Thiomer solidification of an ASR bottom ash: Optimization based on compressive strength and the characterization of heavy metal leaching

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A B S T R A C T
This study examines the function of Thiomer solidification as a novel environment friendly construction material and its immobilization capacity over heavy metals in the automotive shredder residue (ASR) bottom ash. The morphology of the mixture using a field emission-scanning electron microscopy consistently illustrated the effective bonding between Thiomer and sand towards ASR bottom ash due to acting as fillers to reduce the gaps in its surface during Thiomer solidification. A D-optimal mixture design was further utilized in order to evaluate and optimize the parameters of Thiomer (25–35 wt%), ASR bottom ash (30–45 wt%) and sand (30–40 wt%) on the response of compressive strength. Result showed that optimum compressive strength of 55.9 MPa can be attained at 33.6, 36.4 and 30.0 wt% of Thiomer, ASR bottom ash and sand, respectively. The solidified Thiomer specimen showed superior structural strength over ordinary Portland cement concrete at curing time of 1 and 7 days. Furthermore, a mean heavy metal concentrations of 0.055 ppm Cu²⁺, 0.105 ppm Zn²⁺, 0.045 ppm Pb²⁺, 0.078 ppm Cr⁶⁺, and 0.002 ppm Cd²⁺ were achieved at various mixture designs in the heavy metal immobilization which satisfies stringent environmental standards. Thus, the application of Thiomer proves to be a promising construction material that can pose as an alternative over common cement due to promoting high durability and being eco-friendly.

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1. Introduction

A marked increase in the amount of automotive shredder residue (ASR) production has become a challenging problem through the years. ASRs are generated approximately 5,000,000 ton/yr worldwide in shredding facilities of end-of-life vehicles (Baek et al., 2016). This residues are either thermally converted or managed in landfills (Mancini et al., 2014; Ni and Chen, 2015; Osada et al., 2008). The environmental concern that is associated to landfilling of ASRs includes the subsequent risk of leaching which may release harmful substances such as inorganic salts and metal elements unto the environment (Cunliffe et al., 2003; Hwang et al., 2008). ASRs are hazardous substances that contains persistent organic pollutants, polychlorinated biphenyls and heavy metals which causes serious environmental and health problems (Ahmaruzzaman, 2010; Ciacci et al., 2010). The aspect of recycling ASRs shows a promising economic value if these were treated prior to its use (Ni and Chen, 2015). In a thermal process, it is approximated that about 1,000,000 tons of ASR are recoverable for fuel usage according to the United States Environmental Protection Agency (Hwang et al., 2008). In Korea, more than 85% of ASRs were incinerated in order to reduce its volume. The ASR in the thermal process are able to partially remove organic materials but this concentrates the heavy metals present in the ASR in the ASR by a factor of 20 as compared to the concentrations in common municipal solid waste incinerator fly and bottom ash (Cunliffe et al., 2003; Hwang et al., 2008).

The Korean directive has initiated to set the thermal recycling to 95% last 2015 for its resource circulation of electrical and electronic vehicles and/or equipment (Lee et al., 2003; Lee and Oh, 2005). In order to achieve this, the implementation of the direct use of ASR in
cement industries or as a secondary source of raw material is essential. The immobilization of heavy metals is needed for the utilization of the residues in an ASR incinerator to avoid detrimental contamination in the natural environment. There are three types of treatment method for the heavy metals condensed in ash residues discharged from a thermal process, this includes heat treatment (Hu et al., 2013; Okada and Tomikawa, 2013), water extraction (Bayuseno and Schmahl, 2011) and solidification/stabilization (Cerbo et al., 2017; Luna Galliano et al., 2011). These treatment methods are able to mitigate the hazardous properties of wastes and some of which are already well-established in reducing toxic substances or rendering non-toxic species (Cerbo et al., 2017). The solidification/stabilization by binding with cement has been a leading treatment process for ASR fly ash but its application in the bottom ash hinders the formation of hydrates in cement solidification due to the presence of inhibitory salts which coexist with heavy metals (Lee, 2007; Mancini et al., 2014). Solidification/stabilization refers to improving the waste matrix which is able to encapsulate contaminants in a solid matrix and by immobilizing hazardous heavy metals through producing chemically stable constituents. Other materials used in the solidification/stabilization process includes asphalt and fly ash (Mirabile et al., 2002). The main disadvantages in these materials are that the hydration of cementitious binder requires extensive setting time, long hardening time and high heating temperatures reaching 1400 °C to form clinker materials (Malviya and Chaudhary, 2004; Moon et al., 2016).

