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Mobility of the Rare Earth Elements with Acid Rainwater Leaching in the Soil Column

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China is abundant in rare earth elements (REEs) resources. REEs have been extensively used in industry and agriculture for many years (Guo et al. 1988; Sun et al. 1996; Yang et al. 1998). As a result, more and more REEs are moving into environment. They may accumulate in soil, bioaccumulate in crops, or enter the groundwater. Due to its increasing exposure and potential harm to environment, the transportation, transformation, fate and environmental effect of the exogenous REEs should be studied carefully to predict or assess their threats to environment in China.

Environmental hazards derived from REEs are closely linked to their mobility, and thus to the concentrations of the REEs in the soil solution. The mobility of REEs in term of leachability depends not only on the total REEs in soil but also on soil properties and environmental factors. The movement of REEs in soil profiles has received considerable attention, since even a slow transport of REEs through soil and subsoil may result in an increased content of REEs in groundwater. Zhu et al. (1992) concluded that the alkaline soil fixed the exogenous REEs more stable than acid soil, due to which more attention should be paid to the area of acid soils. Zhu et al. (1996) found that migration distance of REEs was limited within 4cm in acid soil under the simulated rain leaching. But the acidity of rain tended upwards year by year, and the strong acidic precipitation happened more and more frequently in China, especially in south China. (Hong, 1995). Ma (1990) found acid rain happened frequently with an average of one in two rainfalls in one year and the lowest pH value of rain was 3.39 in Nanjing, located in south China. Unfortunately, few investigations have been made on REEs transport under acid rain (Chen et al. 1995). Chen studied REEs migration through a model supposing the micro-REEs fertilizer was added to soil by plane. This model imitated what we called instant pollution and didn't take consideration of accumulation of REEs in soil. In fact, the micro-REEs fertilizers have been used for many years in China and caused accumulation of REEs in soil, which we called accumulated pollution. Up to now, no information has been available about REEs migration in the two types of

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pollution of the contaminated soil (accumulated pollution and instant pollution) under the acid rainwater leaching.

In this paper, we selected the red soil purposely because it is major type of acid soil and cover large area in south China. The micro-REEs fertilizers and artificial acid rainwater were used to test the mobility of REEs in two different pollution ways under the acid rain leaching in soil column. The primary purpose of this study was (1) to determine and compare the mobility of REEs in the two pollution ways. (2) to provide information about the effect of applying micro-REEs fertilizers on environment during agriculture practice.

MATERIALS AND METHODS

The red soil (collected from Jiangxi, China) was taken from the surface (0-20cm). The soil was air dried, and ground to pass through a sieve (2mm) for the experiment. The solution containing REEs (1mg/ml) was prepared by using micro-REEs fertilizers. The physicochemical characterizations of soil and the constitutions of micro-REEs fertilizers were listed in table 1 and table 2.

Table 1. Physico-chemical proprieties of the red soils

Soil	pH	Organic matter(g/kg)	Cation exchange capacity(cmol/kg)	Clay% (<0.002mm)
Red soil	5.45	0.63	5.07	32.3

Table 2. The constitution of micro-rare earth elements fertilizer

Element	Lanthanum	Cerium	Neodymium	Praseodymium	Samarium
Content(%)	26.85	46.44	18.53	7.32	0.86

Polyvinyl chloride columns (10cm inside diameter and 20cm in length) were adopted in this study. Each column was filled with soil (about 500g) to the height of 4cm so that the bulk density was similar to the bulk density in the fields. The columns were shaken during filling soil and water was aided to improve soil compacting. Details of filling columns were described as following:

(i)Soil without adding exogenous REEs was filled in column I , as a blank control. (ii)Column II was filled with soil which has been incubated for equilibrium for 15 days after saturated with distilled water and added with 50ml REEs solution. It simulated instant pollution. (iii) ColumnIII was filled with untreated soil to the height of 3cm with another treated soil filling above to the height of 4cm, which was pretreated in the following procedure:(1)flooded with distilled water, mixed with 50ml REEs solution and air-dried. (2) the drying soil was ground, and sieved (2mm). It simulated accumulated pollution.

