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# Novel synthesis and applications of Thiomer solidification for heavy metals immobilization in hazardous ASR/ISW thermal residue

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ABSTRACT

The present paper reports the novel synthesis and application of Thiomer solidification for heavy metal immobilization in hazardous automobile shredder residues and industrial solid waste (ASR/ISW) thermal residues. The word Thiomer is a combination of the prefix of a sulfur-containing compound "Thio" and the suffix of "Polymer" meaning a large molecule compound of many repeated subunits. To immobilize heavy metals, either ASR/ISW thermal residues (including bottom and fly ash) was mixed well with Thiomer and heated at 140 °C. After Thiomer solidification, approximately 91–100% heavy metal immobilization was achieved. The morphology and mineral phases of the Thiomer-solidified ASR/ISW thermal residue were characterized by field emission-scanning electron microscopy, energy dispersive X-ray spectroscopy and X-ray diffraction (XRD), which indicated that the amounts of heavy metals detectable on the ASR/ISW thermal residue surface decreased and the sulfur mass percent increased. XRD indicated that the main fraction of the enclosed/bound materials on the ASR/ISW residue contained sulfur associated crystalline complexes. The Thiomer solidified process could convert the heavy metal compounds into highly insoluble metal sulfides and simultaneously encapsulate the ASR/ISW thermal residue. These results show that the proposed method can be applied to the immobilization of ASR/ISW hazardous ash involving heavy metals.



## 1. Introduction

Automobile recycling produces about five million tons of automotive shredder residues (ASR) in the world every year, and most of this residue ends up in landfill or is thermally converted (Patnaik and Satapathy, 2009; Chung, 2010; Ahmaruzzaman, 2010). ASR can be classified as 'hazardous waste' owing to its high heterogeneity and variable composition of hazardous substances, such as heavy metals, polychlorinated biphenyls (PCBs), and brominated flame retardants (BFRs) added to the list of POPs (persistent organic pollutants) (Darnell, 1996; Cunliffe et al., 2003; Ciacci et al., 2010; Ahmaruzzaman, 2010). Similarly, industrial solid waste (ISW) is mostly dangerous in nature as it can be highly inflammable, reactive or toxic, and consist, of hazardous heavy metals (Ioannidis and Zouboulis, 2003; Ioannidis and Zouboulis, 2006; Ioannidis et al., 2006). In Korea, incineration is an important method for treating municipal and industrial solid waste including ASR (Environmental Protection Agency (EPA), 2010). In recent years, more that 85% of ASR/ISW was incinerated to decrease its volume in Korea. According to the U.S. Environmental Protection Agency, approximately one million tons of ASR could be recovered for fuel by a thermal process (Hwang et al., 2008). On the other hand, the ASR/ISW thermal process removes some of the organic material but concentrates the heavy metals and POPs present in the ASR/ISW by a factor of up to 20 in the ash residues (Kalb et al., 1985). As a consequence, the amount of heavy metals and POPs in the residues obtained from the ASR/ISW thermal processes can be remarkably high compared to the common municipal solid waste incinerator (MSWI) bottom and fly ash (Kalb et al., 1985, Cunliffe et al., 2003; Hwang et al., 2008).

According to the Korea's Ministry of Environment (MOE) new policy, fly ash/bottom ash containing toxic substances were treated only in hazardous waste landfill sites following strict treatment procedures (Kalb et al., 1991). The major environmental concerns in relation to the short and long-term impact of landfilling of ASR/ISW residues are connected to the risk of leaching and the subsequent release of potentially harmful substances into the environment, particularly inorganic salts and metals/trace elements (Kalb et al., 1985; Cunliffe et al., 2003; Hwang et al., 2008). The Korea directive set the recycling target including thermal recycling as 85% by 2006 and 95% by 2015 on the resource circulation of electrical and electronic (EE) equipment and vehicles. In addition, to

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achieving 95% recycling by 2015 in Korea, several procedures on ASR can be implemented, such as the direct use of ASR residue in the cement industry, and/or the direct use of ASR as a secondary raw material (Katsuura et al., 1996). Despite this, many of these recovery options appear to be limited, due to the possible low acceptability of ASR/ISW-based products on the market. The recovery of slag, bottom and fly ash after an ASR thermal treatment is an option that is not normally considered due to the excessive amount of contaminants, particularly heavy metals. Therefore, a heavy metals immobilization treatment is needed before any disposal/use for these residues from the ASR incinerator.

In view of the treatment of heavy metals condensed in ASR/ISW fly ash and bottom ash discharged from thermal processes, there are three treatment methods according to their purpose. One is metal removal recovery, the second is the immobilization for landfill disposal and the third is the treated wastes should comply with building material standards, thereby increasing the potential for recycling in the construction industry. The removal of heavy metals by acid extraction has been studied (Kim et al., 2004), but its practical use has not been realized. On the other hand, immobilization by binding with cement, which has been the leading immobilization method for MSW incineration fly ash, particularly from an economical view, is difficult to apply for this bottom ash because the inhibitory salts that coexist with heavy metals in bottom ash prevent the formation of hydrates in cement solidification (Lee, 2007; Mancini et al., 2014). An immobilization method using asphalt instead of cement as a binder has been reported (Suzuki et al., 1979; McBee et al., 1981; McBee and Weber, 1990). This method aims to use the appropriate characteristics of asphalt as a solidification matrix, such as adhesive property, water repellency, and binding characteristics power. The heavy metals concentration in the eluted solution is decreased by adding sodium hydroxide to the mixing fly ash and asphalt (Mirabile et al., 2002). On the other hand, it is difficult to achieve the severe heavy metal emission standards for disposal today, because the dissolution characteristics of heavy metals depends on the pH of the eluted solution.

