E3S Web of Conferences 573, 01001 (2024) https://doi.org/10.1051/e3sconf/202457301001
SDER 2024

Soil Improvement after Reclamation of Rare Earth Tailings in Northeast Guangdong, China

Qihe Yang[1,2*], Jiaoqing Li[2], Jianhua Xiao[1,2], Lihui Mou[1,2]

[1]Guangdong Provincial Key Laboratory of Conservation and Precision Utilization of Characteristic Agricultural Resources in Mountainous Areas, Meizhou 514015, China
[2]Jiaying University, Meizhou 514015, China

Abstract: In order to explore the soil improvement effect of guest soil reclamation, the main physical and chemical properties of the soil in-situ extracted rare earth tailings after reclamation in Pingyuan County, Meizhou city were tested. Using 5 point sampling method, soil samples were taken from a 0-20 cm soil layer to detect NH_4^+ residues, pH value, content of organic matter, available N, available K, available P, and heavy metal in the soil. The results were shown that the NH_4^+ content in the soil decreased from 96.67 to 15.29 ($mg\cdot kg^{-1}$) after reclamation, the pH value increased from 4.58 to 5.40, and the organic matter increased from 2.12 to 2.75 ($g\cdot kg^{-1}$). However, the available N, P, and K decreased, and the soil fertility index also decreased from 0.55 to 0.49. The reclamation did not significantly improve soil fertility. The Nemero comprehensive index of non-rare earth heavy metal elements decreased from 0.58 to 0.44, but the pollution of non-rare earth heavy metals in the soil before and after reclamation was at a clean level, and there was no heavy metal pollution. The total RE (rare earth) content in tailings soil, reclaimed soil, and control soil was higher than the soil environmental background value in Guangdong Province. Heavy RE content in tailings soil exceeded 50% of total RE content, while light RE was mainly in the reclaimed soil. The pollution levels of total RE metals in soil before and after reclamation were non-pollution to moderate pollution level and non-pollution level, respectively. The control soil was the most severely polluted, reaching a strong pollution level. The three RE metals, Y, Sm and Ce, accounted for the highest proportion of the total soil REs, and the pollution levels of the latter two elements were above strong pollution in control soil. After 4 years of land reclamation, the NH_4^+-N pollution, soil acidification, and heavy metal pollution in the soil of tailings could be significantly improved, but the soil fertility was still low and required a long remediation process. In the future reclamation work, in addition to continuing to pay attention to the improvement of soil environment, the improvement of soil fertility and the control of RE pollution should also be strengthened, and when using foreign soil for reclamation and improvement, the quality of foreign soil, especially fertility, should also be considered.

1. Introduction

In 1983, the national mineral survey found that 12 towns in Pingyuan County, Guangdong Province had RE (rare earth) distribution with reserves of nearly 90,000 tons, mainly distributed in Renju, Bachi and other towns. Since the large-scale mining began in the mid-1980s, it has a history of over 40 years, and tailings are mainly concentrated in Renju. Long-term disorderly mining and backward extraction technology has brought serious environmental problems, such as vegetation destruction, soil pollution, tailings accumulation, etc.[1-2]. Since 2010, the Ministry of Land and Resources and the Ministry of Environmental Protection of China have required the remediation of environmental damage in tailings. Ecological restoration is an indispensable task, and the development of soil reclamation and improvement technologies has become an urgent task. The mining process has shifted from traditional pool and heap leaching to in-situ leaching[3]. In situ leaching, in short, involves directly dissolving the ore body with chemical solvents and extracting required elements from leaching solution. This involves injecting leaching solution containing electrolyte ions (Na^+, NH_4^+, H^+, and Mg^{2+}) into the ore body, exchanging with RE ions resolved from minerals, and then collecting RE mother liquor through pipelines or collection ditches for extraction[4-7]. Compared with the other two mining processes, in-situ leaching mining has higher efficiency, resource utilization, and less environmental damage. Therefore, this process has been commonly used in the RE tailings of Jiangxi and Guangdong for over 20 years, resulting in the formation of many ion-adsorption RE tailings. There are residual heavy metals (including REs) and ammonia nitrogen in these tailings. Determining these residues can help understand the efficiency of RE extraction and evaluate the nature and severity of soil pollution, providing scientific basis for subsequent pollution remediation and ecological reconstruction[4,8-9]. The reclamation of ion-

*Corresponding author: yangqh@jyu.edu.cn

adsorption RE tailings currently mainly adopts the method of soil reclamation, which is an economically effective method[10]. Although land reclamation has been gradually carried out in tailings of Meizhou, there is few researches on the changes in physical and chemical properties of tailings soil before and after reclamation. This is of great significance for the effectiveness evaluation and feasibility analysis of reclamation methods. The existing researches on RE tailings soil are mainly focused on the environmental factors of surface soil in tailings, risk assessment of non-RE heavy metals and REs in surrounding soil, and their impact on surrounding water bodies. However, there are few reports on the degradation characteristics of tailings soil and the comparison of soil environmental factors before and after reclamation. This article analyzed and compared the changes in soil physical and chemical properties before and after reclamation in RE tailings of Renju Town, Pingyuan County, including soil acidity and alkalinity, residual leaching agent (NH_4^+), main nutrients, REs, and non-RE heavy metals, and evaluates the soil improvement effect of reclamation measures.

2. Materials and Methods

2.1. Sample Collection

The reclamation area was the stepped terrain, and the upper soil (0~30 cm) was formed by mixing guest soil and upper soil of tailings. 5 terraces were selected from top to foot of the slope, and mixed samples were collected by the 5-point method in each step, and 5 soil samples represented the soil of reclamation area. 5 soil samples represented the control soil at different height locations of the slope with good vegetation cover around the tailings. At each sampling point, shallow soil (0~20 cm) was used to form mixed soil samples. Approximately 1 kg mixed soil samples were extracted by 4 fraction method and sealed and bagged for backup.