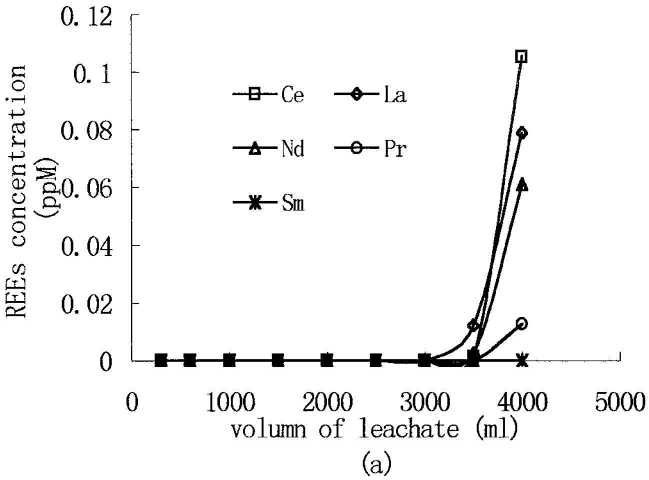
The artificial acid rainwater was prepared according to the composition analysis of the real rainwater in Nanjing area and was adjusted to pH 3.0.Artificial acid rain dripped on each column with total volume of 4000ml to simulate five years rainfall. During the leaching, the surface of acid rainwater in the soil column was controlled 1 cm higher than the soil surface and effluent flow was kept steadily with the rate of an average 50ml/h. Acid rain dripped 10 hours every day. The leaching process was taken 8 days and Samples were collected at 500ml intervals. The concentrations of REEs in the leachates were determined by ICP-AES

After leaching, the soil in the column was divided into 4 layers at even heights. Soil samples were collected at each layer in plastic bag, dried, ground and stored in the drying bottle. Each soil sample of 1g was added with 5g Na_2O_2. Then put them into muffle and melted them 10 minutes at 700℃. The residue was dissolved by 10% triethanolmine solution, then filtered it through quantitative filter paper. The left residue was dissolved in 40ml of 0.8ml/l HCL and it was added to the filtered solution above. After that, the total solution was transferred to columns (8 x 200mm) packed with 1 x 8 strong cation exchangers (Dowex 50 x 8) and 70ml of 1.8 mol/l HCL was added to the column for 1 h. The REEs adsorbed by resin were finally eluted by another 110ml of 4.0mol/l HCL. The eluant was evaporated to about 1ml and transferred to 10ml volumetric flask and made up to volume with distilled water. The resultant solution was subsequently used for analysis by ICP-AES. In order to estimate the error of the procedure, the REEs concentration was also carried out for the recommended sample GSS-5, which was geological reference materials provided by Institute of Geophysical and Geochemistry prospecting (IGGP), Ministry of Geology and Mineral resources. The REEs concentration of GSS-5 measured in this experiment was in range of the recommended REEs concentration. The results obtained by the parallel test of the same soil sample indicated that the mean relative error was smaller than 5%.

RESULTS AND DISCUSSION

The soil column method used in this study represent a simplification of the natural process and the REEs migration in field will be slower than that in the columns in this experiment. So the results of leaching REEs obtained in our lab may reflect a long period behavior of REEs in natural condition.

In this study, the leachate from column I was considered to be an blank control and REEs concentration in the leachate was subtracted from REEs of other two columns. The REEs concentration in the leachate of column II and columnIII was showed in figure1.



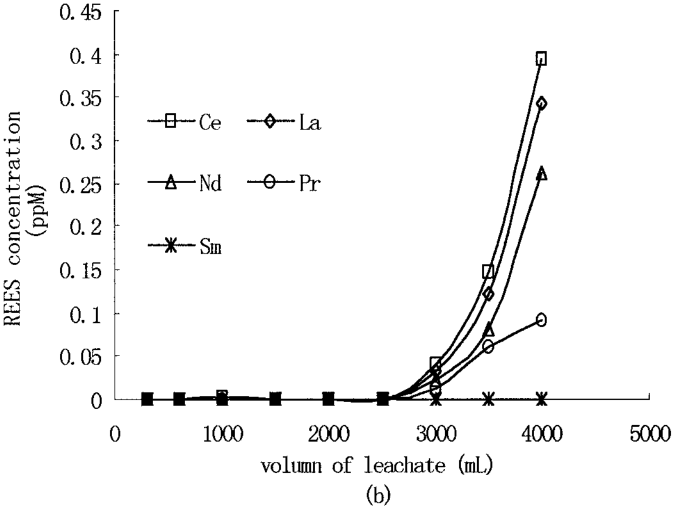


Figure 1. The REEs concentration in the leachate of the red soil column under acid rainwater. (a) simulated instant pollution (column II) (b) simulated accumulated pollution (columnIII)

