated sites were used in this study. Microwave assisted aqua regia digestion was used to determine the total metal contents of two contaminated soils. Clinkers were produced from raw materials using a muffle furnace at 1350°C for 12 h. Performance evaluations were then carried out to ensure that cement products manufactured meet ASTM C150/C150M-20 standard specifications of Portland Type-I cement (ASTM, 2020). Four leaching procedures including TCLP, SPLP, EDTA-mediated TCLP and RALP were used to evaluate the environmental compatibility of cement powders and cement mortars with an incubation period of 28 days. A maximum of 28-day incubation was employed to achieve the maximum strength of cement analogous to real situations.



- To investigate the maximum percentages of raw materials that can be replaced by heavy metal-contaminated soils in cement kiln co-processing for Portland Type-I cement production.
- To evaluate the environmental compatibility of cement products by measuring the heavy metal leaching potentials in different leaching procedures.
- To conduct an economic analysis to evaluate the benefits received by both cement industry and soil polluters.

Figure 3. Flowchart of overall experiments.

3.2 Materials and chemicals

Two contaminated soils obtained from registered contaminated sites in New Taipei City and Taoyuan City (hereinafter called site 1 and site 2) were used in this study (Figure 4). The moisture contents of the two soils were 4.8% and 5.5%, respectively.

Limestone, clay, silica sand, and iron slag are conventional raw materials for cement production. Kaolinite was used to elevate the amount of Al_2O_3 in the cement raw mixture due to the amount of aluminum oxide in clay below the general value. After sintering, gypsum was added into the clinker (Figure 5a) to become cement powder (Figure 5b). Standard sand was used to mix with cement to form cement mortar (Figure 5c).

Ethylene glycol and phenolphthalein indicator (Merck, Germany) were used to detect the content of free lime in the cement. HCl (Merck, Germany) was used to determine the content of free lime, to prepare aqua regia, and to adjust the pH of solutions in RALP. HNO_3 (J.T. Baker) was used to prepare aqua regia for microwave assisted aqua regia digestion and used as the leaching agent in SPLP. H_2SO_4 (Honeywell Fluka, UK) was used as the leaching agent in SPLP. Acetic acid (Merck, Germany) was used as the leaching agent in TCLP and EDTA-mediated TCLP. Disodium EDTA (Merck, Germany) was used in the EDTA-mediated TCLP. NaOH (Honeywell Fluka,

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UK) was used to adjust the pH of solutions in RALP. All experimental solutions were prepared using deionized water obtained from a PURelAB classic system (ELGA, UK).

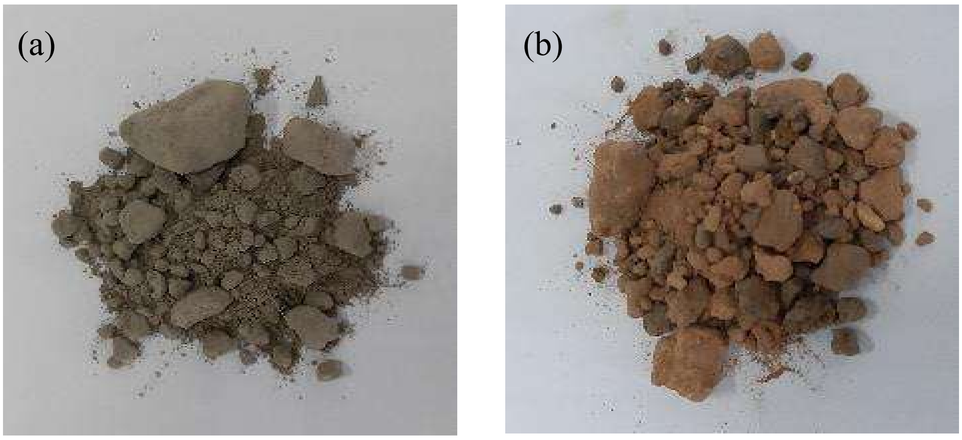

Figure 4. Pictures of (a) site 1 soil in New Taipei City, (b) site 2 soil in Taoyuan City.

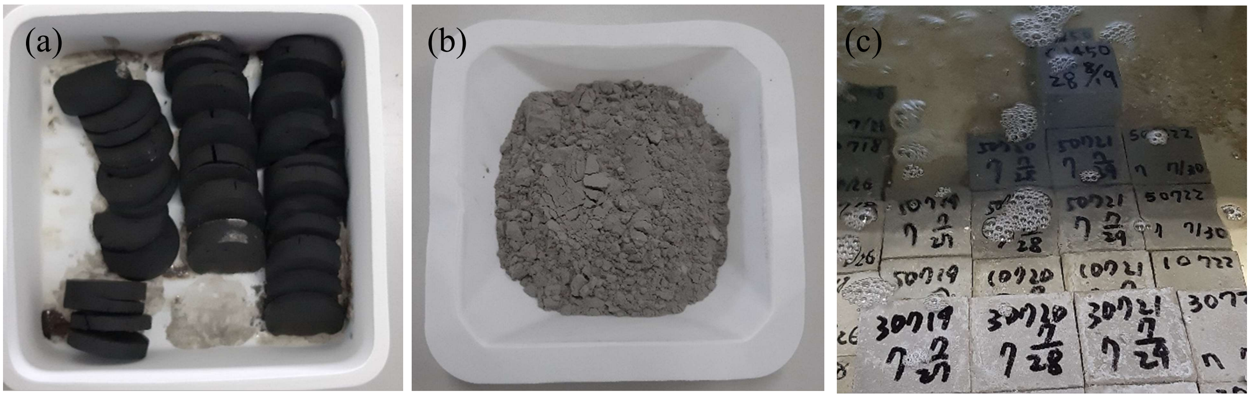

Figure 5. Pictures of (a) the clinker after sintering, (b) cement powder, and (c) cement mortar in cured period.

3.3 Microwave assisted aqua regia digestion

Microwave assisted aqua regia digestion was used to determine the heavy metal content of two contaminated soils. Approximately 0.5 g of homogeneous soil sample was digested with 6 mL HCl and 6 mL HNO_3 in a polytetrafluoroethylene (PTFE) vessel. The temperature rose to 175°C in 20 min and remained for 10 min. After cooling down to the ambient temperature, the solution was diluted with deionized water to a total volume of 50 mL and filtered through a 0.45 μm Nylon filter. The metal concentration in the solution was detected by ICP/OES.

3.4 Cement manufacture

Two contaminated soils and all raw materials were dried at 105°C for 24 h and grounded to ASTM 200 mesh size (<0.074 mm) with a mill. After pretreatment, 20.0 g of the raw material was heated in the muffle furnace at 1000°C to measure the loss on ignition (LOI) which represents the actual material lost during smelting or refining in a furnace or smelter. Then, the chemical compositions of these raw materials were analyzed using the lithium borate fusion method. 0.2 g of the burned material was put in a platinum crucible and mixed with 0.3 g boric acid and 1.0 g lithium carbonate. The mixture was then placed in the muffle furnace at 1500°C to form a glassy crystal as shown in Figure 6. The glassy crystal was immersed in 110 mL nitric acid solution

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(HNO_3: H_2O=1:10 (v/v)) and oscillated to ensure complete dissolution. The elements in the solution were measured by ICP/OES.

Figure 6. The glassy crystal formed using lithium borate fusion method.

The moduli of Portland Type-I cement clinkers was controlled by three parameters, i.e., the hydraulic modulus (between 1.7 and 2.3), the silica modulus (between 1.9 and 3.2), and the alumina modulus (between 1.5 and 2.5). The equations for determining the three parameters are shown in Equations (11)-(13):

$$\text{Hydraulic modulus (HM)} = CaO/(SiO_2+Al_2O_3+Fe_2O_3) \tag{11}$$

$$\text{Silica modulus (SM)} = SiO_2/(Al_2O_3+Fe_2O_3) \tag{12}$$

$$\text{Iron modulus (IM)} = Al_2O_3/Fe_2O_3 \tag{13}$$

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In these experiments, HM, SM, and IM of cement clinkers were maintained at 2.10 ±0.10, 2.50±0.10, and 1.45±0.10, respectively. According to preliminary experiments, 10% contaminated soil was the maximum amount of substitution for clay in raw material or the three parameters cannot reach the scope of set values. Thus, the amount of contaminated soil in the raw mixture was set at 0%, 3%, 7.6%, and 10%, respectively. The formulas of raw materials mixtures used to make different cement samples are shown in Table 4. The raw mixture was compressed to form a cylindrical sample (30 mm in diameter×15 mm in height) with a pressure of 20 MPa and collected in an alumina crucible. The alumina crucible was put into the muffle furnace at room temperature, heated to the predetermined temperature (i.e., 1350ºC) at the rate of 10ºC/min, and maintained for 12 h to simulate a real situation in the rotary cement kiln. The clinker was then taken out from the muffle furnace after cooling to room temperature. All cylindrical clinkers were ground to a fineness of 360 m^2/kg for further analysis and experiments.

Table 4. Formulas of raw materials mixtures (%).

