

Available online at www.sciencedirect.com**SciVerse ScienceDirect**

Procedia Environmental Sciences 12 (2012) 917 – 925

Procedia

Environmental Sciences

2011 International Conference on Environmental Science and Engineering

(ICESE 2011)

Transport kinetics of Pollutants in In-Situ Leaching of Ionic Type Rare-Earth Ore

Feng Xiujuan^{1,2,a}, Tao tao^{1,b*}, Zhu yichun^{2,c}¹School of Environmental Science and Engineering, HuaZhong University of Science and Technology, WuHan HuBei 430074²School of Architectural and Surveying & Mapping Engineering, Jiangxi University of Science and Technology, Ganzhou, Jiangxi 341000^axiujuanf@126.com, ^btaocaiye@vip.sina.com, ^czyc_79_0@126.com

Abstract

Taking Ganzhou city longnan zudong in-situ leaching of ionic rare earth ore soil as the research object, $(\text{NH}_4)_2\text{SO}_4$ as the leaching agent, we forecast and analyze leaching residues pollutants' diffusion rule over time in the soil layer. Constructing pollutants dispersion model, fitting pollutant dispersion changes based on Matlab platform, results show: As time increases, both NO_3^- -N concentration in two soil layers decreased. But the NO_3^- -N migration rate in the soil layer without leaching was clearly slower than the other which had already been leached and extracted. As time increases, both NH_4^+ -N concentration in two soil layers decreased. But the NH_4^+ -N rate in the soil layer without leaching was clearly slower than the other which had already been leached and extracted. As time increases, both SO_4^{2-} concentration in two soil layer decreased, but the SO_4^{2-} migration rate in the soil layer without leaching was clearly slower than the other which had already been leached and extracted.

© 2011 Published by Elsevier B.V. Selection and/or peer-review under responsibility of National University of Singapore.

Open access under [CC BY-NC-ND license](https://creativecommons.org/licenses/by-nc-nd/4.0/).

Keywords: In-situ leaching; pollutants; Transport kinetics;

There are three main Jiangxi Gannan ion adsorption-type rare-earth ore mining process, which are: pool leaching, heap leaching and in-situ leaching^[1,2]. The main leaching agent is ammonium sulphate [the full name is ammonium sulfate, and the molecular formula is $(\text{NH}_4)_2\text{SO}_4$], the main process is that injecting the leaching agent through the injection fluid wells to weathering ore bodies under the condition of natural bury. Under the condition of static pressure infiltration, leaching agent was infiltrated in the seepage field, and ore was transitioned from the non-saturated to the saturation state, seepage was transitioned from the unstable state of the transition to a stable state, so that a steady flow was produced. In the process, when the rare earth cations adsorbed on the mineral surface encountered the more lively chemical properties

[1] * Corresponding author

[2] the National Natural Science Foundation of China (21067003); Jiangxi Science and Technology Department ([2007] 189).

leaching cations (H^+ , NH_4^+), they were exchanged by the more lively cations and desorbed into the solution, forming the rare earth mother liquor. The rare earth mother liquor was gathered to the set liquid pool, then transported to the water plant for processing to get the wet rare earth. The mining process demand for ammonium sulfate is more than 30%, adjusting pH by adding sulfuric acid, and $(NH_4)_2SO_4$ was injected into the mountains, playing down the mountain tunnel to collect ore fluid. Because of large numbers of digging wells, holes, a large number of long-term perfusion with liquid sulfuric acid, excess ammonium ions, part of the sulfate ion remains in the soil, which are not only completely changed the original soil properties, but also the loss part of ammonium sulfate went into farmland together with the rare earth elements, result in crop failures occasionally.

1. Research Methods

1.1. Sampling areas

Ganzhou city longnan zudong rare earth ore represents the typical ionic rare earth ore and in-situ leaching mining in China. This article took the leaching soil and the mineral soil without leaching as the study object, to research and analyze rare earth leaching agent residue diffusion rule in the different soil layers with time.