Figure1 showed that REEs concentration were detectable when the leaching volume reached 3000ml. After that, all the REEs concentration in the leachate became higher with more volume of acid rainwater applied Samarium in the leachate from column II and columnIII was so low that it could be negligible. It was found that Ce leached first and then La, Nd, with Pr last. The REEs could be listed by their

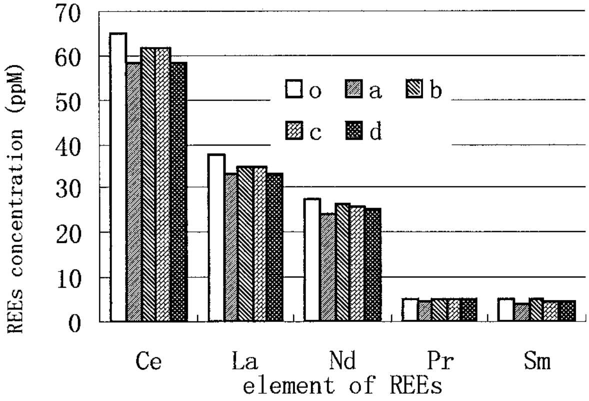


Figure 2. The REEs concentration in the uncontaminated red soil column (column Ⅰ). o represents the original red soil without leaching. a, b, c and d represent 0-1cm, 1-2cm, 2-3cm, 3-4cm depth in the soil column respectively.

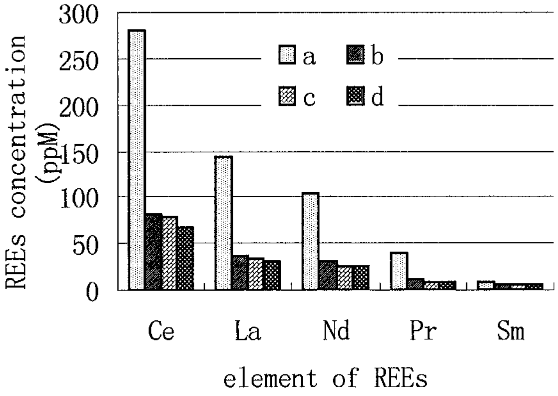


Figure 3. The REEs concentration in the red soil column (column II) which simulated instant pollution. a, b, c and d represent 0-1cm, 1-2cm, 2-3cm, 3-4cm depth in the soil column respectively.

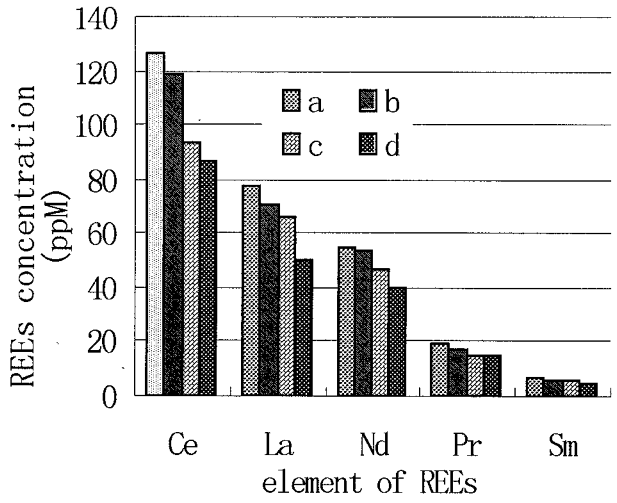


Figure 4. The REEs concentration in the red soil column (columnIII) which simulated accumulated pollution. a, b, c and d represent 0-1cm, 1-2cm, 2-3cm, 3-4cm depth in the soil column respectively.

concentration in leachate with the order Ce > La > Nd > Pr at some specific leaching volume (more than 3000ml), correlated with the order of REEs in the micro-REEs fertilizers. The results showed the mobility of exogenous REEs was related to the REEs concentration in soils. The higher the concentration of exogenous REEs in soil, the higher mobility the REEs have. It can be explained that these REES have similar chemical and physical properties, so the interaction of REEs among the system of soil-acid rain greatly depended on their amount.