A proposed general schematic diagram on the heavy metal immobilization and encapsulation is shown in Fig. 1. The sulfur polymer binder (SPB) came from the octasulfur (S8) rings which when heated turns to S8 chains and are converted to a polymeric sulfur (covalent bond) in form (McBee and Sullivan, 1982, 1979). The solidification/stabilization process using SPB was undertaken for the purpose of the treatment of incineration ash that contained high concentrations of heavy metals such as copper (Cu2+), zinc (Zn2+), lead (Pb2+), chromium (Cr6+) and cadmium (Cd2+). SPB has shown to effectively convert heavy metals into insoluble metal sulfides and is simultaneously encapsulated (Mohamed and El Gamal, 2007; Mohamed and Gamal, 2009). The heavy metals of Cu2+, Zn2+, Pb2+, Cr6+ and Cd2+ were assumed to be attached with the sulfur present in the SPB through a double ionic bond of X = S (X: heavy metal) (Sawada et al., 2005). The Cr6+ on the other hand also can be attached to a double ionic bond with sulfur of X = S but this still retained four free protons.

Thiomer is our brand name for a new type of SPB that proposes a novel approach to improve the performance of asphalt and Portland cement as a binder. Thiomer has a prefix of Thiо for a sulfur-containing compound and a suffix of Polymer for a compound with a large molecule and repeated subunits (Baek et al., 2016). The synthesis of Thiomer concrete does not utilize water and cement. Heating temperature for its aggregate is normally at 140 °C which is more favorable than in Portland cement concrete. Thiomer concrete shows superior performances in terms of its chemical resistance and mechanical strength than ordinary concrete upon adding smaller size filler materials (Saleh and Mustafa, 2011). The addition of Thiomer can also decrease the heavy metal leachability due to a lower solubility of metal sulfides than metal compounds. For example, the solubility at 293 K in water for copper(II) sulfide (CuS: 2.41 × 10⁻¹⁶ g/L), lead(II) sulfide (PbS: 6.77 × 10⁻¹² g/L) and cadmium sulfide (CdS: 1.292 × 10⁻¹³ g/L) are substantially lower than its copper(II) chloride (CuCl2: 730 g/L), lead(II) chloride (PbCl2: 10.8 g/L) and cadmium chloride (CdCl2: 1350 g/L) counterparts (Haynes, 2017). This implies that the formation of metal sulfides in the concrete product would have a low leachability capacity. Currently, only our previous work in Baek et al. (2016) have reported the novel synthesis of Thiomer solidification through different compositions of Thiomer, ASR fly ash mixed with industrial solid waste and fine aggregate sand (Baek et al., 2016). However, the utilization of ASR bottom ash and the aspect of mixture design optimization with respect to its compressive strength have yet to be established. In process optimization, D-optimal mixture design under the response surface methodology (RSM) is widely used due to its capacity to have a multivariate statistical analysis at a least number of experimental runs (Eriksson et al., 1998; Muteki et al., 2007). Furthermore, this can statistically identify interacting variables and allow changes in process parameters in a real-time basis to simultaneously determine the response of the model as opposed to a traditional mixture design formulation technique.

In this study, the solidification of Thiomer and immobilization of heavy metals in ASR bottom ash were investigated. The compositions of Thiomer, ASR bottom ash and sand were characterized. The D-optimal mixture design in RSM was carried out for the system optimization in order to statistically assess essential parameters that affect compressive strength. A comparative assessment of ordinary Portland cement concrete and the result from Thiomer solidification was examined. Furthermore, the immobilization of heavy metals (Cu2+, Zn2+, Pb2+, Cr6+ and Cd2+) was tested at various mixture design combinations.

