In order to reveal the impact of a high concentration of CO\(_2\) on the soil in the coal mining subsidence area, the surface above the goaf before CO\(_2\) injection is regarded as a subsidence area model. Based on the actual vertical depth of 70∼80 m shallow buried coal seam geological conditions, CO\(_2\) diffusion in the goaf is regarded as a short-term high-concentration CO\(_2\) leakage model. The surface soil samples before and after 60 tons of direct injection of liquid CO\(_2\) in the goaf of Huojitujing in the Daliuta Coal Mine could be collected to conduct the experimental observation. By measuring the changes in the five indicators of soil air-dried and fresh sample including pH, available nitrogen, available potassium, water-soluble salt, and total organic carbon, the changes of pH and mineral content in the soil could be analyzed quantitatively and qualitatively at different time periods before and after CO\(_2\) injection. This proves that the injection of CO\(_2\) into the goaf has an impact on the chemical properties of the surrounding soil.

1. Introduction

In the analysis and research of soil chemical properties in subsidence areas, most scholars study the influence of subsidence on soil chemical properties by analyzing soil nutrients. The uneven surface and ground fissures formed by the collapse cause soil nutrients to migrate to the goaf or low-lying areas under the action of runoff, resulting in a nonuniform distribution of soil nutrients and adversely affecting the growth of plants in the collapsed area. Nitrogen, phosphorus, and potassium are the basic indicators of soil nutrients, and soil nutrients determine the level of soil fertility. The available phosphorus and alkali-hydrolyzable nitrogen in soil nutrients are easily absorbed by crops, and their content directly reflects the soil quality. Comparing the soil nutrient content in the collapsed area and the control area shows that the total nutrient, available nutrient, and organic matter content of the soil do not change regularly after the collapse, and the soil nutrient changes in different collapsed areas are not consistent. Shun et al. measured the soil nutrient content of coal mining subsidence in the Baili Rhododendron forest area and found that: the collapse significantly reduced the soil available phosphorus, available potassium, and organic matter content and increased the total soil nutrient and available nitrogen content [1]. Zhang et al. studied that the collapse significantly reduces the content of total nitrogen, total phosphorus, and available potassium [2]. Wan et al. have shown through research that the collapse reduces the total nitrogen and organic matter content of the soil, increases the total phosphorus content, and does not change the total potassium content significantly [3]. The available nitrogen, phosphorus, and potassium content all show varying degrees of loss [3]. Zhou shows that the difference in soil nutrient content between nonsagging areas and subsiding areas is not significant, but there are differences in the spatial distribution in the Ordos region [4]. Many scholars have made corresponding studies on the law of soil nutrient loss caused by the collapse. The
The main research content is the law of soil nutrient loss on the collapsed slope and on the vertical section of the collapse. On the collapsed slope surface, the law of soil nutrient content at different locations appears as follows: upslope point < middle slope point < downslope point < collapse center point, indicating that soil nutrients are lost to varying degrees under the influence of the collapse; among them, available nutrient loss is more significant [2]. Due to a large number of cracks in the upslope point, the loss of water and fertilizer is serious, and the soil nutrient is the shortest. The nutrient content of the collapse center is different from that of the upslope point. When the collapse depth is shallow, the nutrient shortage in the collapse center is relatively short. When the collapse depth is deep, the soil nutrients on the upper and middle slopes moved with the water to the center of the subsidence, resulting in enrichment of soil nutrients. If cracks are developed in the middle slope and the cracks are large, the quick-acting nutrients that migrate from the top of the slope to the bottom of the slope will be interrupted and lost at the cracks. On the vertical section of the collapse, Ren et al. measured a large loss of alkali-hydrolyzable nitrogen and available phosphorus in the soil above a depth of 40 cm, and the nutrient content in the soil below a depth of 60 cm remained basically unchanged [5]; Wang measured the loss of total nitrogen and total phosphorus content in the soil above 40 cm in collapsed dunes but very little total potassium content loss [6].

The soil nutrient content in the collapsed area could change with the extension of the collapse time. Shun et al. measured the soil organic matter, total nitrogen, and total phosphorus content in the subsidence area gradually decreased with time, and the total potassium content gradually increased; the soil available nutrient content in the soil layer above 30 cm gradually decreased; and the soil available nutrient content in the soil layer below 30 cm and above 60 cm gradually increased [7]. Zhang et al. analyzed the soil nutrient content of the cracks in the collapsed area after 3 years of collapse and found that the total nitrogen and total phosphorus contents of the cracks were generally significantly reduced [8]. Wang et al. studied the changes in soil nutrient content in the collapsed area and noncollapsed area and 17 years after the collapse and concluded that the soil nutrient can only gradually recover 12 to 17 years after the collapse [3]. Monokrou sos et al. studied the variation of the chemical properties of soil organic matter, organic nitrogen, and available phosphorus at the deposition site after mining over time and concluded that the content of these nutrient elements gradually increased over time [9]. Zhao et al. used the surface soil (0–60 cm) in the coal mining subsidence area of Dalu as the research object, using traditional statistical methods to study the vertical variability of soil water content and using the kriging local interpolation method in geostatistics to study the planar variability of soil moisture content [10].

It can be seen from the above that the soil is a continuum of inhomogeneity and change. The distribution of soil in nature is extremely complex. Even in an area with the same soil texture, various physical and chemical properties of the soil at the same time have obvious differences in different spatial positions. This nonuniformity of the spatial distribution of soil properties is called spatial variability of soil characteristics [11].

