

Cylindrical Electrolyser Enhanced Electrokinetic Remediation of Municipal Solid Waste Incineration Fly Ashes

Tao Huang, Lulu Zhou, Junjun Tao and Longfei Liu*

School of Chemistry and Materials Engineering, Changshu Institute of Technology,
215500, China

*Email: ht1104705720@qq.com

Abstract. The paper discusses enhancement and efficiency of removing spiked heavy metal (HM) contaminants from the municipal solid waste incineration (MSWI) fly ashes in the cylindrical electrolyser device. The characterization parameters of the electrolyte solution pH, electric current, electrical conductivity, voltage gradient were discussed after the experiment. The chemical speciation of HMs was analysed between the original samples and remediated ones by BCR sequential extraction. The detoxification efficiencies of Zn, Pb, Cu and Cd in the column-uniform device were compared with that in the traditional rectangular apparatus. The pH value changed smoothly with small amplitude of oscillation in general in cathode and anode compartments except the initial break. The electrical current rapidly increased on the first day of the experiment and steadily declined after that and the electrical conductivity presented a clear rising trend. The residual partition of detoxified samples were obviously lifted which was much higher than the analysis data of the raw materials. The pH and the electrical conductivity in sample region were distributed more uniformly and the blind area was effectively eliminated in the electrolytic cells which was indirectly validated by the contrastive detoxification result of the spiked HMs between the rectangular and cylindrical devices.

1. Introduction

Recently, the total capacity of the municipal solid waste for burning dispose and power generation is more than 15 kt/d in China, and a large number of facilities for the service have been built [1-3]. If without being properly treated after capture, the toxic substance will go into the ecological system through different pathways under different conditions. MSWI fly ashes have a lasting toxicity which can cause headache, dizziness, insomnia, forgetfulness, insanity, joint pain, stones, cancer, etc., especially serious to the urinary system and digestive system of organs [4-6]. The ashes should be treated to make them harmless. Electrokinetic remediation (EKR), based on environment friendliness, compatibility, multifunctional adaptability and low requirement for reaction condition, has made itself to be one of the preferred methods to detoxicate the fly ashes and change the characteristics of the hazardous solid waste [7]. During the EKR process, a direct-current (DC) electric field is imposed on the sample region, the contaminants are electro-transferred by the combined mechanisms of electroosmosis, electromigration and electrophoresis. The DC crosses the areas of the fly ashes, resulting in physicochemical and hydrological changes in the mass of ashes. As DC electric field is a much more effective force in driving fluid through interspace of the fly ash grains than the natural hydraulic gradient, electrochemical remediation is particularly applicable to fine-grained solid materials of low hydraulic conductivity and large specific area. However, regardless of promising results, this method has its own drawbacks [8-10]. The EKR process is extremely dependent on acidic conditions during the application, which in return facilitates the release of the HM compound into the



solution phase [11]. However, the achievement of these acidic condition is pretty difficult and time-consuming due to the high buffering capacity of MSWI fly ash grains. The remediation process is also a very energy-extensive and discrete application. The remediation time for fly ash may vary from several days to several months which would consume a significant amount of electricity energy and make the process discontinuous. In this paper, the traditional cuboid electrolyser device was tentatively modulated and converted into cylindrical one to solve the above limitations from the view of engineering application [12]. The ERK experiments for MSWI fly ashes were operated under identical trial conditions and the recorded data on characterization parameters and detoxification efficiencies were comparatively analyzed and displayed to demonstrate the reinforcement of the condition by the cylindrical apparatus. The research content of this article is beneficial to provide a strengthening reference for the engineering application in a way.

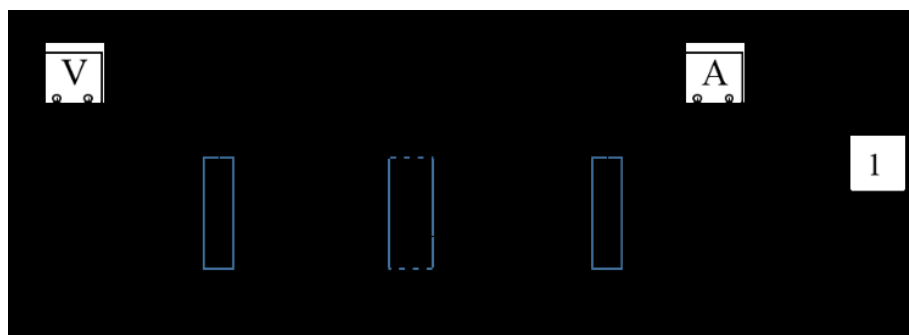
2. Materials and Methods

2.1. Sample Preparation

The MSWI fly ash samples were captured and collected from the cloth bag of the waste incineration and power generation site in Jiangsu, China. The fly ashes were sieved through a 20-mesh sieve to remove stones after naturally air-dried and then dried by thermostatic heater at 120°C. The pre-dried samples were then sieved by using the 300-mesh and prepared for the experiments.