### 2. Materials and methods

#### 2.1. Materials

Thiomer (elemental analysis: 95% S, 2.3% C and 0.1% H) was obtained from Micro Power Co. (Korea). ASR bottom ash was procured from an incinerator plant nearby Ulsan (Korea). Sand (properties: 2.65 g/cm³ density, 2.8 coarseness and 1.63% absorbance rate) was acquired from Kwang Duk Co., Ltd. (Korea). Sulfuric acid (H₂SO₄, 95% purity) and nitric acid (HNO₃, 60% purity) were purchased from OCL Company Ltd. (Korea). Hydrofluoric acid (HF, 48–51% purity) was supplied from Avantor Performance Materials, Inc. (USA). Perchloric acid (HClO₄, 70% purity) was obtained from Junsei Chemical Co., Ltd. (Japan) while hydrochloric acid (HCl, 35% purity) was procured from Daejung Chemicals & Metals Co., Ltd. (Korea).

#### 2.2. Instruments

A pH meter with model HQ40D portable multi-parameter from HACH (USA) was utilized to monitor pH. The microstructure of the
materials was determined by a JSM-7600F Schottky field emission-scanning electron microscope (FE-SEM) made from JEOL (Japan). The compressive strength of the solidified material was tested by a JI-108A compression testing machine from JEIL Precision (Korea). The concentration of heavy metals for the leaching test analysis was quantified by the AA-6300 atomic absorption spectrophotometer (AAS) manufactured from Shimadzu (Korea).

2.3. Determination of pH and surface morphology

The pH of the materials was measured through a waste disposal method in Korea. Around 10 g of the sample was mixed with 25 mL of distilled water in a 50 mL beaker for 30 min. This was then subjected through a centrifuge at 3000 rpm for 10 min. A pH meter was used to monitor the pH of the samples.

A FE-SEM analysis was carried out to determine the surface morphology before (Thiomer, ASR bottom ash and sand) and after solidification/stabilization. In the FE-SEM analysis, the size of the particles was pulverized to 10 μm in a mortar bowl. The specimens were sputter coated with platinum coating. The images in the FE-SEM micrographs were operated at magnification of 500.

2.4. Solidification/stabilization experiment and optimization methodology

Thiomer solidification/stabilization procedure in the present work followed the approach of Baek et al. (2016) except that the component mixture is comprised of Thiomer, ASR bottom ash and sand. Moreover, this was subjected to a comprehensive response surface optimization analysis in terms of compressive strength.

The optimization studies utilized a D-optimal mixture design using Design Expert 7.0.0 to determine the effects of process parameters such as the compositions of Thiomer (X1: 25–35 wt%), ASR bottom ash (X2: 30–45 wt%) and sand (X3: 30–40 wt%) on the compressive strength (Y: MPa) in Thiomer solidification. The mixture design has a total of 14 experimental runs which comprise of minimum model points (6 runs), lack of fit estimation (4 runs) and replicates (4 runs). A regression analysis was performed following the quadratic model to describe the relationship between depended and independent variables shown in Eq (1):

\[ Y = \sum \beta_i X_i + \sum \beta_{ij} X_i X_j \]  

(1)

where \( \beta_i \) and \( \beta_{ij} \) refer to the coefficient of linear and interacting factors, respectively. The results were statistically examined using the analysis of variance (ANOVA). Furthermore, a comparative study for the compressive strength of the specimen was conducted at varying mixture concentration at 1 and 7 days curing time. In order to measure the compressive strength of after Thiomer solidification, a compression testing machine was utilized. Triplicate runs were conducted in this study and its averaged value was used to represent the results.

