

Dynamic Leaching of Iron and Manganese from Coal Gangue under Periodic Infiltration

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Abstract: A dynamic column leaching experiment was conducted to characterize the release behavior of Fe and Mn from coal gangue under periodic infiltration. Leachate samples were collected daily for 11 days and analyzed for Fe, Mn, pH, and total dissolved solids (TDS), while scanning electron microscopy (SEM) was used to compare the microstructures of raw and leached gangue. Both metals showed strong early-stage release followed by progressive attenuation. Fe concentration decreased from 387 mg/L on day 1 to 71.5 mg/L on day 6, whereas Mn declined from 24.709 mg/L to 1.70 mg/L over the same period, with a transient rebound on day 3. Meanwhile, pH increased from 5.49 to 7.84 and TDS decreased from 2700 to 444 mg/L, indicating strong coupling between metal release and hydrochemical evolution. SEM observations showed surface roughening, crack development, layer detachment, and improved pore connectivity after leaching, which created more reactive interfaces for mineral dissolution and metal migration. The cumulative release masses reached 388.65 mg for Fe and 23.04 mg for Mn by the end of the test. Kinetic fitting showed that Fe was best described by the Elovich equation ($R^2 = 0.993$), whereas Mn was better represented by a polynomial model ($R^2 = 0.929$). These results indicate that Fe release was dominated by rapid dissolution of readily available surface-associated phases followed by site depletion, while Mn release was controlled by multiple coupled processes and was more sensitive to changes in the leaching environment.

Keywords: Coal gangue, Dynamic leaching, Iron release, Manganese release, Periodic infiltration, pH, TDS.

1. Introduction

Coal gangue is a major solid waste generated during coal mining and washing. Under long-term rainfall and seepage, soluble salts and metal-bearing phases in gangue may be mobilized and released to the surrounding environment, thereby creating potential risks to soil and groundwater [1].

Fe and Mn are among the most common elements detected in gangue leachate, and their release is controlled by both mineral occurrence and the evolution of the leaching environment [2]. Although previous studies have documented rapid early-stage metal release, the coupled changes in Fe, Mn, pH, and TDS during dynamic infiltration are still insufficiently described [3].

This study therefore carried out a dynamic column leaching experiment under periodic infiltration to characterize the temporal variations of Fe and Mn, identify the hydrochemical evolution of the leachate, and discuss the factors controlling metal release during different stages of leaching.

2. Materials and Methods

2.1. Experimental Setup and Leaching Procedure

A laboratory leaching column was used to simulate pollutant release from coal gangue during natural infiltration. The gangue packing height was 40 cm, and approximately 5 cm thick quartz sand layers were placed at the top and bottom to ensure more uniform flow and filtration. A 400-mesh nylon cloth was installed between the gangue and quartz sand layers and at the outlet to prevent particle migration and blockage [4].

Before the test, the gangue sample was washed three times to remove surface dust. Distilled water was then introduced from the top of the column using a peristaltic pump. The daily leaching volume was 300 mL and the experiment lasted 11

days [5]. Leachate was sampled at the same time each day. A 50 mL aliquot was filtered through a 0.45 μm membrane for Fe and Mn analysis, while pH and TDS were measured immediately after sampling.



Figure 1. Dynamic column leaching apparatus used in this study

2.2. Release Indices and Kinetic Evaluation

To characterize the overall release scale, the daily concentration data were converted into released mass and cumulative release. The daily released mass was calculated as $m_i = C_i V_i$, where C_i is the metal concentration in the leachate and V_i is the daily leaching volume. The cumulative release after n sampling events was calculated as $q_n = \sum(C_i V_i)$, and the average release rate for two adjacent sampling times was expressed as $r_n = (q_n - q_{n-1}) / (t_n - t_{n-1})$.

To compare the release kinetics of Fe and Mn, four empirical models were evaluated: the double-constant model, parabolic model, polynomial model, and Elovich model. Model performance was assessed by the coefficient of determination (R^2). The model with the highest R^2 and the most reasonable fit to the release trend was considered the optimal kinetic expression for each element.

3. Results and Discussion

3.1. Fe and Mn concentrations During Dynamic Leaching

Figure 2 shows the temporal variations of Fe and Mn concentrations during 11 days of dynamic leaching. Both metals were released intensely in the early stage, but their patterns were different. Fe decreased continuously from 387 mg/L on day 1 to 251.3 mg/L on day 2 and 177.3 mg/L on day 3, and further to 71.5 mg/L on day 6, corresponding to a reduction of about 81.5% within the first six days. This behavior indicates rapid depletion of readily soluble or weakly bound Fe-bearing phases.

