

Detoxification of Hazardous Organic/Inorganic Contaminants in Automobile Shredder Residue by Multi-Functioned Nano-Size Metallic Calcium Composite

Srinivasa Reddy Mallampati, Byoung Ho Lee, Yoshiharu Mitoma, Simion Cristian

Abstract—In recent years, environmental nanotechnology has risen to the forefront and the new properties and enhanced reactivities offered by nanomaterial may offer a new, low-cost paradigm to solving complex environmental pollution problems. This study assessed the synthesis and application of multi-functioned nano-size metallic calcium (nMC) composite for detoxification of hazardous inorganic (heavy metals (HMs)/organic chlorinated/brominated compound (CBCs) contaminants in automobile shredder residue (ASR). ASR residues ball milled with nMC composite can achieve about 90-100% of HMs immobilization and CBCs decomposition. The results highlight the low quantity of HMs leached from ASR residues after treatment with nMC, which was found to be lower than the standard regulatory limit for hazardous waste landfills. The use of nMC composite in a mechanochemical process to treat hazardous ASR (dry conditions) is a simple and innovative approach to remediate hazardous inorganic/organic cross-contaminates in ASR.

Keywords—Nano-sized metallic calcium, automobile shredder residue, organic/inorganic contaminants, immobilization, detoxification.

I. INTRODUCTION

ASR can be classified as hazardous waste based on the presence of inorganic HMs, organic polychlorinated biphenyls (PCBs), brominated flame retardants (BFRs), and other persistent organic pollutants (POPs) [1], [2]. ASR residues mostly includes unburned substance (*i.e.* soil/sand) which is the most controlled mineral composition present in ASR dust, which also encloses about 4 wt% of initial ASR. Recent studies have revealed that the HMs leached from different ASR residues were found to be higher than the regulatory limit for hazardous waste landfills. In order to reassure the public and render ASR-based materials completely safe, HMs and CBCs must be immobilized or eliminated before the residues can be disposed of or used.

Cross-contaminated wastes with both HMs and CBCs are

Srinivasa Reddy Mallampati is with the Department of Civil and Environmental Engineering, University of Ulsan, Ulsan 680-749, Republic of Korea (corresponding author, phone:+82-52-259-1412; fax: +82-52-259-2629; e-mail: srireddys@ulsan.ac.kr, srireddys@hotmail.com).

Byoung Ho Lee is with the Department of Civil and Environmental Engineering, University of Ulsan, Ulsan 680-749, Republic of Korea.

Yoshiharu Mitoma is with the Department of Environmental Sciences, Prefectural University of Hiroshima, 562 Nanatsuka-Cho, Shobara City, Hiroshima, 727-0023, Japan.

Simion Cristian is with the Politehnica University of Bucharest, Department of Organic Chemistry, 060042, Bucharest Romania.

notoriously hard to remediate, even when taking advantage of the most suitable technologies [3]. Immobilization processes use a large variety of binders, such as hydroxyapatites [4], zeolites and calcium hydroxides [5], and phosphates and biochars [6], as well as a cement-based stabilization/solidification treatment process, are generally preferred for treating HM-contaminated wastes [7]. On the other hand, the general methods proposed for waste removal and/or degradation of CBCs are physical, chemical, or microbial. Among the physical methods, the most prominent are high-temperature incineration, ultrasonication, and photochemical degradation [8]. Chemical methods can be classified into two main categories: dehalogenation and hydrodehalogenation processes [9]. However, these wet methods is expensive and energy consuming and often engenders a high risk for the generation of other organic pollutants. Therefore, the necessity of dry, water-free, cost effective methods should be considered with possible industrial application. Mechanochemical processing is a relatively simple and dry method to treat cross-contaminated wastes. This process consists of introducing into a ball mill one or several immobilization/dechlorination additives, along with the contaminated substrate. This study assessed the synthesis and application of nMC composite for detoxification of hazardous HMs and CBCs contaminants in ASR.

