

LEACHING BEHAVIOR OF HEAVY METALS FROM BROKEN TON BAGS FILLED WITH FLY ASH IN ACID RAIN ENVIRONMENT

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ABSTRACT: The column leaching experiment of landfill stabilized fly ash was established by simulating acid rain with "sulfuric acid + nitric acid" type extractant to study the influence of acid rain seepage path on the leaching behavior of heavy metals in fly ash under the condition that the fly ash ton bag in the landfill was damaged. The results showed that the six seepage paths all promoted the leaching of Pb, Zn, Cu, Cd, Cr, and Ni from landfill stabilized fly ash in varying degrees. Under the double influence of gravity potential energy and matrix potential, compared with the horizontal seepage path of "upper left inflow - lower right outflow", the vertical seepage path of "upper inflow - lower outflow" was more likely to promote the leaching of heavy metals in fly ash. Under the mode of "dynamic scouring + static soaking + dynamic scouring", the cumulative leaching amount of heavy metals was higher. Under the seepage path of "upper left inflow - upper right outflow", the fluctuation of pH value of leachate was the smallest, the cumulative leaching amount of heavy metals was the lowest, and the stability of heavy metals (especially Pb, Zn, and Cr) in stabilized fly ash matrix was the best. The research results can provide a scientific basis for the evaluation of the leaching behavior of heavy metals from landfill stabilized fly ash in extreme acid rain environment and the environmental risk management and control when the fly ash ton bag in the actual landfill was damaged.

KEYWORDS: fly ash landfill; broken ton bag; acid rain; seepage path; heavy metal leaching

INTRODUCTION

In China, more than 146.076 million tons of raw municipal solid waste (MSW) was incineration in 2020, accounting for 62.3% of the total harmless treatment. As the scale of municipal waste incineration grows, large amounts of fly ash rich in heavy metals and dioxin pollutants are generated. According to GB 16889-2008, fly ash can only be landfilled in domestic landfills alone after pretreatment to meet the standards. Dithiocarbamate (DTC) chelating agents can combine with heavy metals to form chelated products with high stabilization coefficients and solid environmental adaptability and thus have been widely used in the industry. However, due to the imperfect management system, fly ash ton bags are not strictly sealed in the actual operation of non-standard storage or landfills. Aging and breakage of the landfill fly ash pile cover and untimely maintenance can further increase the risk of exposure of fly ash in broken ton bags to the adverse external environment which increases the environmental risk of heavy metal leaching from landfill-stabilized fly ash. In addition, acid rain is one of the possible risks of environmental exposure for fly ash landfills—acid rainfall, often present south of the Yangtze River and in the southeastern coastal areas. Acid rain with "sulfuric acid + nitric acid" type is the primary type of acid rain

evolution in recent years.

In contrast to static batch leaching, the leaching column experiment is a dynamic scouring model of leachate based on realistic permeation conditions. Leaching column experiments can better simulate the dynamic scouring process of contaminants in wastes and thus have received more extensive attention from researchers [1-3]. The analysis found that the studies on metal leaching behavior in fly ash were based on the acid leachate in a single direction of vertical seepage path conditions. However, in the actual landfill process, the breakage of ton bags can significantly affect the seepage path of acid leachate in the landfill fly ash pile. Few relevant studies consider the effect of acid rain leachate seepage paths on the leaching behavior of heavy metals in landfill-stabilized fly ash based on the location of ton bag breakage. Based on this, this study investigates the effect of acid rain on the leaching behavior of heavy metals in landfill stabilized fly ash under diversified seepage path conditions by simulating acid rain with "sulfuric acid + nitric acid" type extractant. This study provides some theoretical references for the standardization of fly ash ton bag material, the landfill disposal operation process, and improving the management system in China.

MATERIALS AND METHODS

Experimental materials

Stabilized fly ash samples were taken from a large domestic waste incineration plant in Qingdao (750 t·d⁻¹), and the chelating agent was DTC. The stabilized fly ash samples were crushed and sieved through 10 mesh sieves, mixed by quadratic method then kept in a sealed reserve, pH=12.34. The preparation of simulated acid rain was based on HJ/T 299-2007 standard. Sulfuric acid and nitric acid were mixed at 2:1 (mass ratio) and added to deionized water, adjusted pH=3.2±0.05.

Acid rain seepage path experiment

The experiments of six seepage paths were designed assuming the possible breakage of stabilized fly ash-filled ton bags (Table 1).