Vadose zone refers to the zone above the diving surface below the ground [12]. The voids between the soil and rocks in this zone are not filled with water and contain air. The main forms of water in the aeration zone are gaseous water, adsorbed water, membrane water, and capillary water. When precipitation or surface water seeps, gravity water can temporarily appear. There have been few reports on the impact of high-concentration CO₂ intrusion on the physical and chemical properties of soil in the aeration zone. Research by Amos et al. found that after CO₂ enters the vadose zone, some toxic metals will be activated due to the decrease of pH, and CO₂ partially replaces O₂, thereby reducing the degradation rate of organic matter [13]. At present, more research has focused on the effects of high-concentration CO₂ leakage by the CCS (Carbon Capture and Storage) project on plant leaf photosynthesis, transpiration and biomass accumulation, plant roots, soil respiration, and changes in soil microbial flora [14]. There are relatively few studies on the impact of high-concentration CO₂ on the physical and chemical properties of plant soils. Nie et al. used high-concentration CO₂ to test the soil chemical properties and fertility of buckwheat and sorghum crops and found that the increase in CO₂ concentration had no significant impact on the soil pH of buckwheat and sorghum crops and would not affect the soil ions and soil ions controlled by acid-base balance and, however, has a different impact on available nitrogen, available potassium, organic matter, and cation exchange capacity [15].

In fact, before CO₂ is injected, the surface above the mined-out area can be regarded as a collapsed area model, and since the actual vertical depth is 70 m–80 m, it belongs to shallow buried coal seams; the CO₂ leaked by the CCS (Carbon Capture and Storage) project on plant leaf photosynthesis, transpiration and biomass accumulation, plant roots, soil respiration, and changes in soil microbial flora [14]. There are relatively few studies on the impact of high-concentration CO₂ on the physical and chemical properties of plant soils. Nie et al. used high-concentration CO₂ to test the soil chemical properties and fertility of buckwheat and sorghum crops and found that the increase in CO₂ concentration had no significant impact on the soil pH of buckwheat and sorghum crops and would not affect the soil ions and soil ions controlled by acid-base balance and, however, has a different impact on available nitrogen, available potassium, organic matter, and cation exchange capacity [15].

In this paper, the surface soil samples were collected before and after 60 tons of direct injection of liquid CO₂ in goaf lower coal seam of Huojitu in the Dalu Coal Mine for laboratory analysis to analyze the gas composition in the soil layer, and the changes in the mineral content in the soil to reveal the degree of impact on the soil after the injection of CO₂.

2. Materials and Methods

2.1. Geological Condition of Sample Site. This project is located in the Dalu Coal Mine of the National Energy Shendong Coal Group. The goaf of the liquid CO₂ injection face is located on the east side of Naogaobulamiaogou, west of Shujiehengou, south of the live chicken and rabbit crossing highway, and north of Zijaie village. The study area was selected as the Huojitu Mine field of the Dalu Coal Mine, Shennu City, Shaanxi Province. This area belongs to the transition zone from the loess hilly landform to the aeolian landform, with an altitude of 1,100–1,300 m. The regional average annual precipitation is 415.0 mm, but it is mainly...
concentrated in June to September and mostly heavy rain, accounting for 76% of the annual precipitation. The annual average evaporation is 1,788.4 mm; the annual average sunshine time is 2875.9 h; the annual average temperature is 8.6°C; and the annual average wind speed is 3.2 m/s. The soil types in the mining area mainly include chestnut soil, coarse bone soil, and aeolian sandy soil. The vegetation communities in the study area are mainly sandy vegetation combinations with *Salix*, *Artemisia sphaerocephala*, *Hedysarum* leave, and *Caragana korshinskii* as the constructive species. The coal-bearing seam in this area is a gentle monoclinic structure, and the coal seam is about 100 m deep. The coal mining method mainly adopts the comprehensive mechanized long-arm mining technology. The fully mechanized mining face is 200–400 m long, 4 m high, and several thousand meters long. There are 20–30 m wide roadway coal pillars between the working faces. With the massive mining of coal, various degrees of mining damage occurred in the overlying rock strata over the goaf, such as caving, cracks, and bending, causing large cracks and step-shaped fractures on the surface, and even collapse pits. The crack width is between 10 and 50 cm, and the vertical displacement is between 0 and 80 cm.

The coal seam at the working face is the lower layer of the complex coal seam; the coal seam structure is simple; and the coal rock type is mainly semidark coal. The average thickness of the coal seam is 6.0 m (4.2–10.0 m). The top coal caving technology is adopted for the fully mechanized caving face of the lower coal seam, and the upper coal seam of the compound area was mined in 2002, and the lower coal seam is now mined. There is no special geological structure inside the working face, and the coal seam structure is simple.

2.2. Experimental Materials. Too low or too high soil pH can affect crop growth [16]. Soil compaction caused by excessively acidic soil and the resulting microelement poisoning will greatly affect the growth of vegetation [17]. The test method selected this time is the potentiometer method, and the instrument used is a pH meter. By measuring the pH of the soil, the impact of CO₂ injection on the pH of the soil environment can be known.

Soil nitrogen is one of the important nutrient elements for plant growth, and what plants absorb and utilize is the available nitrogen in the soil [18]. In this test, the effective nitrogen content of the soil was tested by the alkaline solution diffusion method, and the experimental instrument was an alkaline burette. The level of available nitrogen in the soil reflects the level of nitrogen supply in the soil in the near term. It is closely related to crop growth and is of great significance in recommended fertilization. The content of available nitrogen in the soil only accounts for a small proportion of total nitrogen. For example, the content of inorganic NH₄⁺ is only 1% to 5% of total soil nitrogen. Therefore, determining the content of available nitrogen in the soil has important practical significance for evaluating soil fertility and evaluating the impact of CO₂ injection on soil fertility.

