

## Effect of Rare Earth Ions on Regular of Nitride Migration in Soil

Z. W. Liu <sup>1\*</sup>, J. Zhang <sup>1</sup>, C. B. Lu <sup>1</sup>, C. H. Wen <sup>1</sup>, F. J. Hu <sup>2</sup>, X. Y. Yang <sup>1</sup>

<sup>1</sup> School of Architectural and Surveying & Mapping Engineering, Jiangxi University of Science and Technology, Ganzhou, 341000, CHINA

<sup>2</sup> School of Resources and Environmental Engineering, Jiangxi University of Science and Technology, Ganzhou, 341000, CHINA

\* Corresponding author: 469346791@qq.com

### Abstract

Ion-adsorption rare earth ore mining with ammonium sulfate as leaching agent in situ leaching is not perfect, due to seepage and other technical measure, which easily results in serious nitride pollution of soil and water in mining and surrounding areas. In this paper, the effect of rare earth ions of different species and different concentration on the migration of nitride in the soil was studied by using soil column simulation experiment. The results showed that the leaching loss of ammonium nitrogen in the school soil was higher than that in the mining soil under the action of leaching. The low concentration of exogenous rare earth could promote the accumulation of ammonium nitrogen in the soil, while the high concentration was inhibited. When the concentration of yttrium, lanthanum and mixed rare earth were 5-10 g/kg, 0-1 g/kg, 0-1 g/kg, the concentration of ammonium nitrogen reached the maximum. The trend of available nitrogen concentration was consistent with that of ammonium nitrogen. The effect of yttrium on the contents of nitrate nitrogen in the soil was not significant, but the lanthanum showed some inhibitory effect, and the mixed rare earth showed the characteristics of "low concentration-promoting and high concentration-inhibiting" in the soil. The conclusion will lay a theoretical foundation for the control of nitrification in soil and water body of ionic rare earth mine.

**Keywords:** rare earth ions, soil, ammonium nitrogen, migration regularity

Liu ZW, Zhang J, Lu CB, Wen CH, Hu FJ, Yang XY (2018) Effect of Rare Earth Ions on Regular of Nitride Migration in Soil. Ekoloji 27(106): 525-534.

### INTRODUCTION

In the mining process of ion-adsorption type rare earth ore, because a large amount of ammonium sulfate is used as ore leaching agent, the formation, accumulation and migration of nitride in the soil of the rare earth mining area lead to serious pollution of the nitride for soil and water around the mining area, thus endangering the ecological security and sustainable development of the soil and water, and bringing difficulty to the reclamation of soil in the rare earth mining area after mining (Liu and Zhang 2013, Luo et al. 2014, Wang et al. 2015, Zhang et al. 2008). At present, the researches on the migration and transformation of nitride in soil of general farmland are mostly studied by scientific researchers, and some achievements have been obtained (Ding et al. 2004, Li et al. 2011, Yang et al. 2014, Zhang et al. 2015). However, there are few reports on the research of nitrogen contamination in soil of ionic rare earth. In this paper, through the establishment of a simulated experimental column to simulate the process of in situ leaching (Liu et al. 2015,

Wang et al. 2014), the effects of different types and concentration of rare earth ions on the migration of nitride in soil were studied. In order to understand the migration and transformation of nitride in rare earth, nitride pollution in the surrounding area lays the theoretical and technical foundation.

### MATERIALS AND METHODS

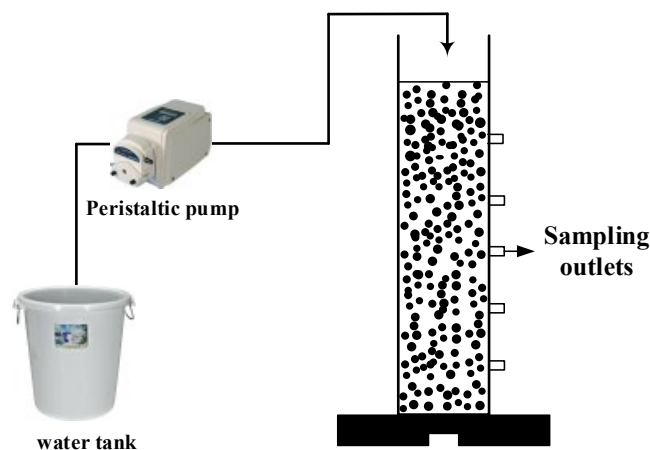
#### Equipment

Main instruments: electronic analytical balance (TY4001), electric oven blast (CSIOI-IAB), UV-visible spectrophotometer (UV-6100), constant temperature water bath oscillator (SHZ-B) and the like.

Experimental reagent is analytical pure, experimental water is distilled water.

#### Sample Collection and Pretreatment

By leaching time, the depth of different profiles (corresponding to the height of sampling holes) for sampling, and then air-dried. After removal of debris, the soil was grounded and screened through 100 mesh



**Fig. 1.** Experimental device

**Table 1.** Experiment design

Condition	Blank	A	B	C
Y (g/kg)	0	1	5	10
La (g/kg)	0	1	5	10
Y+La (g/kg)	0	1	5	10

sieve. 20 g sample was applied and placed in a clean beaker.

### Experimental Device

In this experiment, a set of experimental apparatus with 4 plexiglass columns was used. The column height is 180 cm and the inner diameter is 20 cm. The sampling holes were set on the wall of the tube. The number of holes was 5 and the hole spacing was 30 cm. Peristaltic pump was used to drip the immersion solution into the rare earth soil. Leaching agent can outflow from the bottom. The experimental setup is shown in **Fig. 1**.