The ionic RE tailings studied in this study was located in Renju Town, Pingyuan County. In-situ leaching was used during mining, mainly using NH_4^+ ($(NH_4)_2SO_4$ or NH_4HCO_3, often mixed) as the leaching agent. In 2018, the terraced land reclamation technology was systematically adopted, with a guest soil cover thickness of 30-40 cm. A survey conducted from Oct to Dec 2022 found the main herbs in the reclaimed area included Miscanthus floridulus, Cynodon dactylon, and Pennisetum glaucum×purpureum. Occasionally, Dicranopteris pedata, Blechnopteris orientalis, Pteris vittata and other distribution would be found. The seedlings and young individuals of Pinus massoniana, P. elliottii, Elaeocarpus sylvestris and Eucalyptus robusta were cultivated and the vegetation coverage was about 50%. While in the tail mining area (i. e., unreclaimed area) there were few plants growing, the vegetation coverage was about 2~5%, the control area (retained woodland) coverage exceeded 70% (Figure 1). The reclamation area had a stepped terrain, and its upper soil layer (0-30 cm) was a mixture of guest soil and the original tailings upper soil layer after leveling. 5 terraces were selected equidistant from top to foot of the slope, and mixed samples were collected through the 5 point method at each level. A total of 5 soil samples were collected to represent the soil in reclamation area. Soil samples were collected from the tailings at similar heights to those collected from reclamation area. 5 soil samples were collected using 5 point method to represent the control soil at different heights of slopes with good vegetation coverage (unmined areas) around the mining area. Each sampling point takes a mixed soil sample composed of shallow soil (0-20 cm), and approximately 1 kg mixed soil sample was extracted using the quartering method and sealed in bags for following use.

2.2. Soil Sample Processing and Analysis

According to the method of Zhou et al. (2019)[4], soil samples were air dried, ground, sieved, and bagged in the laboratory for following use. Then, soil pH, organic matter, available N, available P, available K, and heavy metal (including RE metals) content were measured. The digestion of soil samples and determination of heavy metal content according to the method of You et al. (2018)[2], while the determination of REs according to Zhou et al. (2019)[4] and You et al. (2018)[2] using inductively coupled plasma chromatography-mass spectrometry (ICP-MS).

Figure 1 Regional division of rare earth tailings

2.3. Soil evaluation methods

2.3.1. Heavy/Light RE ratio

REs were classified into light REs (LREEs) and heavy REs (HREEs) based on their differences in physi-chemical properties and the need for mineral processing and extraction. According to the methods of Jin et al. (2014) [11]and Zhou et al. (2019)[4], the ratio of heavy to light REs was calculated as follows: HREEs/LREEs=$\sum$([Gd] - [Lu]+[Y])/$\sum$([La] - [Eu]).

2.3.2. Comprehensive soil fertility evaluation method

Referring to the method of Zhou et al. (2019) [4], soil fertility single index and improved Nemero comprehensive index method (NY/T 1749-2009) were used. The calculation formula for soil single fertility index (P_i) was $P_i=C_i/S_i$, where P_i was the fertility index of evaluation factor i, and the larger its value, the higher the fertility. When $P_i \geq 3$, the fertility index was calculated as $P_i=3$; C_i was the measured value of evaluation factor i; S_i was the evaluation standard for participating factor i (the evaluation standard in this article adopted reference standard values recommended by the main physi-chemical indicators in soil fertility evaluation in Southern China).

The formula for calculating soil comprehensive fertility (P_z) was as follows: $Pz = \sqrt{\frac{(P_i^2 min + P_i^2 ave)}{2}} \times \frac{N-1}{N}$, where Pi^2_{min} was the minimum value of all single fertility indices (P_i) among all soil indicators; P^2_{ave} was the average value of each individual fertility index; N was the number of fertility indicators determined. When grading soil fertility based on P_z values, a value below 0.9 was considered poor; $0.9 \leq Pz < 1.7$ was average; 1.7 or above was fertile.

2.3.3. Nemero comprehensive pollution index method

The Nemero comprehensive pollution index was a widely used method to evaluate the pollution levels of various heavy metal elements in soil [4, 12-13].

2.3.4. Index of geoaccumulation method

The index of geoaccumulation (I_{geo}) method was used to evaluate heavy metal pollution [4, 12-13].

2.4. Data Analysis

The computational analysis and mapping were performed using the Microsoft Excel software, the data statistical analysis was performed using the SPSS 13.0 statistical software. One-way ANOVA and Duncan's multiple comparisons were conducted of pH values, organic matter, effective N, quick P, quick K, heavy metals (including REs) in different soil (α=0.05).

3. Results and Analysis

3.1. Residual NH4+ leaching agent

Through the determination of NH_4^+ content in three soils, it was found that the NH_4^+ content was in the following order: tailings soil >control soil> reclaimed soil. The NH_4^+ content in tailings soil was the highest and significantly higher than that in the other two soils ($P<0.05$), while in the other two soils, the reclaimed soil was significantly higher than the control soil (Figure 2). This indicated that a large amount of leaching agent NH_4^+ remained in tailings soil after mining, and the content significantly decreased after reclamation, indicating that reclamation could remove some residual NH_4^+.