Available potassium, also known as available potassium, refers to the potassium in the soil that is easily absorbed and utilized by crops, including soil solution potassium and soil exchangeable potassium [19]. The content of available potassium is one of the important indicators to characterize the supply of potassium in the soil, and it is a substance that plants can directly absorb and utilize. Da et al. illustrate NH₄OAC extraction-flame photometer method and flame atomic absorption spectrophotometer were utilized to determine the content of soil available potassium. By measuring the content of available potassium, the impact of a high concentration of CO₂ on soil potassium in a short period of time can be obtained [20].

Soil water-soluble salt is an important attribute of saline-alkaline soil and an obstacle to crop growth. It plays a certain role in reflecting the changing trend of soil salinization [21]. Tian et al. state that the main instrument is an analytical balance [22]. By measuring the total amount of water-soluble salt, the degree of influence of a high concentration of CO₂ on soil salinization in a short time can be obtained.

Although soil organic carbon (SOC) accounts for a small proportion of the total soil organic matter, it plays a key role in the regulation of soil quality and function [23]. This test uses the potassium dichromate volumetric method, and the equipment used is the same as the water-soluble salt test. By testing the soil organic carbon content, the impact of high concentration CO₂ on soil quality in a short time can be obtained.

2.3. Experimental Methods

2.3.1. Method of Direct Injection of Ground Liquid CO₂. A scheme of the process is illustrated in Figure 1. The target area for direct injection of liquid CO₂ is deep gob in the lower coal seam. The surface power and water supply holes in the cutting hole area are utilized as drill holes. The surface of the borehole is used as a system installation site; the power supply hole is used as a vertical transmission hole for liquid CO₂; and the low-temperature high-pressure resistant pipeline is about 84 m long. It is connected by a special welding method to the surface-pressure-holding device and to the surface liquid CO₂ tank through an austenitic metal body hose. The downhole direct injection pipeline is connected with the end of the ground-drilling straight pipe through an austenitic metal hose. The terminal is connected to a long-distance automatic pressure-holding device, and the austenitic metal hose is connected to the observation hole through the roof of the tunnel. Arched steel plates and expansion screws are installed. Warning signs are installed to ensure safety. The monitoring substation is installed as well; 1,500 m communication optical fiber is laid, to connect computers by means of a ring network. The signal line starts from the substation and connects the pipeline-pressure-holding device, the CO₂ sensor, and the ground and surface pipes through the water supply drilling. The length of the signal line is about 1,200 m for the connection of the pressure-holding device at the road terminal.
During the direct injection of liquid CO₂, a value of 300 m³/min for the safe ventilation flow rate has been calculated and adopted, taking into account the limits of safe concentration of CO₂ in a workplace.

Liquid CO₂ was infused for 3 hours (14:00 to 17:00). The cumulative infusion amount was 60 t. The perfusion flow was 17.14∼20.96 t/h. The depth of injection is around 140 m.

2.3.2. Sampling Method. pH value and chemical indicators are selected as test objects. In order to reduce the impact of CO₂ in the air on the samples, GPS positioning technology was used to take soil at five locations at a depth of 1 m above the surface fissure above the #30 lane where liquid CO₂ was injected and mark P1, P2, P3, P4, and P5. The soil samples are taken three times before the liquid CO₂ injection and 1 day and 5 days after the liquid CO₂ injection, and the air-dried and fresh samples are taken each time. A total number of samples are 30.

For the rationality of the sample, a five-point sampling method is adopted, with each point separated by a certain distance. In order to avoid lack of representativeness when sampling, ditches, forest belts, ridges, roadsides, old building foundations, bottoms of dung piles, and uneven terrain should be avoided. In order to facilitate subsequent procession, each air-dried sample and fresh sample were repeatedly collected at three small sample points (i.e., a drill soil sample) to form a mixed sample. The location, depth, and quantity of the soil at each sample point should be consistent. Sample should be removed simply from the debris and bagged. The fresh samples are stored and tested in wet soil. They cannot be spread out for a long time to clean up the debris. They should pass through a 2 mm screen and put them into a ziplock bag.

A soil cylindrical pit is dug with a depth of 1 m using an undisturbed soil drill (length 1 m, diameter 50 mm) at the sampling point in each fissure. The drill bit to rotate the soil is used, and then the soil samples are loaded into cloth and ziplock bags. The samples in the cloth bags are brought back indoors to dry naturally. The ziplock bag is kept fresh with an ice bag and sent to the laboratory for freezing and preservation for subsequent soil index determination and analysis. Figures 2 and 3 are the soil borrowing instruments used. On-site sampling is shown in Figure 4.

Numbering rule: according to the sample volume of five air-dried samples (F1∼F5) and five fresh samples (X1∼X2), there were three different periods: before injection, 1 day after injection, and 5 days after injection (D1∼D3). The complete sample is shown in Table 1.

2.3.3. Sample Processing. The P1∼P5 soil samples were dried in the shade and cryopreserved; the differences are shown as follows:

Air-dried soil samples are collected from the field and placed in a clean indoor ventilated place until they are naturally dried in the shade. The time of drying should last for around 3–5 days. Exposure to the sun is strictly prohibited, and attention should be paid to the pollution sources such as acid, alkali, dust, gas, and so on that may affect the test results. During the air-drying process, it is necessary to frequently move soil samples, crush large soil blocks, and remove intrusions other than soil such as rocks. Air-dried soil samples can
analyze indicators such as soil nutrients and organic matter but cannot detect volatile indicators. Due to a large number of mixed samples, all the soil is put on a plastic sheet to dry in the shade and crushed by hand to remove the sundries, and then the “quarter method” is utilized to reduce it to the required number, and exposure to the sun should be avoided before sending it to the testing organization.