2.2. EKR Experiment Instrument and Process

The device is consisted of an ERK cell (sample region), two electrode compartments, two rinsing reservoirs and a DC power supply. The cylindrical apparatus was made of toughened glass. The outer and inner diameters of the anode compartment are 36 cm and 28 cm, respectively, and the diameter of the cathode compartment is 4cm. The platinum wire was selected as the conductor to connect the electrodes with the power source. Graphite bar ($\Phi 4\text{ cm} \times 8\text{ cm}$) was used as the electrode (i.e. anode and cathode). The periphery of the cathode compartment was wrapped by a piece of cation exchange membrane. The pores ($\Phi 5\text{mm}$) were evenly drilled on the surfaces of two internal hollow cylinders to ensure the circulation of electrolyte. Figure 1 shows the process of EKR experiment in the cylindrical device. Details of the operating parameters are displayed in Table 1. The electrode distance is the difference of the radius between the internal two cylinders, not the distance between the electrodes.



1. DC power supply; 2. Ampere meter; 3. Voltmeter; 4. Anode compartment and graphite electrode; 5. Cathode compartment and graphite electrode; 6. Sample region

Figure 1. Process of EKR experiment in the cylinder device

Table 1. Operating parameters

Experimental parameters	Electrode distance (cm)	Voltage drop (V)	Initial water content (%)	Duration (d)
Value	10	20	25	21

2.3. Speciation Analysis

The chemical speciation of HM contaminated samples were analyzed through BCR sequential extraction procedure (proposed by SM&T of the European Union) for the determination of Zn, Pb, Cd and Cu. The HMs were partitioned into four chemical fractions (operationally defined): acid exchangeable, reducible, oxidizable and residual, separately. The concentrations of HMs were analyzed using flame atomic absorption spectrophotometry (FAAS). The results were compared with total metal concentrations obtained by using microwave digestion procedures. The sample region of cylindrical electrolyser was divided into five parts along the radius direction, from anode to cathode, S1, S2, S3, S4 and S5. The region was also separated into three sub-regions, from anode to cathode, a, b and c when measured the voltage drop (gradient) of the sample. Figure 2 unfolds the divisions of the sample regions. When measuring the voltage drop (gradient) of the sample, the region was separated into three sub-regions, from anode to cathode, a, b and c. Figures 3 unfolds the divisions of the sample regions.

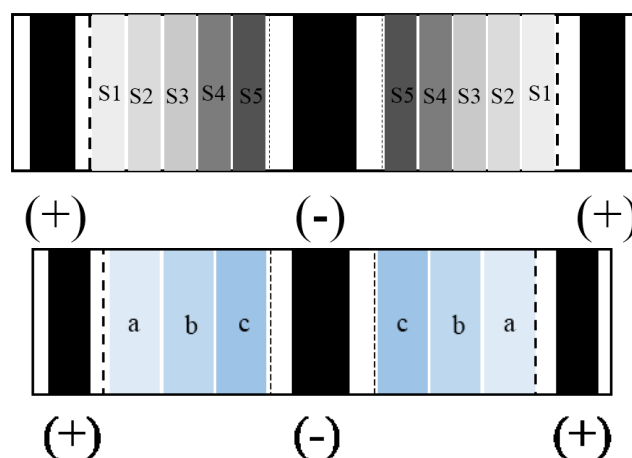


Figure 2. Divisions of the sample regions

3. Experimental Results

3.1. PH and Electric Current over the EKR Process

The EKR process relies on several interacting mechanisms in total, including advection, diffusion of the acid front to the cathode, and the migration of cations and anions towards the respective electrode. The initial pH of the electrolyte was 11.03 which was quite high (Figure 3a). The plummet was observed with the pH value in the anode chamber being dramatically reduced just one day later, which was contributed into the continuous hydrolysis and the numerical advantage of anode electrodes placed at the intra-periphery of the hollow cylinder. However, the pH of the electrolyze fluid in the cathode compartment (Figure 3a) has a tendency to slowly rise with a whiff of oscillation. The fluctuation of pH over the time directly indicated the dissolution of some minerals in the fly ashes during the electrokinetics.