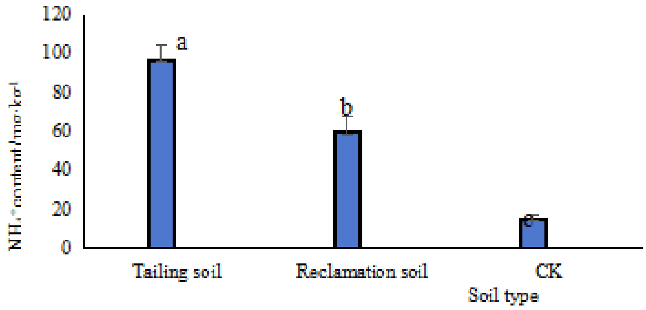

Figure 2 Soil NH_4^+ content of different soils

3.2. Soil pH value

There was no significant difference in pH value between reclaimed soil and tailings soil or control soil, but compared with the latter two, pH value of the tailings soil was significantly lower than that of control soil (Figure 3), indicating that the original leaching treatment changed the acidity of the soil. The pH value of soil in South China was mostly below 7 (mostly concentrated in 4.5-5.5), and all the three soils were no exception[14]. According to the soil pH grading standards of the second national soil surveyin China, tailings soil belonged to acidic category. This was mainly due to the use of ammonium salts such as $(NH_4)_2SO_4$ for RE extraction, which was a physiological acidic salt. The residues in soil could lead to soil acidification, the reclaimed soil and the control soil were weakly acidic. Due to plant absorption and rainwater flushing, the concentration of ammonium salts decreased, and the soil pH had significantly increased, similar to the control soil. This indicated that soil acidification had improved after reclamation, but it was not significant. The pH value of tailings soil was significantly lower than that of control soil, indicating that the acidity was stronger than that of control soil.

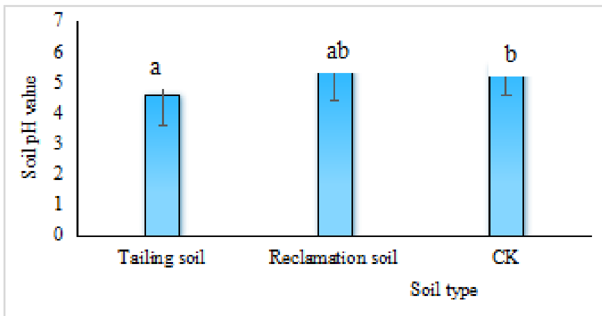

Figure 3 PH value of different soils

3.3. Soil fertility degradation

The content of organic matter, available N, available K, and available P in soil can to some extent reflect soil fertility. The degradation of soil fertility mainly refers to the gradual decrease of The aforementioned soil nutrients, and even the overall deterioration of soil environment[4,6]. The determination results showed significant differences in the aforementioned four nutrients among the three soils. The available N content was highest and the organic matter content was lowest in tailings soil, but there was no significant difference in organic matter content between tailings soil and reclaimed soil. The average content of available P, organic matter, and available K in the control soil was the highest, and the content of available P and organic matter was much higher than the other two soils. However, there was no significant difference in the content of available K compared to tailings soil. The content of available N, P, and P in the reclaimed soil was the lowest and significantly lower than that of the other soils. However, there was much residual NH_4^+-N in the leaching agent in the tailings soil, resulting in a higher content of available N (Table 1). Compared with the control soil, the content of four nutrients in reclaimed soil was relatively low, indicating that the soil still lacked these nutrients after reclamation, and the fertility was still insufficient, making it difficult to ensure the normal growth of plants. The soil viscosity of tailings was the worst, with the highest content of fine and coarse sand. The control soil had the strongest viscosity, mainly because its structure had not been damaged by mining, and the content of fine and coarse sand was the least. The viscosity of reclaimed soil was in between the two aforementioned soils (Table 2). If the soil had poor viscosity and high content of fine and coarse sand, its water retention performance was weak. Soil with high fertility must had a good aggregate structure. According to the soil nutrient evaluation grading indicators (organic matter and macro-element content grading), the control soil belonged to level 5 (nutrient deficiency), and the fertility level of reclaimed and tailings soil both belonged to level 6 (extremely nutrient deficient).

From the perspective of single factor fertility index, except for P_{AK}, which was above 1, P_{AN}, P_{AP}, and P_{SOM} were all below 1 (Table 3), indicating that the soil's N, P, and organic matter content were all very low, lower than the reference standard values for soil fertility evaluation in Southern China. The P_z values of the three soils were in the order of control soil>tailings soil>reclaimed soil, but the difference between tailings soil and control soil was very small. The P_z values of three soils were all below 0.9, indicating that their comprehensive fertility was at level III (poor). The surveyed tailings was located in low mountain and hilly area of South China, with abundant and concentrated precipitation. The leaching effect of mineral elements was extremely strong, and the soil was mostly acidic red soil, so the fertility was not high. The control soil was taken from the surrounding forest land of the tailings, not farmland. Currently, the soil classification standards in China are mainly based on the nutrient requirements of crops. The fertility of forest land soil was usually weaker than that of various types of farmland, so the soil had lower fertility.