Raw materials	Control	Site 1			Site 2		
		S1:3%	S1:7.6%	S1:10%	S2:3%	S2:7.6%	S2:10%
Limestone	76.1	76.2	78.1	79.0	76.8	77.6	78.0
Clay	7.60	4.60	0.00	0.00	4.60	0.00	0.00
Silica sand	10.4	10.2	9.40	7.00	9.50	8.60	7.10
Iron slag	4.20	4.10	3.90	3.40	4.00	3.60	2.90
Kaolinite	1.70	1.90	1.00	0.60	2.10	2.60	2.00
Site 1 soil	-	3.00	7.60	10.0	-	-	-
Site 2 soil	-	-	-	-	3.00	7.60	10.0
Sum	100	100	100	100	100	100	100

The produced clinker was mixed with 5% gypsum to form cement powder. The cement mortar was prepared by mixing cement powder with deionized water at a water-to-cement (W/C) weight ratio of 0.484 and sand (ASTM 30-70 mesh) at a sand-to-cement weight ratio of 2.75. The mortar was then filled in 50×50×50 mm molds and kept in the thermostat/humidistat incubator at 20±2ºC and relative humidity at 95% for 24 h before being removed from the molds.

3.5 Performance evaluation

Chemical compositions and free lime of cement were determined first followed by the performance evaluation using several tests, including fineness, initial setting time and compressive strength.

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The chemical compositions of the clinker were determined using XRF and used to estimate the major mineral phases in clinkers using Bogue’s calculations (Equations (1)~(4)). The mineral phases were then used to calculate HM, SM, IM. Free lime (f-CaO) was detected by ethylene glycol titration method (Swenson and Thorvaldson, 1951). Fineness was determined using the air permeability apparatus (Figure 7a). Initial setting time was measured using the Vicat apparatus (Figure 7b), in which a 1 mm diameter needle was inserted in the cement ball and the height was recorded every 15 min until the penetration was 25 mm or below. Cuboid cement mortars with incubation periods of 7 d and 28 d were placed into the compression tester machine (Figure 7c) to determine the maximum compressive strength of respective incubation period. The determined clinker performance parameters and the corresponding ASTM standard specifications of Portland Type-I cement are shown in Table 5. In addition, the presence and proportion of the major mineral phases were quantified by Quantitative X-ray Diffraction (QXRD) (ASTM, 2018d). Surface microanalysis and element composition were investigated by field-emission scanning electron microscope coupled with energy dispersive X-ray analysis (FESEM-EDS). The autoclave expansion test was not conducted in this study due to the limited cement samples.

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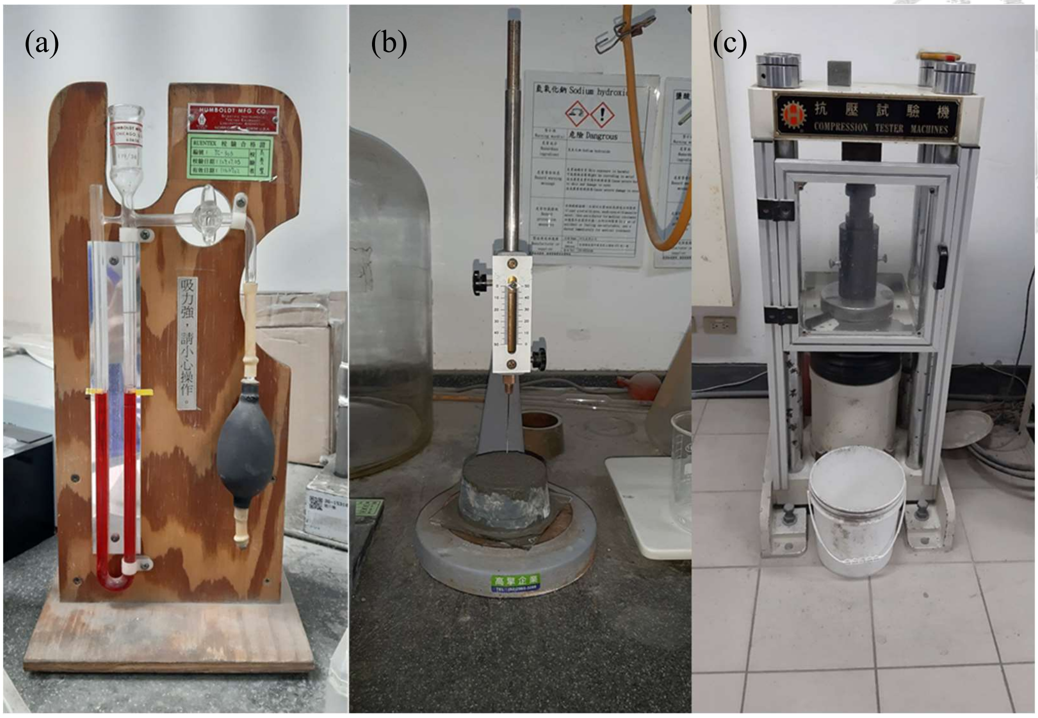

Figure 7. Pictures of (a) air permeability apparatus, (b) Vicat apparatus, and (c) compression tester machine.

Table 5. The values of parameters of clinker and Portland Type-I cement in ASTM cementitious standard specifications (ASTM C150/C150M-20).

Parameters	Value	Unit	Reference
Free lime (f-CaO)	<1.2	%	(ASTM, 2018b)
Fineness	>260	m^2/kg	(ASTM, 2011)
Initial setting time	45-375	min	(ASTM, 2017)
Autoclave expansion	0.8	%	(ASTM, 2018c)
Compressive strength			
7 days	>19	MPa	(ASTM, 2018a)
28 days	>28		

3.6 Leaching test

For cement products (i.e., cement powder and cement mortar), the leachability of heavy metal was determined to assess the mobility of heavy metals. Four leaching tests were employed in this study including TCLP, SPLP, EDTA-mediated TCLP, and RALP. The TCLP was conducted following the USEPA Method 1311 (US EPA, 1992), which is the mandated leaching test for hazardous waste characterization in the US. The samples were crushed and sieved with a 9.5 mm sieve to remove oversize particles. Acetic acid (pH 2.88 or 4.92) was used as the leaching solution with a liquid/solid ratio (L/S) of 20:1. The experimental setup was shown in Figure 8. The extraction was performed using capped polypropylene (PP) bottles loaded on a rotary tumbler at 30±2 rpm for 18±2 hours. After the extraction, the final pH of the leachate was measured and the leachate was filtered through a 0.7 μm pore size glass microfiber filter. The filtrate was collected and mixed with 4 ml nitric acid and 1 ml hydrochloric acid in the PTFE vessel. The microwave digestion was carried out to dissolve metal particles into a solution. After the digestion, the solution was filtered through a 0.45 μm PTFE filter prior to ICP/OES measurement. The SPLP (USEPA Method 1312) (US EPA, 1994) simulates exposure of waste to acid rain in the environment. Sulfuric acid and nitric acid mixed at a 60/40 wt.% mixture in deionized water (pH 4.20 or 5.20) was used as the leaching solution with a L/S of 20:1. The subsequent steps of SPLP are the same as those of TCLP.

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EDTA-mediated TCLP follows identical TCLP procedures but with the addition of EDTA. It has been proposed as a good alternative to simulate the leaching of heavy metals from alkaline wastes under continuous acidic environment. It was found that 7 mM EDTA could leach similar levels of heavy metals as those determined from (Lu et al.) at pH 4-5. 7 mM EDTA was employed in the leaching test. RALP used deionized water as the extraction fluid at a L/S ratio of 10. The initial pH value of the solution was adjusted to 6.00±0.10. In this method, the cement mortar was placed in a plastic container (Figure 9) and stirred for 6 h at 200 rpm. All leaching experiments were carried out in duplicate.

Figure 8. The experimental setup of TCLP, SPLP, and EDTA-mediated TCLP.

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Figure 9. The experimental setup of RALP.

3.7 Analytical method

The chemical composition of clinker was determined using the X-ray fluorescence spectrometer (XRF, PANalytical B.V. Axios Cement). The major mineral phases in each clinker were determined using the Quantitative X-ray diffraction (QXRD, Bruker D2 PHASER). The crystalline phases were identified by referencing the International Center for Diffraction Data database (JCPDS-ICDD). The surface morphology of formed minerals was analyzed using the field-emission scanning electron microscope coupled with energy dispersive X-ray analysis (FESEM-EDS) (JSM-7600F, JEOL). A microwave digestion system (Milestone Srl ETHOS EASY) was used to digest

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contaminated soil samples. The metal concentrations were measured using the inductive coupled plasma optical emission spectrometry (ICP/OES, Agilent 700 series). The method detection limits (MDL) of target metals detected by ICP/OES are shown in Table 6. The pH value in the solution was measured using a calibrated pH meter (Suntex, SP-2100).

Table 6. Method detection limits (MDL) in ICP/OES measurement.

Metal	Ag	As	Ba	Cd	Cu	Cr
MDL (mg/L)	0.015	0.023	0.011	0.017	0.021	0.020
Metal	Hg	Mn	Ni	Pb	Se	Zn
MDL (mg/L)	0.028	0.016	0.015	0.036	0.038	0.017

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Chapter 4 Results and discussion

4.1 Characterization of heavy metal-contaminated soils

The XRD diffractograms of the two contaminated soils are shown in Figure 10. The mineral composition of site 1 soil was more complex than that of site 2 soil. The main composition of the two soils was quartz, which possessed a major peaks at 2θ around 21° and minor peaks at 36 to 60°. This result indicated that the two contaminated soils could be employed as a substitute to replace clay for cement production.