Fresh soil samples are also called fresh samples, which generally refer to soil samples used for analysis and testing immediately after being collected from the field or after cryopreservation. It is often used for the analysis of components such as divalent iron, nitrate nitrogen, ammonium nitrogen, and so on that change significantly during the air-drying process and can more truly reflect certain chemical properties of the soil in the natural state of the field. After the fresh samples were shipped back to the laboratory, they were stored at −25°C until they were sent to the testing organization.

3. Results and Discussion

3.1. Soil Test Results. The changes in the five indicators (pH value, available nitrogen, available potassium, water-soluble salt, and total organic carbon (TOC)) of soil air-dried and fresh sample at #1, #2, #3, #4, and #5 sampling points and three different periods (before CO2 injection, 1 day after injection, and 5 days after injection) are shown in Tables 2–6.

3.2. Soil pH Analysis. The acidity and alkalinity (pH) of soil is a good indicator to describe the process of soil formation and maturation. It is affected by the concentration of free H⁺ and OH⁻ in the soil solution and the plasma concentration of H⁺, Al³⁺, Na⁺, and Ca²⁺ adsorbed in the soil colloid. Under normal circumstances, the pH value of the soil is lower than 4 and higher than 9; the normal metabolism of plants is hindered or even destroyed, and it is unable to absorb and transport minerals. In addition, the soil pH value also seriously affects the availability of ions in the soil medium, such as Ca, Mg, N, P, K, and other elements. In a soil environment with a neutral pH value, plant roots can be well absorbed and utilized. However, many elements such as Fe, Mn, and Cu are difficult to be used in alkaline soil media. The pH of the soil also has a great influence on the type and quantity of active bacteria in the soil. Therefore, it is necessary to grasp the change characteristics of CO₂’s influence on soil pH value for studying ecological environment changes. Soil pH classification is shown in Table 7.

In Figure 5, the red column represents the air-dried sample, and the blue column represents the fresh sample (the following are the same). The pH value in the soil is generally between 4.01 and 6.22, which is acid to extremely acid soil, which may be related to the particularity of soil cracks, and the physical and chemical properties of soil cracks are different from other places. It can be seen that among the five samples of air-dried samples, the value of four samples decreased, and the value of one sample increased, and the pH value decreased by 0.046 on average. Among the five fresh samples, the value of four samples decreased, and the value of one sample increased, and the pH value decreased by 0.15 on average. Both the air-dried sample and the fresh sample rose at P4, which was related to soil variability.

After the CO₂ is injected, the pH value decreases for the first time. The reason is that after CO₂ enters the soil, it reacts with the water in it and ionizes more H⁺ and HCO⁻. The pH value rises during the second measurement and lies between the initial value and the first detection value, indicating that CO₂ makes the pH value drop in the short term. However, due to the short duration of the CO₂ environment, the pH value will return to the initial value within a certain period of time. Therefore, it can be concluded that CO₂ can cause a decrease in soil pH to varying degrees. In general, the difference between the air-dried sample and the fresh sample is relatively small in terms of value and change trend. This
### Table 1: Number correspondence table [24].

| Sample number | Sample category | Sampling time | Number |
|----------------|-----------------|---------------|--------|
| #1 (P1)       | Air-dried sample F | Before infusion (D1) | P1FD1 |
|               |                 | 1 day after infusion (D2) | P1FD2 |
|               |                 | 5 days after infusion (D3) | P1FD3 |
|               | Fresh sample X  | Before infusion (D1) | P1XD1 |
|               |                 | 1 day after infusion (D2) | P1XD2 |
|               |                 | 5 days after infusion (D3) | P1XD3 |
| #2 (P2)       | Air-dried sample F | Before infusion (D1) | P2FD1 |
|               |                 | 1 day after infusion (D2) | P2FD2 |
|               |                 | 5 days after infusion (D3) | P2FD3 |
|               | Fresh sample X  | Before infusion (D1) | P2XD1 |
|               |                 | 1 day after infusion (D2) | P2XD2 |
|               |                 | 5 days after infusion (D3) | P2XD3 |
| #3 (P3)       | Air-dried sample F | Before infusion (D1) | P3FD1 |
|               |                 | 1 day after infusion (D2) | P3FD2 |
|               |                 | 5 days after infusion (D3) | P3FD3 |
|               | Fresh sample X  | Before infusion (D1) | P3XD1 |
|               |                 | 1 day after infusion (D2) | P3XD2 |
|               |                 | 5 days after infusion (D3) | P3XD3 |
| #4 (P4)       | Air-dried sample F | Before infusion (D1) | P4FD1 |
|               |                 | 1 day after infusion (D2) | P4FD2 |
|               |                 | 5 days after infusion (D3) | P4FD3 |
|               | Fresh sample X  | Before infusion (D1) | P4XD1 |
|               |                 | 1 day after infusion (D2) | P4XD2 |
|               |                 | 5 days after infusion (D3) | P4XD3 |
| #5 (P5)       | Air-dried sample F | Before infusion (D1) | P5FD1 |
|               |                 | 1 day after infusion (D2) | P5FD2 |
|               |                 | 5 days after infusion (D3) | P5FD3 |
|               | Fresh sample X  | Before infusion (D1) | P5XD1 |
|               |                 | 1 day after infusion (D2) | P5XD2 |
|               |                 | 5 days after infusion (D3) | P5XD3 |