In the first experiment, two plexiglass columns were filled with mining soil and campus soil. The filling height was 148 cm and the sampling depth was 0 cm, 30 cm, 60 cm, 90 cm and 120 cm, respectively. Before the experiment, two soil columns were leached with ammonium sulfate solution of 1.5% concentration for one week in order to ensure sufficient nitrogen content in the experimental soil. The leachate was simulated acid rain, simulated rainfall with reference to the average annual rainfall of 1587 mm in recent years, and sampled from each sampling port every 6 days.

In the second experiment, four plexiglass columns were used, which were marked as blank column, A column, B column and C column, respectively. The column was filled with raw mineral soil, and different types and concentration of exogenous rare earth were added into the soil. Sampling depth is 10 cm and 40 cm, respectively. Leachate was 1.5% ammonium sulfate solution. The leaching amount simulated the dosage of

rare earth leaching, and continuous leaching is carried out. The upper and lower cross-samples are taken every two days. The experimental design is shown in **Table 1**.

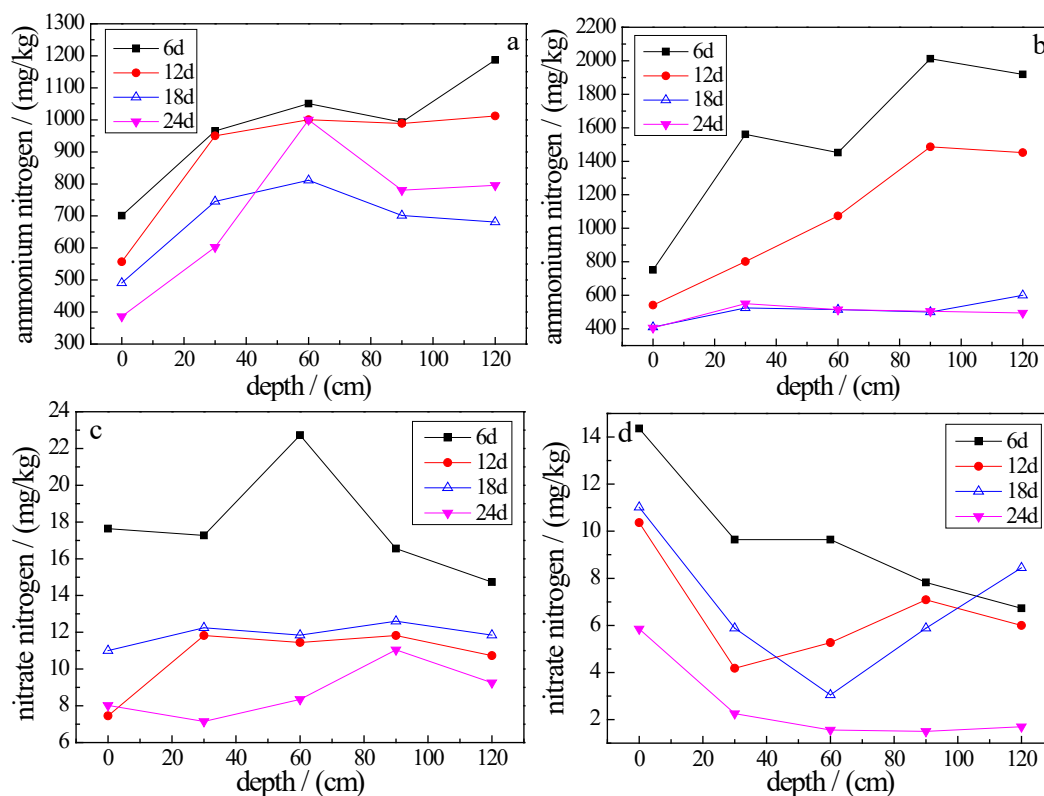
### Measurement Items and Methods

Test items: ammonium nitrogen, nitrate nitrogen, available nitrogen (including ammonium nitrogen, nitrate nitrogen and some easily decomposed organic nitrogen). The determination of ammonium nitrogen was  $\text{CaCl}_2$  solution extraction-spectrophotometry; the determination of nitrate nitrogen was KCl solution-spectrophotometry. The available nitrogen was determined by alkali diffusion method.

## RESULTS AND DISCUSSION

### Effect of Endogenous Rare Earth Ions on the Transport of Nitride in Soil

The variation and distribution characteristics of ammonium nitrogen content in mining soil and campus soil with time variation and depth are shown in **Fig. 2a** and **Fig. 2b**. As can be seen from **Fig. 2a**, the content of ammonium nitrogen in mining soil decreases gradually with the increase of leaching time. When the leaching is completed, the content of ammonium nitrogen in the soil decreases obviously (the average decrease of 300 mg/kg). The contents of ammonium nitrogen in each period showed a trend of migration from the upper layer to the lower layer and accumulated in the lower layer. The downward trend of surface soil was stable while the middle layer was relatively steep. The contents of ammonium nitrogen in 60 cm and 90 cm



**Fig. 2.** Distribution of nitride in mining soil and campus soil. (a) the content of ammonium nitrogen in mining soil; (b) the content of ammonium nitrogen in campus soil; (c) the content of nitrate nitrogen in mining soil; (d) the content of nitrate nitrogen in campus soil

the initial leaching loss was small, but its migration rate increased gradually in the later stage, and the contents of ammonium nitrogen in the lower soil layer was consistent with the surface soil. As can be seen from **Fig. 2b**, the content of ammonium nitrogen in campus soil also shows the tendency of migrating from the upper layer to the lower layer, which is consistent with the characteristics of the variation of the mining soil. the contents of ammonium nitrogen in the initial stage of leaching was much higher than that in the final stage of leaching. With the leaching, the contents of ammonium nitrogen in each depth soil decreased gradually. After 24 days, the amount of ammonium nitrogen was about 500 mg/kg, and the leaching amount was between 350 and 1300 mg/kg, which is much higher than that of the mining soil.