Mn also showed an overall declining trend, but with stronger fluctuations. Its concentration dropped from 24.709 mg/L on day 1 to 12.496 mg/L on day 2, rebounded to 24.171 mg/L on day 3, and then declined rapidly to 1.70 mg/L on day 6. By day 11, Fe and Mn had further decreased to approximately 15.5 mg/L and 0.33 mg/L, respectively. These results indicate that the leaching risk of coal gangue was highest at the beginning of infiltration, with Fe showing a more continuous attenuation pattern and Mn responding more sensitively to short-term geochemical changes.

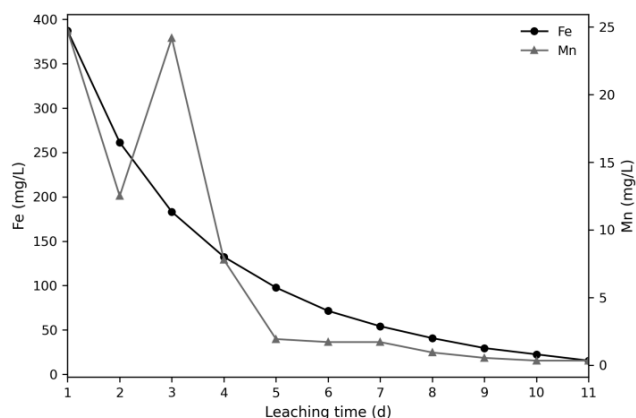


Figure 2. Temporal variations of Fe and Mn concentrations during dynamic leaching

3.2. Hydrochemical Evolution of pH and TDS

The first six days of pH and TDS data are summarized in Table 1, and their temporal trends are shown in Figure 3.

As leaching proceeded, pH increased continuously from 5.49 to 7.84, whereas TDS decreased sharply from 2700 to 444 mg/L within the first six days. The overall decline of TDS was consistent with the decrease in Fe and Mn concentrations, indicating that the dissolution intensity of soluble components weakened progressively during repeated flushing.

The inverse relationship between pH and Fe/Mn concentration indicates strong hydrochemical control on metal release. At the beginning of the experiment, the leachate was weakly acidic, which favored dissolution of Fe- and Mn-bearing minerals and desorption of metal ions from the particle surface. As the experiment continued, neutralization by carbonate dissolution increased the pH of the system. Under near-neutral to weakly alkaline conditions, Fe was more likely to hydrolyze, precipitate, or become readsorbed, while Mn release was also increasingly suppressed after its short-lived fluctuation.

Table 1. pH and TDS values of the leachate during the first six days

Day	TDS (mg/L)	pH
1	2700	5.49
2	1844	5.94
3	1247	6.67
4	1254	6.92
5	1123	7.52
6	444	7.84

Overall, the leaching system evolved from a low-pH, high-TDS, metal-rich state to a higher-pH, lower-TDS, and lower-metal state. This transition confirms that Fe and Mn release was tightly coupled to the ongoing evolution of water chemistry during dynamic infiltration.

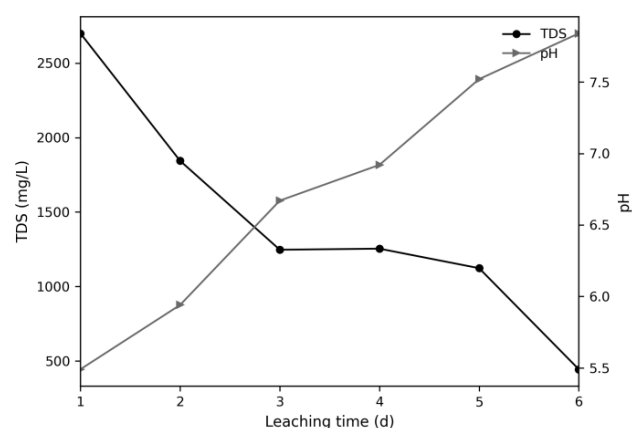


Figure 3. Temporal variations of pH and TDS during the first six days of dynamic leaching

3.3. Microstructural Evolution of Coal Gangue

SEM images before and after leaching are compared in Figure 4. The raw gangue was characterized by relatively dense particle aggregation, smoother particle surfaces, and comparatively intact lamellar or platy structures. Pores and interparticle voids were present but not strongly developed, indicating that the original material had a compact framework with limited externally induced disturbance.

