Dechlorination of auto shredder residues

Hua-Shan Tai *, Chia-Ming Liu, Yun-Jou Wu

Department of Safety, Health and Environmental Engineering, National Kaohsiung First University of Science and Technology,
2, Juoyue Road, Nantsu District, Kaohsiung 811, Taiwan, ROC

Abstract

Dechlorination of ASR (auto shredder residual) wastes has been studied in the present work. ASR was predechlorinated with $Ca(OH)_2$ extraction as well as dechlorinated with $Ca(OH)_2$ during incineration or pyrolysis. Experimentally, pre-dechlorination of ASR via extraction of Cl with a $Ca(OH)_2$ solution (pH 12.5) may reduce Cl contain in the ASR by 15%. Extraction of Cl at elevated temperatures (such as 373 K), interestingly, led to a further reduction of Cl in the ASR to 33.5%. A small amount of HCl and light hydrocarbons (C_1–C_5) were yielded during pyrolysis of the ASR in the presence of $Ca(OH)_2$ at 773 K. On the contrary, 75–85% of Cl may be mineralized ($CaCl_2$) with $Ca(OH)_2$ (or CaO) during incineration at 1100 K.
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1. Introduction

After shredding of waste automobiles and recycling of valuable metals, the residual matters (20–30%) are known as the shredder residue (ASR) [1,2]. About 4000 tons/year of ASR discharged from automobile shredding plants were generally treated by incineration [3,4]. ASR that contains combustible materials such as foam, rubber and plastics with a high heating value may be recycled as residue derived fuels (RDFs) [5,6]. RDFs may be combusted with coal or natural gas in boilers [7–10]. However, ASR frequently contains 1–4% of Cl [11]. Direct incineration of ASR may lead to yield toxic species such as dioxins in the flue gas. In addition, HCl formed during incineration of ASR may reduce the service life of main incineration equipments and instruments via mainly chemical corrosion. Thus, it is of great importance in dechlorination of ASR prior to incineration or other thermal treatment processes.

In the presence of $Ca(OH)_2$ (Ca/Cl = 13), a high reduction (>70%) of HCl in the flue gas was found during incineration of ASR [12]. $CaCl_2$ was the main chloride in the incineration ashes ($Ca(OH)_2 \rightarrow CaO + H_2O$, $CaO + 2HCl \rightarrow CaCl_2 + H_2O$).

In addition to reduction of HCl emissions, Tagashira et al. [13] also observed a highly reduction of dioxins in the flue gas as $CaCO_3$ or $Ca(OH)_2$ was added with the ASR feeding to incinerators. At Ca/(S + 0.5Cl) = 2, a removal efficiency of Cl (60%) in the flue gas might be achieved. Thus, the main objective of this work was to investigate dechlorination of ASR with $Ca(OH)_2$ via extraction, incineration and pyrolysis.

2. Experimental

The ASR wastes were sampled from a waste automobile shredding plant in Taiwan. Glass, electrical wires, gravel and metal components in the ASR wastes were separated by a pulverizer with 5 and 0.5 mm sieves. The proximate and elemental analyses of the ASR samples were determined by standard EPA methods (moisture (NIEA R203.00T), ashes (NIEA R204.00T), combustible portion (NIEA R204.00T), volatile matter (NIEA R212.00C), and elemental analyses (Thermo Quest, EA1110)) [14].

Pre-dechlorination of the ASR sample by extraction was conducted in the $Ca(OH)_2$ solution at 298 K for 0.5–5 h. Dechlorination of ASR with $Ca(OH)_2$ during incineration and/or pyrolysis was carried out at 1100 and 500 K, respectively. Effectiveness of dechlorination was determined with a sulfur–chlorine analyzer (Mitsubishi, TSX-10).

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* Corresponding author. Tel.: +886 7 6011540; fax: +886 7 6011608.
E-mail address: huashan@ccms.nkfust.edu.tw (H.-S. Tai).

Table 1
Proximate and elemental analysis of the ASR wastes

Proximate analysis (%)	
Water	1.0
Ash	18.4
Volatile	65.2
Fixed carbon	15.4
Elemental analysis (%)	
Carbon (C)	57.7
Hydrogen (H)	6.6
Oxygen (O)	30.7
Nitrogen (N)	2.6
Sulfur (S)	0.52
Chlorine (Cl)	1.8
Higher heat value (cal/g)	7000

3. Results and discussion

Table 1 shows the proximate and elemental analyses of the ASR samples. Typically, the ASR contains 18.4% ash and 80.6% combustibles that provide a heating value of 7000 cal/g approximately. Note that approximately 1.8% of Cl was found in the ASR.

Extraction of Cl in the ASR sample with a $Ca(OH)_2$ solution (pH value = 12.5) for 0.5–5 h at 298 K is shown in Fig. 1. The Cl removal efficiency during extraction was 14% approximately at the early stage. Prolong the extraction time to 5 h, the Cl removal efficiency was further increased to 14.8%.

Extraction of Cl in the ASR sample with the $Ca(OH)_2$ solution was also conducted at 293–373 K for 1 h (see Fig. 2). It is clear that at $T < 333$ K, the extraction might not be an activated process. Mainly inorganic Cl was extracted by $Ca(OH)_2$. At $T > 333$ K, organic Cl might be extracted, to some extent. The activation energy for extraction at 330–373 K was presumably a first order reaction involved.