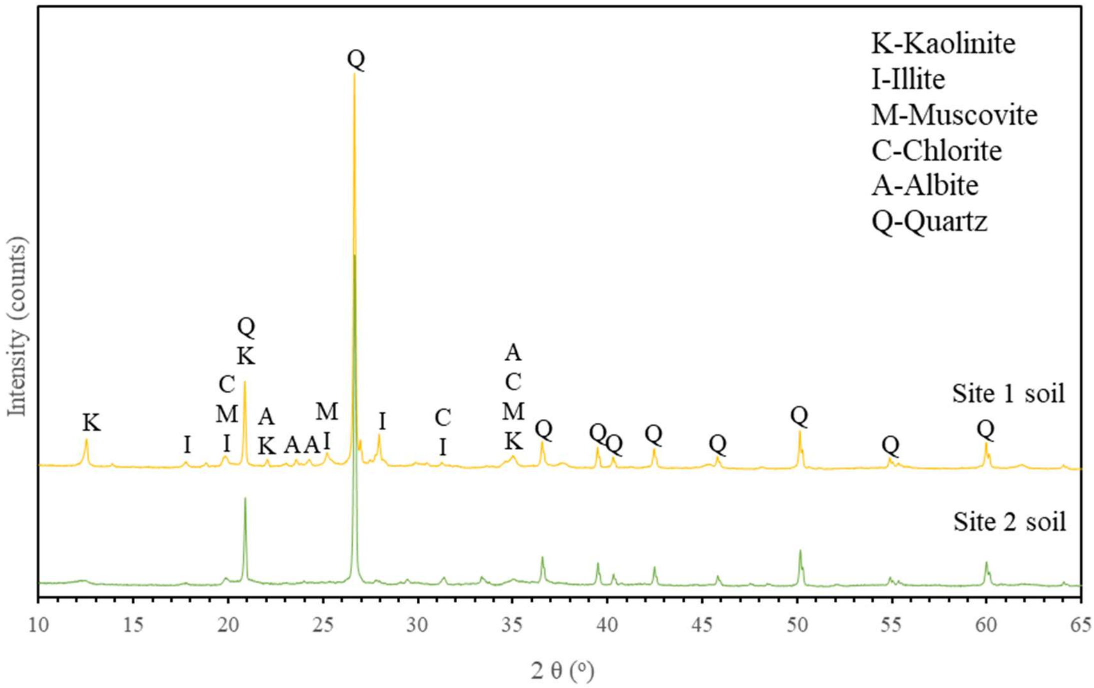

Figure 10. XRD pattern for two heavy metal-contaminated soils

The levels of heavy metals in these two soils are shown in Table 7, along with the levels reported by the Taiwan EPA. The measured levels indicated that site 1 soil contained Cr, Cu, Mn and Zn, in which the Cr level was about 30 times higher than the regulatory limit. Site 2 soil contained Cr, Cu, Mn and Zn, Pb, and Ba, in which Cr and Zn were higher than the regulated levels. Although the soil also contained high levels of Mn and Ba, they are not currently regulated by Taiwan EPA (Taiwan EPA, 2011). In general, the levels reported by Taiwan EPA were much higher than those determined in this study because the Taiwan EPA levels were the maximum concentrations detected in the contaminated sites. The soil samples used in this study were obtained by random sampling and the levels of heavy metals could be affected by the sampling location and depth.

Table 7. The heavy metal content of soil samples in two sites (mg/kg-soil).

Site 1						
Element	Cr	Cu	Mn	Zn		
This study	7327±675	264±0.89	291±36	443±95		
Taiwan EPA	14300	4050	-	2130		
Site 2						
Element	Cr	Cu	Mn	Zn	Pb	Ba
This study	262±20	200±10	5043±342	3370±310	447±11	612±20
Taiwan EPA	786	670	-	51500	5600	-
Regulatory limit	250	400	-	2000	2000	-

Figure 11 showed the heavy metal leaching concentrations of site 1 soil using TCLP, SPLP and EDTA-mediated TCLP. It was found that EDTA-mediated TCLP yielded the highest levels among the three procedures. The Cr concentration obtained using TCLP was higher than the regulated level (5 mg/L). To be noted, the Cr concentration obtained using EDTA-mediated TCLP was 21.4 mg/L. Cu was not detected using TCLP, but was observed in the EDTA-mediated TCLP. Mn and Zn were also detected using EDTA-mediated TCLP, but they were not regulated.

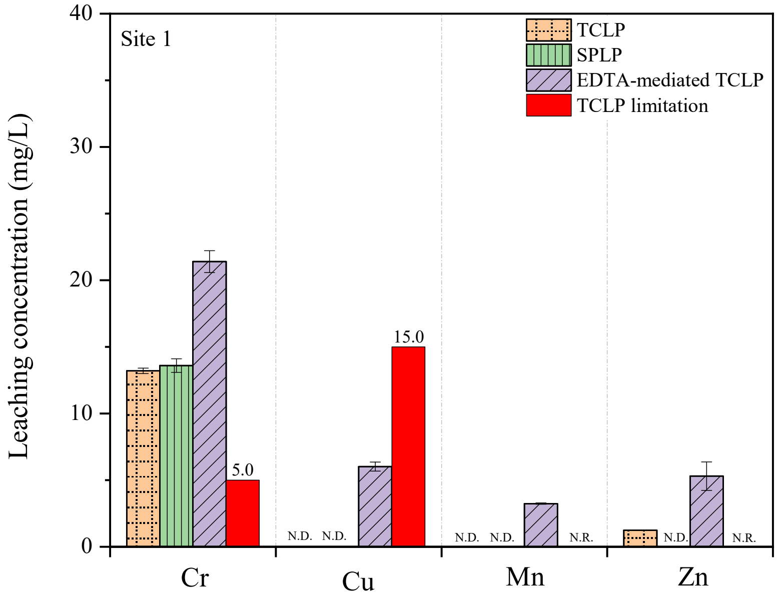

Figure 11. The leaching concentrations of heavy metals in site 1 soil under three leaching procedures. N.D. represented not detected and N.R. represented not regulated and the error bar represented the difference between the duplicate.

The heavy metal leaching concentrations of site 2 soil are shown in Figure 12. Similarly, EDTA-mediated TCLP yielded the highest metal concentrations among the three procedures. Due to the excessive content of Zn in site 2 soil, it was found in all three procedures. Mn could only be observed using TCLP and EDTA-mediated TCLP. Pb was only found using EDTA-mediated TCLP. The results indicated that different metals have different mobilities in the simulated conditions, implying that using total metal content (Table 7) to evaluate the environmental hazards of contaminated soils could not provide a sound picture of their associated risks (Yang et al., 2010).

The final leachate pH values in the three leaching procedures are shown in Table 8. TCLP and EDTA-mediated TCLP yielded a final pH of about 5.0 and lower than that using SPLP (6.0-7.0). In general, metal leaching concentrations decreased in the following order: EDTA-mediated TCLP>TCLP>SPLP, reflecting that facts that the mobility of metal is higher at a lower pH and chelation based on the considerations of solubility and complexation. EDTA-mediated TCLP led to the highest leaching concentration, which could be considered as a stricter method.

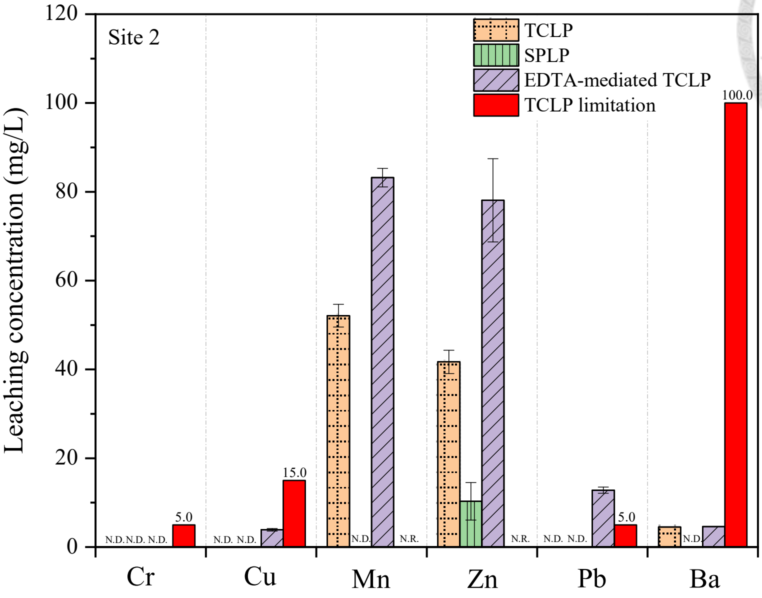

Figure 12. The leaching concentrations of heavy metals in site 2 soil under three leaching procedures. N.D. represented not detected and N.R. represented not regulated and the error bar represented the difference between the duplicate.

Table 8. The final pH of leaching solutions in the end of leaching procedures.

Leaching procedure	Final pH	
	Site 1	Site 2
TCLP	5.1	5.0
SPLP	6.3	7.0
EDTA-mediated TCLP	4.7	4.8

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4.2 Characterization of raw materials and cement products

In the cement industry, it is required to characterize the chemical compositions of raw materials before cement production using the lithium borate fusion method. The results for the raw materials employed in this study are shown in Table 9, in which those of heavy metal-contaminated soils from site 1 and site 2 are also shown. It was found that the compositions of both soils were similar to that of clay. Hence, they can be used to replace clay for cement production. The main substituted compounds were SiO_2 and Al_2O_3.

