

Sustainable Processes for the Recovery of Heavy Metals and Soluble Salts from Municipal Solid Waste Incineration Fly Ash

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論 文 名： Sustainable Processes for the Recovery of Heavy Metals and Soluble Salts
from Municipal Solid Waste Incineration Fly Ash
(都市固形廃棄物焼却飛灰からの重金属および可溶性塩回収のための
持続可能なプロセス)

区 分： 甲

論 文 内 容 の 要 旨

In Europe, particularly in Switzerland, acid leaching processes have been applied to the resource recovery of municipal solid waste incineration (MSWI) fly ash. This method enables both the resource recovery and harmless treatment of fly ash, making it an ideal, sustainable approach. However, existing processes such as FLUWA (acidic filter and fly ash washing) and HaloSep® suffer from low leaching efficiency for Pb and Cu. Additionally, the recovered heavy metals predominantly form metal hydroxides, which despite the high zinc content, cannot be separated using flotation processes commonly employed by ore processing industries. To recover the heavy metals, a new process called FLUREC (Zn recycling) was developed. While this process enhances the system's complexity and increases treatment costs, it still presents certain challenges. Additionally, there is no effective method to separate calcium chloride from the salts recovered from fly ash. To overcome these issues, this thesis developed three processes: an ammonium leaching process, an acid leaching process, and a salt separation process.

Chapter 1 introduces MSWI fly ash, covering both conventional treatment methods and resource recovery approaches. It focuses particularly on resource recovery methods, with an emphasis on acid leaching processes. The chapter presents the research motivation, purpose, and objectives, and provides a brief outline of the thesis structure.

Chapter 2 evaluates the metal recovery potential (Zn, Pb, Cu, Sb, K) of two fly ash samples, as well as the impact of waste input and water washing pretreatment on the recovery value of fly ash. The results show that both fly ash samples have recovery potential, with waste input significantly affecting the metal recovery value of the fly ash, and water washing pretreatment significantly enhancing the recovery value.

Chapter 3 introduces the ammonium leaching process developed in this study for recovering Zn and Cu from fly ash. This process uses ammonium chloride (NH_4Cl) as the leaching agent and includes several steps; ammonium leaching, ammonia removal, heavy metal removal, and carbonation, which allow for the recycling of NH_4Cl within the system. This chapter investigates the combined effects of ammonium leaching and ammonia removal on the recovery of Zn and Cu from fly ash, the metal concentrations in the heavy metal precipitate, and the changes in the properties of fly ash before and after ammonium leaching. The overall recovery rates for Zn and Cu from fly ash, employing both the ammonium leaching and ammonia removal processes, reached 52.2 % and 85.3 %, respectively. The resulting precipitate from these recovery efforts contained substantial metal concentrations, with 33.6 % Zn and 14.2 % Cu, making it an excellent candidate for further application as a raw material in metal smelting. The mass of the treated fly ash was reduced to just 30.6 % of its original weight. However, the form of heavy metals in the leached fly ash

showed no significant changes and remained primarily in the exchange/carbonate form.

Chapter 4 introduces the acid leaching process developed in this study for recovering heavy metals (Zn, Pb, Cu) and soluble salts from fly ash. This process comprises five key steps. In the first step, HCl, water, and air are used to extract heavy metals from the fly ash. In the second step, Na₂S is employed to precipitate the extracted heavy metals. The third step involves the addition of an alkaline solution to remove impurities such as Al, Si, Mg, and Fe, while also further eliminating any remaining heavy metals. In the fourth step, an oxidizing agent and ferric chloride (FeCl₃) are applied to remove divalent sulfur antimony, and arsenic. Finally, the process concludes with the evaporation step to recover salts. Compared to the FLUWA process and HaloSep® process, this process has two main advantages. First, aeration in the first step enhances the leaching efficiency of Pb and Cu, thereby improving the recovery of heavy metals. Second, the process recovers heavy metals in the form of metal sulfides, enabling their separation via flotation. This characteristic allows the recovered heavy metal precipitates to be directly utilized by mineral processing companies, significantly increasing the feasibility and economic efficiency of resource recovery. This chapter mainly investigates the effect of aeration on the leaching efficiency of Pb and Cu from fly ash. The experimental results show that aeration significantly improved the leaching efficiency of Pb and Cu in fly ash. Additionally, after leaching, the heavy metals in the fly ash are present in more stable forms.

Chapter 5 primarily investigates the second, third, and fourth steps of the acid leaching process developed in this study. In the second step, a method for controlling the amount of sodium sulfide added was developed. This method allows for a slight excess of sodium sulfide, ensuring a high recovery rate (over 99%) of heavy metals. Approximately 30 mg/L of divalent sulfur ions generated in this step are utilized in the third step as a heavy metal removal agent, reducing the concentrations of all heavy metals to below discharge standards, except for Sb. In the fourth step, calcium hypochlorite and FeCl₃ were used to remove Sb and divalent sulfur, while effectively lowering the concentrations of As and P. Additionally, the heavy metal precipitate recovered in the second step showed high metal concentrations. One of the precipitates contained Zn 35.6 %, Cu 11.6 %, and Pb 11.5 %, while another contained Zn 26.6 %, Cu 2.7 %, and Pb 7.1 %. These precipitates serve as excellent raw materials for heavy metal recovery.

Chapter 6 compares the proposed acid leaching process with the currently applied FLUWA+FLUREC+WWT (acid fly ash washing) process. The proposed process demonstrates several significant advantages, such as higher heavy metal recovery rates, simpler equipment requirements, lower equipment costs, and lower operational costs. The acid leaching process stands out as a cost-effective and efficient alternative, offering considerable benefits in terms of both economic and environmental performance.

Chapter 7 introduces the salt separation process developed in this study. This process takes advantage of the significant differences in the solubility of calcium chloride, sodium chloride, and potassium chloride in ethanol to separate calcium chloride from the mixed salts. The purity of the separated calcium chloride is approximately 98 %, and the calcium chloride concentration in the separated mixed salts is less than 1 %. Additionally, this chapter evaluates the safety of the recovered mixed salts. The heavy metal concentrations in the mixed salts (mercury was not measured) meet Japan's safety standards for edible salt, and the dioxin toxicity equivalent concentration meets the EU food safety standards, demonstrating their safety.

Chapter 8 summarizes the entire study and provides an outlook for future research.