Table 1 Soil nutrient contents of different soils

Soil type	Available nitrogen(AN) /mg.kg^{-1}	Available phosphorus(AP) /mg·kg^{-1}	Available potassium(AK) /mg·kg-1	Organic matte(SOM) /g·kg^{-1}
Tailing soil	65.23±3.85a	2.06±0.15b	102.56±2.86a	2.12±0.42b
Reclamation soil	18.20±1.78c	0.92±0.12c	88.57±2.94b	2.75±0.52b
CK	34.47±5.37b	3.36±0.27a	108.82±2.99a	6.90±1.42a

Table 2 Particle composition of soil

Soil type	Clay content (<0.002mm)/ %	Powder (fine sand) particle content (0.002~0.02mm)/ %	Sand (coarse sand) particle content (0.02~2.0mm)/ %
Tailing soil	5.50	16.50	78.0
Reclamation soil	15.0	18.50	66.5
CK	25.0	20.50	54.5

The P_z value of reclaimed soil was lower than that of tailings soil, indicating that the comprehensive fertility of the soil had not improved after reclamation. This was mainly because the residual NH_4^+-N in the leaching agent in tailings soil led to a higher effective N content. The content of available P and K in reclaimed soil was relatively low, with lower levels of P_{AP} and P_{AK} compared to tailings soil. This may be due to the fact that the reclaimed land was more easily leached by rainwater after leveling, or because the plants on it absorbed P and K from the soil, resulting in a lower content than tailings soil. It might also be due to use of guest soil during reclamation, which was not arable soil and had low fertility. Compared with control soil, the pH of reclaimed soil was both 1, P_{SOM} was higher than the latter, but P_{AP}, P_{AK}, and P_{AN} were all lower than the latter. Overall, the comprehensive fertility of reclaimed soil was still lower than that of control soil. To achieve the level of fertility of control soil, a long restoration process was needed, and the current reclamation duration was only 4 years. In the reclaimed soil, P_{AP}, P_{AK}, and P_{AN} were all the lowest, indicating that the content of available P, available K, and available N was insufficient to support the normal growth of plants, and vegetation restoration was slow. Therefore, when reclaiming tailings, it is necessary to consider the fertility of soil and choose soil with high fertility as much as possible. If the fertility of soil is low, appropriate fertilization is needed to supplement the nutrients it lacks.

Table 3 The fertility index of different soils

Soil type	Individual fertility index/P_i					Comprehensive fertility index /P_z
	P_{pH}	P_{AN}	P_{AP}	P_{AK}	P_{SOM}	
Tailing soil	1	0.62	0.27	1.28	0.25	0.55
Reclamation soil	1	0.17	0.12	1.11	0.68	0.49
CK	1	0.33	0.45	1.36	0.55	0.59

3.4. Soil heavy metal pollution

After mining, the physical structure (such as particle structure) of soil is damaged, and the permeability, permeability, water retention performance, nutrients, and pH value will all decrease. Heavy metal elements (including REs) in these areas will migrate and transform due to various physi-chemical reactions, causing changes in the soil and water environment in mining areas and their surrounding areas[2,9-10]. The pollution of non-RE heavy metals in soil is the main environmental problem in some RE tailings, and there is currently more research. However, there are relatively few researches on RE pollution, and the conclusions are not consistent[4,15]. In order to further explore the nature of heavy metal pollution and the degree of single element pollution in tailings soil, it is divided into two categories for analysis: non-RE heavy metal pollution and RE pollution.

3.4.1. Non-RE heavy metal pollution

The determination results of 7 non-RE heavy metals in three soils showed that the Pb content in reclaimed soil was significantly lower than in tailings soil, but there was no significant difference in the content of other 6 elements between reclaimed soil and tailings soil. Compared with control soil, there was no significant difference in the content of these 7 elements in reclaimed soil (Table 4), which might be due to that the guest soil used during the reclamation also came from other surrounding forests and had a great similarity to the control soil.

The Zn content in tailings soil was significantly higher than that in control soil, but there is no significant difference in the content of the other 6 elements compared to the control soil. The heavy metal content of three soils was far below the second level soil environmental quality standard (GB15618-1995), and the single pollution index of Cr, Ni, and As elements was below 0.1, indicating that these three heavy metal elements did not exceed the standard. Using the Nemero comprehensive evaluation, the results showed that tailings soil had the highest P_{Nem} pollution, followed by reclaimed soil, and the control soil had the smallest P_{Nem}. However, the P_{Nem} of all three soils was below 0.7. Therefore, the heavy metal pollution level was evaluated as safe (clean) level, namely there was no pollution, but in comparison, the control soil had the highest safety level.

Table 4 The content of non-RE heavy metals in the soil of tailings areas

Soil type	Pb	Cr	Ni	Cu	Zn	Cd	As	PNem
Tailing soil	70.38±16.80a	2.13±4.16a	0.92±0.40a	5.96±0.89b	105.85±6.33a	0.16±0.12a	0.35±0.23a	0.58
Reclamation soil	54.45±5.21b	2.84±0.84a	2.73±1.86a	7.25±5.48ab	76.97±14.48ab	0.12±0.05a	0.39±0.21a	0.44
CK	48.32±10.58ab	1.95±0.45a	1.78±0.82a	8.56±0.31a	74.52±7.56b	0.07±0.04a	0.26±0.12a	0.40
Environmental quality standards grade II in China (GB15618—1995)	250	150	40	50	200	0.30	40	—
Environmental background values of soil elements in Guangdong	30.0	36.0	9.6	10.5	36.0	0.041	6.8	—
Environmental background values of soil elements in China	24.0	54.0	23.4	20.0	68.0	0.074	9.2	—