Table 9. The chemical compositions of raw materials and two contaminated soils by lithium borate fusion method.

Raw materials	LOI[a]	SiO_2	Al_2O_3	Na_2O	K_2O	MgO	CaO	Fe_2O_3	Zn	Cr	Mn	Pb	Cu
Limestone	37.1	0.02	0.28	0.09	0.38	2.57	59.2	0.29	0.00	0.00	0.00	0.00	0.00
Clay	15.2	42.2	9.70	0.31	1.86	1.76	24.9	3.47	0.00	0.00	0.00	0.00	0.00
Silica sand	3.21	80.4	7.58	0.18	2.27	0.59	2.72	2.55	0.00	0.04	0.00	0.00	0.00
Iron slag	-4.81	23.5	9.56	0.32	0.99	2.87	17.8	48.0	0.00	0.00	0.00	0.00	1.15
Kaolinite	14.0	29.4	50.3	0.00	0.30	0.21	4.12	0.54	0.00	0.00	0.00	0.00	0.00
Site 1 soil	5.65	45.0	9.14	0.33	1.84	1.26	31.4	3.76	0.03	0.96	0.03	0.00	0.03
Site 2 soil	5.96	58.0	10.3	0.11	1.24	2.92	11.2	8.38	0.28	0.16	0.67	0.04	0.02

[a] LOI: Loss on ignition at 1000°C. The negative value of iron slag was due to its formation under a reducing atmosphere that contained sulfide.

After sintering at 1350ºC for 12 h, seven cement clinkers with 0%, 3%, 7.6% and 10% of heavy metal-contaminated soils were produced (Figure 5a). The clinker made with 0% contaminated soil is referred as the control in this study. The chemical compositions and physical performance of the clinkers are shown in Table 10. The SM, HM and IM (Equations (11)-(13)) of each clinker were controlled at pre-determined values (SM=2.10, HM=2.50 and IM=1.45). The free lime contents of the clinkers were between 0.2 and 0.7%, which met the ASTM cementitious standard specifications (<1.2%). The fineness was maintained at 360 m^2/kg.

The mineral species of the clinkers determined using XRF indicated that the proportions of C_3S ranged from 45% to 65% and C_2S ranged from 15% to 30%. In control, C_3S content was the highest and C_2S content was the lowest. For clinkers made with both contaminated soils, the proportions of C_3S decreased with the increasing percentage of soil added, whereas C_2S showed the opposite trend. This resulted from the decomposition of C_3S and generation of C_2S and calcium oxide by heavy metals present in the added contaminated soils (Stephan et al., 1999; Wu et al., 2011). Chen et al. (2009) indicated that Zn and Cr had a positive influence on C_2S formation, while Cu had a negative influence. Moreover, different heavy metals possess different influences on the solid solution of cement due to the different bonding abilities of metals to the crystalline phases. It was found that Cr in soils collected from site 1 had more adverse effects on

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the reduction of C_3S, which plays an important in the formation of cement, than Pb and Zn in soils collected from site 2. Cr is stabilized by incorporating into C_2S (Chen et al., 2009). Zn can be trapped by C_3A (Stephan et al., 1999). The proportions of C_3A and C_4AF were almost identical for all clinkers, indicating that the formation of these phases was unaffected by the soils added.

The results for the initial setting time of cement were between 255 and 330 min, which met ASTM cementitious standard specifications. The initial setting time was prolonged with the addition of contaminated soils because C_3S had a faster hydration rate than C_2S (Clavier et al., 2019).

Most research indicated that lower W/C produce stronger Portland cement, and tended to set a maximum ratio between 0.40 and 0.50 (Levy, 2012). Based on our operating conditions (W/C=0.484), the cement may have lower strength in the suggested interval. Figure 13 displays the compressive strength of cement mortars in 7 d and 28 d. The results indicated that the strength decreased with the increasing addition of soils collected from site 1. Specifically, the strengths of S1:10% after 7 and 28 d incubation did not meet the ASTM cementitious standard specifications (19 and 28 MPa). Although the proportions of C_2S elevated, the 28-d compressive strength still decreased, likely due to the retardation of the hydration of C_3A by Cr (Fernández Olmo et al., 2001). If the incubation time prolonged, the strength in end age may recovery.

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Meanwhile, the addition of soils collected from site 2 had no effects on the strength. Interestingly, the cement had slightly greater strength than that of control after 7 d and 28 d incubation. This observation is consistent with the results of Hamilton and Sammes (1999) that a small addition of Zn and Pb may accelerate the hydration of cement and increase the strength after 28 d incubation. Overall, the addition of Cr was the major reason causing the prolonged initial setting time and the loss of compressive strength. Based on these criteria, the maximum allowable addition of site 1 soil was determined to be 7.6% while that of site 2 soil was 10%.

Table 10. The chemical analysis by XRF and performance evaluation of clinkers and cement samples.

	Control	S1:3%	S1:7.6%	S1:10%	S2:3%	S2:7.6%	S2:10%	Unit
Mineral species								
SiO_2	21.8	22.4	22.6	22.9	21.8	21.7	22.0	%
Al_2O_3	5.17	5.30	5.49	5.64	5.31	5.33	5.44	%
Fe_2O_3	3.56	3.65	3.72	3.75	3.79	3.66	3.65	%
CaO	66.2	65.3	64.5	65.0	66.2	65.5	65.8	%
MgO	2.16	1.93	2.26	1.43	1.69	2.45	1.91	%
SO_3	0.26	0.28	0.29	0.24	0.21	0.21	0.23	%
C_3S	63.5	54.2	47.6	47.4	62.1	59.9	59.3	%
C_2S	14.5	23.3	29.0	29.9	15.6	17.5	18.3	%
C_3A	7.70	7.80	8.30	8.40	7.70	7.90	8.00	%
C_4AF	10.8	11.1	11.3	11.4	11.5	11.1	11.1	%
Performance								
HM	2.17	2.08	2.03	2.02	2.14	2.14	2.12	-
SM	2.49	2.50	2.46	2.43	2.40	2.44	2.42	-
IM	1.45	1.45	1.48	1.51	1.40	1.46	1.49	-
Fineness	361	358	353	357	371	373	370	m^2/kg
f-CaO	0.6	0.7	0.3	0.5	0.5	0.2	0.6	%
IST*	255	285	300	330	270	285	285	min

*IST: Initial setting time

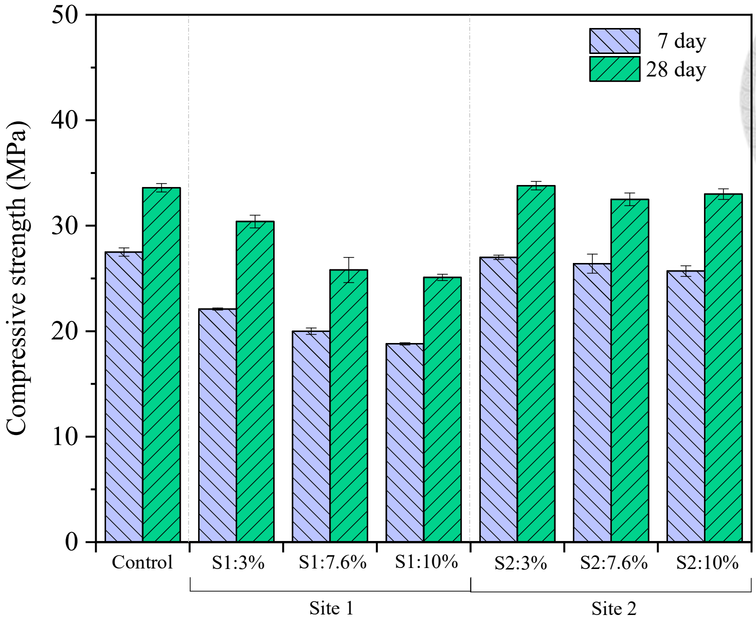

Figure 13. Compressive strength of cement mortars after 7 and 28 d incubation.

QXRD was performed to determine the crystalline phases present in cement samples. The XRD patterns are shown in Figure 14 and the mineral phases present in all cement samples are summarized in Table 11. The four primary phases including C_3S, C_2S, C_3A and C_4AF were found for all cement samples. For those produced from co-processing with contaminated soils, the proportions of C_3S decreased and that of C_2S increased with the increasing addition of soils. It has been reported that metal oxides or sodium salts in soils may promote the decomposition of the C_3S during co-processing (Yang et al., 2014). There was no significant difference between the proportions of C_3A and C_4AF. The proportion of mineral phase (C_3S, C_2S, C_3A and C_4AF) received from XRF and QXRD was similar, but the data obtained from QXRD were more accurate.