### Table 2: P1 soil test results.

| Number | pH value | Available nitrogen (mg/kg) | Available potassium (mg/kg) | Water-soluble salt (g/kg) | Total organic carbon (TOC) (g/kg) | Total carbon (TC) (g/kg) | Bicarbonate ions (HCO$_3^-$) (mg/kg) | Carbonate ions (CO$_3^{2-}$) (mg/kg) |
|--------|----------|-----------------------------|----------------------------|---------------------------|-----------------------------------|-------------------------|--------------------------------------|-------------------------------------|
| P1FD1  | 4.20     | 420.94                      | 37.5                       | 1.3                       | 2.4                               | 4.12                    | 18.55                               | 0                                   |
| P1FD2  | 4.03     | 432.43                      | 28                         | 2.3                       | 1.8                               | 3.2                     | 19.35                               | 0.7                                 |
| P1FD3  | 4.05     | 423.00                      | 32                         | 1.5                       | 2.3                               | 4.11                    | 18.95                               | 0                                   |
| P1XD1  | 4.05     | 412.33                      | 28                         | 3.0                       | 1.1                               | 1.98                    | 19.35                               | 0                                   |
| P1XD2  | 4.20     | 387.94                      | 31                         | 2.5                       | 1.1                               | 2.01                    | 20.2                                | 0.85                                |
| P1XD3  | 4.01     | 398.66                      | 30                         | 1.4                       | 2.8                               | 3.68                    | 18.65                               | 0                                   |

### Table 3: P2 soil test results.

| Number | pH value | Available nitrogen (mg/kg) | Available potassium (mg/kg) | Water-soluble salt (g/kg) | Total organic carbon (TOC) (g/kg) | Total carbon (TC) (g/kg) | Bicarbonate ions (HCO$_3^-$) (mg/kg) | Carbonate ions (CO$_3^{2-}$) (mg/kg) |
|--------|----------|-----------------------------|----------------------------|---------------------------|-----------------------------------|-------------------------|--------------------------------------|-------------------------------------|
| P2FD1  | 4.52     | 416.97                      | 34                         | 1.9                       | 2.1                               | 3.62                    | 19.15                               | 0                                   |
| P2FD2  | 4.51     | 485.05                      | 30                         | 1.6                       | 7.1                               | 8.7                     | 20.2                                | 0.95                                |
| P2FD3  | 4.40     | 459.44                      | 30                         | 1.5                       | 0.6                               | 1.34                    | 19.35                               | 0                                   |
| P2XD1  | 4.39     | 364.45                      | 32                         | 2.4                       | 1                                 | 2.19                    | 19.45                               | 0                                   |
| P2XD2  | 4.36     | 327.29                      | 32                         | 1.3                       | 0.3                               | 0.75                    | 20.35                               | 0.85                                |
| P2XD3  | 4.20     | 433.62                      | 27                         | 1.9                       | 2.4                               | 4.12                    | 19.5                                | 0                                   |
shows that CO₂ injection reduces the pH of the soil in a short period of time, and the pH change trend of different sampling points is not obvious. Therefore, the injection of CO₂ has little effect on the pH of the soil.

3.3. Analysis of Available Nitrogen Content. Available nitrogen refers to the nitrogen in the soil that is easily absorbed by crops. There are mainly ammonium nitrogen (NH₄⁺-N), nitrate nitrogen (NO₃⁻-N), amino nitrogen (Gly-N), amide nitrogen ((NH₂)₂CO-N), and some simple peptide and protein compounds. The determination methods include acid hydrolysis and alkaline hydrolysis. The former is called acid hydrolysis available nitrogen, and the latter is called alkaline hydrolysis available nitrogen. Although the absolute values of the two are different, they are highly positively correlated, and both are important parameters of soil fertility. This test uses the alkaline hydrolysis diffusion method, so it is also called alkaline hydrolysis effective nitrogen. Most of the nitrogen in the soil is the combined form of organic matter, and inorganic nitrogen (NH₄⁺-N and NO₃⁻-N) generally only accounts for 1% to 5% of total nitrogen. The growth and decline of soil organic matter and nitrogen are mainly determined by the relative strength of bioaccumulation and decomposition, climate, vegetation, farming systems, and other factors, especially soil temperature and moisture.

As a carbon source for plant growth, CO₂ is also involved in bioaccumulation and decomposition. The total available nitrogen value in the soil tested this time is between

| Number | pH value | Available nitrogen (mg/kg) | Available potassium (mg/kg) | Water-soluble salt (g/kg) | Total organic carbon (TOC) (g/kg) | Total carbon (TC) (g/kg) | Bicarbonate ions (HCO₃⁻) (mg/kg) | Carbonate ions (CO₃²⁻) (mg/kg) |
|--------|----------|----------------------------|----------------------------|--------------------------|---------------------------------|------------------------|--------------------------------|-------------------------------|
| P3FD1  | 5.74     | 384.61                     | 28                         | 2.1                      | 3.2                             | 5.49                   | 22.35                          | 0                             |
| P3FD2  | 5.50     | 386.76                     | 27                         | 1.9                      | 1.2                             | 2.63                   | 23.6                           | 1.25                          |
| P3FD3  | 5.18     | 437.75                     | 28                         | 1.3                      | 2.9                             | 4.97                   | 22.85                          | 0                             |
| P3XD1  | 5.50     | 325.41                     | 27                         | 0.5                      | 0.4                             | 0.89                   | 24.3                           | 0                             |
| P3XD2  | 4.91     | 324.44                     | 28                         | 0.2                      | 0.9                             | 1.96                   | 23.15                          | 1.45                          |
| P3XD3  | 4.78     | 346.73                     | 29                         | 1.2                      | 2.7                             | 4.66                   | 22.95                          | 0                             |