1.2. Sampling and sample preparation^[3,4]

The time of sampling is on the June 18, 2010. Samples have been gathered under the conditions of using the highest point of the major mining as the center and according to the dominant wind direction, wind power and terrain and other factors in Ganzhou as well as the type of the pollution in leaching areas. By S distribution method, random samples were fixed vertically, with the soil sampler collection, and sampling depth was 0-3cm, 10cm, 20cm, 30cm and 40cm, respectively. The soil of each location was collected by the mixture of multi-point acquisition. Each sample's weight was 1kg and was placed in Teflon bags to back to the laboratory for use. The content of SO_4^{2-} , NH_4^+-N , $NO_3^- -N$ in different depths would be measured.

Put the soil samples down to the plastic film to dry slowly in cool place, crush the samples and remove the plant roots, leaves, stones and other debris when they come to semi-dry state, pave a thin layer, turn frequently, be fully air-dried and prevent direct sunlight and dust as well as the pollution of acid, alkali and other gases. After the soil samples dried, crush them with plexiglass and through the 2mm nylon sieve to remove more than 2mm gravel and plant residues. The dried fine soil will be repeatedly abandoned by quartering to take, and take some samples, bottling for use. The left samples should be further pulverized with a mortar plexiglass, and through 100 mesh nylon sieve, then shake them well and bottling for analysis.

1.3. Method^[3,4]

SO_4^{2-} was measured with $BaSO_4$ turbidimetry. Weigh 7.00g soil samples and leaching them by 35.0ml deionizer water. According to predictions, draw 5.00ml soil extract, and accurate dilution with water to 25.00mL, into 50.00mL Erlenmeyer flask. Add 1.00mL stabilizer and 1.0g $BaCl_2$ crystal grains, and turn the flask immediately to dissolve the grain until the end. Turbid fluid in the above should be compared the turbidity within 15min at 480nm (to be shaken one by one before comparing turbidity). Add 1.00mL stabilizer to the same soil extract, without $BaCl_2$. Measure its absorbance value by UV spectrophotometer, and subtract it from the absorbance value of cloudy soil liquid, then get the content of SO_4^{2-} .

(mg/25mL) in the cloudy soil liquid from the working curve. Record the room temperature when measured.

NH_4^+ -N was measured as follows: weigh 1.00g soil samples which were dried, skived and divided to the Erlenmeyer flask, add 5.0mL 20% NaCl solution, oscillate for 30min, and filter with qualitative filter paper. Draw 1.00mL filtrate to the color-metric tube and dilute to 20mL around with water. Then, add 0.1mL potassium sodium tartrate solution and 0.15mL 20% NaOH solution, shake completely, stewing for 15min, and add 0.05mL Nessler reagent while shaking the plus side, and then to the mark. After a period of time, the absorbance value could be read with UV spectrophotometer at 390nm. The interference of Ca^{2+} , Mg^{2+} and other metal ions could be excluded when potassium sodium tartrate - sodium hydroxide solution are use as masking agent.

NO_3^- -N was measured as follows: Accurately weigh 1.00g full mix of fresh soil, place in 100ml Erlenmeyer flask with a stopper, and add 0.01g CaSO_4 and 5.00mL redistilled water. After 10min of the oscillation on the oscillator, filter the upper clean solution of the suspension with dry filter papers, draw 1.00-20.00mL (determined by the concentration of NO_3^- -N) filtrate placed in 25mL grinding mouth colorimetric tube, diluted with water and accurate to the scale. The absorbance value could be read with UV spectrophotometer at the wavelengths of 203nm and 230nm. The method has good selectivity, high sensitivity, easy operation, wide measurement range, and can effectively eliminate the interferences of nitrite, chloride and organic matters.