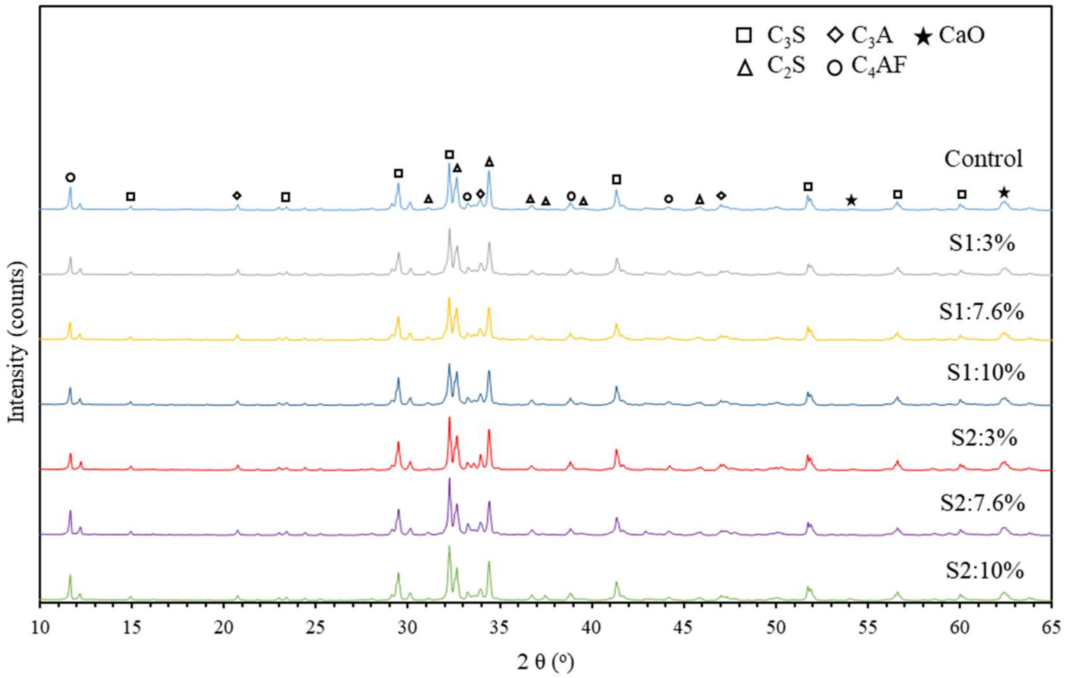

Figure 14. XRD patterns for all cement samples.

Table 11. QXRD results for all cement samples.

Parameter	Control	S1:3%	S1:7.6%	S1:10%	S2:3%	S2:7.6%	S2:10%
C_3S	66.9	57.4	55.2	51.7	71.3	59.1	58.3
C_2S	8.48	17.2	19.0	25.3	5.21	12.2	16.7
C_3A	2.44	2.68	3.06	3.14	2.78	3.15	3.28
C_4AF	13.2	13.6	13.4	12.5	13.4	14.6	12.7
Lime	0.24	0.20	0.20	0.33	0.18	0.19	1.66
Portlandite	1.49	1.30	0.47	0.18	0.69	0.07	0.31
f-CaO	1.36	1.18	0.55	0.47	0.7	0.25	1.89
Periclase	1.68	1.36	1.75	1.41	0.94	2.33	1.05
Quartz	0.05	0.04	0.03	0.02	0.01	0.00	0.00
Arcanite	0.46	0.43	0.50	0.33	0.54	0.58	0.40
Langbeinite	0.05	0.13	0.16	0.15	0.00	0.13	0.17
Aphthitalite	0.19	0.32	0.28	0.28	0.13	0.25	0.24
Gypsum	4.70	4.43	4.72	3.71	3.95	4.16	4.18
Anhydrite	0.05	0.00	0.00	0.13	0.00	0.01	0.00
Calcite	0.11	0.31	0.93	0.86	0.84	1.25	0.96

The SEM-EDS images of cement mortars, including the control, S1:10%, and S2:10% cured for 28 d are shown in Figure 15 and Table 12. In control (Figure 15a and 15b), prismatic structures were observed, in which C-S-H gel and ettringite could be seen in cement mortars. In S1:10%, trace Cr was found to be associated with prismatic crystal in cement powder and fibrous C-S-H gel and acicular ettringite (Figure 15c and 15d). In S2:10%, Zn was found in C-S-H gel and ettringite (Figure 15e and 15f), but Pb and Mn were not observed in those structures. These results indicated that heavy metals can be trapped through calcination process and C-S-H gel and ettringite can also effectively encapsulate heavy metals after the hydration process.

Table 12. Elemental compositions (%) of cement powder and cement mortar (Control, S1:10%, and S2:10%) determined by EDS. The value was average of duplicate.

Element	Cement powder			Cement mortar		
	Control	S1:10%	S2:10%	Control	S1:10%	S2:10%
C	13.3	11.6	7.82	16.9	15.1	14.5
O	56.3	60.2	61.0	57.6	61.4	61.1
Mg	0.42	1.09	0.55	0.71	0.77	0.32
Al	1.26	1.04	0.72	1.02	1.02	1.45
Si	5.39	7.41	7.69	7.45	5.34	6.44
S	0.31	0.41	-	0.88	0.63	0.52
Ca	20.8	17.2	22.2	15.5	14.6	13.7
Cr	-	0.79	-	-	1.16	-
Zn	-	-	0.11	-	-	0.03

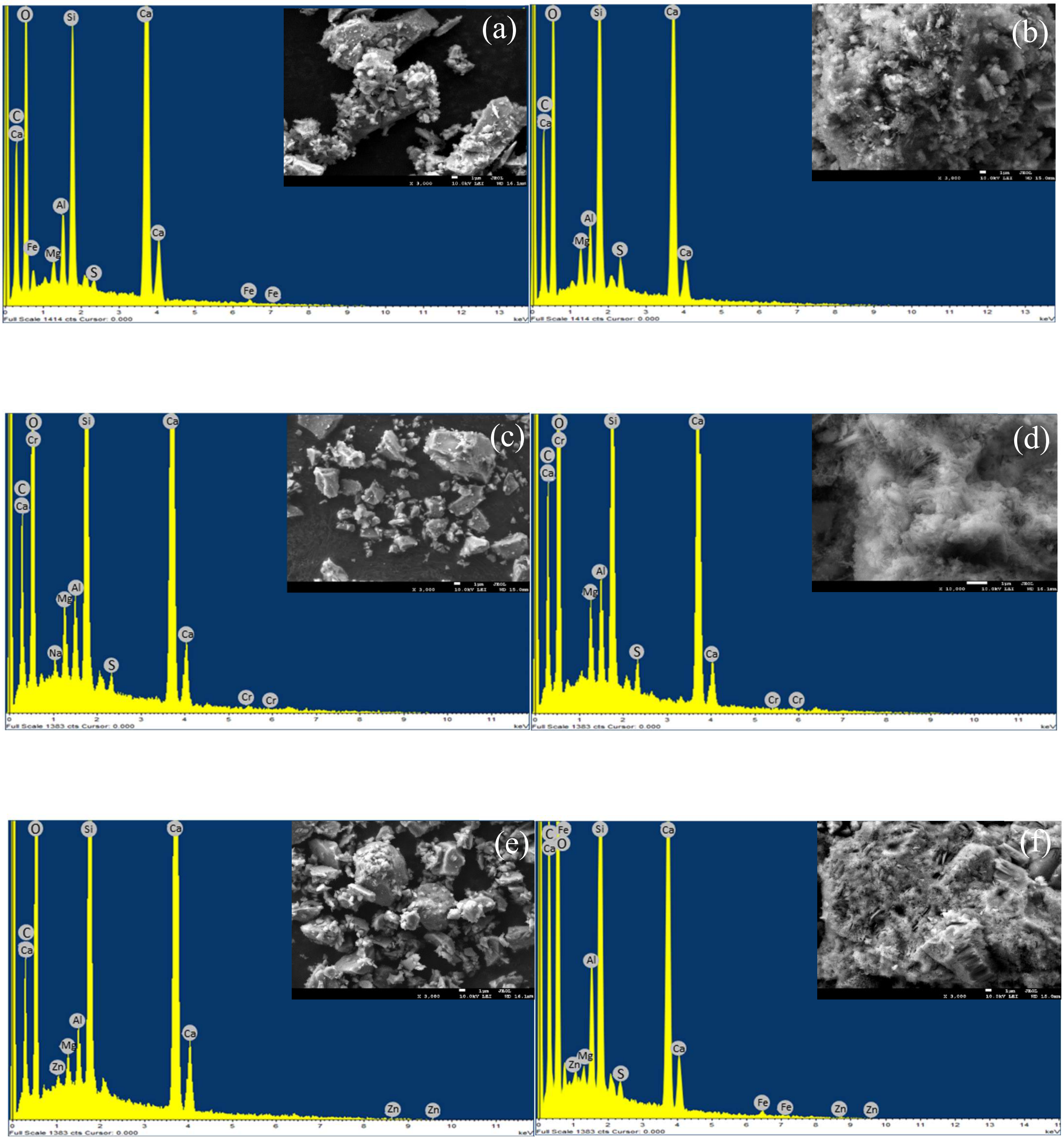

Figure 15 SEM-EDS of cement powders of (a) control, (c) S1:10%, (e) S2:10% and cement mortars of (b) control and (d) S1:10%, (f) S2:10% after 28 d incubation.

4.3 Leaching test

The metal leachability of cement powders produced from co-processing of two contaminated soils at different mass ratios and that of cement mortars incubated for 28 d were examined using three different leaching tests including TCLP, SPLP, and EDTA-mediated TCLP. The environmental compatibility of the cement products was evaluated using RALP.