| Number | pH value | Available nitrogen (mg/kg) | Available potassium (mg/kg) | Water-soluble salt (g/kg) | Total organic carbon (TOC) (g/kg) | Total carbon (TC) (g/kg) | Bicarbonate ions (HCO₃⁻) (mg/kg) | Carbonate ions (CO₃²⁻) (mg/kg) |
|--------|----------|----------------------------|----------------------------|--------------------------|---------------------------------|------------------------|--------------------------------|-------------------------------|
| P4FD1  | 5.45     | 444.27                     | 29                         | 1.9                      | 4.1                             | 7.03                   | 21.85                          | 0                             |
| P4FD2  | 5.10     | 408.41                     | 33                         | 2.8                      | 5.1                             | 8.63                   | 22.15                          | 0.35                          |
| P4FD3  | 6.22     | 473.45                     | 30                         | 2.7                      | 2.7                             | 4.63                   | 21.9                           | 0                             |
| P4XD1  | 4.87     | 385.23                     | 31                         | 14.8                     | 1.2                             | 2.4                    | 22.4                           | 0.25                          |
| P4XD2  | 4.79     | 378.81                     | 32                         | 14.9                     | 5.9                             | 8.4                    | 22.65                          | 0.25                          |
| P4XD3  | 6.01     | 374.84                     | 29                         | 1.6                      | 2.8                             | 4.7                    | 22.45                          | 0                             |

| Number | pH value | Available nitrogen (mg/kg) | Available potassium (mg/kg) | Water-soluble salt (g/kg) | Total organic carbon (TOC) (g/kg) | Total carbon (TC) (g/kg) | Bicarbonate ions (HCO₃⁻) (mg/kg) | Carbonate ions (CO₃²⁻) (mg/kg) |
|--------|----------|----------------------------|----------------------------|--------------------------|---------------------------------|------------------------|--------------------------------|-------------------------------|
| P5FD1  | 5.40     | 424.40                     | 32                         | 1.1                      | 2.9                             | 4.97                   | 21.25                          | 0                             |
| P5FD2  | 5.30     | 424.42                     | 33                         | 1.9                      | 2.9                             | 4.99                   | 21.55                          | 0.15                          |
| P5FD3  | 5.23     | 471.75                     | 34                         | 0.5                      | 2.5                             | 4.77                   | 21.3                           | 0                             |
| P5XD1  | 5.74     | 332.91                     | 31                         | 1.6                      | 1.4                             | 2.8                    | 21.6                           | 0                             |
| P5XD2  | 4.56     | 361.67                     | 36                         | 1.9                      | 4.1                             | 6.78                   | 21.85                          | 0.35                          |
| P5XD3  | 4.80     | 354.92                     | 33                         | 1.8                      | 3.8                             | 6.45                   | 21.6                           | 0                             |

| pH     | Soil acidity and alkalinity       |
|--------|-----------------------------------|
| <4.5   | Very strong acidic                |
| 4.5~5.5| Strong acidic                     |
| 5.5~6.0| Acidic                           |
| 6.0~6.5| Weak acidic                       |
| 6.5~7.0| Neutral                          |
| 7.0~7.5| Alkaliescent                      |
| 7.5~8.5| Alkaline                         |
| 8.5~9.5| Strong alkaline                   |
| >9.5   | Very strong alkaline              |
324.44 mg/kg and 473.45 mg/kg. According to Figure 6, the available nitrogen values of the five air-dried samples are increasing, with an average increase of 34.84 mg/kg at each point. Among the five fresh samples, the value of three samples increased, and the value of two samples decreased, with an average increase of 17.69 mg/kg. In general, after the injection of CO2, the air-dried samples showed a trend of increasing, with an average increase of 34.84 mg/kg at each point. Among the five fresh samples, the value of three samples increased, and the value of two samples decreased, with an average decrease of 0.2 mg/kg. This is because the increase in CO2 concentration under different nitrogen levels increases crop biomass, which leads to an increase in the uptake of soil potassium by crop growth, resulting in a decrease in available potassium. The effective potassium value of air-dried samples showed irregular changes during the process of CO2 injection, but the overall change was small, which was related to the spatial variability of the soil. Fresh samples showed a trend of rising first and then falling, indicating that the air-drying process will affect the change of the effective potassium value.

The small difference in overall values between air-dried and fresh samples indicates that the effective potassium value is not very volatile. Taken together, the injection of CO2 causes a slight change in the effective potassium value. However, due to the short duration of the high-concentration CO2 environment, the effective potassium value will return to the initial value within a certain period of time.

### 3.5. Analysis of Soil Water-Soluble Salt Content

#### 3.5.1. Carbonate and Bicarbonate Ions Content Analysis

The results of bicarbonate and carbonate ions are shown in Figures 8 and 9, respectively. From the results of carbonate and bicarbonate content in the soil, it can be seen that there is almost no CO$_3^{2-}$ in the soil, but a very small amount of CO$_3^{2-}$ appears in individual soils, and the content of HCO$_3^-$ is between 18.8 and 25.9 mg/kg. The CO$_3^{2-}$ in the anion is almost zero, probably because the CO$_3^{2-}$ in the soil extract can be measured by the titration method when the soil pH is greater than 8.5. However, more CO$_3^{2-}$ exists only when the pH is greater than 10, which is consistent with the maximum pH value of 6.01 after CO$_2$ invasion. The content of HCO$_3^-$ is relatively small and does not change much, possibly because CO$_2$ forms H$_2$CO$_3$, and H$_2$CO$_3$ ↔ H$^+$ + HCO$_3^-$, HCO$_3^-$ ↔ H$^+$ + CO$_3^{2-}$ series reactions occur.

Water-soluble salt refers to the water-soluble salt contained in the soil that is leached out with a certain water-soil ratio and within a certain period of time. When the
soluble salt in the soil reaches a certain amount, it will directly affect the normal growth of crops. Because of its different compositions, soluble salt is also harmful to crops. This is also closely related to the salt tolerance of various crops. Therefore, analyzing the total amount and composition of soluble salt in the soil and understanding the dynamics of soil salt are not only important bases for the classification of saline soil, crop planting, soil improvement, and irrigation and drainage measures but also indispensable data for predicting and forecasting soil secondary salinization.