II. MATERIALS AND METHODS

A. Synthesis of nMC/CaO

Solvent-free production of the reagent, a dispersed mixture of nMC and CaO, was prepared through a planetary ball-milling process [10]-[12]. Granular particles of metallic Ca (Kishida Chemicals, 99%, particle size distribution: 1.0-2.5 mm, surface area: 0.43-0.48 m²/g) and fine grade CaO (Kishida Chemicals, 98%, previously dried at 825°C for 2h) were introduced into the planetary ball-mill (Retsch PM-100; 20 pieces SUS, 32g/ball) at a weight ratio of Ca/CaO = 2/5. The Ca and CaO were then milled for 1h at room temperature in an Ar gas atmosphere at 600 rpm, to a rotation-to-revolution ratio of 1:-2. The average observed size of the nMC solid, porous, spherical and amorphous particles were 183 nm (Figs. 1 (a) and (b)). Through XRD analysis, the broad peaks at 2θ of 30°, 40° and 50° confirmed the presence of calcium (Ca) and calcium oxide (CaO) in the nMC sample (Fig. 1 (c)).

B. ASR Samples Collection and Ball Milling Treatment with nMC

In the present study, we collected a fraction of ASR residue (0.250 mm). Quantitative analyses of the main inorganic components in the samples of ASR were analyzed by X-ray fluorescence spectrometry (XRF) (EDX-720; Shimadzu Corp.) and the values were presented in Table I [10]-[12]. ASR residue (0.250 mm) alone and mixtures of ASR (10 g) and 0.5 g (5 wt%) of nMC additive were introduced into a 250 mL stainless steel pot along with five stainless steel balls (20 mm diameter). At the end of each ball-milling interval, samples were taken for further analysis. Total HM concentrations in content (acid digested solutions) and eluted

solutions were measured using inductively coupled plasma optical emission spectrometry (ICP-OES, 720-ES; Varian). CBC concentrations before and after ball-milling treatments were measured as elemental Cl and Br, using XRF with high accuracy. HM immobilization and CBC decomposition mechanisms, as well as eventual after-treatment ASR alterations, were analyzed through microstructural characterization and elemental mapping, with the aid of SEM combined with electron dispersive spectroscopy (SEM/EDS). Further analyses of the crystalline phases and constituents on the surface of solid samples, before and after treatment, were conducted using an XRD. XRD data were collected at 2 θ values of 10 $^{\circ}$ – 80 $^{\circ}$.

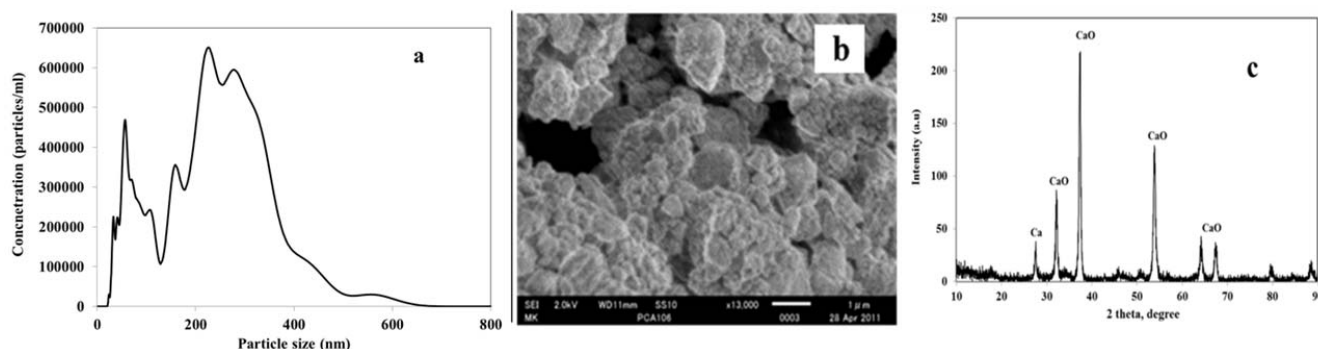


Fig. 1 nMC (a) particle size distribution, (b) SEM microstructure ($\times 5 \times 10^3$) and (c) XRD spectra

TABLE I
MAIN INORGANIC CHEMICAL COMPOSITIONS IN ASR (WT%).