2. Leaching agent residues diffusion model with time ^[4to 7]

Analyzing the migration and diffusion process of lateral contamination elements in soil occurs over time. This article takes the migration and diffusion process of contamination elements in the porous medium as a two-dimensional, thus the two-dimensional steady-state model was constructed as follows:

$$\left\{ \begin{array}{l} \frac{\partial C}{\partial t} = D_{xx} \frac{\partial^2 C}{\partial x^2} + D_{yy} \frac{\partial^2 C}{\partial y^2} - v \frac{\partial C}{\partial x} + Q C_0 \delta(x, y), \begin{cases} -\infty < x < +\infty, t > 0 \\ -\infty < y < +\infty, t > 0 \end{cases} \\ \text{Initial : } C(x, y, t) \Big|_{t=0} = 0, \begin{cases} -\infty < x < +\infty \\ -\infty < y < +\infty \end{cases} \\ \text{Boundary: } \lim_{x \rightarrow \pm\infty} C(x, y, t) = 0, \lim_{y \rightarrow \pm\infty} C(x, y, t) = 0, t > 0 \\ P : \delta(x, y) = \begin{cases} 1, (x = x_p, y = y_p) \\ 0, (x \neq x_p, y \neq y_p) \end{cases} \end{array} \right. \quad (1)$$

Among them, taking P as the origin of coordinates, the analytical solution can be obtained by two-dimensional Fourier transform:

$$C(x, y, t) = \frac{C_0 Q}{4\pi h v \sqrt{a_{xx} a_{yy}}} \exp\left(\frac{x}{2a_{xx}}\right) [W(0, b) - W(t, b)] \quad (2)$$

In this equation,

$$D_{xx} = a_{xx}v, D_{yy} = a_{yy}v, b^2 = \frac{x^2}{4a_{xx}^2} + \frac{y^2}{4a_{xx}a_{yy}}, \tag{3}$$

$$W(t, b) = \int_t^\infty \frac{1}{y} \exp\left(-y - \frac{b^2}{4y}\right) dy,$$

Hantush function; a_{xx} represents the dispersion for x direction; Other symbols mean the same with the former.

3. Leaching agent residues of rare earth in-situ leaching trend analysis

3.1. rare earth leaching agent residues NO_3^- -N migration and diffusion diagram

Research on leaching agent residues NO_3^- -N diffusion difference in soil layer between the leaching mining soil and the mining soil without leaching .Results are shown in Figure 1,2,3,4.

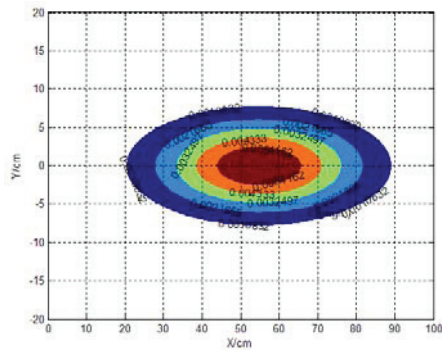


Fig 1 NO_3^- -N migration and diffusion diagram after one year mining

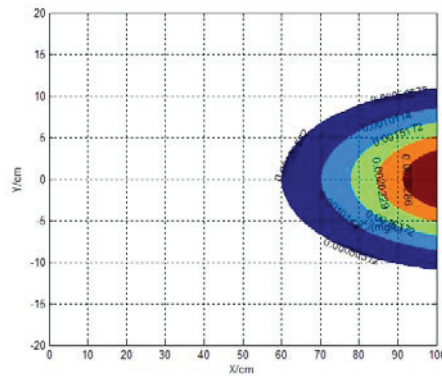


Fig 2 NO_3^- -N migration and diffusion diagram after two years mining

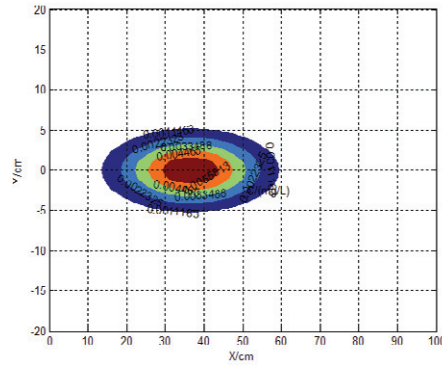


Fig 3 NO₃⁻-N migration and diffusion diagram of the soil without leaching after one year mining

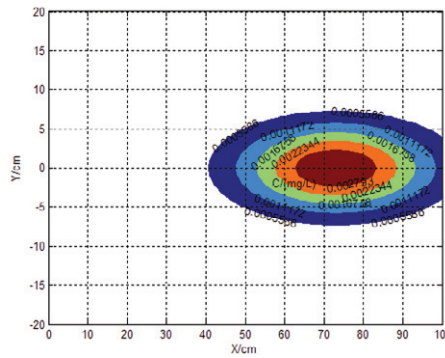


Fig 4 NO₃⁻-N migration and diffusion diagram of the soil without leaching after two years mining

As shown in Figure 1~4, both NO₃⁻-N concentration in two soil layers decreased with time. But the NO₃⁻-N migration rate in the mining soil layer without leaching was clearly slower than the other which had already been leached and extracted.