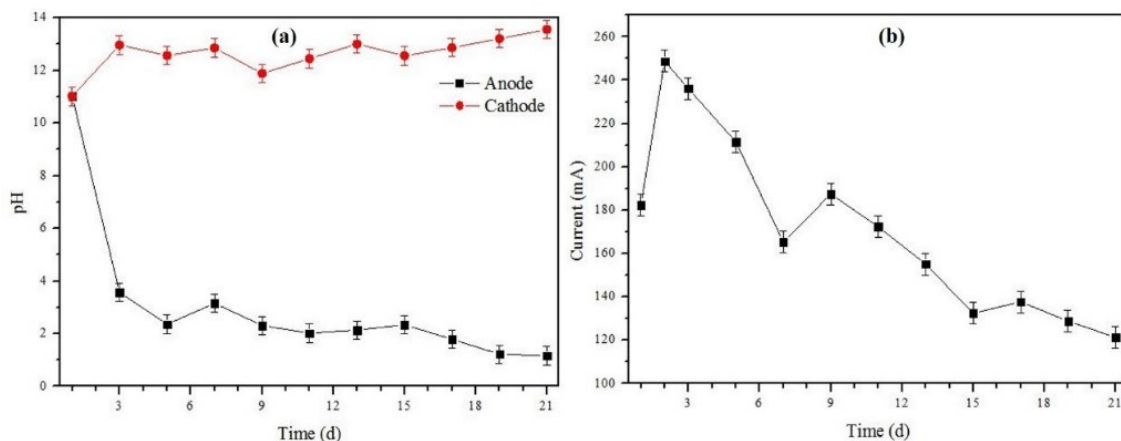


Figure 3. Changing curves of pH and electric current, (a) pH changes in the electrode compartments; (b) the change of electric current over the time

At the last day of the experiment, the pH values in the anode and cathode compartments were 1.16 and 13.56 separately. In the electrolytes, the electric current is formed by the flow of both positively and negatively charged particles at the same time. The magnitude of the current density is the electric current per cross-sectional area which indicates the concentration of the charged particles per unit time and unit area. The initial value of the DC current was 182.36mA and it reached the maximum 248.76mA at the end of the first day. The sharp variation was mainly caused by the rapid dissolution and desorption of some contaminants in the MWSI fly-ash samples. The decreasing trend of the electricity change was synchronous with the change of pH in the electrode areas.

3.2. Conductivity and Voltage-Drop in the EKR Process

As shown in Figure 4, the initial conductivities in the anode and cathode chambers were 63.47 and 76.92 mS/cm, separately. The conductivities in the electrode chambers both increased from the first day to achieve the maximums (166.46 and 141.13 mS/cm) at the fifth day and gradually diminish until to the end. The total variation of conductivity in the anode compartment was larger than the counterpart in the cathode with little disturbance. The results indicated that the concentration of mobile ions in anode electrolyte solution mounted faster than the opposite one during the experiment and was also more sensitive to the potential factors under the same experimental conditions. During the recording of the voltage gradient, the sample cell was hypothetically divided into three sections. The voltage-drops in the three regions were obviously different with each other (Fig. 4b). The voltage gradients in the whole sample region were all maintained constant until to the fifth day before a progressive descend. The steady decline of the gradient manifested the distribution of pH in the sample cell was relatively uniform, which was totally propitious to favor in desorption of pollutant from the matrix surface and transportation from one side to the other. Generally, the voltage gradient in the region-b was larger than that in the region-c while lower than the counterpart in the region-a. The voltage gradient of the middle section was maintained in a relatively stable state which majorly controlled the status of the concentration polarization. In the late stage of experiment, the amplitude was attenuating, indicating the environment was improving and the condition of the concentration polarization was offset. The voltage gradient in the region-c revealed the growing unrest and the maximal amount of increase among the three line graphs. Overall, the results supported the existence of the large resistance production (precipitation, sorption, solidification and electroplate etc.) near the cathode and the deterioration of migration path for the cations.