Soil particles and colloidal surface with a negative charge have strong adsorption of ammonium ions. Ammonium nitrogen adsorption by the soil, mainly in water-soluble, exchangeable, fixed-state existence of three forms, water-soluble ammonium is easy to be extracted by deionized water and the exchangeable ammonium can be displaced by neutral salt. Fixed ammonium and clay minerals to form intracuster complexes, the binding force between three forms of

ammonium and soil surface is: fixed ammonium, exchangeable ammonium and water-soluble ammonium. Mining soil contains endogenous rare earth ions, before the experiment, two soil column was immersed ammonium sulfate solution, rare earth ions were displaced out, ammonium ions are adsorbed by the soil. Therefore, under the same conditions, the leaching loss of ammonium nitrogen in mining soil is less than that of the soil in the campus.

The variation and distribution characteristics of nitrate nitrogen contents in mining soil and campus soil with time variation and depth are shown in **Fig. 2c** and **Fig. 2d**. As can be seen from **Fig. 2c**, in the initial stage of leaching, the contents of nitrate nitrogen in mining soil is between 14-22 mg/kg, and in the depth of 60 cm reaches 22.73 mg/kg. With the increase of leaching time, the contents of nitrate nitrogen in each soil layer decreased gradually, showing the trend of migration from surface to deep. As can be seen from **Fig. 2d**, in the initial stage of leaching, the contents of nitrate nitrogen in campus soil decreased gradually with the increase of depth. At leaching time of 12 d and 18 d, with the increase of soil depth, the contents of nitrate nitrogen decreased first and then increased, and the contents of nitrate nitrogen was the lowest at 30 cm and

60 cm. Nitrate nitrogen migrated gradually to the lower soil and the lower soil appeared the accumulation. After leaching to 24 d, except the surface soil, nitrate nitrogen contents in each depth soil reached the maximum leaching loss. The leaching amount of nitrate nitrogen in the mining soil was between 5-14 mg/kg, while that of the campus was 5-9 mg/kg. Generally speaking, the leaching amount of nitrate nitrogen in the mining soil was much larger than that of the campus soil.

Due to the surface soil is well-ventilated, the nitrification reaction is easy to occur under the action of microorganisms. Ammonium nitrogen can convert into nitrate nitrogen, so the nitrate nitrogen contents in the surface soil is higher. Subsequently, under the action of leaching, the nitrate nitrogen in the surface soil migrated gradually to the deep soil. When the concentration of nitrate ion in the soil layer was lower than the concentration of nitrate ion in the soil solution, negative adsorption phenomenon would occur. Nitrate nitrogen contents in the soil layer increases in the short term. Continuously sampling could easily lead to hollowness inside the soil layer, and the leachate would stay briefly for a short time. As a result, nitrate ions were dissolved in the soil solution and gradually infiltrated until they were discharged out of the column. Because of its ore-bearing mineral rock, large particle size, strong sand and large porosity, will make the nitrate nitrogen in the mining soil migration rate greater than the campus soil.

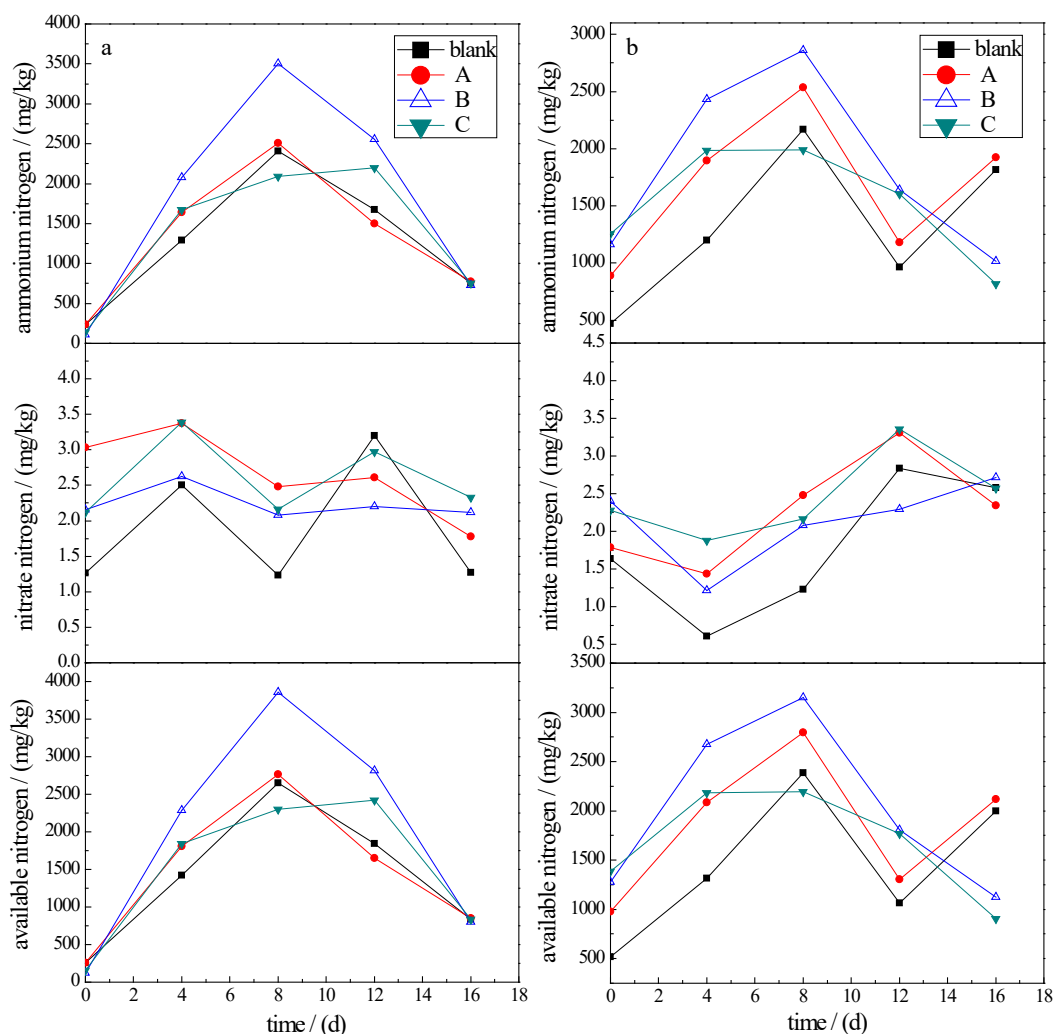
### **Effect of Exogenous Rare Earth Ion on the Transport of Nitride in Soil**