3.2 rare earth leaching agent residues NH₄⁺-N migration and diffusion diagram

Research on leaching agent residues - NH₄⁺-N diffusion difference in soil layer between the leaching mining soil and the mining soil without leaching. Results are shown in Figure 5,6,7,8.

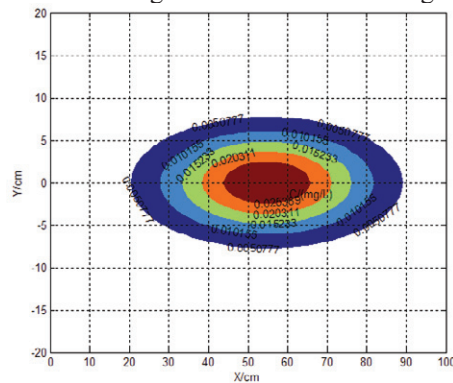
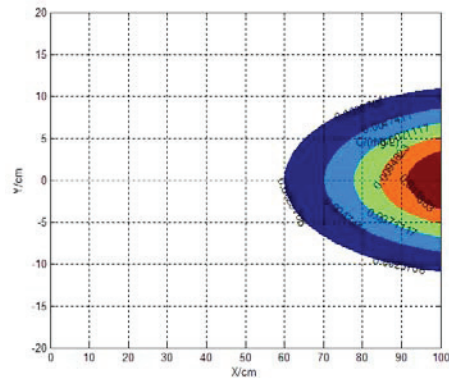
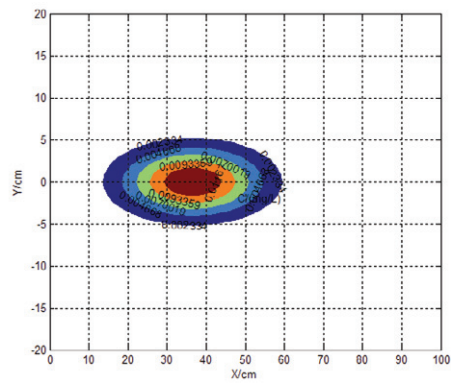
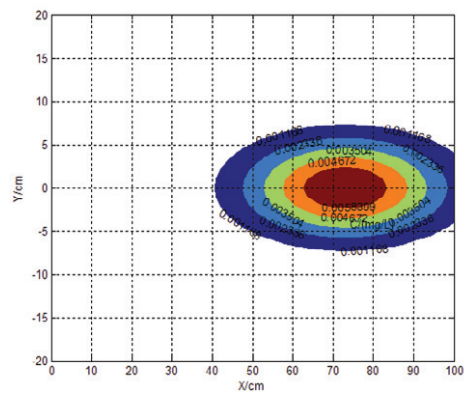


Fig 5 NH_4^+ -N migration and diffusion diagram after one year miningFig 6 NH_4^+ -N migration and diffusion diagram after two years miningFig 7 NH_4^+ -N migration and diffusion diagram of the soil without leaching after one year miningFig 8 NH_4^+ -N migration and diffusion diagram of the soil without leaching after two years mining

What can be seen from the comparison of Figure 5 to 8 is that both NH_4^+ -N concentration in two soil layers decreased with time. But the NH_4^+ -N rate in the unleaching soil layer was clearly slower than the other which had already been leached and extracted.

3.3. rare earth leaching agent residues SO_4^{2-} - migration and diffusion diagram

Research on leaching agent residues SO_4^{2-} diffusion difference in soil layer between the leaching mining soil and the mining soil without leaching. Results are shown in Figure9,10,11,12.