In the soil (layer A) of Guangdong Province, the background values of these 7 elements are all below the national soil background values[16], located in the low background value area (Table 3). In this study, the content of Pb, Zn, and Cd in the three soils exceeded the background values of soil elements in Guangdong Province and China, but the content of Cr, Ni, Cu, and As, the four heavy metal elements, was lower than the aforementioned two background values. Li et al. (2021)[17]found that in the soil (layer A) of Shaoguan City in northern Guangdong, Pb, Zn, and Cd were relatively enriched, while Ni was severely poor, similar to the soil in this mining area. The reason is that the parent rock of soil is mostly acidic granite, and one of its characteristics is that the content of many mineral elements (such as Fe, Mg, etc.) is low. Over 80% of the soil in South China is acidic, and nearly 60% has a pH value between 4.5 and 5.5. Metal ions are easily displaced into soil solution and leached out. The South Subtropics are hot and rainy, with strong soil chemical weathering. After being washed and leached by rainwater, mineral elements (including some heavy metal elements) are easily lost. Vegetation has suffered serious damage in history, and the existing forests around the tailings are mostly secondary forests. Soil erosion is severe, with a low proportion of clay and powder particles in soil, low organic matter content, and reduced adsorption of mineral elements, resulting in low soil content[14,16]. In addition, the rice paddy soil widely distributed in Guangdong, has relatively high levels of heavy metals such as Pb, Zn, and Cd[17]. This may be related not only to soil genesis, but also to frequent human activities. For example, there are some lead-zinc tailings with earlier mining history around the surveyed tailings.

3.4.2. RE pollution

The determination results of 16 REs in three soils (Table 5) showed that the total content of heavy REs in control soil and tailings soil accounted for 52.83% and 56.71% of total RE content, namely the total content of heavy REs exceeded 50%, and the proportion of heavy RE element Y to the total RE content exceeded 1/3, which was 33.66% and 35.27%, respectively. The heavy light RE ratios (HREEs/LREEs) were 7.56 and 5.01, respectively, which confirmed that the RE ore in this study was a Y-rich heavy RE ore and similar to some RE tailings in neighboring Longnan County, Ganzhou, but with a higher ratio of heavy to light REs [2,4]. The total amount of heavy REs in reclaimed soil accounted for only 34.21% of the total RE content, with a heavy to light RE ratio of 3.22. This was likely due to the higher proportion of heavy RE extraction during leaching and the higher proportion of residual light REs. The order of total RE content (∑REEs) in three soils was control soil>tailings soil>reclaimed soil. The total content of control soil was much higher than that of tailings soil and reclaimed soil. The total RE content in reclaimed soil, tailings soil, and control soil was 1.73, 3.35, and 6.00 times the background value of soil in

Guangdong Province, respectively, and 1.48, 2.86, and 5.13 times the background value of soil in China (Table 5). The high RE content in control soil was due to the fact that its REs had not been extracted. Compared with the three types of soil, in tailings soil, the elements with higher content in descending order were Y, Sm, Ce, Nd, and La, with the total content of these 5 elements accounting for nearly 80% of the total RE content, while in the reclaimed soil, Sm, Ce, Y, Nd, and La accounted for 77.26%. In contrast, the control soil contained Y, Sm, Ce, Gd, and Nd, accounting for 77.59%. Among three soils, Y, Sm, and Ce had the highest content, but their order was different. The total amount of heavy RE, light RE, and RE in tailings soil were significantly lower than those in the control soil, with the former only accounting for 51.90%, 60.91%, and 55.79% of the latter. The total content of heavy RE, light RE, and REs in reclaimed soil were also significantly below those in the control soil, with only 17.47%, 43.71%, and 28.78% of the latter.

The total content of heavy REs in tailings soil, reclaimed soil, and control soil accounted for 52.83%, 34.53%, and 56.89% of the total content of REs, respectively, while that of light REs accounted for 47.07%, 65.47%, and 43.11%, respectively. This indicated that heavy REs were mainly present in tailings soil and control soil, while light REs were mainly present in reclaimed soil. The total content of REs, light REs, and heavy ones in control soil were all the highest, followed by tailings and reclaimed soil. This indicated that the control soil also contained relatively abundant REs, while the decrease in their content in tailings soil and reclaimed soil was likely due to extraction. However, the total content of RE, light and heavy RE of reclaimed soil were lower than those of tailings soil, which was likely due to that the sampling area of reclaimed soil was located outside the tailings area (Figure 1), which was more prone to weathering and rainwater erosion, and REs were more prone to loss.

Table 5 The contents of 7 REs of different soils in the tailings area ($mg\cdot kg^{-1}$)

Soil type	Tailing soil	Reclamation soil	CK	Background value in Guangdong	Soil background value in China
Y	234.45±55.21b	58.32±20.58c	440.38±76.80a	29.10	34.20
Sc	4.13±4.16a	2.84±0.84a	4.95±0.45a	9.10	10.31
Gd	20.92±7.40a	15.73±8.86a	81.78±10.82b	4.64	6.01
Tb	15.96±0.89a	8.25±1.48a	17.56±0.31a	0.59	0.90
Dy	7.52±7.56a	6.92±4.48a	10.85±6.33a	5.09	6.27
Ho	10.16±6.12a	3.12±1.05a	20.07±6.54a	1.06	1.22
Er	30.35±7.23a	7.39±3.21b	70.26±9.12c	3.39	3.90
Tm	6.25±4.58ab	1.15±0.54a	12.50±6.40b	0.48	0.49
Yb	30.27±4.22a	18.22±3.24b	35.96±6.82c	3.45	3.40
Lu	8.65±0.75a	2.15±0.76b	15.96±0.89c	0.54	0.51
∑HREES	368.66	124.09	710.27	57.44	67.21
La	50.38±16.80a	24.45±5.21b	68.45±10.24a	37.50	45.00
Ce	102.13±14.16a	72.84±9.84b	181.95±12.45a	79.40	79.90
Pr	10.92±5.40a	13.73±6.86a	21.78±8.82a	5.95	10.34
Nd	55.96±7.89ab	47.25±9.48a	78.56±10.31b	22.10	33.30
Sm	106.97±14.48a	74.52±7.56b	185.85±26.33a	4.96	6.64
Eu	1.16±0.12a	2.12±0.65a	1.47±0.74a	0.75	1.02
∑LREES	327.87	235.3	538.32	150.66	176.2
∑REEs	696.53	359.39	1248.59	208.10	243.41