First, the final pH values of all three leaching tests are shown in Figure 16, in which the lines represent the initial pH of leachates used in the three tests. All final pH values rose substantially to pH 11-14 with the following order: EDTA-mediated TCLP<TCLP<SPLP. In addition, the final pH values in leachates of cement powders were consistently higher than those of cement mortars due to the large surface areas of small particles present in the cement powders (Halim et al., 2003).

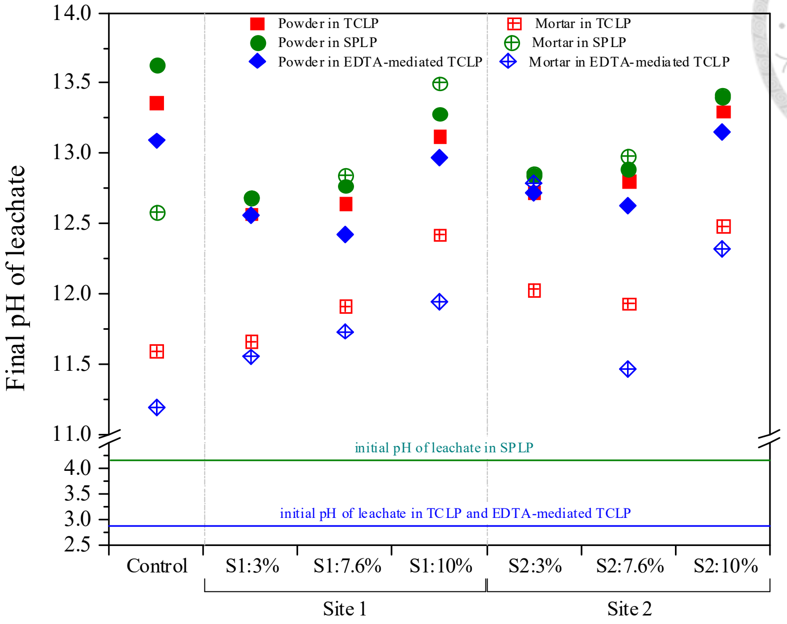

Figure 16. The final pH in leachates of cement products using three leaching tests. The lines represented the initial pH of extractions in three tests.

TCLP results showed that only Cr exceeded the TCLP standard (5 mg/L) (Appendix Table S1). The limited Cu and Mn could be due to the alkaline pH values in the leachates, leading to the formation of hydroxide precipitates. Pb-containing compounds are relatively insoluble at pH 5-12 and become more soluble at higher pH due to the formation of $Pb(OH)_3^-$ and $Pb(OH)_4^{2-}$ complexes (Halim et al., 2004a; 2004b). However, the release of Pb was negligible in all experiments even in the presence of EDTA, a known chelation agent that can enhance the leaching of metals (Karlfeldt Fedje et al., 2010). Similar result was found for Zn. The low concentrations of these metals indicated that co-processing with cementitious materials can fix these metals and make them immobile even in harsh environments. Based on these results, the influence of replacements of heavy metal-contaminated soils was focused on the leachability of Cr in the three leaching tests.

The leachates of cement powders and cement mortars produced by replacement with site 1 soil had higher Cr concentrations than those with site 2 soil (Figure 17). In general, the leaching of Cr increased with the increasing replacements of contaminated soils. In TCLP, the leachate of cement powders produced by co-processing with greater than 7.6% of site 1 soil surpassed the regulatory limit, whereas those of all cement mortars met the regulation. This result indicated that incubation required for cement mortar could encapsulate more Cr via the hydration process and prevent its leaching. The mass of Cr in the raw material of S1:3%, S1:7.6%, and S1:10% was 1.2, 3.04, and 4.0 mg, respectively. Based on the Cr leaching concentration, the percentage of Cr encapsulation calculated was 83% in cement powder, and 92% in cement mortar. The results in chapter 4-2 showed the proportions of C_2S increased with the addition of site 1 soil, indicating more Cr could be encapsulated by C_2S. However, the Cr concentration still increased. This is because Cr(III) is liable to become Cr(VI) through sintering due to an oxidizing atmosphere provided by cement kiln co-processing. Once the Cr(VI) retains in clinkers, it cannot be trapped by C_2S, and the leaching of it may release to environment. In the leachates, Cr(VI) presents as a further soluble material at all pH,

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and would easily release together with portlandite particles upon exposure to leaching extractions (Halim et al., 2004a). Similarly, Chen et al. (2012) indicated that the clinkers produced under the oxidizing atmosphere had significantly higher concentrations of Cr in the TCLP leachates, whereas those produced under the reducing atmosphere had much lower leaching concentrations. Consequently, the reducing atmosphere can prevent Cr(III) from oxidizing to Cr(VI) during the sintering process and leaching in the environment. In SPLP, the Cr concentrations in leachates were much lower than those observed for TCLP. In EDTA-mediated TCLP, cement powders co-processed with 7.6% and 10% site 1 soils and cement mortar co-processed with 10% site 1 soils exceeded the TCLP standard and higher than those obtained in the TCLP test, reflecting that Cr could leach in harsh environments such as consistently acidic conditions (Karlfeldt Fedje et al., 2010). If the alkalinity of cement is wholly consumed, the C-S-H gel will be destroyed, causing the loss of compressive strength (Halim et al., 2004a). Based on these results, it was concluded that the maximum mass ratio of site 1 soils that can be added for cement co-processing was 3% and that the maximum mass ratio of site 2 soils was 10%. It was estimated that a kilogram of cement was capable of accommodating 220 mg Cr.

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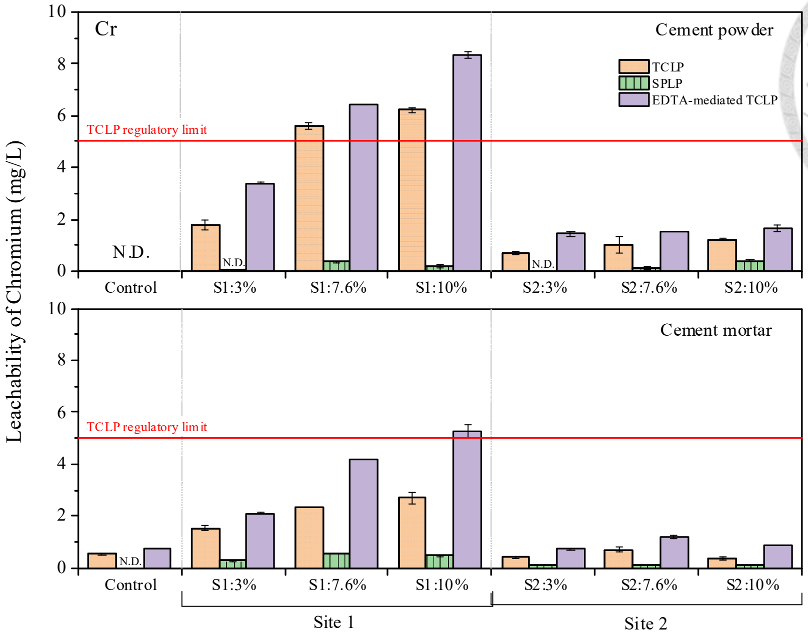

Figure 17. Cr concentrations in leachates for cement powders and cement mortars using TCLP, SPLP and EDTA-mediated TCLP. The red lines represent Cr regulatory limit in TCLP (5 mg/L). N.D. represents nom-detectable and the error bar represents the range of duplicate.

RALP is currently used by Taiwan EPA to determine the environmental compatibility of incineration recycled aggregates. Figure 18 showed the final pH and metal concentrations in leachates of cement mortars in RALP tests, in which the purple line represents the initial pH of the leachate and the red dotted lines and blue solid lines represent the primary and secondary regulatory levels of Cr and Zn, respectively. Other metals regulated in the RALP test were not detected. The final pH values were all about pH 13. The Cr concentrations in all leachates, including the control without contaminated soils, exceeded the primary but were below the secondary regulatory levels, suggesting that the cement mortars can be reused but only outside the environmentally sensitive regions. Zn was detected in leachates using cement mortars produced by co-processing 7.6% and 10% doping ratios of site 2 soil, while the levels were lower than the primary and secondary levels. Cement mortars manufactured in this study, therefore, could be reused in non-sensitive regions.