Table 1 Experimental design grouping of acid rain infiltration paths

NO.	Seepage path way
A1	upper inflow - lower outflow
A2	lower outflow - upper inflow
B1	upper left inflow - lower right outflow
B2	upper left inflow - upper right outflow
A3	After soaking, upper inflow - lower outflow
B3	After soaking, upper left inflow - lower right outflow

The experiment was performed using six PVC columns, which were external leachate collection bottles and simulated acid rain reservoirs. The experiments were conducted in a stage-feed mode, with each stage (S1 to S3) spaced 25 days apart, and each stage time of operation referred to the experimental design of EPA Method 1314 [4], in which the cumulative liquid-to-solid ratio (L/S) reached ten as the end point of the individual stage operation. The leachate sampling sites for the S1, S2, and S3 stages were set at cumulative L/S of 0.2/0.5/1.0/1.5/2.0/4.5/5.0/9.5/10, 0.2/0.5/1.0/2.0/5.0/10 and 0.2/2.0/10, respectively. At the end of each experiment phase, samples of residual landfill fly ash solids in the column were taken.

RESULTS AND DISCUSSION

pH, EC change

During the cleaning process of municipal solid waste incineration flue gas, excessive lime makes the fly ash matrix highly alkaline. Therefore, the fly ash matrix will rapidly neutralize the H⁺ introduced by the simulated acid rain when it comes in contact with it. As shown in Fig. 1 (a), the pH change increases in the leachate of each stage S1. For the B2 system, acid rain must flood the whole design before generating the leachate, B2 leachate pH=12. After

the cumulative L/S exceeded 2 in the S2 stage, all of them showed an increasing trend of pH. The seepage path was stabilized in phase S3, and each device showed a decreasing trend in leachate pH.

As shown in Fig. 1 (b), from S1 to S3, the acid rain invasion causes the soluble salts in the fly ash matrix to be continuously washed out and transferred to the leaching solution. Therefore, with the increase of cumulative L/S, the EC of each leachate path showed a tendency to

increase, followed by a decrease, and gradually stabilized. At the beginning of the S2 stage, EC of the B2 leaching solution showed a transient upward trend. That's attributed to the B2 mode of operation, which allows full reconnection of the stabilized fly ash with acid rain resulting in increased EC. It decreases with increasing cumulative L/S when the seepage is stabilized in the path.

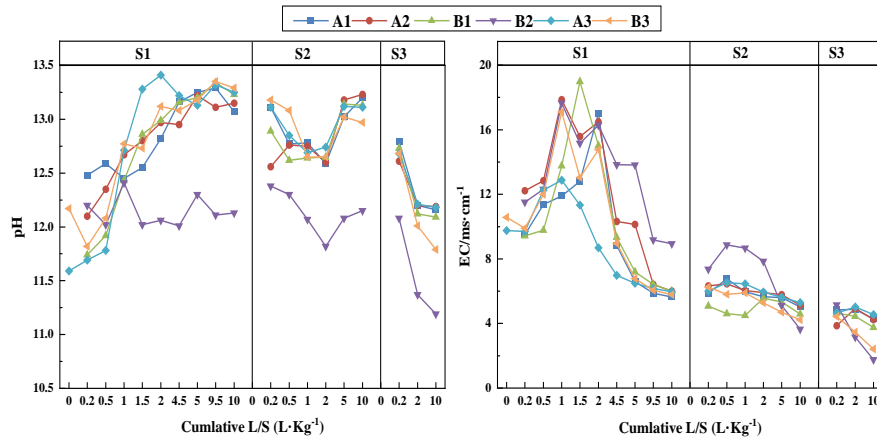


Fig. 1 Changes in pH and EC of fly ash leachate at each stage under different seepage path conditions

Changes in leaching behavior of major elements

Figure 2 shows the trend variation of the cumulative leaching amounts of Cl, K, Ca, Na and Mg in the stabilized fly ash leachate from the S1 to S3 stages. In this case, the cumulative leaching amount (M ; $\text{mg} \cdot \text{kg}^{-1}$) was calculated using equation (1), where is the sampling concentration ($\text{mg} \cdot \text{L}^{-1}$) and is the sampling liquid-solid ratio ($\text{L} \cdot \text{kg}^{-1}$).

$$M = \sum_{i=1}^n C_i \times (t_i - t_{i-1}) \quad (1)$$

During the S1~S3 stage of acid rain invasion, soluble ions were flushed out in large quantities, and the cumulative leaching amounts of Cl, K, Ca, Na and Mg in the leachate of each

device all increased with the increase of cumulative L/S. One of the most obvious trends was leaching in the S1 stage.