The pollution level of REs was evaluated according to I_{geo} in other literature [4,18](Table 6), and the results confirmed that the RE pollution level of control, tailings, and reclaimed soil decreased sequentially, with significant differences, namely moderate, non-pollution to moderate, and non-pollution. The reclaimed soil did not have RE pollution. From a single element perspective, the element Y with the highest proportion reached three levels of strong pollution, moderate to strong pollution, and non-pollution to moderate pollution in control, tailings, and reclaimed soil, respectively. Tb and Sm both reached strong pollution or strong to extremely strong pollution in three soils. The I_{geo} values of heavy REs, except Sc and Gd, in tailings and control soil ranged from 2.0 to 4.3, indicating that the pollution in tailings and control soil reached moderate to strong level. Whether a single REs or an overall RE pollution, the pollution level of control soil was relatively high, which was likely due to the extraction of these REs from tailings soil and reclaimed soil, and the control soil was likely in areas with abundant REs.

Table 6 The geoaccumulation index (I_{geo}) of REs of different soils in the tailings area

Soil type	Tailing soil	Reclamation soil	CK
Y	2.43	0.42	3.33
Sc	-1.72	-2.26	-1.46
Gd	1.59	1.18	3.55
Tb	4.17	3.22	4.31
Dy	-0.02	-0.14	0.51
Ho	2.68	0.97	3.66
Er	2.58	0.54	3.79
Tm	3.12	0.68	4.12
Yb	2.55	1.82	2.80
Lu	3.42	1.41	4.30
∑HREES	2.09	0.53	3.04
La	-0.16	-1.20	0.28
Ce	-0.22	-0.71	0.61
Pr	0.29	0.62	1.29
Nd	0.76	0.51	1.24
Sm	3.85	3.32	4.64
Eu	0.04	0.91	0.39
∑LREES	0.54	0.06	1.25
∑REEs	1.16	0.20	2.00

4. Discussion

After mining of ionic RE mine, the tailings soil often had desertification, acidification, sterilishment and chemical pollution (including ammonia nitrogen pollution and heavy metal pollution), leading to the deterioration of soil physi-chemical properties to prevent vegetation recovery[4-5,10], which had also been confirmed in this study. During the mining of REs in Northeastern Guangdong, ammonium salts had been used as leaching agents and some of them remained in the tailings soil. $(NH_4)_2SO_4$ is a physiological acid salt causing soil acidification. This is also a common phenomenon of ionic RE tailings. Except for a few acidic soil plants, such as Osmunda japonica, Osmanthus fragrans, and Pteris vittata, other plants were extremely difficult to grow. The precipitants used in the extraction of ionic REs, like leaching agents, also caused a decrease in soil and groundwater pH values. After soil acidification, it also led to secondary pollution[2,9]. The soil of RE tailings had poor viscosity, low content of organic matter and nutrient element, and was mainly composed of sand. After reclamation, although there had been some improvement, it had not yet reached the level of control soil. The leaching agents $(NH_4)_2SO_4$ and NH_4HCO_3 remained in the soil and continued to accumulate and disrupt the stability of soil aggregates, and migrated through rainfall leaching and infiltration and led to soil acidification, loss of nutrients such as Ca, Mg, and K, decreased soil fertility, and NH_4^+-N pollution. After being polluted by NH_4^+-N, the concentration of NH_4^+-N in the surrounding water of tailings exceeded the standard, which could easily lead to water eutrophication[7-9]. NH_4^+-N in tailings soil would continuously transform into NO_3-N. During the process of rainfall leaching, soil NO_3-N continuously migrated to the surrounding environment to cause persistent harm. Therefore, NH_4^+-N pollution is also considered one of the main problems to be solved in ecological restoration of ionic RE tailings[7,9,19], but NH_4^+-N is relatively easy to purify and circulate in the natural environment compared to other metal ions.

In this study, the NH_4^+ content and pH value of the RE tailings soil decreased after reclamation in Northeastern Guangdong, the organic matter content also increased, the leaching agent residue decreased, soil acidification decreased, and the physical structure of the soil was significantly improved. The soil was improved to a certain extent, but the fertility of reclaimed soil and tailings soil was still poor, belonging to level 6 (extremely deficient), which is consistent with the research results of other tailings in the South China[4,20]. After land reclamation, the soil quality had improved, but the problem of tailings soil fertility deficiency had not been completely solved. The control soil belonged to level 5 (nutrient deficiency), indicating that the soil had not yet reached the level of control soil, and even lower than the tailings soil. The ecological restoration effect of reclaimed soil is closely related to the fertility of guest soil. In this study, the soil used for reclamation came from other forest areas around the tailings, and its fertility was also as poor as other mountain soil. Generally, it is not allowed to use cultivated land for reclamation in the local area, which may be an important reason for the poor reclamation effect of certain tailings soil. Research has shown that planting deep rooted plants such as eucalyptus and bamboo has a certain elimination effect on $(NH_4)_2SO_4$[5,21]. Tailings soil was formed after leaching with $(NH_4)_2SO_4$ or other immersion agents in mining areas. During the RE extraction process, K^+ was exchanged and carried away by NH_4^+, resulting in a lower available K content in tailings soil compared to the control soil. Although there was a decrease of available K content in this study compared to control soil, it was not significant. The loss of P in soil was mainly through leaching and surface runoff. In South China, there is more rainfall, and the content of available P in forest soil is usually lower. More plants grew in the reclamation area than in the tailings, and perhaps the plants absorbed more rapid effect P resulting to lower content.