The sulfur polymer binder (SPB) process can be used to convert heavy metal compounds into the highly insoluble metal sulfides and simultaneously encapsulate the waste (Sullivan and McBee, 1976; Mishras and Shimpi, 2005; Mohamed and El Gamal, 2007; Mohamed and El Gamal, 2009). This paper proposes a novel method of immobilizing heavy metals by chemical reaction substitution, in which heavy metals involved in ASR/ISW fly ash or bottom ash are reacted with Thiomer. Thiomer is a new name for eco-friendly construction materials that is a combination of the prefix of a sulfur-containing compound "Thio" and the suffix of "Polymer" meaning a large molecule compound of many repeated subunits. Thiomer is our brand name of SPB (sulfur polymer binder) however; it includes customized fly ash as filler. Fly ash, an industrial waste, can be used as a potential filler material in polymer matrix composites because it is a mixture of oxide ceramics. It improves the physical and mechanical properties of the composites (Patnaik and Satapathy, 2009). Reduction in filler size gives better enhancement in properties due to uniform distribution of particles in polymer matrix and increases degree of cross linking of matrix (Mishras and Shimpi, 2005). A mechanical property such as tensile strength, impact strength and hardness of Thiomer is enhanced with the addition of smaller size filler materials (Najat and Samir, 2011). In all particulate filled systems, the adhesion between the matrix and the filler plays a significant role in determining key properties such as strength and toughness. The size of the interface is generally dependent on the specific surface area of the filler. Modification of surface properties of the fillers can yield significant changes in strength (Najat and Samir, 2011). Fly ash mainly consists of alumina and silica, which are expected to improve the composite properties. Fly ash also consists to some extent, hollow spherical particles (termed cenospheres) which aid in maintenance lower density values for the composite, a feature of considerable significance in weight specific applications (Pedlow, 1978; Rothon, 1997). Therefore, it is cost effective and safe to store or use it (Fuhrmann et al., 2002; Randall and Chattopadhyay, 2004). The addition of Thiomer can to decrease the leachability of heavy metals if heavy metals are converted to metal sulfides because most metal sulfides have lower solubility than the other metal compounds. The durability of Thiomer solidified ASR/ISW specimens was also evaluated in terms of its ability to absorb water, resist acid and salt penetration, and leachability as function of the medium and time.

## 2. Materials and methods

### 2.1. ASR/ISW thermal residue sample collection and characterization

ASR/ISW thermal residue (bottom ash and fly ash), a by-product of burning an ASR/ISW sample, was collected over several days at an ASR/ISW incineration plant at Ulsan, Korea. The ash residue samples collected over several days were mixed well to obtain a homogenized sample composition and the heavy metals were characterized. The fly ash residues include the particulate material (ash) from the bag filter or captured after reagent injection in the acid gas treatment units prior to effluent gas discharge into the atmosphere (Cunliffe et al., 2003). The material is a very fine, powdery material, predominantly comprised of silica, with particles in the form of tiny hollow spheres consisting of oxides of silica, aluminum and iron with smaller amounts of calcium, magnesium and potassium oxides. In contrast, the bottom ash is odorless and composed of heterogeneous materials of various sizes in the form of powder or granules mixed with pulverulent char-like black powder. This stream represents the main product of ASR/ISW gasification and, on average, constitutes approximately 16–18% of the total ASR burnt (Cunliffe et al., 2003). The fine aggregate (sand) was commercially obtained from a store. The inorganic components in the samples of fly ash/bottom ash and aggregate were analyzed quantitatively by X-ray fluorescence (XRF, EDX-720; Shimadzu Corp.) with high accuracy, and the results are listed in Table 1.

The total heavy metal concentrations in the ASR/ISW thermal residue were measured using the method described by Baker and Amacher (Baker and Amacher, 1982; Najat and Samir, 2011), which consisted of the digestion of fly ash samples in a mixture of HF–$HNO_3$–$HClO_4$–$H_2SO_4$. Approximately 1 g of fly ash was kept in a 250 mL Teflon beaker and mixed sequentially with 4 mL of 40% hydrofluoric acid, 2 mL of 30% perchloric acid, 5 mL of 60% nitric acid, and 5 mL of 60% hydrochloric acid. The mixture was stirred and heated continuously after the addition of each reagent. The mixture was then dissolved in 50 mL HCl 0.1 M to yield a solution of total metal concentrations. The total heavy metal content in the acid solutions was measured by inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent 720). All experiments were conducted in triplicate and the average value was taken.

**Table 1**
Main inorganic chemical composition of ASR materials (wt%) used.

| | $Al_2O_3$ | CaO | $Fe_2O_3$ | $K_2O$ | MgO | $SiO_2$ | $SO_3$ | Cl |
|---|---|---|---|---|---|---|---|---|
| ASR fly ash | 0.55 | 40.34 | 3.07 | 1.05 | 0.39 | 2.65 | 2.65 | 30.1 |
| ASR bottom ash | 1.88 | 32.19 | 19.54 | 0.52 | 0.89 | 9.16 | 3.65 | 4.2 |
| ISW bottom ash | 1.01 | 30.2 | 15.43 | 0.48 | 0.81 | 10.1 | 2.9 | 6.2 |
| Sand | 0.47 | 16.35 | 0.68 | 0.13 | 1.16 | 74.43 | – | – |

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