2.5. Toxicity characterization

2.5.1. Determination of heavy metal concentrations in ASR bottom ash

The concentration of various heavy metals was tested in order to determine the presence of hazardous substances in ASR bottom ash. The measurement for the total heavy metal concentration was carried out based on the method of Baker and Amacher (1982). ASR bottom ash was composed of particles with irregular size and shape. This was passed through a 5 mm sieve. Approximately 2 g of ASR bottom ash, 25 mL of distilled water and 2 mL of HNO3 were mixed in a Teflon beaker. The solution was dried up and cooled adequately. Three drops of H2SO4 and 10 mL of HF were then added in the solution and heated to 200 °C to allow evaporation to occur until it is completely dried up. After cooling, 15 mL of HNO3, 2 mL of H2SO4 and 5 mL of HClO4 were added followed by having a sufficient drying time. The cooled filtrate solution was then filtered by adding distilled water using 1.0 μm glass-fiber filter paper through a 50 mL round flask. The concentration of various heavy metals (Cu2+, Zn2+, Pb2+, Cr6+ and Cd2+) in the filtered sample was then quantified using AAS. The measured heavy metal concentration (M) was calculated using Eq (2):

\[ M = \frac{(C_d - C_b)(V)(F)}{W} \]  

(2)

where \( C_b \) and \( C_d \) are the concentration of metal (mg/kg) in the original and blank sample, respectively, \( V \) is the volume of the digested solution (ml), \( W \) is the dry weight of sample (g) and \( F \) is the dilution factor.

2.5.2. Heavy metal leaching procedure

To elucidate and compare the heavy metal immobility, the ASR bottom ash and solidified Thiomer specimen were subjected to a leaching test using the Korea standard leaching procedure (Park et al., 2013). A 100 g of grounded samples with less than 5 mm uniform particle size and a solvent with pH 5.8–6.3 using diluted HCl were separately prepared. The sample was mixed together using a solid to liquid ratio of 1:10 to a total volume of 500 mL. The mixture was kept in a container for 6 h at 200 rpm with 4–5 cm shaking widths. The mixture was then subjected to a centrifuge at 3000 rpm for 20 min and filtered using a 0.45 μm membrane filter. The heavy metals (Cu2+, Zn2+, Pb2+, Cr6+ and Cd2+) in the filtrate solution were analyzed by AAS to evaluate its potential leachability. All experimental runs were done in triplicates and the averaged value was taken for the results represented in this study.

3. Results and discussion

3.1. pH and surface morphology of materials

The measured pH for Portland cement, sand, Thiomer and ASR bottom ash were 12.9, 6.1, 4.2 and 11.7, respectively. The Portland cement showed high alkalinity while sand exhibited a slightly acidic condition. For Thiomer, the sulfur reacting with oxygen in water resulted to a moderately acidic condition. The ASR bottom ash resulted to have a high alkaline condition due to the slaked lime cation/stabilization procedure in the present process (Brereton, 1996).

The FE-SEM analysis was performed at 500 magnifications in order to determine the surface morphology of Thiomer, ASR bottom ash, sand and Thiomer solidification shown in Fig. 2.

The FE-SEM micrographs of Thiomer and sand are shown in Fig. 2(a) and (c), respectively; similar surface textures of non-porous, smooth and uniform surface were observed for the samples. The morphology of the ASR bottom ash in Fig. 2(b) illustrates a coarser and porous surface area which is ideal to have a ball bearing effect in improving the material structure. In Fig. 2(d), the SEM micrograph after Thiomer solidification exhibited a structure similar to ASR bottom ash but with lesser pores. The mixture of the Thiomer and sand onto ASR bottom ash lessened the porosity of the ASR bottom ash particles. The utilization of ASR ash can improve the durability towards alkali silica reaction and sulfate attack in Thiomer solidification (Baek et al., 2016). The sand acts as a binder for the aggregates by enabling the sulfur to effectively adhere in its surface (McBee et al., 1981).
3.2. Compressive strength of Thiomer solidification

In the optimization experiments, the effect of the compositions of Thiomer, ASR bottom ash and sand on Thiomer solidification were examined using the D-optimal mixture design. Table 1 illustrates the observed responses of the runs with respect to its compressive strength after Thiomer solidification. The compressive strength at various compositions was observed to be in the range of 36.5–55.6 MPa and 38.0–53.7 MPa for the observed and predicted response, respectively.