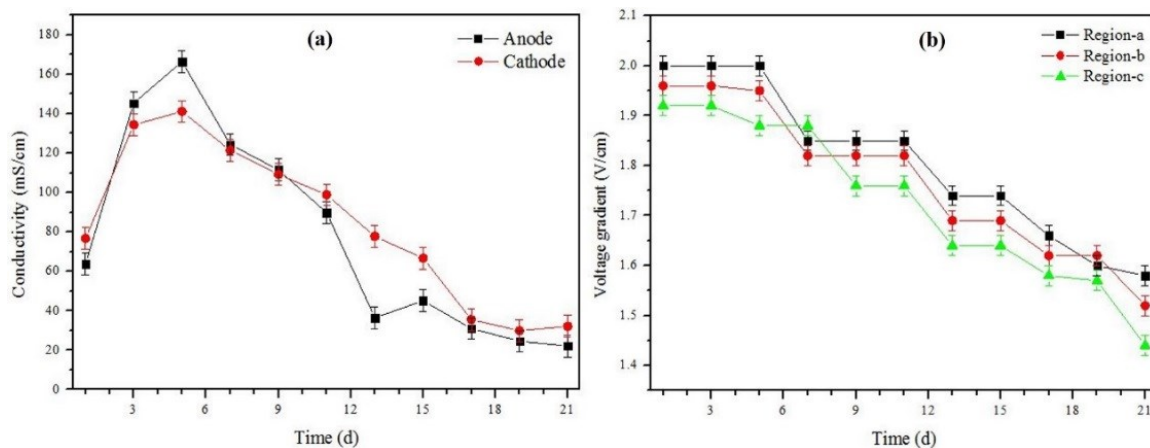


Figure 4. Changing curves of conductivity and voltage gradient, (a) conductivity in the electrode compartments; (b) voltage gradient over the time in the three regions

3.3. Detoxification Efficiency

The detoxification efficiencies of HMs in the MSWI fly ash sample section were calculated following as:

$$\omega = \frac{C_0 - C}{C_0} \times 100\% = 1 - \frac{C}{C_0} \quad (1)$$

Where ω represents the detoxification efficiency of specific HM element. C_0 is the original leaching concentration and C is the leaching concentration after the electrokinetic remediation. From the formula 1, it can be found that the smaller the C/C_0 , the bigger the ω .

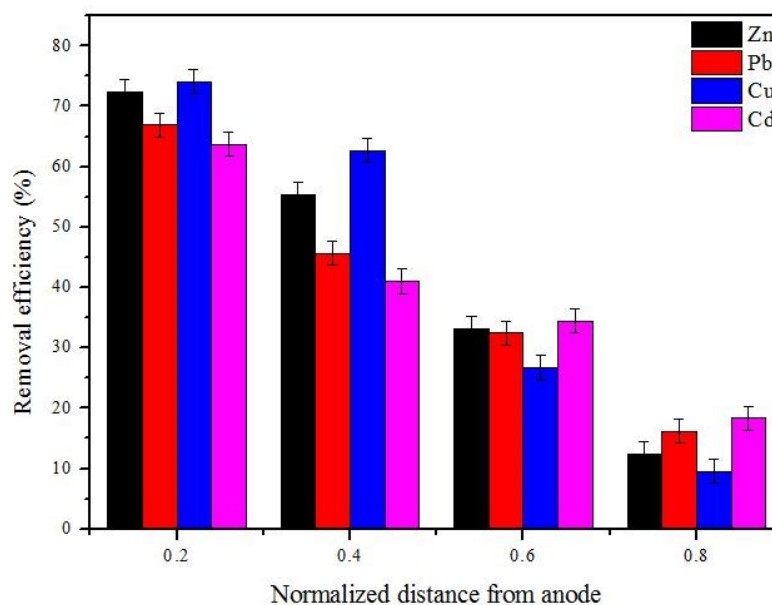


Figure 5. Leaching concentration ratios of Zn, Pb, Cu and Cd

The detoxification efficiencies of some HMs (including Zn, Pb, Cu and Cd) in the fly ash grains with normalized distance from anode are shown in Fig.5. It is clear that the general changing trend was moderate and the differences between the each sub-region to each element was not obvious. The C/C_0 values close to the anode electrode were smaller than that near the cathode. The maximal efficiencies of Zn, Pb, Cd and Cu were 72.45%, 66.89%, 63.71% and 74.13%, respectively, obtained

near the anode (0.2 of normalized distance from anode). The removal efficiency of each element was gradually reduced from the anode and cathode, which directly demonstrated the effect of electromigration on the cations of HMs.