The REEs in the leachate from columnIII were always higher than that from column II at the same leaching volume (more than 3000ml). The REEs in the leachate from columnIII could be detected earlier than that from column II. The comparing result showed the leaching potentiality of REEs in the accumulated polluted soil was higher than that in the instant polluted soil.

The REEs concentration in column I was listed in figure2. Figure2 showed the five REEs concentration decreased with the depth in the column except for the first layer, which is abnormal and may be caused by the complex physcio-chemical characteristic of the soil or the error in the experiment. The five REEs concentration in all layer of column I was lower than that of original red soil without leaching, which showed REEs in the red soil can be washed away by the acid rainwater.

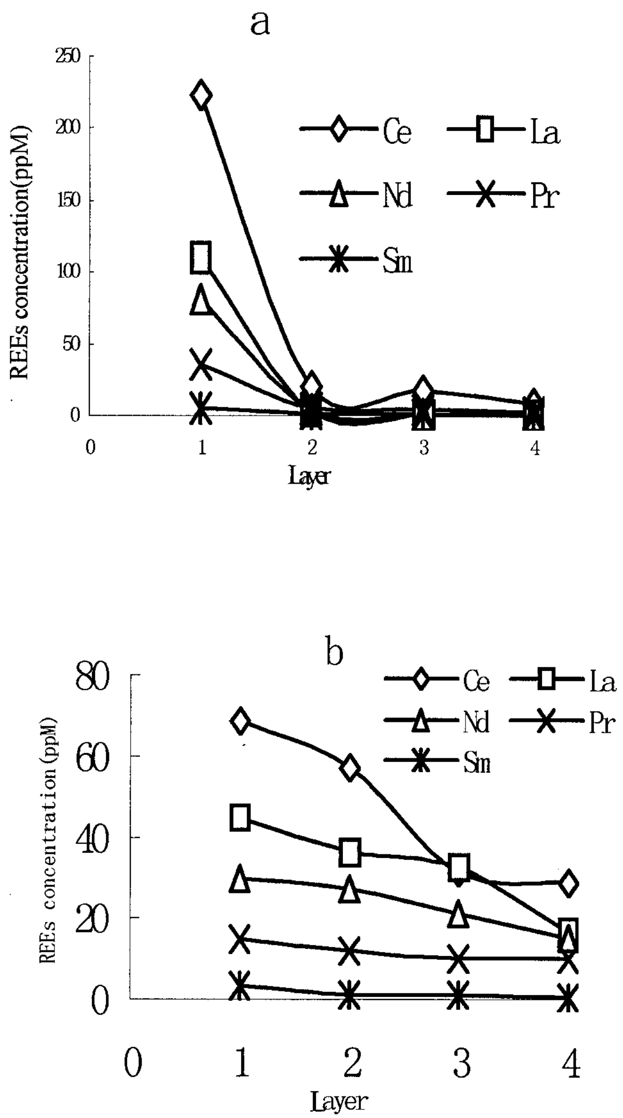


Figure 5. The exogenous REEs in the red soil column
(a) simulated instant pollution (column II)
(b) simulated accumulated pollution (columnIII)

In column II (figure3), the REEs in the first layer (0-1cm) were much higher than that in other layers, indicating most of REEs were retained by soil. We can find the REEs concentration decreased with the depth in the column. From the result, it can be concluded that the REEs could be retained by the soil strongly, which makes the migration of REEs in soil very difficult.

The REEs in the first layer (0-1cm) of columnIII, which simulated accumulated pollution ,is higher than the REEs in other layers (figure 4), but the difference is not big enough compared with the column II.

In order to study the distribution of the exogenous REEs in column II and columnIII, the REEs concentration in each layer of column II and columnIII was subtracted from the REEs concentration in column I respectively (figure5). Figure5 shows the most of exogenous REEs accumulated in the first layer of column II and in column III, the REEs concentration decreased slowly with the depth, which indicated the exogenous REEs concentration in the columnIII has greater mobility than that in the column II. It means that the accumulated pollution of REEs will pose more serious threat to environment than the instant pollution. So it is very necessary to change the present way of applying micro-REEs fertilizer to prevent accumulation of REEs in soil caused by agriculture activities and many techniques, such as chemical stabilization or phytoremediation, should be adopted to recover polluted soil by the REEs.

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