#### ***Distribution of nitride in soil with different concentration of yttrium ions***

The trend of the nitride contents in the upper soil (10 cm) containing different concentration of yttrium ions with time variation is shown in **Fig 3a**. As can be seen from **Fig. 3a**, the trend of the change of ammonium nitrogen and available nitrogen is basically the same. The contents of ammonium nitrogen in four soil columns showed the trend of increasing at first and then decreasing. The contents of ammonium nitrogen in blank column, column A and column B reached the maximum value when the leaching time is 8 days. Column D reached the maximum value when the leaching time is 12 days. Comparing the trend of ammonium nitrogen contents in blank column, column A and column B with time prolonging, it can be seen that the higher in the concentration of yttrium ion, the higher the contents of ammonium nitrogen in the upper soil. By comparing the C column and the D column, it can be concluded that the content of

ammonium nitrogen in the soil is decreased obviously when the concentration of the yttrium ion is added to a peak value. The above result shows that exogenous rare earth will have some impact on morphology of nitride because the addition of higher concentration exogenous rare earth inhibited the nitrification of the soil. The changes of nitrate nitrogen contents in four soil columns are consistent, showing a trend of first increasing, then decreasing, then increasing and then decreasing again. In the initial stage of leaching, the contents of nitrate nitrogen were 1.26, 3.04, 2.16 and 2.12 mg/kg, respectively. The contents of nitrate nitrogen in the soil were 1.27, 1.78, 2.12 and 2.33 mg/kg respectively at the end of leaching. Small, almost negligible compared to ammonium nitrogen. The trend of available nitrogen contents is basically the same as that of ammonium nitrogen, which is due to the less organic matter and the small amount of nitrate nitrogen in the soil. So the ammonium nitrogen occupies the vast majority section of available nitrogen in the mining soil. The effective nitrogen contents of four soil columns increased from 260.34, 259.12, 118.53 and 159.02 mg/kg at the initial stage of leaching to 832.62 mg/kg and 852.35, 798.38 and 833.78 mg/kg at the end of leaching.

The trend of the nitride contents in the lower soil (40 cm) containing different concentration of yttrium ions with time variation is shown in **Fig. 3b**. As can be seen from **Fig. 3b**, the contents of ammonium nitrogen in blank column and column A increase first, then decrease and then increase with time prolonging. While in column B and column C, the contents of ammonium nitrogen first increase and then decrease. In the initial stage of leaching, the more the concentration of exogenous yttrium was added, the higher the contents of ammonium nitrogen in the lower soil layer. The initial ammonium nitrogen contents in the four soil columns were 467.92, 886.40, 1159.59 and 1255.50 mg/kg, respectively. After leaching for one week, the content of ammonium nitrogen reaches its maximum, which is consistent with the change of ammonium nitrogen contents in the upper soil. After leaching to half a month, the contents of ammonium nitrogen in the lower layer soil were 1813.55, 1923.99, 1017.22 and 819.59 mg/kg, while the contents of ammonium nitrogen in the upper layer soil were 755.65, 733.08, 723.68 and 755.65 mg/kg, respectively, which shows a trend of migration from the upper layer to the lower layer and accumulated in the lower layer. The surface of the soil particles and colloids is negatively charged, which make it has a strong adsorption of ammonium ions, yttrium ions with the ammonium ion



**Fig. 3.** Distribution of nitrides in soil with different concentrations of yttrium ions. (a) the content of the nitride in the upper soil containing different concentration of yttrium ions; (b) the content of the nitride in the lower soil containing different concentration of yttrium ions

displacement reaction. With leaching, ammonium ions are constantly being retained and adsorbed soil particle surface, ammonium nitrogen contents continued to rise until it reaches its saturation adsorption value. The contents of nitrate nitrogen in B column tended to decrease first and then increase, while the other three columns showed the trend of decreasing firstly, then increasing and then decreasing again. The content of nitrate nitrogen was in the range of 0.62-3.35 mg/kg. The low content of nitrate nitrogen is due to the negative charge of nitrate, which is consistent with the charge on the surface of soil particles and colloids. Therefore, the nitrate nitrogen is not easily adsorbed by the soil particles. Under the constant erosion of the leaching solution, the residual nitrate in the soil easily dissolved in water, and gradually migrated to the underlying soil and leachate. Nitrate will accumulate in a short period of time when the nitrate contents is low and the amount of nitrate transported downward with