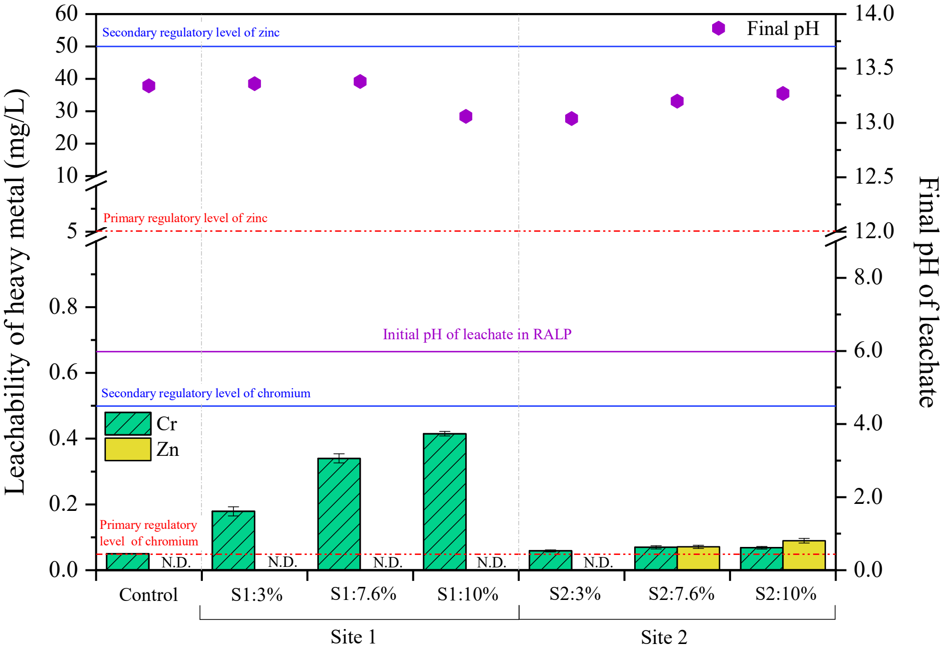

Figure 18. The final pH and metal concentrations in leachates of cement mortars using RALP. The purple line represented the initial pH of extractions in RALP. The red dotted lines and blue solid lines represented the primary and secondary regulatory levels of chromium and zinc, respectively. N.D. represented not detected and the error bar represented the difference between the duplicate.

4.4 Economic analysis

The economic analysis was conducted to assess the benefits of both cement industry and soil polluter in the regeneration of metal-contaminated soils by co-processing. The assumptions used in the analysis were as follows:

1. The analysis was reflecting a local cement company that manufactures 0.8 million ton-cement/yr. The proportions of limestone, clay, silica sand, and iron slag used for cement production are 85%, 9%, 3%, and 3%, respectively.
2. The contaminated soil is used to replace 33% of clay for cement production, representing a replacement of 3%, which can meet the metal leaching regulation based on our data, of total weight of raw materials.
3. The soil shipping fee to the cement plant is the same as that to the treatment facility if the contaminated soil is ex-situ treated using the S/S technology followed by landfill.
4. The shipping fee is borne by the polluter.

Based on these assumptions, the total amounts of soils that can be substituted for clay can be calculated. Since the LOI is 33%, the weight of raw materials for cement production therefore is 1.2 million tons. The clay substitution (3%) counts for about 36,000 ton/yr. Table 13 showed the prices of soil treatment by co-processing and S/S technology.

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Table 13. The related prices of soil cleaning by co-processing and S/S technology and landfill.

Category	Clay cost	Shipping fee of clay	Co-processing fee	Total price of S/S technology and landfill
Price (USD/ton)	3.3	8.3 (for 100 km)	500 (current price in Taiwan)	850~1700 (Assume 1200)

For soil polluter, the total cost of S/S treatment and landfill for 36,000 tons of contaminated soil is 43.2 million USD. Alternatively, the use of co-processing to treat the same amount of soil only costs 18 million USD, representing a 58% or 25.2 million USD reduction in expenses.

For cement company, treating contaminated soils by co-processing can not only save the material and shipping costs of clay, but also make profits from soil cleaning income. In this case, sum savings of clay and shipping costs is 0.42 million USD and the income is up to 18 million USD.

The above economic analysis suggests that using cement kiln co-processing to treat contaminated soils can bring benefits for both the cement industry and the soil polluters.

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Chapter 5 Conclusions and recommendations

5.1 Conclusions

Cement kiln co-processing is a technology using wastes as the substitute for raw materials or fossil fuels in cement production to minimize the consumption of environmental resources. The use of heavy metal contaminated soils as a replacement of clay for cement production was investigated in this study. The engineering performance and heavy metal leachability of cement powders and cement mortars were specifically examined.

The results showed that the proportions of C_3S decreased with the increasing percentage of soil added, whereas C_2S showed the opposite trend. Specifically, the presence of Cr resulting from the use of contaminated soils was the major reason causing the prolonged initial setting time and the loss of compressive strength.

In TCLP tests, leaching of Cr was the major concern. Co-processing of 3% of the contaminated soil collected from site 1 could meet the performance requirements and metal leaching standards, while all leachates of cement samples co-processing with site 2 soil met the TCLP standards. It was determined that each kilogram of cement could accommodate 220 mg of Cr. EDTA-mediated TCLP could potentially release higher Cr concentrations, indicating that cautions were still needed when applying the cement products in harsh environments. In RALP, cement sample using a replacement by 10 %

contaminated soil was feasible for reuse as CLSMs at non-sensitive regions.

Finally, based on economic analysis, it was concluded that using cement kiln co-processing is an attractive alternative compared to traditional S/S technology and landfill to treat heavy metal contaminated soils. It brings benefits to both the cement industry and soil polluters for the remediation of contaminated soil.

5.2 Recommendations

1. Due to the gap of Cr leaching between the cement powders co-processing with 3% site 1 soil (1.76 mg/L) and the TCLP Cr standard (5 mg/L), a higher addition of contaminated soil (e.g., 5%) in the cement production may still meet the TCLP standard. Therefore, co-processing with a higher contaminated soil fraction should be conducted to determine the maximum Cr accommodation per kilogram of cement, which could bring higher benefits for cement company and soil polluters.
2. The Cr leaching concentration in a cement sample manufactured using S/S by adding the same amounts of soil with Portland cement could be attempted to compare with the results obtained in this study to determine a more suitable method to treat Cr-containing wastes.
3. Different types of Portland cement could be explored for better Cr encapsulation.
4. The exhaust emission from cement kiln co-processing should be monitored to explore potential metal vaporization in sintering to prevent secondary pollution.

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Appendix

Table S1. Heavy metal leaching concentrations of cement powders and mortars using three leaching tests.

No.	Sample	Leaching mode	Leaching concentration of heavy metal (mg/L)																								
			Ag*	Al	As*	B	Ba*	Bi	Ca	Cd*	Co	Cr*	Cu*	Fe	Ga	In	K	Li	Mg	Mn	Na	Ni	Pb*	Se*	Sr	Tl	Zn
Control	powder	TCLP	N.D.	N.D.	N.D.	8.50	15.4	N.D.	3597	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.28	N.D.	N.D.	N.D.	15.4	N.D.	N.D.	N.D.	17.8	N.D.	N.D.
		SPLP	N.D.	N.D.	N.D.	5.57	11.7	N.D.	1216	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	15.31	N.D.	N.D.	N.D.	29.7	N.D.	N.D.	N.D.	16.4	N.D.	N.D.
		EDTA-mediated TCLP	N.D.	N.D.	N.D.	3.61	9.56	N.D.	2963	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.929	N.D.	N.D.	N.D.	12.6	N.D.	N.D.	N.D.	9.77	N.D.	N.D.
	mortar	TCLP	N.D.	0.981	N.D.	1.51	2.46	N.D.	3112	N.D.	N.D.	0.538	N.D.	N.D.	N.D.	N.D.	9.67	N.D.	N.D.	N.D.	7.71	N.D.	N.D.	N.D.	4.98	N.D.	N.D.
		SPLP	N.D.	0.474	N.D.	0.554	2.84	N.D.	891	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	7.99	N.D.	N.D.	N.D.	6.31	N.D.	N.D.	N.D.	3.69	N.D.	N.D.
		EDTA-mediated TCLP	N.D.	0.239	N.D.	0.350	1.91	N.D.	2973	N.D.	N.D.	0.745	N.D.	N.D.	N.D.	N.D.	8.62	N.D.	0.488	N.D.	8.60	N.D.	N.D.	N.D.	5.23	N.D.	N.D.
S1:3%	powder	TCLP	N.D.	N.D.	N.D.	N.D.	1.95	N.D.	3129	N.D.	N.D.	1.76	N.D.	N.D.	N.D.	N.D.	27.3	N.D.	N.D.	N.D.	30.6	N.D.	N.D.	N.D.	7.76	N.D.	N.D.
		SPLP	N.D.	0.536	N.D.	N.D.	8.27	N.D.	1041	N.D.	N.D.	0.040	N.D.	N.D.	N.D.	N.D.	22.9	N.D.	N.D.	N.D.	41.4	N.D.	N.D.	N.D.	10.3	N.D.	N.D.
		EDTA-mediated TCLP	N.D.	N.D.	N.D.	N.D.	1.46	N.D.	4985	N.D.	N.D.	3.39	N.D.	N.D.	N.D.	N.D.	23.7	N.D.	N.D.	N.D.	28.6	N.D.	N.D.	N.D.	6.96	N.D.	N.D.
	mortar	TCLP	N.D.	0.558	N.D.	0.724	2.24	N.D.	2472	N.D.	N.D.	1.53	N.D.	N.D.	N.D.	N.D.	13.1	0.0490	0.265	N.D.	8.48	N.D.	N.D.	N.D.	4.16	N.D.	N.D.
		SPLP	N.D.	0.336	N.D.	0.335	2.35	N.D.	836	N.D.	N.D.	0.262	N.D.	N.D.	N.D.	N.D.	8.94	0.0417	N.D.	N.D.	7.33	N.D.	N.D.	N.D.	2.92	N.D.	N.D.
		EDTA-mediated TCLP	N.D.	0.295	N.D.	0.102	1.91	N.D.	2790	N.D.	N.D.	2.10	N.D.	N.D.	N.D.	N.D.	13.1	0.0482	0.356	N.D.	9.78	N.D.	N.D.	N.D.	4.44	N.D.	N.D.
S1:7.6%	powder	TCLP	N.D.	N.D.	N.D.	1.70	0.968	N.D.	4997	N.D.	N.D.	5.62	N.D.	N.D.	N.D.	N.D.	22.2	N.D.	N.D.	N.D.	28.3	N.D.	N.D.	N.D.	5.98	N.D.	N.D.
		SPLP	N.D.	0.402	N.D.	0.619	6.25	N.D.	1286	N.D.	N.D.	0.366	N.D.	N.D.	N.D.	N.D.	19.4	N.D.	N.D.	N.D.	35.5	N.D.	N.D.	N.D.	8.96	N.D.	N.D.
		EDTA-mediated TCLP	N.D.	N.D.	N.D.	0.253	1.06	N.D.	4096	N.D.	N.D.	6.41	N.D.	N.D.	N.D.	N.D.	21.0	N.D.	N.D.	N.D.	29.2	N.D.	N.D.	N.D.	5.73	N.D.	N.D.
	mortar	TCLP	N.D.	0.492	N.D.	0.260	2.32	N.D.	2319	N.D.	N.D.	2.33	N.D.	N.D.	N.D.	N.D.	11.6	0.0549	0.226	N.D.	10.1	N.D.	N.D.	N.D.	4.00	N.D.	N.D.
		SPLP	N.D.	0.295	N.D.	0.146	2.21	N.D.	934	N.D.	N.D.	0.532	N.D.	N.D.	N.D.	N.D.	8.55	0.0492	N.D.	N.D.	9.12	N.D.	N.D.	N.D.	2.91	N.D.	N.D.
		EDTA-	N.D.	0.299	N.D.	0.101	1.92	N.D.	3155	N.D.	N.D.	4.17	N.D.	N.D.	N.D.	N.D.	11.2	0.0560	0.332	N.D.	11.2	N.D.	N.D.	N.D.	4.34	N.D.	N.D.