Component	0.250 mm
SiO ₂	32.0 \pm 1.2
Fe ₂ O ₃	35.4 \pm 1.4
Al ₂ O ₃	5.0 \pm 0.25
TiO ₂	4.3 \pm 0.02
CaO	16.4 \pm 1.0
MgO	0.46 \pm 0.1
SO ₃	3.0 \pm 0.01
Na ₂ O	0.4 \pm 0.10
K ₂ O	2.1 \pm 0.20

III. RESULTS AND DISCUSSION

A. HM Immobilization and CBCs Decomposition

It is obvious that ball-milling has a certain effect on HM mobility, since after a simple treatment, HMs leached concentrations are lower. However, when nMC dispersion is added to the process, there is a drastic drop of HM concentrations in the leachate. These concentrations correspond to an intrinsic HM immobilization efficiency of about 95–100%, regardless of ASR dimensions (Fig. 2). Even though a simple ball-milling treatment resulted in greatly decreasing the leachable concentrations of many HMs, they were still higher than the regulation limits. Thus, the treatment with nMC is necessary, in order to lower the concentration of leachable HMs to a level lower than the leachate regulatory standard limits (i.e., Co, Cd 0.3 mg L⁻¹, Cr 1.5 mg L⁻¹, Fe, Pb and Zn 3.0 mg L⁻¹, Mn and Ni 1 mg L⁻¹). Generally, CaO

increases ASR pH, and favors the formation of oxides, metal carbonate precipitates and complexes that decrease metal mobility. In particular, n-Ca/CaO generates a high pH when mixed with ASR in the presence of moisture, due to the formation of Ca(OH)₂, a strong base. High pH value is another effort in the mobilization of HMs. On the other hand, nMC can also react with moisture and CO₂ to yield insoluble pozzolanic-like cements that can enclose or bind HMs. When combined with the formation of Ca-associated salts (CaCO₃/Ca(OH)₂), this leads to the formation of an almost impenetrable shell layer [10], [11]. As a result, immobile Ca salts remarkably inhibit the mobility of HMs in ASR. On the other hand, the halogenated organic compound concentrations were measured before and after ball-milling treatment, and Table II presents the values as gross chlorine [Cl] and bromine [Br] content.

TABLE II
CBC CONCENTRATIONS IN ASR BEFORE AND AFTER BALL-MILLING TREATMENT (WT.%)

Elements	Before treatment	0.250 mm	
		Simple BM	BM with n-Ca/CaO
Cl	1.74 \pm 0.45	0.44 \pm 0.05	0.04 \pm 0.0
Br	36.4 \pm 2.02	9.4 \pm 1.5	0.48 \pm 0.09

After simple ball-milling, the concentrations of Cl and Br diminished by 75% (Fig. 2 (b)). While, the concentrations of Cl and Br in ASR residues decreased dramatically after ball-milling with nMC, which corresponds to an intrinsic Cl and Br removal efficiency of 90–99% by decomposition (Fig. 2 (b)).

This may be due to the high surface area made by ball milling treatment. The particle surface area increases and the Cl and Br decomposition increases because of the increased adsorption area [11]. Therefore, the fine fraction showed high decomposition of Cl and Br. Considering that the hydrodechlorination/hydrodebromination processes are probably radical in nature, metallic calcium is more prone to generate free electrons than its oxide, which in turn is available to trap Cl and Br atoms formed in the process. Thus,

adding to the sum of Ca salts that contribute to the immobilization of HMs. In other words, in the particles that immobilize both HMs and [Cl]/[Br], HMs are in the core, surrounded by the impenetrable wall of Ca salts (including [Cl]/[Br] Ca salts that are decomposed inside the shell), surrounded by a stronger shell of $[\text{CaCO}_3/\text{Ca}(\text{OH})_2]$ mixed salts that contribute to the low permeability of HMs and/or CBCs.