The quadratic model was utilized in correlating the experimental data and obtaining the regression equation. The determination of the response coefficients ($\beta_i$ and $\beta_{ij}$) for the independent variables ($X_1$, $X_2$ and $X_3$) was done using the experimental data. The response surface predictive model for the compressive strength ($Y$) is in Eq (3):

$$Y = 48.4X_1 + 43.9X_2 + 34.9X_3 + 30.6X_1X_2 + 31.1X_1X_3 + 0.43X_2X_3$$

3.2.1. Statistical results

Table 2 summarizes the results of the ANOVA for the compressive strength in Thiomer solidification to test the significance of the fit of the response surface quadratic model where the level of confidence is assumed to be 0.05. The significance of the interaction of process parameters is determined using the Fisher variance ratio ($F$-value) and calculated probability ($p$-value). A $p$-value less than 0.05 indicates that a corresponding independent variable is statistically significant while a high $F$-value indicates the variation in the mean data can be accurately described by the variables in the quadratic model equation (Baskan and Pala, 2010; Choi et al., 2016a). Based on the $F$-value (39.0) and $p$-value (<0.0001), it

Table 1

<table>
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<tr>
<th>Run</th>
<th>Thiomer (wt%)</th>
<th>ASR bottom ash (wt%)</th>
<th>Sand (wt%)</th>
<th>Compressive strength (MPa)</th>
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<td></td>
<td>Observed</td>
<td>Predicted</td>
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</tr>
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<td>30.0</td>
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<td>33.75</td>
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<td>30.0</td>
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</tr>
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<td>30.0</td>
<td>40.0</td>
<td>46.9</td>
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<tr>
<td>7</td>
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<td>35.0</td>
<td>30.0</td>
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<td>8</td>
<td>32.5</td>
<td>33.75</td>
<td>33.75</td>
<td>50.7</td>
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<td>40.0</td>
<td>35.0</td>
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<td>40.0</td>
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Table 2

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<th>$F$-value</th>
<th>$p$-value</th>
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<td>16.5</td>
<td>8.4</td>
<td>0.0202</td>
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$R^2 = 0.9606$ Adj-$R^2 = 0.9360$ Pred-$R^2 = 0.8766$ Adeq precision = 17.0 C.V.% = 3.0.
Fig. 3. Diagnostic plots: (a) predicted versus actual compressive strength values and (b) normal plot of residuals.
implies that the generated quadratic model and terms used are statistically significant. The interactive terms of \(X_1X_2\) and \(X_1X_3\) were significant, whereas \(X_2X_3\) was not significant towards the compressive strength in Thiomer solidification. Moreover, a small \(F\)-value (1.57) and a high \(p\)-value (0.3354) in the lack of fit test imply that there is no significant lack of fit that is relative to the pure error in the quadratic model.

The quality of fit in the quadratic model was expressed by the coefficient of determination (\(R^2\)), adjusted coefficient of determination (\(\text{Adj-}R^2\)) and predicted coefficient of determination (\(\text{Pred-}R^2\)). The high \(\text{Adj-}R^2\) (0.9360) confirms that the model has a good fit in predicting the range of the experimental variables which denotes the sufficiency of the model that could be utilized in the optimization of compressive strength. The adequate precision (Adeq precision) is the ratio of signal to noise which describes the adequacy of its signal. This measures the contrast in the predicted response based on the associated error. A ratio of greater than 4 imply that the signal is adequate (Sengupta, 2014). Therefore, the obtained ratio of 17.0 for the Adeq precision in the quadratic model for compressive strength indicates an adequate signal to navigate the design space. This implies that the generated model equation based on the mixture of Thiomer, ASR bottom ash and sand can adequately predict the response of the compressive strength in the solidified product with only a minimal associated error. The degree of precision, where treatments are compared, is measured by the coefficient of variation (C.V. %). A high reliability of the experiments is shown in a low C.V. % value (Li et al., 2009). Hence, the C.V. % of 3.0 calculated based on the compressive strength of the mixture design demonstrated a high reliability in the experimental runs for Thiomer solidification.