In stage S1, except B2, the cumulative leaching of major elements basically reached leaching stability at $L/S = 4.5$. Ca increased significantly with cumulative L/S. B2 leached slowly in the early stage of S1, but the cumulative total leaching of Cl, K, and Na accounted for the highest in the stages of S2~S3. In general, the total leaching of major elements in A1 and A3 was relatively high. Furthermore, the contact area between A3 and B3 and the fly ash matrix was larger, which led to the rapid leaching of the major metal elements from the fly ash.

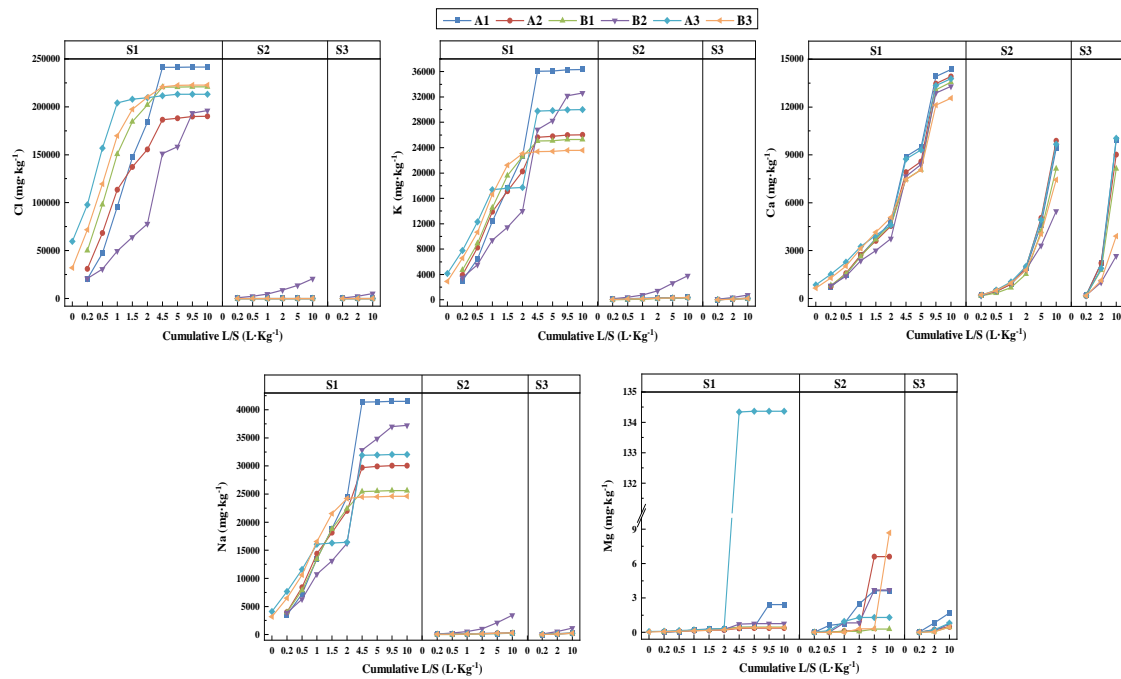


Figure 2 Cumulative leaching of significant elements (Cl, K, Ca, Na and Mg) from fly ash leachate at each stage under different seepage path conditions

Changes in leaching behavior of heavy metals

Calculating the cumulative leaching amount of each heavy metal (M ; $\text{mg} \cdot \text{kg}^{-1}$) in stages S1~S3 still used equation (1), and the variation of the results is shown in Figure 3.

The stage acid rain leaching process, early stage of acid rain leaching is a critical period for the leaching of heavy metals in landfill-stabilized fly ash. Among them, Pb was leached at the beginning of the S1 set, while the other heavy metals were leached slowly with the increase of cumulative L/S. A3 showed a significant jump in the cumulative Cd leaching at cumulative L/S=4.5. In addition, the leaching amount of Cd throughout the S1 phase was minimal. The leaching of heavy metals from the fly ash continues in the S2 and S3 phases.

Regarding acid rain infiltration paths, different infiltration paths significantly influence

the cumulative leaching of heavy metals. S1 stage, A1 and A3 are more easily leached. S2 and S3 stages, the cumulative leaching of heavy metals from B1 and B3 leachate is significantly increased. In contrast, the long-term stability of heavy metals in landfill-stabilized fly ash is reduced under the transverse seepage path. A2 The whole process is only influenced by the acid rain matrix potential. It lacks the influence of gravitational potential energy, and the accumulated leaching of heavy metals is in a slowly activated release state throughout the stage. Therefore, heavy metal concentrations are lower in the S1 location while significantly higher in S2 and S3 steps. It is noteworthy that B2 has the lowest cumulative leaching of heavy metals of all seepage paths. In addition, the leaching of heavy metals is also affected by the "dynamic scouring" and "static soaking" of acid rain.