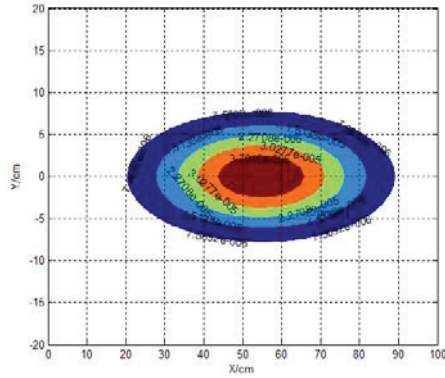


Fig 9 SO_4^{2-} migration and diffusion diagram after one year mining

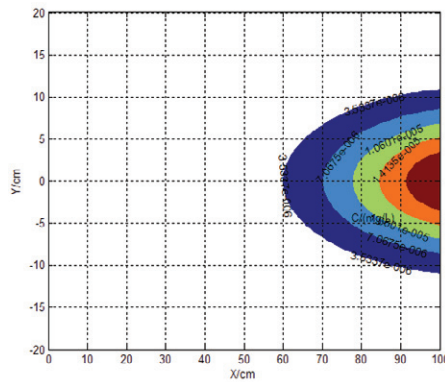


Fig 10 SO_4^{2-} migration and diffusion diagram after two years mining

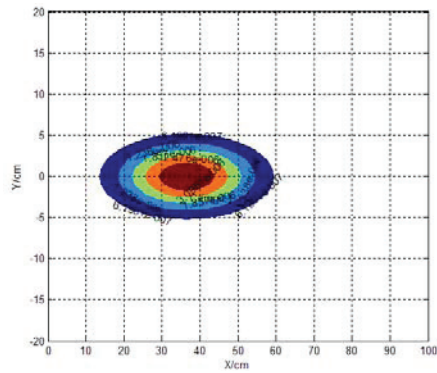


Fig 11 SO_4^{2-} migration and diffusion diagram of the soil without leaching after one year mining

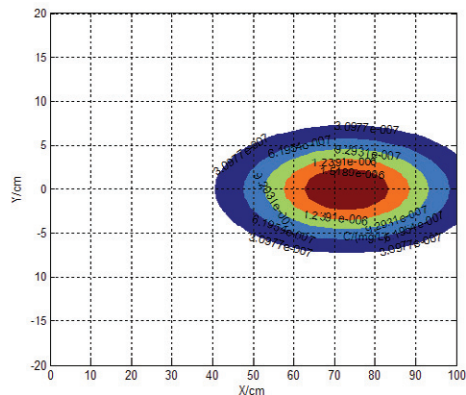


Fig 12 SO_4^{2-} migration and diffusion diagram of the soil without leaching after two years mining

As shown in Figure Figure 9 ~ 12, both SO_4^{2-} concentration in two soil layer decreased with time, but the SO_4^{2-} migration rate in the unleaching soil layer was clearly slower than the other which had already been leached and extracted.

From the analysis above we can see that the mining soil is more vulnerable to pollution elements erosion, which need more soil environmental protection. Meanwhile, mine vegetation needs fast recovery for the prevention of soil desertification and environmental pollution.

References

- [1] Chi, R.A., Tian, J., 2006. Chemical and metallurgy process of weathered crust rare earth ore. Science Press, Beijing, China.
- [2] Zhao, Q.G., 2002. The temporal and spatial variation, mechanism and regulation of the soil degradation in red regions in eastern China. Science Press, Beijing, China.
- [3] Lu, R.K., 1999. Chemistry analysis of agricultural soil. China Agricultural Science and Technology Press, Beijing, China.
- [4] Nanjing Agricultural University, 1986. Agricultural soil analysis. China Agricultural Science and Technology Press, Beijing, China.
- [5] Li H, Yang Z.H., 2002. The evolution analysis of earth pollution based on genetic algorithm. Gold 5(6), 37-41.
- [6] Shi, R.G., 2009. The pollution characteristics, spatial distribution and ecological risks of the interface of soil and water in peri-urban. Doctoral dissertation, Nankai University Tianjing.

- [7] Zhang L.B., 2007. The research of experimental genetic algorithm and its application in the problems of water system. Doctoral dissertation, Yangzhou University, Yangzhou