		mediated TCLP																									
S1:10%	powder	TCLP	N.D.	0.354	N.D.	0.297	1.02	N.D.	3511	N.D.	N.D.	6.21	N.D.	N.D.	N.D.	N.D.	14.8	0.0675	0.0416	N.D.	23.3	N.D.	N.D.	N.D.	7.51	N.D.	0.0744
		SPLP	N.D.	0.459	N.D.	0.138	5.24	N.D.	1163	N.D.	N.D.	0.206	N.D.	N.D.	N.D.	N.D.	12.5	0.173	N.D.	N.D.	32.4	N.D.	N.D.	N.D.	9.87	N.D.	0.109
		EDTA-mediated TCLP	N.D.	0.404	N.D.	0.119	0.795	N.D.	3981	N.D.	N.D.	8.34	N.D.	N.D.	N.D.	N.D.	14.3	0.0576	0.0635	N.D.	22.5	0.0472	N.D.	N.D.	6.91	N.D.	0.167
	mortar	TCLP	N.D.	0.195	N.D.	0.260	1.75	N.D.	2363	N.D.	N.D.	2.70	N.D.	N.D.	N.D.	N.D.	10.3	0.0596	0.296	N.D.	9.77	N.D.	N.D.	N.D.	4.69	N.D.	0.0529
		SPLP	N.D.	0.151	N.D.	0.197	2.05	N.D.	871	N.D.	N.D.	0.463	N.D.	N.D.	N.D.	N.D.	9.41	0.0617	0.0769	N.D.	9.87	N.D.	N.D.	N.D.	3.58	N.D.	0.105
		EDTA-mediated TCLP	N.D.	0.221	N.D.	0.161	1.44	N.D.	3221	N.D.	N.D.	5.27	N.D.	N.D.	N.D.	N.D.	9.96	0.0570	1.17	N.D.	11.2	0.0837	N.D.	N.D.	5.22	N.D.	0.0616
S2:3%	powder	TCLP	N.D.	0.0577	N.D.	0.66	1.79	N.D.	4220	N.D.	N.D.	0.705	N.D.	N.D.	N.D.	N.D.	1.15	N.D.	0.0614	N.D.	2.78	N.D.	N.D.	N.D.	10.1	N.D.	0.135
		SPLP	N.D.	0.499	N.D.	0.329	8.00	N.D.	1246	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.510	0.0469	0.0386	N.D.	4.15	N.D.	N.D.	N.D.	12.3	N.D.	0.114
		EDTA-mediated TCLP	N.D.	0.0415	N.D.	0.179	1.47	N.D.	3972	N.D.	N.D.	1.44	N.D.	N.D.	N.D.	N.D.	0.405	N.D.	0.0456	N.D.	2.68	0.0651	N.D.	N.D.	9.60	N.D.	0.0944
	mortar	TCLP	N.D.	0.464	N.D.	0.315	3.25	N.D.	2434	N.D.	N.D.	0.395	N.D.	N.D.	N.D.	N.D.	7.44	N.D.	0.1459	N.D.	5.34	N.D.	N.D.	N.D.	4.69	N.D.	0.202
		SPLP	N.D.	0.358	N.D.	0.178	2.94	N.D.	865	N.D.	N.D.	0.0807	N.D.	N.D.	N.D.	N.D.	5.40	N.D.	N.D.	N.D.	5.17	N.D.	N.D.	N.D.	3.66	N.D.	0.133
		EDTA-mediated TCLP	N.D.	0.313	N.D.	0.133	2.60	N.D.	3013	N.D.	N.D.	0.717	N.D.	N.D.	N.D.	N.D.	6.93	N.D.	0.3230	N.D.	6.29	0.118	N.D.	N.D.	4.99	N.D.	0.0854
S2:7.6%	powder	TCLP	N.D.	0.439	N.D.	0.276	2.16	N.D.	3403	N.D.	N.D.	1.03	N.D.	N.D.	N.D.	N.D.	4.36	0.0567	N.D.	N.D.	11.1	N.D.	N.D.	N.D.	6.75	N.D.	0.172
		SPLP	N.D.	0.621	N.D.	0.135	7.80	N.D.	1264	N.D.	N.D.	0.124	N.D.	N.D.	N.D.	N.D.	3.54	0.106	N.D.	N.D.	16.8	N.D.	N.D.	N.D.	9.19	N.D.	0.128
		EDTA-mediated TCLP	N.D.	0.0707	N.D.	0.0959	1.52	N.D.	3529	N.D.	N.D.	1.51	N.D.	N.D.	N.D.	N.D.	4.98	0.0378	0.0556	N.D.	9.25	N.D.	N.D.	N.D.	5.90	N.D.	0.106
	mortar	TCLP	N.D.	0.525	N.D.	0.408	2.01	N.D.	2444	N.D.	N.D.	0.706	N.D.	N.D.	N.D.	N.D.	7.84	0.0394	0.247	N.D.	6.14	N.D.	N.D.	N.D.	3.85	N.D.	0.143
		SPLP	N.D.	0.567	N.D.	0.178	2.12	N.D.	861	N.D.	N.D.	0.117	N.D.	N.D.	N.D.	N.D.	5.76	0.0308	N.D.	N.D.	5.37	N.D.	N.D.	N.D.	2.41	N.D.	0.127
		EDTA-mediated TCLP	N.D.	0.501	N.D.	0.175	1.55	N.D.	2979	N.D.	N.D.	1.19	N.D.	N.D.	N.D.	N.D.	8.14	0.0455	4.29	N.D.	7.73	N.D.	N.D.	N.D.	4.24	N.D.	0.0956
S2:10%	powder	TCLP	N.D.	0.106	N.D.	0.382	1.04	N.D.	3491	N.D.	N.D.	1.23	N.D.	N.D.	N.D.	N.D.	3.16	0.0542	0.0379	N.D.	7.23	N.D.	N.D.	N.D.	6.54	N.D.	0.329
		SPLP	N.D.	0.0919	N.D.	0.177	2.75	N.D.	1184	N.D.	N.D.	0.397	N.D.	N.D.	N.D.	N.D.	2.42	0.0910	0.0298	N.D.	9.65	N.D.	N.D.	N.D.	8.90	N.D.	0.224

	EDTA-mediated TCLP	N.D.	0.0670	N.D.	0.124	0.831	N.D.	3975	N.D.	N.D.	1.63	N.D.	N.D.	N.D.	N.D.	3.00	0.0415	0.0747	N.D.	7.66	N.D.	N.D.	N.D.	5.85	N.D.	0.188
mortar	TCLP	N.D.	0.226	N.D.	0.266	2.41	N.D.	2667	N.D.	N.D.	0.331	N.D.	N.D.	N.D.	N.D.	8.10	0.0520	0.528	N.D.	5.64	N.D.	N.D.	N.D.	4.59	N.D.	0.2980
	SPLP	N.D.	0.145	N.D.	0.211	2.24	N.D.	987	N.D.	N.D.	0.0818	N.D.	N.D.	N.D.	N.D.	6.02	0.0506	0.0438	N.D.	5.22	N.D.	N.D.	N.D.	3.50	N.D.	0.176
	EDTA-mediated TCLP	N.D.	0.161	N.D.	0.146	1.74	N.D.	3044	N.D.	N.D.	0.847	N.D.	N.D.	N.D.	N.D.	7.80	0.0493	0.434	N.D.	6.45	0.0545	N.D.	N.D.	4.83	N.D.	0.122

*Heavy metal is regulated by TCLP limitations.

N.D.: not detected

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