At present, new non-ammonia-nitrogen solvents are being sought, for example, magnesium and aluminum salt have been used to replace ammonia nitrogen solvent in some mining areas[9]. After the reclamation of tailings soil, the overall soil quality had improved, the resident plants and vegetation coverage had increased. When planting some trees and shrubs in the reclamation area of Northeastern Guangdong for greening, these trees and shrubs do not grow weakly in the early stages (seedling and juvenile stages). However, as the seedlings grow, the roots continuously penetrate deeper into the soil, they grow poorly, the roots of some individuals rot and even die. This is mainly because the reclamation soil is usually 20-30 cm thick, and the original tailings soil below it is insufficient in terms of acidity, alkalinity, and fertility to support plant growth. Therefore, land reclamation can only improve shallow (0-30 cm) soil in the short term, while deep soil requires other measures or longer duration.

The in-situ leaching tailings not only contain REs, but also associate non-RE heavy metals causing heavy metal pollution. Their content in the soil is usually related to the type and dosage of leaching agents[5,10]. The soil heavy metal pollution of ionic RE tailings is different from the general heavy metal pollution, including not only RE heavy metals, but also non-RE heavy metal pollution. In some ionic RE tailings in Southwestern China, there was often severe non-RE heavy metal pollution[5]. However, in this study, no non-RE heavy metal pollution was found, which is similar to these RE tailings in Longnan County and Xinfeng County, Jiangxi Province, adjacent to Northeast Guangdong[4,12,18]. The pollution level of non-RE heavy metal in the control soil, tailings soil and reclaimed soil was clean, and the pollution level of non-RE heavy metal pollution was even lower after reclamation. In this study, the reclamation reduced the overall pollution level of REs, but through I_{geo} evaluation of a single RE metal, the heavy RE element Tb and light element Sm both reached the levels above strong pollution in the three soils. Y. Sm and Ce, the three REs, had the highest proportion of quality in the three soils, and were also the least polluted in reclamation pollution. Compared with some RE tailings in Longnan County and Xinfeng County of Ganzhou, adjacent to Northeastern Guangdong, Y, Ce, and La elements were all REs with higher content[4,12,18]. In this study, Sm content was also higher. However, many researches has confirmed that some REs have strong ecological toxicity, and the accumulation of REs can inhibit the distribution, growth, development, and reproduction of some soil organisms[15], but these conclusions are not consistent. At present, the divergence of these research conclusions may be due to differences in the concentration and chemical form of REs, exposure conditions, regional soil physi-chemical characteristics, and soil animal community structure, so further researches are needed on their toxicity and toxicity mechanisms. Although this study did not find severe total RE pollution or non-RE heavy metal pollution, which might be due to the study site located in the middle and upper slopes of mountains, the soil in the upstream mining area may be washed into the downstream farmland soil by the river with soil erosion, and the cumulative effect of heavy metal pollution cannot be ignored. For example, Zhang et al. (2023) found that there were sample points with heavy metal pollution in the middle and lower reaches of a RE tailings in Southern Jiangxi, but other sample points were not polluted or lightly polluted[13].

In the RE tailings soil studied in this study, the top 5 elements in the order from high to low were Y, Sm, Ce, Nd and La, Sm, Ce, Y, Nd, and La in the reclaimed soil, while Y, Sm, Ce, Gd, and Nd in control soil, the top 5 elements accounted for above 77% of the total RE content. In the three soils, Y, Sm and Ce all were one of the top 5 elements with the highest content, although the order was different. The content of Y, Ce, Nd, Yb, and Dy REs in control soil and tailings soil of a RE mine in Longnan County was relatively high, with the total content of the 5 REs accounting for 74-75% of the total RE content, the content of Ce, Nd, La, Sc, and Pr in the reclaimed soil was relatively high, with a total content of about 78% of the total REs[4]. In contrast, in a RE tailings in Xinfeng County, the top 4 REs with highest content in control soil and leaching area soil was Ce, Y, La, and Nd, respectively, while was Y, La, Nd, and Ce. The soil in the mining area[18]. Ganzhou and Meizhou are adjacent, so these RE tailings have significant similarities, with higher content of Y, Ce and Nd in the tailings and control soil.

5. Conclusion

In this study, after 4 years of soil reclamation, the NH_4^+ content in the soil significantly decreased, the pH value increased, and the organic matter content increased. However, the available N, P, and K decreased, and the soil fertility index also decreased. Overall, reclamation did not significantly improve soil fertility. The pollution level of non-RE heavy metals decreased, but non-RE heavy metal pollution in soil before and after reclamation was at a clean level. The total RE content in tailings, reclaimed, and control soil was all above the soil environmental background value in Guangdong Province. The RE in tailings soil was mainly composed of heavy REs, while in reclaimed soil mainly light ones. The pollution levels of total REs in soil before and after reclamation were non to moderate pollution level and non-pollution level, respectively, while in the control soil reached a strong pollution level. Among REs, Y, Sm, and Ce had the highest quality proportion, and the pollution levels of the latter two elements were above strong pollution in control soil. Therefore, in the future reclamation work, in addition to continuing to pay attention to the improvement of soil environment, the improvement of soil fertility and the control of rare earth metal pollution should also be strengthened. At the same time, when choosing foreign soil for reclamation, the quality of foreign soil, especially its fertility, so as to improve the reclamation effect more effectively. Moreover, according to other research and practice, attention should be paid to selecting acid-resistant and barren-tolerant native plants for reclamation and appropriate fertilization is applied to accelerate ecological restoration.