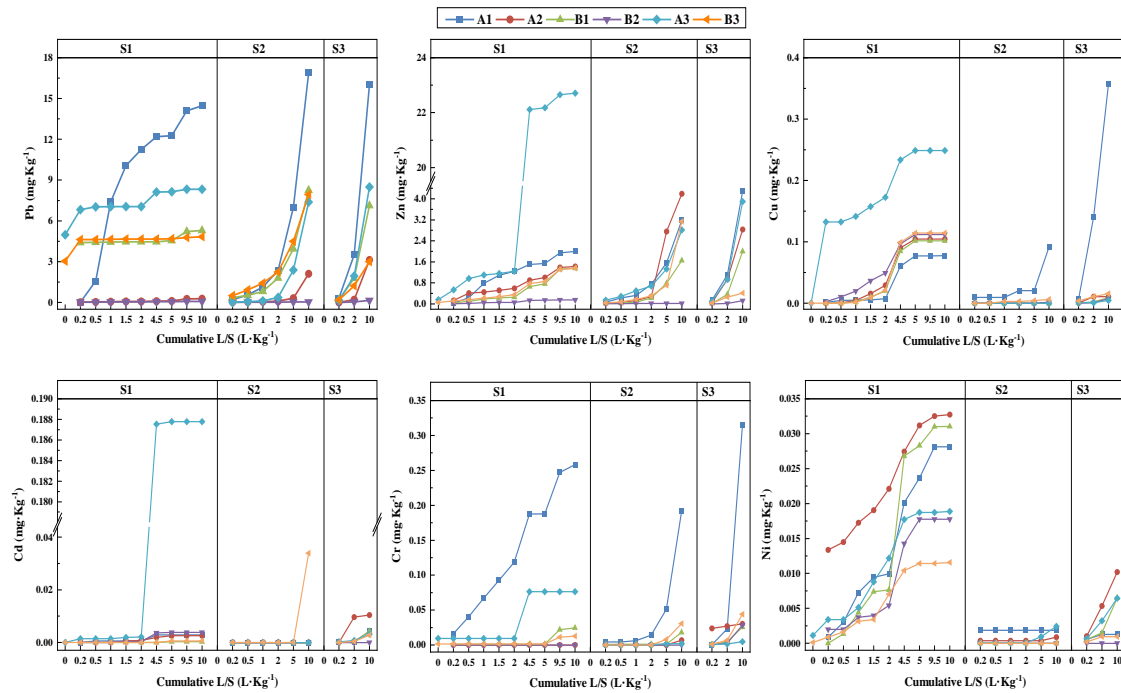


Figure 3 Cumulative leaching of heavy metals (Pb, Zn, Cu, Cd, Cr and Ni) from fly ash leachate at each stage under different seepage path conditions

CONCLUSION

S1~S3 phased acid rain intrusion can significantly affect the stability of heavy metals in landfill-stabilized fly ash. The initial acid rain leaching is the main period affecting the leaching of rich gold from landfill-stabilized fly ash.

A1 and A3 with "upper inflow - lower outflow", heavy metals in fly ash are more likely to enter the leachate due to the influence of both gravitational potential energy and matrix potential at the early stage of acid rain invasion. Heavy metals in leaching cycles are longer than others because of B1 and B3 lack gravitational potential energy. The leaching of heavy metals and significant elements is mainly reflected in the S2 and S3 stages. Compared with the single acid rain dynamic scouring process, the total accumulated leaching of heavy metals is higher in the "dynamic scouring + static soaking + dynamic scouring" mode. The leachate pH was the lowest in B2 with a "upper left inflow - upper right outflow", and the leaching of heavy metals

(especially Pb, Zn, and Cr) was the least affected.

Therefore, enhancing the anti-seepage capability of fly ash ton bags and standardizing the landfill operation process plays a vital role in reducing the leaching of heavy metals. Meanwhile, attention should be paid to the long-term stability of heavy metals in landfill-stabilized fly ash.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant Nos. 52000111, 51978350). Thanks for the support of the Open Fund Project of Zhejiang Provincial Key Laboratory of Solid Waste Treatment and Recycling (Grant No. SWTR-2021-01), Shandong Postdoctoral Innovation Project Fund (Grant No. 202103026), and Qingdao Postdoctoral Applied Research Project.

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