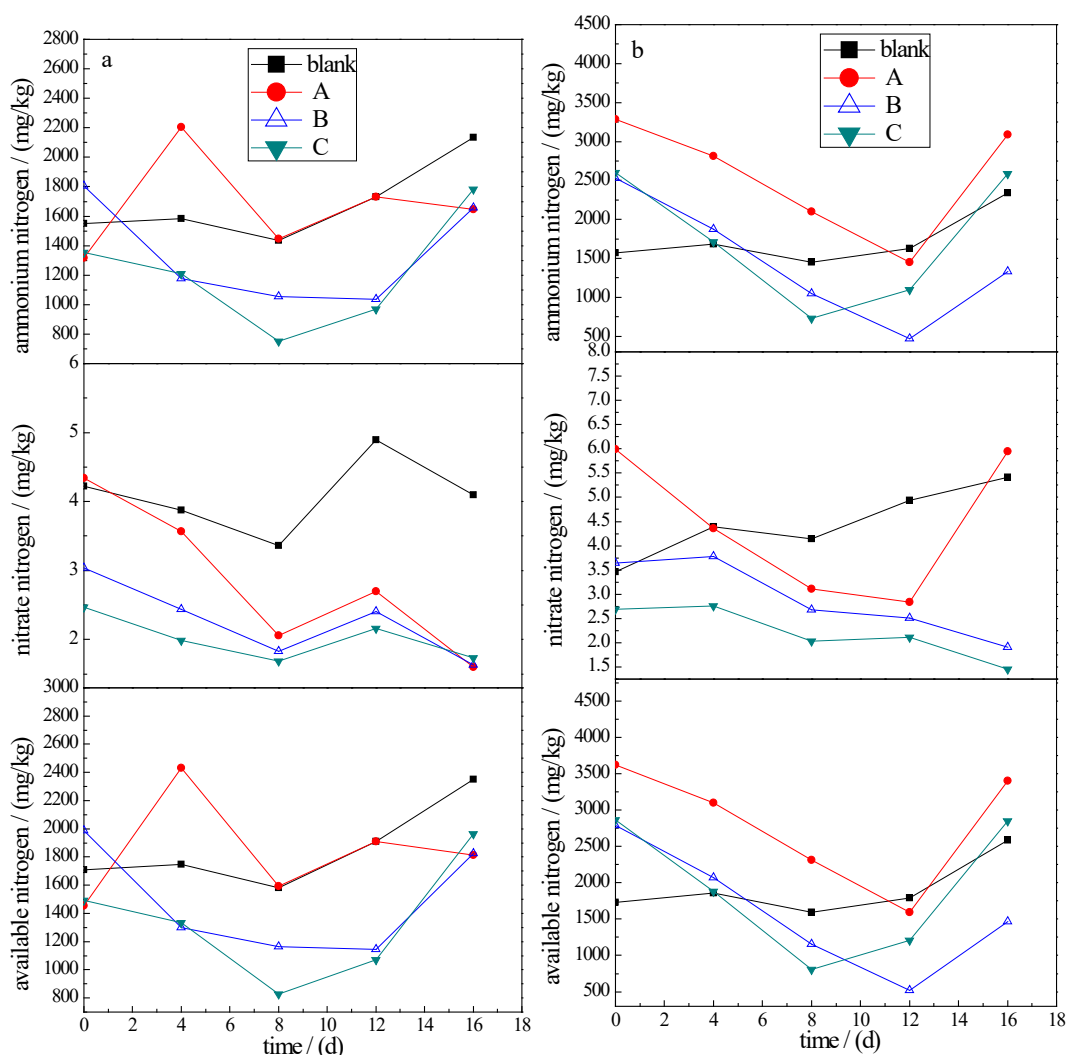
the leachate is less than its retention in this layer. In the initial stage of leaching, the effective nitrogen content in the lower column of the blank column was 516.51 mg/kg. While the effective nitrogen content in the other three columns was in the range of 1000-1400 mg/kg. The higher the concentration of exogenous yttrium ions was, the more the initial effective nitrogen contents. With the passage of time, four soil column effective nitrogen contents increased, and reached a peak value after a week. The available nitrogen contents in B and C columns decreased with time prolonging, while the blank column and A column showed the trend of decreasing and then increasing. The trend of available nitrogen in four soil columns is consistent with that of ammonium nitrogen, which indicates that ammonium nitrogen is the most dominant form of available nitrogen in the mining soil.

***Distribution of nitride in soil with different concentration of lanthanum ions***

The trend of the nitride contents in the upper soil (10 cm) containing different concentration of lanthanum ions with time variation is shown in **Fig. 4a**. As can be seen from **Fig. 4a**, the trend of the change of ammonium nitrogen and available nitrogen is basically the same, which is similar to that of the upper soil with different concentration of yttrium ions added. In the initial stage of leaching, the content of ammonium nitrogen in B column soil was higher than blank column, while the other two columns were lower than the blank column. In the subsequent leaching process, the A, B and C columns were lower than the blank column, and ammonium nitrogen contents was inversely proportional to the concentration of lanthanum ions, because higher-concentration lanthanum ions inhibit the ammonification of the soil. The contents of ammonium nitrogen in B and C column firstly decreased and then increased with the passage of time, while the blank column and A column showed a “M” trend. The initial concentration of ammonium nitrogen in the four soil columns was 1549.08, 1316.57, 1804.83 and 1354.35 mg/kg, respectively. At the end of leaching, the content of ammonium nitrogen was 2133.25, 1647.89, 1656.61 and 1784.49 mg/kg, respectively. The ammonium nitrogen accumulated in the upper soil. The change trend of nitrate nitrogen in the upper soil of the four soil columns was basically the same, showing a trend of first decreasing, then increasing and then decreasing again. Besides, the contents of nitrate nitrogen in the blank column was lower than that of the A column at the initial stage of leaching, higher than the other three columns. In the initial stage of leaching, nitrate contents in four-column was 4.23, 4.34, 3.04 and 2.47 mg/kg, respectively. At the end of leaching, nitrate content was 4.10, 1.60, 1.63 and 1.74 mg/kg, leaching loss is inversely proportional to the concentration of lanthanum ions. Leakage of the blank column is least, because lanthanum ions may have a fixed effect on the nitrate nitrogen. Compared with the blank column, the accumulation of lanthanum ions will reduce nitrate nitrogen, which is consistent with Qian Xiaoqing et al. (Qian et al. 2000). The trend of available nitrogen contents in upper soil is consistent with that of ammonium nitrogen, which is because ammonium nitrogen is the main form of available nitrogen in the mining soil. In addition to the initial stage of leaching, the effective nitrogen content of the blank column is higher than that of the other three columns. Studies by Chu et al. (2001). Showing that lanthanum ion has an