Fig. 3 illustrates the diagnostic plots based on the quadratic model generated from the Thiomer solidification process. The actual and predicted compressive strength are in good agreement based on Fig. 3(a) which indicates a reliable and good fit in the model. In Fig. 3(b), the internally studentized residuals showed that the experimental data points rest along or are close to the normal line which indicates an acceptable fit in the model. No apparent problems in the response transformation and normality were observed.

3.2.2. Analysis of response

To investigate the effect of Thiomer, ASR bottom ash and sand on the compressive strength in Thiomer solidification, RSM was utilized to draw out a contour and 3-D plot. Based from the ANOVA of Table 2, the interaction of Thiomer towards ASR bottom ash (\(p\)-value = 0.0064) and sand (\(p\)-value = 0.0202) were found to have a significant effect on compressive strength, whereas the interaction of ASR bottom ash and sand (\(p\)-value = 0.9608) provided the least effect on the response. The response surface plots and two component mixtures of the results for Thiomer solidification based

![Fig. 4. Effect of Thiomer (\(X_1\), wt%), ASR bottom ash (\(X_2\), wt%) and sand (\(X_3\), wt%) compositions on compressive strength (MPa): (a) contour plot, (b) response surface plot, (c) Thiomer and ASR bottom ash component graph and (d) Thiomer and sand component graph.](image-url)
on compressive strength are shown in Fig. 4. The contour and 3-D plots for the effect of Thiomer, ASR bottom ash and sand mixture composition is shown in Fig. 4(a) and (b), respectively. This consistently illustrates the significant interactive effects of Thiomer and ASR bottom ash as well as Thiomer and sand. Therefore, the mixing and proportioning of Thiomer, ASR bottom ash and sand would affect the final serviceability and quality of the solidified product in terms of its compressive strength. The reaction of the ASR bottom ash along with sand in Thiomer is beneficial to increase the workability and consistency of the mixture due to its appropriate size and shape to act as a filler material to improve the strength of the material (Mohamed, 2002; Mohamed and Gamal, 2009; Na and Lee, 2013). This also shows that the compressive strength increases with higher Thiomer content. This trend is associated to the modified sulfur present in Thiomer that strengthens and binds the aggregates efficiently in forming the solidified product (Baek et al., 2016; Mohamed and El Gamal, 2007). In Fig. 4(c), it is observed that the interaction of Thiomer and incineration ash improves the durability in Thiomer solidification. However, increasing further the Thiomer mix would cause a partial decrease in the resulting compressive strength due to the presence of additional polymerized sulfur that makes the mixture viscous which reduces the rate of crystal growth and formation in the solidified product (Vroom, 1981). Moreover, the interaction of the components of Thiomer and sand is shown in Fig. 4(d). An increase in compressive strength is attributed to the promotion of an easy adherence of the sulfur in Thiomer to the surface of the sand grains (McBee et al., 1981). The illustrated curvature is due to a slower increase in compressive strength at higher Thiomer to sand ratio. This is due to a thicker layer of sulfur that is starting develop around the sand particle that tends to form brittle products (Mohamed and El Gamal, 2011).

### 3.2.3. Optimal result

The optimized conditions for the maximum compressive strength in the Thiomer solidification process were obtained by the simultaneous analysis of the response surface plots and solving the regression equation. The predicted compressive strength of 54.0 MPa could be attained using 33.6 wt% Thiomer, 36.4 wt% ASR bottom ash and 30.0 wt% sand. In the statistical approach of D-optimal mixture design, a predicted interval for the compressive strength provided a range of 50.5–57.5 MPa. This accounts for the uncertainty and error of the outcome of the response (Choi et al., 2014). Therefore, there is a 95% chance that the validation of the response should fall within the specified interval to confirm the generated quadratic model.