3.4. Chemical Speciation Analysis

The speciation variations of Zn, Pb, Cu and Cd before and after EKR experiments are shown in Figure 6. The label information of the measuring areas are detailed in Figure 2. The percentages of residue partition were on the decline from S1 to S5 (from anode to cathode) for the four HMs, and were contrary to the changing trend of the acid exchangeable partition. The rest of the speciation basically kept the same line with local and small change. The average percentages of residue partition were broadly increased for all the four specific HMs compared with the condition of the original sample, and in return the other three partitions were lower than that of the primary one. The total variation of the speciation largely supported the experimental data of the detoxification efficiencies. Te-maxD between S1 and original for the four HMs were 29.0%, 25.6%, 46.4% and 28.1% respectively, the transform of cadmium was the most obvious.

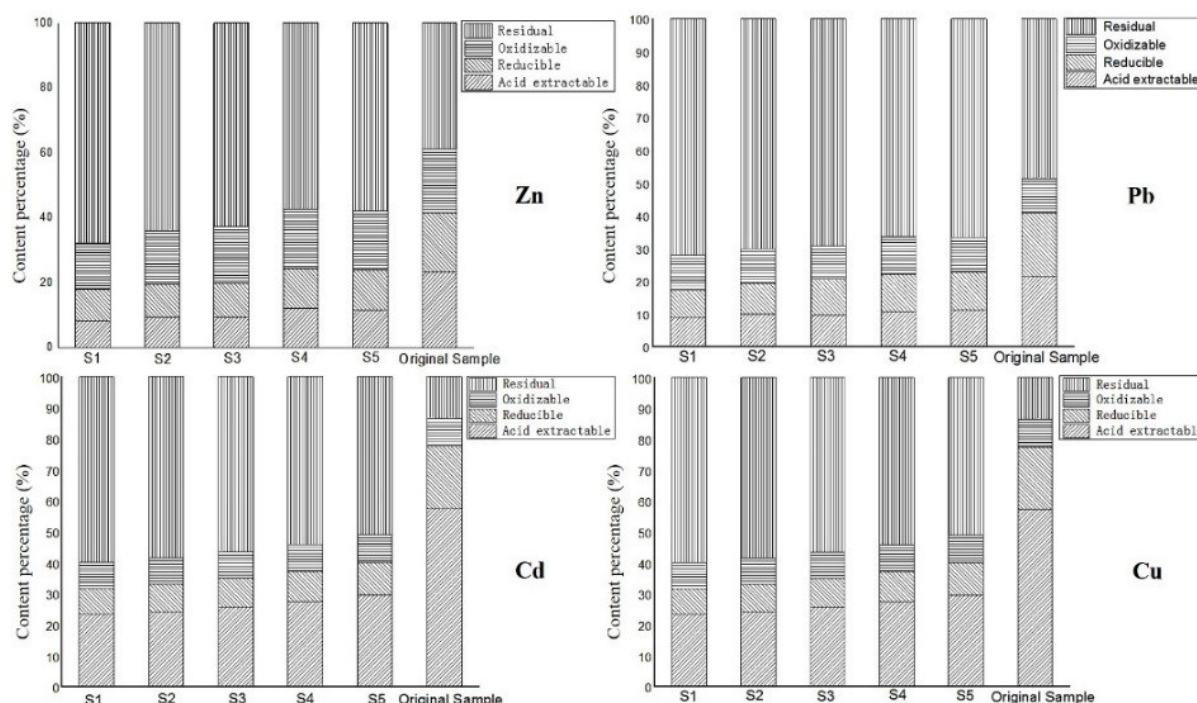


Figure 6. Speciation analysis of Zn, Pb, Cd and Cu before/after EKR experiments

4. Conclusion

The pH of the electrolyte solution at the anode zone experienced a sharp plunging only after a day of the time and the pH in the cathode compartment was maintained within a narrow range over the EKR course. The general variation of the DC was matched by the pH change with a gradual downward trend which reflected the contaminant dissolution and desorption to some extent. The total variation of the anode conductivity was bigger than that of the cathode over the process which indicated that the ion concentration near the anode was higher than that near the opposite one. The three curves of the voltage gradient represented the distinct changing situation. The steady decline adjacent to the anode demonstrated the uniform distribution of pH in the sample cell. The drop (gradient) improved the condition of the concentration polarization. After the end of the EKR process, the maximal detoxification efficiencies of Zn, Pb, Cd and Cu were 72.45%, 66.89%, 63.71% and 74.13% respectively. Te-maxD between S1 and original for the four HMs were 29.0%, 25.6%, 46.4% and 28.1%. In conclusion, the pH in the cylindrical electrolyser device was quickly lowered at short time which facilitated the solubilization of contaminants and render them in mobile states.

5. References

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