inhibitory effect on soil available nitrogen, and the experimental results also verify this feature.

The trend of the nitride contents in the lower soil (40 cm) with different concentration of lanthanum ions with time variation is shown in **Fig. 4b**. As can be seen from **Fig. 4b**, in the initial stage of leaching, the greater the concentration of exogenous lanthanum ions, the less the contents of ammonium nitrogen in the mining soil, and the trend of ammonium nitrogen contents in three soil columns with the addition of lanthanum ion is consistent, all showed a trend of first decreasing and then increasing. According to the change trend of ammonium nitrogen contents from 8 to 16 days, the low concentration of lanthanum ion can increase the concentration of ammonium nitrogen in the lower soil layer, while the high concentration of lanthanum ion reduces the concentration of ammonium nitrogen. This is consistent with the results of Lu et al. (1999). The initial concentration of ammonium nitrogen in the four soil columns were 1569.42, 3285.32, 2531.42 and 2601.17 mg/kg, respectively, while the concentration of ammonium nitrogen at the end of leaching were 2342.51, 3086.53, 1331.10 and 2586.64 mg/kg. Except for the accumulation of ammonium nitrogen in the blank column, the contents of ammonium nitrogen in the other three columns decreased compared with the initial ammonium nitrogen, which was different from that of the upper mining soil. By comparing the change of contents of ammonium nitrogen in mining soil, the ammonium nitrogen in the upper soil migrated to the lower layer, and the accumulated amounts of A, B and C columns were 1968.75, 726.59 and 1091.27 mg/kg, respectively. The contents of nitrate nitrogen in B and C column decreased with time prolonging, while the contents of nitrate nitrogen in blank column increased gradually. The contents of nitrate nitrogen in each column were blank > A column > B column > C column, which indicated that the accumulation of lanthanum ions would decrease nitrate nitrogen contents, which is consistent with the changes of upper soil with the addition of yttrium ions. In the initial stage of leaching, the effective nitrogen contents in the lower soil layers of four soil columns were 1730.17, 3620.44, 2788.57 and 2864.25 mg/kg, respectively. There was no significant correlation between the initial available nitrogen contents and the concentration of lanthanum ions. With the passage of time, effective nitrogen contents of A, B and C columns gradually reduced. At the end of the experiment, the effective nitrogen contents of the four soil were 2582.72, 3401.72, 1466.31 and 2846.91 mg/kg, except for the blank columns, and



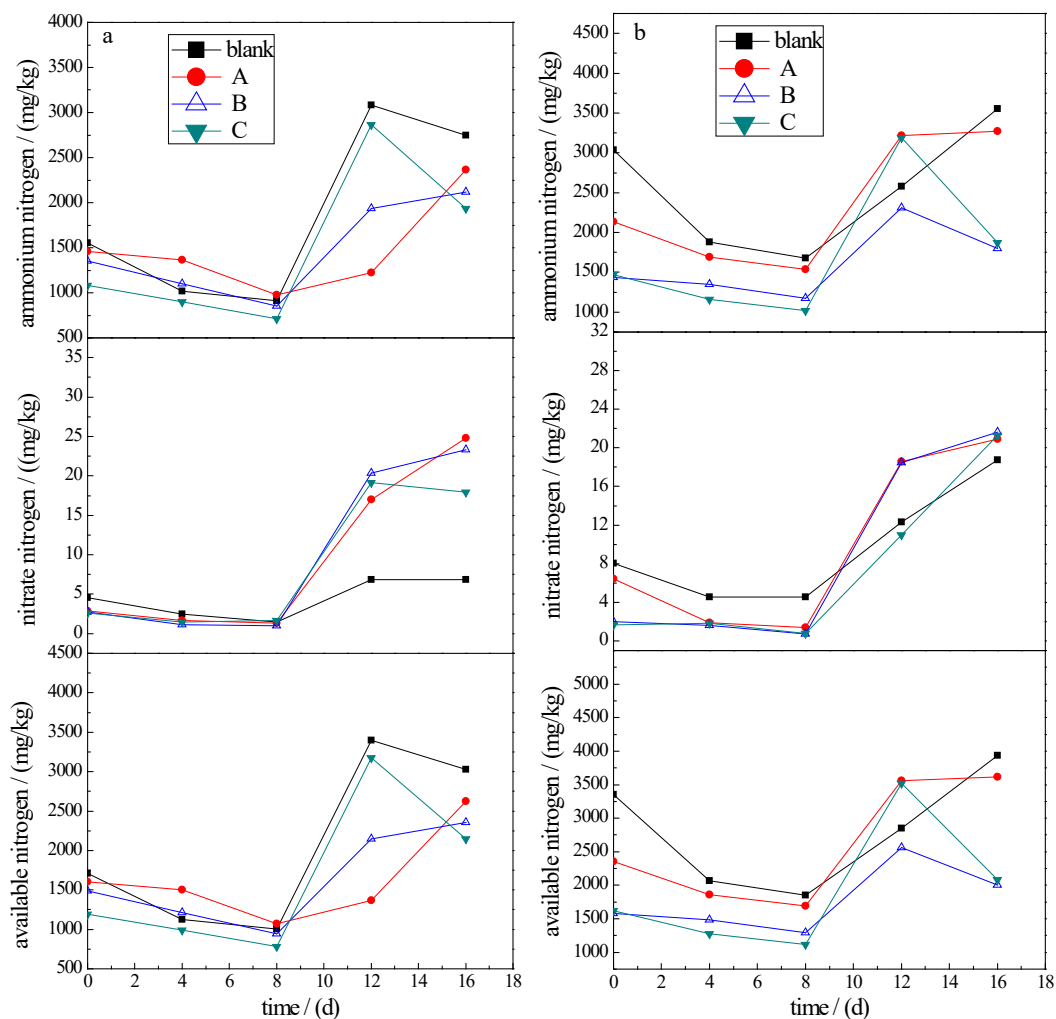
**Fig. 4.** Distribution of nitrides in soil with different concentration of lanthanum ions. (a) the content of the nitride in the upper soil containing different concentration of lanthanum ions; (b) the content of the nitride in the lower soil containing different concentration of lanthanum ions