Acknowledgement

This study is financially supported by Special Fund for Guangdong Provincial Science & Technology Innovation and Rural Revitalization Strategy in 2021 (2021A0305), Guangdong Base Hakka Research Institute Bidding Project in 2020 (20KYKT09), Characteristic Innovation Project of Guangdong General Universities in 2019(2019KTSCX171),Guangdong Provincial Special Projects in Key Areas in 2020 (2020ZDZX1036), and Guangdong Rural Science and Technology Commissioner Project (Yue Ke Han Nong Zi[2020]No. 1056).

References

1. Gu J W, Wang Q, JIN H X, Liu Y Y, Qiu W. (2023) Heavy metal pollution of soil and chronic diseases among residents around an abandoned rare earth ore in Jiangxi [J]. Shanghai J. Prevent. Med., 2023,35(5): 494-499.
2. Guan H B. (2023) Ecotoxicological effects of rare earth accumulation on soil animals in desert grassland around rare earth mine [D]. Beijing: Minzu University of China.
3. Guo Z Q, Zhao K, Jin J F, Wang G S, Zhu Y C. (2019) Reviews on environmental assessment and pollution prevention of ion adsorption type rare earth ores[J]. Chinese Rare Earths, 40(3): 115-126.
4. Guo Z Q, Zhao K, Jin J F, Yuan W, Liang C. (2019) Problems facing ion adsorption type rare earth exploitation and research progresses on green extraction [J]. Chem. Ind. Eng. Prog., 38(07): 3425-3433.
5. Jin S L, Huang Y Z. (2014) A review on ecological toxicity of rare earth elements in soil [J]. Asian J. Ecotoxicol., 9(2): 213-223.
6. Li T T, Liu Z N, Jia L, Zhang W. (2021) Analysis on background value of soil elements and influencing factors in Shaoguan, Guangdong Province [J]. J. Geol., 45(03): 254-261.
7. Liu E H, Huang J, Tan W, Liang X L, Ma L Y. (2022) Constraints on the REE enrichment-fractionation in weathering crust by the mineral evolution in the weathering and leaching processes: a case study of the renju REE deposit in the Meizhou Area, Guangdong, China [J]. Bull. Miner. Petrology Geochem., 41(3): 517-526+464.

8. Luo J, Zhang Q, Luo M M, Wan G Y, Zhao X M, Chen X L.(2022) Degradation characteristics of soil in different functional areas of an ion type rare earth mine[J]. J. Chin. Soc. Rare Earths, 40(02): 329-338.
9. Mao J. (2022) Study on the effect of different vegetation restoration measures on soil ammonium sulfate elimination in rare earth tailings area of Xunwu County [J] Mod. Hortic., 45 (21): 15-17, 22.
10. Ren F T, Zhang Q, Yang G, Bai Y W, Gao H J, Li Z, Liu S B, Wang J Q. (2022) Characteristics of ammonium nitrogen pollution in deep soil profile of ionic rare earth ore tailings and influencing factors[J]. Acta Pedol. Sin., 59(2): 517-527.
11. Shi X Y, Chen H W. (2019) Contamination and restoration of abandoned pool and heap leaching sites of rare earth mine [J]. J. Chin. Soc. Rare Earths, 37(4): 409-417.
12. Wang M, Hong K, Li J. (2022) Exploitation of ionic rare earth ore and its impact on ecological environment [J]. Nonferrous Metals (Mining Section), 74(6): 95-100.
13. Wei F S, Chen J S, Wu Y Y, Zheng C J. (1991) Study on the background contents on 61 elements of soils in China [J]. Chinese J. Enviro. Sci., 12(4): 12-19.
14. Xu L F, Liu T H. (1996) The Zonal differentiation of of soil environmental background values and critical contents in Guangdong . J. South China Agric. Univ., 17(4): 61-65.
15. Xu Z, Yang J L, Zhao Y, Zhang G L. (2023) Study on the characteristics of soil nitrate nitrogen accumulation of rare earth tailing in Southern Jiangxi[J]. APS, 60: 1-11. http://kns.cnki.net/kcms/detail/32.1119. P.20230118.1845.003.html.
16. Yang Q H, Lin Q Y, Lai W N, Yang H S, Kuang W. (2013) Investigation on vegetation restoration in Pingyuan rare earth tailing [J].Guangdong Agri. Sci., 40(16): 150-154, 166.
17. You L. (2018) Study on pollution status and remediation technology in specific southern rare earth diggings [D]. Jiangmen: Wuyi University.
18. Zhang D Q, Wang Y N, Qiao W, Wang Y, Bai G Y. (2023) Evaluation of heavy metal pollution in soils from a mining area in Southern Jiangxi [J]. Multipurpose Utilization of Mineral Resources, (3): 181-191.
19. Zhang Q Y, Shu W, Li F, Lie M, Zhou J, Tian C, Liu S B, Ren F T, Chen G. (2022) Nitrate source apportionment and risk assessment: A study in the largest ion-adsorption rare earth mine in China [J]. Environ. Pollut., 302: 119052.
20. Zhou D, Luo C G, Su J, Luo X P. (2014) Soil ecological restoration in ionic rare earth mining area [J]. Metal Mine, 460 (10): 103-109.
21. Zhou C Y, Zhang Q, Zhao X M, Wan G Y, Cheng X D, Guo X. (2019) Soil quality changes of rare earth tailings before and after reclamation in south Jiangxi Province, China[J]. J. Agric. Res. Environ., 36(1): 89-95.