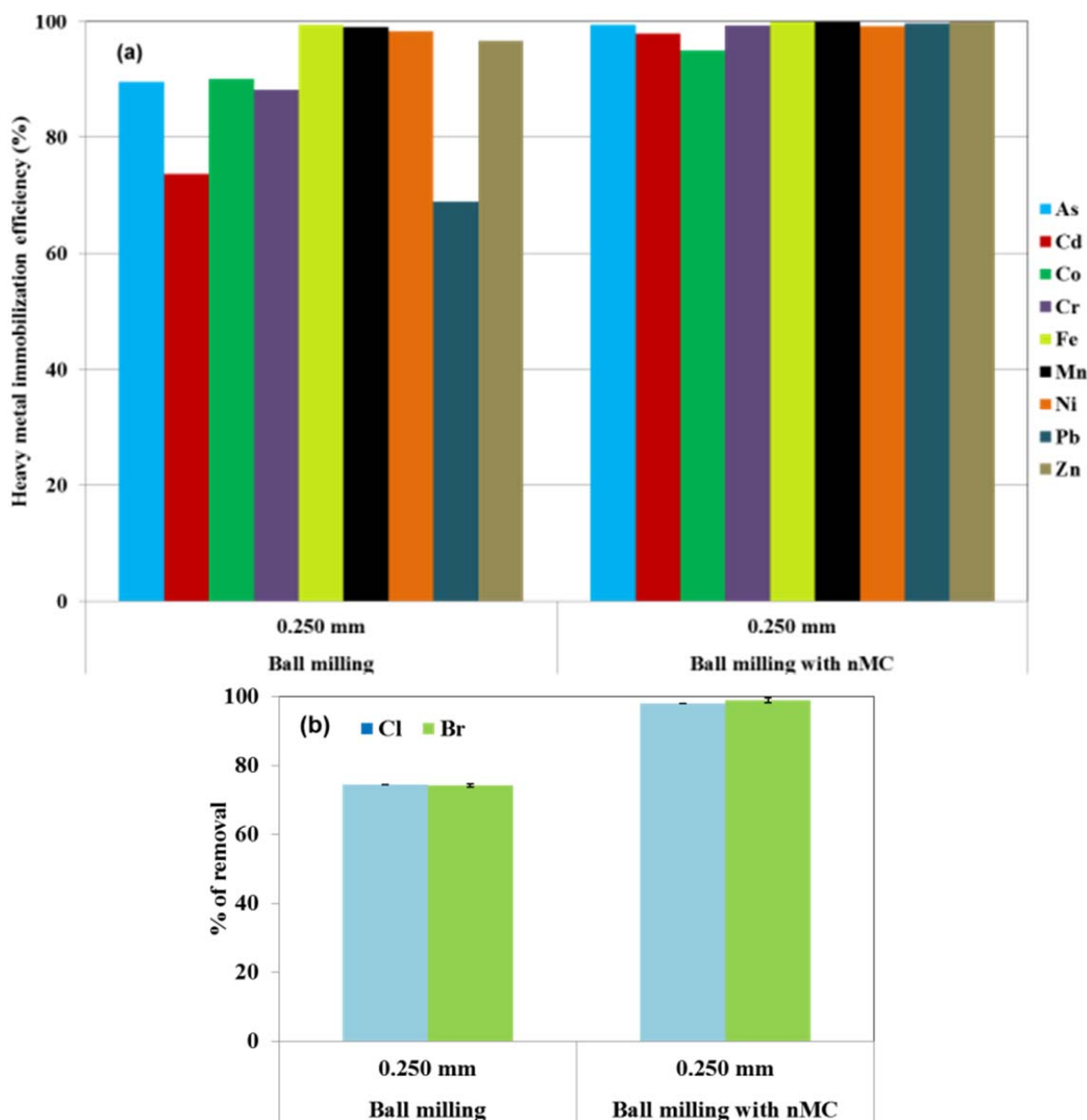


Fig. 2 (a) HMs immobilization and (b) CBC trapping efficiency in ASR residues after treatment with nMC

Fig. 3 presents a schematic of a possible pathway for the enhanced HM immobilization and CBCs decomposition capacity attained by ball-milling treatment with nMC. When ASR is contaminated by HMs and halogenated compounds, we may assume that these are adsorbed onto ASR particles through a surface coordination process (Fig. 3 (a)). While, the

ball-milling process starts, ASR particles are subjected to high energetic collisions that may promote both aggregation and breaking processes, as well as an accumulation of crystalline defects and vacancy amorphization (Fig. 3 (b)) [3], [10]. The aggregation phenomenon with the subsequent formation of stable aggregates results in a net increase of ASR particle size.