the remaining three columns were leached loss. From the above analysis, it can be seen that ammonium nitrogen is the most important form of available nitrogen in mining soil. The change trend of available nitrogen in four-column is consistent with that of ammonium nitrogen. The upper soil layer with lanthanum ion also has this feature.

#### *Distribution of nitride in soil with different concentration of mixed rare earth*

The trend of the nitride contents in the upper soil (10 cm) containing different concentration of mixed rare earth with time variation is shown in **Fig. 5a**. As can be seen from **Fig. 5a**, the initial concentration of ammonium nitrogen in the four soil columns are 1551.61, 1456.07, 1351.45 and 1084.06 mg/kg, respectively. The initial ammonium nitrogen concentration is inversely proportional to the mixed

rare earth concentration. With the passage of time, the contents of ammonium nitrogen in the upper soil layer of four soil columns first decreased and then increased, and reached the lowest value on the eighth day after leaching, then the contents of ammonium nitrogen in the blank column and C column sharply increased to the maximum. At the end of leaching, the contents of ammonium nitrogen were 2744.12, 2362.85, 2115.81 and 1935.62 mg/kg, respectively, which still accorded with the higher concentration of ammonium and the lower contents of ammonium nitrogen, which indicated that the addition of different concentrations of exogenous mixed rare earth had certain influence on the contents of ammonium nitrogen in the soil. The high concentration of rare earth mixed could inhibit the production of ammonium nitrogen. The nitrate nitrogen contents of four soil columns decreased first and then increased with time prolonging. In the initial



**Fig. 5.** Distribution of nitrates in soil with different concentration of mixed rare earth. (a) the content of the nitride in the upper soil containing different concentration of mixed rare earth; (b) the content of the nitride in the lower soil containing different concentration of mixed rare earth

stage of leaching, the nitrate nitrogen content of the blank column was 4.54 mg/kg, while that of the other three columns was between 2.6 and 2.8 mg/kg, with a more concentrated distribution. With the passage of time, the contents of nitrate nitrogen in blank column changed little and the other three columns increased gradually. At the end of leaching, the content of nitrate nitrogen in blank column was 6.85 mg/kg and the other three columns were 24.79, 23.34 and 17.96 mg/kg, respectively, much higher than the initial stage of leaching. Comparing the nitrate nitrogen contents of three columns A, B and C at the beginning and the end of the leaching, the higher the concentration of the mixed rare earth, the lower the contents of the nitrate nitrogen, which is consistent with the above-mentioned ammonium nitrogen. The change of available nitrogen contents is consistent with that of ammonia nitrogen. When leaching to the 8th day, the contents of each column reached the lowest, then increased gradually.

The available nitrogen content of each column is negatively correlated with the concentration of mixed rare earth. Low concentration of rare earth ions will increase the available nitrogen concentration of soil, but the application of high concentration of rare earth ions will reduce the effective nitrogen concentration. This is consistent with the conclusion of Lu et al. (1999).

The trend of the nitride contents in the lower soil (40 cm) with different concentration of mixed rare earth with time variation is shown in **Fig. 5b**. As can be seen from **Fig. 5b**, the contents of ammonium nitrogen in blank column and column A first decreases and then increases with the passage of time. However, column B and column C show the first decrease then the increase and then decrease. The contents of ammonium nitrogen of four soil columns reached the lowest value on the eighth day after leaching. The order of the ammonium nitrogen contents in the soil column was