In order to validate the reliability and accuracy of the model, confirmatory runs were carried out using the optimum conditions. The mean observed compressive strength is 55.9 MPa. This implies that the quadratic model is effective and adequate for the optimization study since the experimental result is in good agreement with the predicted interval values.

### 3.2.4. Effect of curing time

Table 3 lists the Thiomer solidification at 1 and 7 days curing time. Results showed that increasing the curing time from 1 to 7 days increases the compressive strength in Thiomer solidification and Portland cement concrete by 1.2–1.5 and 2.0 to 4.0 times, respectively. At a longer curing time, the excessive water is able to block the pores of the specimen resulting to a decrease in its porosity (Pan et al., 2016). This indicates the further hydration of uncarbonated binder that increases its compressive strength (He et al., 2016). The results of the synthesized Thiomer solidification in this study was compared to a common type of Portland cement concrete presented in Çolak (2006). The solidified Thiomer specimen showed a promising alternative over the ordinary Portland cement concrete due to having a superior compressive strength at different curing time.

### 3.3. Leaching characteristics of Thiomer solidified ASR bottom ash

Table 4 lists the content of various heavy metal concentrations in ASR bottom ash and solidified Thiomer matrices before and after leaching. Metals were commonly found components in the ASR bottom ash and this comprise mainly of Cu²⁺ (5741.6 ppm) and Zn²⁺ (1631.9 ppm). It is observed that the concentration of Cu was significantly higher; this is followed by Zn²⁺, Pb²⁺, Cd²⁺, and Cd²⁺. Copper is mainly found in small electric wire segments. All the metals present in the untreated ASR bottom ash exceeded the Korean regulatory levels of 3.0 ppm for Cu²⁺, Zn²⁺ and Pb²⁺, 1.5 ppm for Cd²⁺ and 0.3 ppm for Cd²⁺. These were the metals that needed to be monitored and treated at the end of the process. Results from the ASR bottom ash alone after leaching was able to comply with the heavy metal concentration limit. However, the solidified Thiomer matrices were able to further lower all the heavy metal concentrations. A decrease of 45.5% Cu²⁺, 91.2% Zn²⁺, 55.0% Pb²⁺, 85.0% Cd²⁺ and 98.0% Cd²⁺ were observed by comparing ASR bottom ash after leaching to the mean of the 14 runs at different mixture composition. This shows that runs 1–14 were able to

### Table 3

Comparison of Thiomer solidification and ordinary cement based on different curing time.

<table>
<thead>
<tr>
<th>Property</th>
<th>Curing time</th>
<th>Thiomer solidification (This study)</th>
<th>SPB/ASR bottom ash/Sand wt%</th>
<th>Ordinary Portland cement concrete (Çolak (2006))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>SpB/ASR/Thiomer (30/30/38)</td>
<td>30/40/30</td>
<td>35/35/30</td>
</tr>
<tr>
<td>Compressive strength (MPa)</td>
<td>1 day</td>
<td>47.7</td>
<td>50.4</td>
<td>55.6</td>
</tr>
<tr>
<td></td>
<td>7 days</td>
<td>59.4</td>
<td>76.6</td>
<td>77.2</td>
</tr>
</tbody>
</table>

### Table 4

Heavy metal leaching test of ASR bottom ash and various Thiomer matrix.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Before leaching</th>
<th>After leaching</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ASR bottom ash</td>
<td>Thiomer solidification (by run)</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>5741.6</td>
<td>57.5</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>1631.9</td>
<td>36.1</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>31.6</td>
<td>19.2</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>9.2</td>
<td>9.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ppm</th>
<th>1 day</th>
<th>47.7</th>
<th>50.4</th>
<th>55.6</th>
<th>2–22</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-day</td>
<td>76.6</td>
<td>77.2</td>
<td></td>
<td>8–43</td>
<td></td>
</tr>
</tbody>
</table>
adequately decrease the concentration of heavy metals from eluting into the solution which proves the effectiveness of Thiomer addition in the mixture. Approximately 99.6—100% of the intrinsic heavy metal immobilization efficiency was achieved through the eluted heavy metal concentrations in the untreated ASR bottom ash with the mean result of the 14 runs. High immobilization efficiency of Thiomer solidification is due to introducing sulfur on the particle surface of ASR bottom ash which converts the heavy metals into highly insoluble metal sulfide form that simultaneously encapsulates the ash waste (Sawada et al., 2001; Simic, 2013).