Reasons for the poison of water-soluble salt to plants are as follows:
The high concentration of salt reduces the soil water potential, and plants cannot absorb water or even seep water out. Therefore, salt damage usually manifests as physiological drought.

The excessive absorption of certain salt ions by crops can cause poisoning or physiological dysfunction. Too high contents of Na⁺, Cl⁻, Mg²⁺, SO₄²⁻, and so on will cause the lack of K⁺, HPO₄²⁻, or NO₃⁻ plasma.

When there is too much exchangeable sodium in the soil, the pores of the soil will be blocked due to the role of sodium ions to disperse the soil particles; the structure will be deteriorated; the permeability will be poor; the activity of microorganisms will be weakened; and the soil fertility will be significantly reduced.

If the soil pH is too high, some effective nutrients such as phosphorus and iron in the soil become ineffective and cannot be used by crops.

Classification standards of saline soil in our country are shown in Table 8. Most of the water-soluble salt in the soil is between 0.2 g/kg and 3.0 g/kg, belonging to light to medium saline soil. It can be seen from Figure 10 that among the five samples of air-dried samples, the value of two samples increased, the value of three samples decreased, and the average value did not change. Among the five fresh samples, the value of two samples increased; the value of three samples decreased; and the average value decreased by 0.3 g/kg. In general, the values of water-soluble samples show irregular changes, but the changes are relatively small, and the values of air-dried samples have smaller changes compared with fresh samples, which indicates that the water-soluble salt has certain volatilization during the air-drying process. The values of P4XD1 and P4XD2 are obviously larger than other values, which may be caused by test errors. On the whole, the amount of water-soluble salt will change due to the injection of CO₂ but the change is small, and the duration of the CO₂ environment is short; the water-soluble salt will return to the initial value within a certain period of time.

### Table 8: Classification standards of saline soil in our country [26].

| Type of saline soil   | Total salt content (g/kg) |
|----------------------|--------------------------|
| Light saline soil    | 1.0–2.0                  |
| Medium saline soil   | 2.0–4.0                  |
| Strong saline soil   | 4.0–6.0                  |
| Saline               | >6.0                     |

### 3.6. Analysis of Total Carbon and Organic Carbon Content

#### 3.6.1. The Carbon Source of Soil

The carbon source emissions formed by mining in coal mining areas are intertwined and coupled with the carbon budget mechanism of the regional ecosystem, forming a carbon cycle system that is open to the external environment. The destruction of surface vegetation, movement of overlying strata, and changes in soil texture caused by coal mining activities all have an impact on the carbon cycle, as shown in Figure 11.

The destruction of surface vegetation reduces the cover area of the surface and reduces the carbon sink capacity of vegetation. The movement of the overlying rock layer destroys the underground gas storage structure, which leads to gas gushing and gas accidents. Gas is either directly discharged into the atmosphere or extracted for use, and CO₂ is emitted into the atmosphere and becomes the main carbon source of the process of coal mining. Changes in soil texture, such as the decrease of microorganisms and organic matter content, result in a decrease in soil carbon sequestration capacity. In addition, plants absorb CO₂ in the atmosphere through photosynthesis; soil and plants emit CO₂ into the atmosphere through respiration; and plants emit organic carbon to the soil through humification. The carbon cycle system in coal mining areas is open to the external environment and exchanges carbon substances with the external environmental system through the circulation of greenhouse gases, industrial products, and carbon sink carriers (coal, grain, and biomass).

Its organic carbon is composed of organic matter in the soil. It is the general term for various decomposition products and synthesis products of all animal and plant residues formed in the soil and added externally at different
stages. It includes highly decomposed humic substances, organic residues with recognizable anatomical structures, and various microorganisms. The inorganic carbon includes HCO$_3^-$ in the soil solution, CO$_2$ in the soil air, and CaCO$_3$ deposited in the soil. The latter mostly exists in the soil profile in the form of nodules and mycelium. In terms of quantity, soil inorganic carbon is dominated by CaCO$_3$.

3.6.2. The Total Carbon and Organic Carbon Content Analysis. Figure 12 shows the changes in soil total carbon content due to CO$_2$ intrusion. It can be seen that the carbon content is between 0.75 and 8.63 g/kg. In general, the intrusion of different concentrations of CO$_2$ did not have a significant impact on the soil organic matter but slightly reduced the carbon content.

Soil organic matter has colloidal properties and can absorb more cations so that the soil has fertility retention and buffering properties. It can also improve the physical properties of the soil, make the soil loose and form a structure, and is also an indispensable carbon source and energy source for soil microorganisms. The average carbon content of organic matter is 58%; organic carbon is a component of organic matter; and soil organic matter is roughly 1.724 times the organic carbon content. Since total organic carbon (TOC) is an easy-to-detect indicator, total organic carbon is generally used to characterize the content of total organic matter. The reduction of organic matter will also cause a series of problems such as loose soil aggregate structure, reduction of microorganisms, and activation of heavy metals. Soil organic matter is the main source of various nutrients in the soil, especially an important source of nitrogen and phosphorus.

The total organic carbon detection value of the soil is between 0.3 and 7.1, which is related to the spatial specificity of the soil. It can be seen from Figure 13 that among the five samples of air-dried samples, the values of five samples all decreased, with an average decrease of 0.75 g/kg, and among the five samples of fresh samples, the values of five samples all increased, with an average increase of 1.88 g/kg. On the whole, the sample values show irregular changes, but the changes are small. The value of the air-dried sample decreased compared with that of the fresh sample, indicating that the organic carbon value of the air-dried sample

![Diagram](image-url)
changed during the air-drying process. From the perspective of fresh samples, the increase in organic carbon will increase the soil quality, which is beneficial to the growth of vegetation. Because the CO$_2$ environment is kept for a short time, the organic carbon value will return to the initial value within a certain period of time.