When aggregation occurs in the presence of nMC, the amount of HMs and halogenated compounds adsorbed into the surface of two overlapping particles may be entrapped within the newly formed aggregates (Fig. 3 (b)). However, nMC can produce immobile salts by reacting with moisture and atmospheric CO₂, yielding pozzolanic cement with specific hydraulic properties. As a result, HMs and halogenated

compounds would be further enclosed in the immobile Ca-associated (CaCO₃/Ca(OH)₂ salts (Fig. 3 (c)) [10], [11]. Consequently, the amount of HMs exposed to leaching is reduced; thereby enhancing the HMs immobilization and CBCs decomposition obtained using this nMC ball-milling treatment.

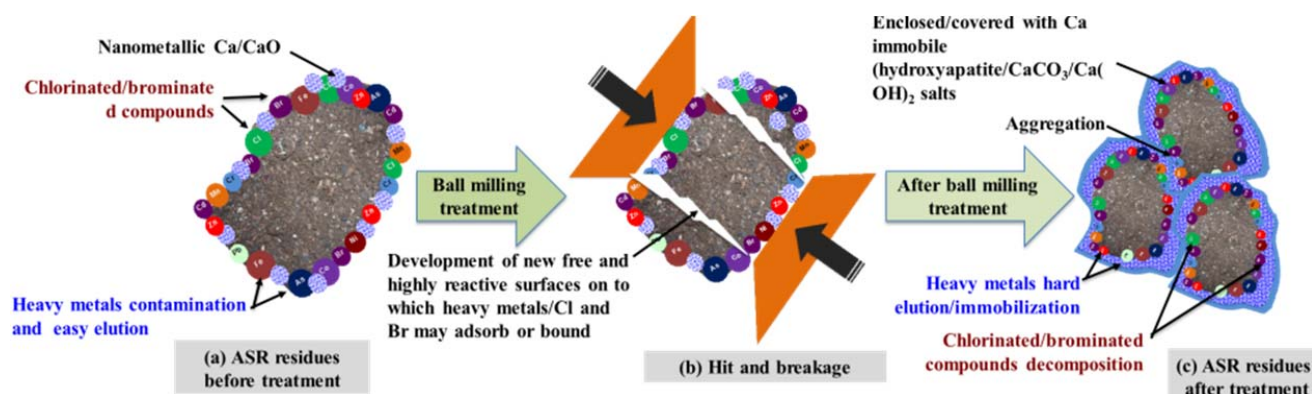


Fig. 3 Schematic representation of possible HM immobilization and CBC decomposition pathways in ASR after ball-milling: (a) HM/CBC adsorption and nMC addition, (b) hit and breakage, and (c) aggregation and surface enclosing (immobilized HMs and decomposed CBCs) [11]

IV. CONCLUSION

The mechanochemical treatment of dually HM/CBC contaminated ASR in the presence of a multi-functional nMC is the most effective method to immobilize harmful compounds. Immobilization efficiencies increase to 95–100% and 90–99% for HMs and CBCs, respectively. The concentration of leachable HMs were substantially decreased after ball-milling with an n-Ca/CaO mixture to a level lower than the leachate regulatory standard limits proposed by the Korean Hazardous Waste Elution Standard regulatory threshold. The use of a nanometallic Ca/CaO dispersed mixture in a ball-milling technique to treat hazardous ASRs in dry conditions is a novel approach for the remediation of cross-contaminated ASRs with HMs and halogenated compounds.

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