3.4. Practical implications of this work

Various solidification/stabilization process of past literature at different component mixtures were compared to the research findings of this study (Cerbo et al., 2017; Li and Poon, 2017; Pesonen et al., 2016). As listed in Table 5, Thiomer has showed superiority based on its compressive strength and heavy metals leaching. Thiomer as the binding material shows to be 5.6—103.5 times higher in terms of compressive strength against Portland cement. The utilization of Thiomer was able to surpass the treatment time of Portland cement due to achieving the highest result in compressive strength at 1 day. This is due waterless characteristic of the modified sulfur in Thiomer that is capable of reaching its full strength in the concrete product (Moon et al., 2016). Furthermore, Thiomer was also able to fully comply with the stringent environmental regulations of Korea in terms of the heavy metals leaching results as compared with the conventionally used Portland cement.

Based on the results in this study, Thiomer proves to be a novel binding material that showed high compressive strength and eco-friendly in terms of its heavy metal immobilization capacity over the conventionally utilized Portland cement binder. Currently, there is a global surplus (6—12 million metric tons) in sulfur generated in gas and refineries processing plants (Mohamed and El Gamal, 2011). The utilization of this sulfur compounds into Thiomer would prove to be beneficial to expand the sulfur consumption in non-traditional markets which is an acceptable sulfur disposal method that does not compromise the environmental situation. This proves to be a potential new market that will avoid the impending sulfur disposal crises and bring new job opportunities especially for the developing countries for the alternative usage of sulfur. In the 21st century, stringent environmental regulations with respect to the limits of sulfur levels and sulfur dioxide emissions in fuel oil brings about the importance of the desulfurization process (Choi et al., 2017a, 2017b, 2016b). After the desulfurization process in fuel oil, using the sulfur products into the development of Thiomer as a potential binding material for concrete products can therefore be a complete step in dealing with the desulfurization of fuel oil without producing sulfur wastes. Furthermore, some future works extending the study of Thiomer in this research may include a cost analysis, up-scale analysis and monitoring other contaminants (ex. radioactive waste) that is present in the ASR bottom ash.

4. Conclusions

In this study, the solidification/stabilization technique upon using the Thiomer matrix has successfully demonstrated high compressive strength and heavy metal immobilization efficiency. The response surface methodology with D-optimal mixture design was used in examining the effects of Thiomer, ASR bottom ash and sand to predict the response of compressive strength for all experimental regions by regression and statistical significance analysis. The analysis of response surface showed Thiomer has a significant interaction towards ASR bottom ash and sand. Results indicated high compressive strength with an increase in Thiomer content. The optimum compressive strength of 55.9 MPa was attained using the following conditions: 33.6 wt% Thiomer, 36.4 wt % ASR bottom ash and 30.0 wt% sand. The solidified Thiomer specimen has shown superior compressive strength than in ordinary Portland cement with 1 and 7 days curing time. Thiomer solidification was also able to immobilize the heavy metals in ASR bottom ash to acceptable regulatory levels using the leaching test. The morphology of Thiomer solidification using FE-SEM illustrated a successful blending synthesis due to the apparent alteration of its surface structure that has led to results of high compressive strength and efficient heavy metal immobilization. Therefore, Thiomer has proven to be an effective construction material that are able to surpass ordinary concrete in terms of compressive strength, and being environmentally friendly in terms of its capacity towards heavy metal immobilization in ASR bottom ash.

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References