Since interaction of $Ca(OH)_2$ with organic Cl may be an activated process, a high Cl removal efficiency may be achieved at
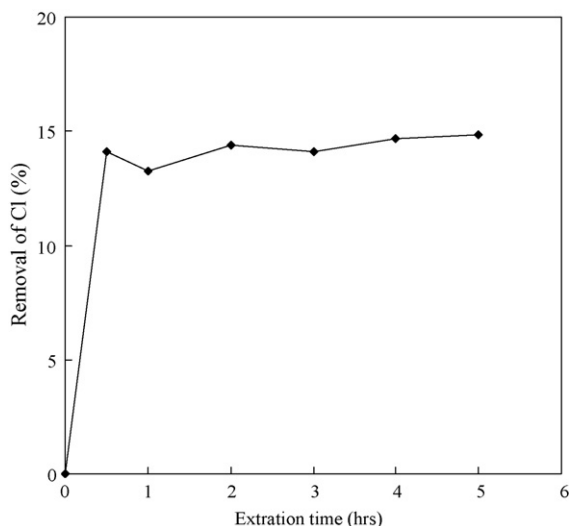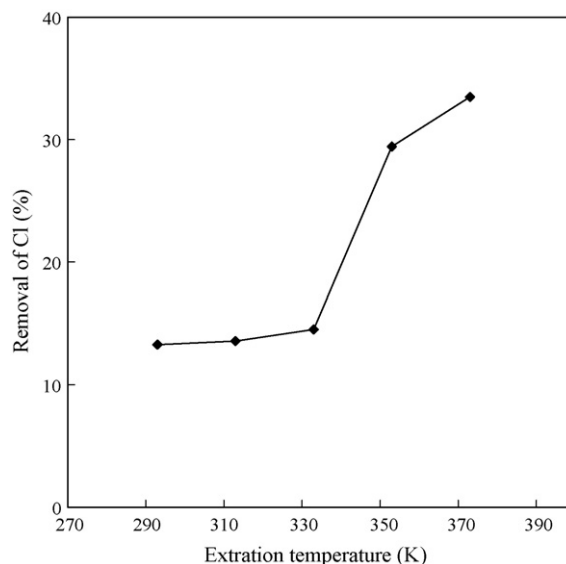
Fig. 2. Removal efficiency of Cl during extraction with the $Ca(OH)_2$ solution at 298–398 K for 1 h.

elevated temperatures. Effect of $Ca(OH)_2$ on Cl removal efficiency during pyrolysis of ASR was also investigated. Fig. 3 shows the IR spectra of HCl yielded during pyrolysis of ASR at 573–773 K in the presence of $Ca(OH)_2$ (with the Ca/Cl ratio of 20). At 773 K, a very small amount of light hydrocarbons (C_1–C_5) as well as HCl were observed during pyrolysis of ASR.

At 1100 K, $Ca(OH)_2$ and ASR was co-incinerated. Fig. 4 shows that the Cl removal efficiency increases as the Ca/Cl ratio increases. At $T > 850$ K, $Ca(OH)_2$ was decomposed and yielded CaO and H_2O. The reaction of CaO and Cl to form $CaCl_2$ is thermodynamically favored. Thus, the emission of Cl containing compounds may be reduced. For instance, the Cl removal efficiencies was 72% and 85% for the Ca/Cl ratios of 10 and 75, respectively, during incineration of ASR at 1100 K (see Fig. 4).
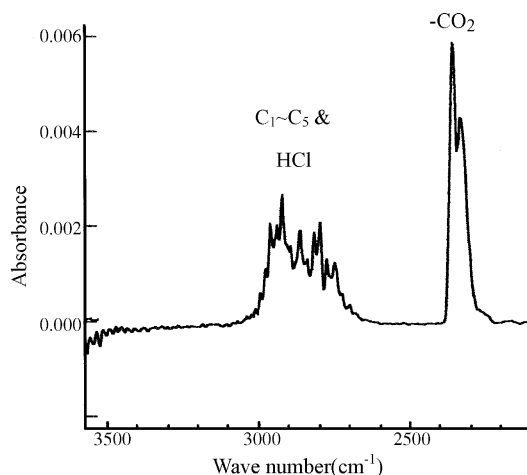
Fig. 1. Removal efficiency of Cl during extraction with the $Ca(OH)_2$ solution at 298 K for 0.5–5 h.

Fig. 3. IR spectra of product gases during pyrolysis of ASR in the presence of $Ca(OH)_2$ at 773 K.
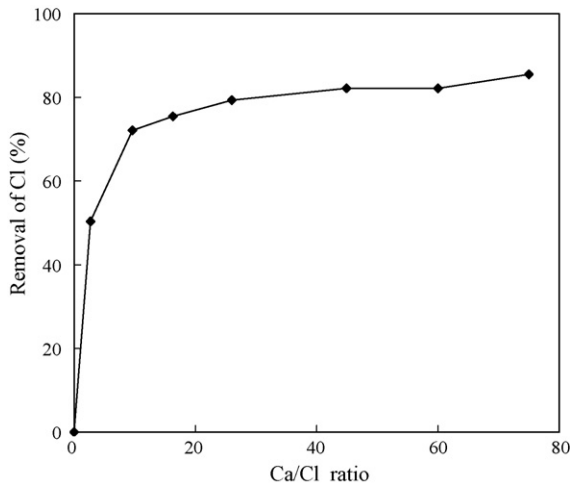
Fig. 4. Effect of Ca/Cl ratios on the removal efficiency of Cl during ASR incineration at 1100 K.

4. Conclusions

Experimentally, pre-dechlorination of ASR via extraction with a Ca(OH)$_2$ solution (pH 12.5) may reduce the Cl contain in the ASR by 15%. Extraction with the Ca(OH)$_2$ solution at 373 K, interestingly, led to a further reduction of Cl in the ASR to 34%. A small amount of HCl and light hydrocarbons (C$_1$–C$_5$) were yielded during pyrolysis of the ASR in the presence of Ca(OH)$_2$ at 773 K. Incineration of ASR with Ca(OH)$_2$ at 1100 K caused significant reductions (75–85%) of Cl emissions.

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