blank column > A column > B column > C column in the initial stage of leaching. However, the concentration of ammonium nitrogen in the blank column remained at 3932.36 mg/kg at the end of leaching, which is consistent with the change of ammonium nitrogen contents in the upper soil. High-concentration mixed rare earth will inhibit the production of ammonium nitrogen, which is agreement with the previous study (Lu et al. 1999, Qian et al. 2000). The contents of nitrate nitrogen decreased firstly and then increased with the leaching time. During the initial leaching period, the contents of nitrate nitrogen in blank column and A column were 8.03 and 6.41 mg/kg, respectively, while that of C and D column was between 0.7-2.0 mg/kg, and then the nitrate nitrogen contents of each soil column increased greatly. When the leaching ended, the contents of nitrate nitrogen were 18.75, 20.9, 21.62, And 21.30 mg/kg, respectively. The trend of nitrate nitrogen accumulation was consistent with that of nitrate nitrogen in the upper soil added with mixed rare earth. According to the change trend of nitrate nitrogen in the upper and lower soil layers, nitrate nitrogen migrated downward from the upper soil in the early stage of experiment. With the passage of time, the migration trend gradually weakened, and even the upper soil nitrate nitrogen content was greater than the lower soil. This is because the topsoil has good aeration conditions, and under the action of microorganisms, nitrification can transform part of the ammonium nitrogen into nitrate nitrogen, resulting in higher nitrate nitrogen contents in the surface soil. Subsequently, under the leaching effect, nitrate in the surface soil gradually migrated to the deeper soil, and when the nitrate concentration in the soil layer was lower than the nitrate ion concentration in the overall soil solution, negative adsorption phenomenon would occur, nitrate nitrogen contents in the soil layer increased in the short term. Continuous sampling is likely to cause the inner hollow in soil layer, leaching water flow in this temporary stay, making the surrounding soil nitrate dissolved in a large number of soil solution and gradually discharged to the outside of the column by gravity. The initial available nitrogen contents of each column was negatively correlated with the concentration of mixed rare earth, and the same trend was observed in the lower and upper soil. The change trend of ammonium nitrogen in each column is consistent with that of available nitrogen, which is because a large amount of ammonium ions in

the leachate and rare earth ions displace, so that most of the nitrides in the soil exist in the form of ammonium. While the contents of organic matter in the mining soil is small, and the contents of nitrate nitrogen has little effect on the change of available nitrogen. Therefore, the nitride in the soil of rare earth mine mainly exists in the form of ammonium, the pollution of soil environment and surrounding water in the mining area is mainly the pollution of ammonium nitrogen.

### CONCLUSIONS

In this paper, the effects of rare earth ions on the migration of nitrides in the soil of rare earth mining area were studied. The following conclusions were drawn:

- (1) After leaching for 24 days, the leaching loss of ammonium nitrogen in mining soil was 500 mg/kg, while that of campus soil was 350-1300 mg/kg. The leaching loss of soil in the campus was higher than that of the mining soil.
- (2) The effects of adding different concentrations of yttrium, lanthanum and mixed rare earth ions on the contents of ammonium nitrogen in the upper and lower soil were as follows: low concentrations of exogenous rare earth ions could promote the accumulation of ammonium nitrogen in the soil, while the high concentration of them inhibited the growth. The concentration of ammonium nitrogen reaches the maximum when the concentration of yttrium ion, lanthanum ion and mixed rare earth ions are 5-10 g/kg, 0-1 g/kg and 0-1 g/kg, respectively. The trend of available nitrogen concentration with time variation is consistent with ammonium nitrogen.
- (3) The effect of different concentration of Yttrium ions on the nitrate nitrogen contents in the upper and lower soil was not significant, but the addition of lanthanum ions showed inhibition. Adding different concentration of mixed rare earth showed "Low concentration showed a promotion effect, high concentration showed inhibition".

### ACKNOWLEDGEMENTS

This study was funded by the National Natural Science Foundation of China (51464014).

**REFERENCES**

- Chu HY, Cao ZH, Xie ZB (2001) Effects of lanthanum on microbial biomass carbon, nitrogen and respiration in red soil. *Journal of the Chinese Rare Earth Society*, 19(2): 158-161.
- Ding SM, Zhang ZL, Liang T (2004) Effects of rare earth on fractionation and transformation of available nitrogen in soil. *Journal of the Chinese Rare Earth Society*, 22(3): 375-379.
- Li XQ, Zhu YN, Yu G (2011) Study on permeation and migration law of ammonia nitrogen in aquitar. *Journal of China Hydology*, 31(3): 71-75.
- Liu YQ, Zhang JL (2013) Research on the market governance mechanism of rare-earth resources development in South Jiangxi to repay the “environmental liability”. *Chinese Rare Earth*, 27(5): 99-102.
- Liu ZW, Wang HS, Zhu Q (2015) Distribution characteristics of nitrides in soil of south china ion-adsorption rare earth ore mining area. *Chinese Rare Earth*, 36(1): 1-5.
- Lu P, Liu DF, Ma F (1999) Effect of REE-fertilizer on soil nitrogen and phosphorus. *Acta Scientiae Circumstantiae*, 19(5): 532-535.
- Luo CG, Luo XP, Su J (2014) Environmental problems and treatment measures in ionic-type rare earth mine. *Metal Mine*, 43(6): 91-96.
- Qian XQ, Shen QR, Wang JJ (2000) Effect of complex compound of rare earth element on transformation of soil nitrogen and crop growth. *Journal of Nanjing Agricultural University*, 23(3): 41-44.
- Wang HS, Liu ZW, Zhu Q (2014) Characteristics of nitrides spatial distribution in the in-situ leaching mining of ion-adsorption rare earth. *Nonferrous Metals Science and Engineering*, 5(6): 132-136.
- Wang JH, Zhang X, Chen DG (2015) Influence of during south ion-absorbed-type rare earth deposit mining on groundwater and it's monitoring. *Science & Technology Review*, 33(18): 23-27.
- Yang LP, Zeng FT, Huang HM (2014) Advances in research of migration and transformation of nitrogen in environmental media. *Water Resources Protection*, 30(5): 1-8.
- Zhang Y, Chi BM, Guan CY (2015) Experimental study on ammonia nitrogen transport in different medium in rainfall process. *Science Technology and Engineering*, 15(12): 260-264.
- Zhang ZH, Zhao ZG, Li T (2008) Experimental study on infiltration and transportation of ammonia nitrogen through the clayey soil layer. *Rock and Soil Mechanics*, 29(1): 28-32.