Table 9: Number correspondence table.

| Sample number | Sample category       | Sampling time              | Number  |
|---------------|-----------------------|----------------------------|---------|
| #1 (C1)       | Air-dried sample F    | Before infusion (D1)       | C1FD1   |
|               |                       | 1 day after infusion (D2)  | C1FD2   |
|               |                       | 5 days after infusion (D3) | C1FD3   |
|               | Fresh sample X        | Before infusion (D1)       | C1XD1   |
|               |                       | 1 day after infusion (D2)  | C1XD2   |
|               |                       | 5 days after infusion (D3) | C1XD3   |
| #2 (C2)       | Air-dried sample F    | Before infusion (D1)       | C2FD1   |
|               |                       | 1 day after infusion (D2)  | C2FD2   |
|               |                       | 5 days after infusion (D3) | C2FD3   |
|               | Fresh sample X        | Before infusion (D1)       | C2XD1   |
|               |                       | 1 day after infusion (D2)  | C2XD2   |
|               |                       | 5 days after infusion (D3) | C2XD3   |
| #3 (C3)       | Air-dried sample F    | Before infusion (D1)       | C3FD1   |
|               |                       | 1 day after infusion (D2)  | C3FD2   |
|               |                       | 5 days after infusion (D3) | C3FD3   |
|               | Fresh sample X        | Before infusion (D1)       | C3XD1   |
|               |                       | 1 day after infusion (D2)  | C3XD2   |
|               |                       | 5 days after infusion (D3) | C3XD3   |
4. Discussion

Because there are still limitations in the study of soil carbon in coal mining areas, the research object should not only inject the poorer soil in the topsoil layer directly above the soil sample but also select the more fertile soil as the contrast soil sample. Therefore, three points of contrast soil samples (labeled C1, C2, and C3) were taken in the forest zone (the area with more fertile soil) on the surface of the surface where the liquid carbon dioxide was injected. The number correspondence of the sample is shown in Table 9. Fresh samples and air-dried soil samples and test the physical and chemical properties of the contrast samples should be taken.

4.1. Analysis of Contrast Sample Results. It can be seen from Figure 14. In the three samples of the air-dried sample, the sample values all show a trend of the first decline and then rise; in the three samples of the fresh sample, the sample value also shows a trend of the first decline and then rise. After the CO₂ is injected, the pH value drops for the first time. The reason is that after CO₂ enters the soil, it reacts with the water in it and ionizes more H⁺ and HCO⁻³. The pH value rises during the second measurement and lies between the initial value and the first detection value, indicating that CO₂ could make the pH value drop in the short term. However, due to the short duration of the CO₂ environment, the pH value could return to the initial value within a certain period of time.

The pH value of fertile soil (C1~C3) and poorer soil (P1~P3) is shown in Figure 15. Compared with the five samples of poorer soils P1~P3, the U-shaped change trend of pH value is more obvious. This shows that the more fertile soil has a higher composition of various microorganisms and other substances, and the internal self-remediation capacity of the soil is stronger than that of the P1~P3 soil sample, and the restoration efficiency is higher.

The total carbon and organic carbon (C1~C3) are shown in Figures 16 and 17. The content of soil organic carbon is between 7.99 and 8.69 g/kg, and the total carbon content is between 10.19 and 11.1 g/kg. However, experiments with different concentrations of CO₂ could not cause significant differences in soil organic carbon and total carbon and could not show regular changes. In general, the organic carbon in the soil is not affected by the soil CO₂ concentration during the test period.

5. Conclusions

This experiment selected five indicators: pH, available nitrogen, available potassium, water-soluble salt, and total organic carbon. The samples before and after CO₂ injection were tested, and the results were analyzed. The results are summarized as follows:

(1) The pH value of the air-dried and fresh soil samples decreased slightly after the CO₂ injection and rose after 5 days. It is expected to return to the initial value soon with little impact.
(2) The injection of CO₂ has a certain effect on the effective nitrogen value of the air-dried and fresh soil samples, which enhances the soil fertility in a short time but will soon return to the initial value.

(3) The effective potassium value of air-dried and fresh soil samples decreased slightly due to the influence of CO₂ injection, which was beneficial to the absorption of potassium by plants, but then rebounded. It is expected to return to the initial value soon, with a small gain.

(4) Under the influence of CO₂, the water-soluble salt of the air-dried soil did not change, and the water-soluble salt of the fresh sample decreased slightly. It is conducive to plant growth in a short period of time, rebounds quickly, and is less affected by CO₂ injection.

(5) The total organic carbon of air-dried samples decreased slightly under the effect of CO₂ injection, and the fresh samples increased. Compared with the air-dried samples, the total organic carbon value of the fresh samples changed greatly, and the fertility increased, which was beneficial to the growth of vegetation. However, it is expected that the value will return to the initial value in a short time, and the impact time will be short.

In general, the injection of CO₂ has little effect on soil chemistry. As far as the measured indicators are concerned, most of them are conducive to plant growth, such as the "carbon source" of plant growth, the increase of available nitrogen, the decrease of a water-soluble salt, and the increase of effective potassium absorption. Factors that are not conducive to plant growth, such as the pH value, dropped slightly but quickly recovered. According to the existing theory and combined test results, it is shown that the injection of CO₂ in the goaf has a certain effect on the chemical properties of the surrounding soil, and it has a promoting effect on the growth of plants. When liquid CO₂ was injected in the goaf, injected liquid CO₂ is not able to make major changes inside the soil because a buffer system inside the soil act as an organic buffer that rebalanced the pH again (no change in pH).

Data Availability

The data utilized to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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