After dynamic leaching, the gangue surface became visibly rougher and more irregular. The images show enhanced edge breakage, local layer detachment, microcrack development, and a more open pore structure. Fine particles were also redistributed on the surfaces of larger grains, and some lamellar boundaries became less regular and more fragmented.

These observations indicate that dynamic leaching mainly modified the outer surface and weakly bonded interlayer zones rather than completely destroying the particle framework. The increase in surface roughness, exposed interfaces, and pore connectivity would facilitate continued water-rock interaction and provide more pathways and reactive sites for the dissolution and migration of Fe and Mn.

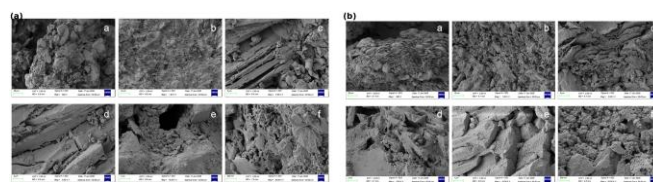


Figure 4. SEM comparison of coal gangue before and after leaching: (a) raw gangue; (b) gangue after dynamic leaching

3.4. Cumulative Release and Kinetic Interpretation

The cumulative release masses calculated from the daily leachate concentrations are listed in Table 2.

Table 2. Cumulative release masses of Fe and Mn during dynamic leaching.

Cumulative leachate volume (mL)	Fe released (mg)	Mn released (mg)
300	116.10	7.41
600	194.50	11.18
900	249.43	18.43
1200	289.14	20.76
1500	318.46	21.34
1800	339.90	21.87
2100	356.15	22.40
2400	368.38	22.68
2700	377.26	22.84
3000	384.01	22.94
3300	388.65	23.04

Both Fe and Mn showed monotonic increases in cumulative release with increasing leachate volume, but the increment became progressively smaller with time. Fe increased from 116.10 mg after the first day to 388.65 mg at the end of the experiment, while Mn increased from 7.41 mg to 23.04 mg. For both elements, the first three days contributed the largest fraction of the final cumulative release, confirming that the early stage dominated the overall pollutant output.

The cumulative release of Fe was much greater than that of Mn, indicating either a higher abundance of releasable Fe in the gangue or a stronger tendency for Fe-bearing phases to dissolve under the initial leaching conditions. By contrast, the lower cumulative release and earlier stabilization of Mn suggest a smaller releasable pool and stronger effects of competing processes such as slow mineral dissolution, readsorption, and secondary fixation.

The fitting performance of the four kinetic models is summarized in Table 3.

Table 3. Comparison of kinetic model performance for Fe and Mn cumulative release

Model	Fe (R^2)	Mn (R^2)	Interpretation
Double-constant	0.950	0.867	Moderate fit for both elements
Parabolic	0.867	0.801	Weakest fit among the tested models
Polynomial	0.984	0.929	Best fit for Mn
Elovich	0.993	0.921	Best fit for Fe

Among the tested models, the Elovich equation gave the best fit for Fe release ($R^2 = 0.993$), with the final fitting expression $q = 119.951 + 117.842 \ln t$. This result suggests that Fe release behaved like a heterogeneous surface-controlled process, characterized by rapid initial dissolution of readily available phases followed by a gradual decline as reactive sites were depleted.

For Mn, the polynomial model showed the highest coefficient of determination ($R^2 = 0.929$), with the fitted expression $q = -0.295t^2 + 4.839t + 4.057$. Compared with Fe, Mn release appears to have been governed by a more complex combination of mechanisms over the observation period, including leaching of labile phases, slower mineral dissolution, and secondary fixation. Therefore, although both elements followed a decreasing release-rate pattern, their dominant controls were not identical.

4. Conclusion

Fe and Mn were released intensively during the initial stage of dynamic leaching, after which their concentrations declined markedly. Fe showed a smoother attenuation pattern, whereas Mn exhibited stronger short-term fluctuation and greater sensitivity to environmental changes.

The leachate evolved from a weakly acidic, high-TDS, metal-rich system to a near-neutral, low-TDS, metal-poor system. This confirms that Fe and Mn release was closely coupled with hydrochemical evolution during repeated infiltration.

SEM observations demonstrated that dynamic leaching mainly enhanced surface roughness, crack development, lamellar detachment, and pore connectivity, thereby increasing the number of reactive interfaces available for continued mineral dissolution and metal migration.

The cumulative release masses reached 388.65 mg for Fe and 23.04 mg for Mn. Fe release was best described by the Elovich model, whereas Mn release was better fitted by a polynomial model, indicating different dominant release controls for the two elements.

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