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Study on Mechanism of Water-Rock Interaction in the Process of Irrigation with Mine Water

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Abstract. This paper studies the concentration rules of different components of exudate based on original soil column test by using coal mine pit drainage and tap water as filter fluid to simulate water-rock interaction in sewage water irrigation, clear water irrigation or precipitation filtration, and the results show that the water-rock interaction is mainly dissolved by soluble salt, followed by cation exchange and adsorption. The carbonic balance movement occurred in both sewage and clear water irrigation, accompanied by the complex cooperation of some ions. These physical chemistry processes contribute to the sulphate and total hardness of groundwater in the irrigated areas.

Keywords. Soil column test, water-rock interaction, irrigation with mine water, groundwater

1. Introduction

Zibo Synclinal Basin is an old industrial mining area, where the coal mines are widely distributed, and the discharge of mines is large and stable. For a long time, local farmers have been using pit water for irrigation, and large-scale sewage irrigation has not only caused soil compaction, crop yield reduction and other adverse reactions, but also caused large areas of groundwater pollution, it has a serious impact on the lives of local residents and on industrial and agricultural production. Sewage irrigation leaks pollution to groundwater, pollutants must penetrate the soil layer of the gas-bearing belt into the underground aquifer, in this process of water-rock interaction, that is, the migration, transformation, degradation and other effects of pollutants in the soil layer of the gas-bearing belt are particularly important in the entire pollution process, which directly determines the type, concentration and form of pollutants that eventually enter the aquifer, which is one of the most critical links in groundwater pollution [1-3]. This article reproduces this process through simulation tests to study the pollution mechanism of groundwater and provides guidance for pollution provention and control

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in this area.

2. Test Design

The simulation test uses the drainage of the coal mine pit as the filtrate, and the original soil column is used as the test soil sample in the corresponding irrigation area to simulate the natural state [4]. At the same time, in order to investigate the leaching effect of clean water irrigation or atmospheric precipitation on the gas belt and pollutants after sewage irrigation, tap water is used for leaching after leaching with pit water, and the main chemical components of the two filtrates are shown in Table 1.

The lithology of the tested soil column is sub-sandy soil, the column height is 45cm, the diameter is 18 cm, the measured dry bulk weight (ρ b) is 1.39g/cm³, and the effective porosity (η e) is 0.22. The test device is mainly composed of two parts: one is the water supply device, using a 25000 mL large Martens bottle, installing the automatic water supply equipment of the water head to keep the water head stable when leaching; the other is the test column, using an inner diameter of 18 cm, an outer diameter of 20 cm PVC pipe to fill the soil sample, and install a graben layer, a filter layer and a screen at the top and bottom of the soil sample to prevent impurities from blocking the pores of the soil sample or the leaching liquid to wash the soil column.

Table 1. Leaching filtrate chemical composition content table (unit: mg/L).

Composition	K⁺	Na ⁺	Ca ²⁺	Mg ²⁺	Cl	SO4 ²⁻	HCO ₃ -	NO ₃	Total hardness	Degree of mineralization	РН
Mine water	13.2	210.0	375.7	99.4	231.0	1413.2	57.4	2.5	1347.7	2402.4	6.3
Tap water	1.2	12.3	95.4	19.2	40.8	53.8	244	9.07	317	518	7.9

3. Test Process

The soil column test lasted a total of 4815 minutes, in which was carried out in two stages. The first stage was the sewage leaching stage, using pit water as the leaching liquid, which lasted 3185 minutes, during the process, a total of 85400 mL of sewage was leached, and 12 penetrating liquid water samples were taken. The second stage was switching to tap water leaching, which lasted 1630 minutes, a total of 28300 mL of tap water was leached, and 3 penetrating liquid water samples were taken. All water samples were analyzed for water quality.

4. Analysis of Test Results

Figures 1 and 2 are penetration curves of concentrations of several major substances such as SO_4^{2-} . The front part of the curve (before break-point) is the penetration curve of the sewage leaching concentration, the posterior section is the penetration curve of the clear water leaching concentration, and the point on the longitudinal axis is the concentration of the water in the pit.



Figure 1. Penetration curve of main anion concentration in soil column test.



Figure 2. Penetration curve of main cation concentration in soil column test.

4.1. Sewage Leaching Process

Obviously, in the process of sewage leaching, the concentration of all anions in the penetrating liquid is always higher than the concentration of the original solution, indicating that during this period, the soil layer not only did not effectively intercept or adsorb Cl⁻, SO_4^{2-} , NO_3^{-} , HCO_3^{-} and other anionic components, on the contrary, due to the addition of sewage, part of the above components in the soil layer were dissolved and filtered out, thus increasing the degree of pollution of the down filtration water.

For groundwater, the soil layer of the gas-laden belt not only does not play a role in isolating these pollutants, but has become a potential second source of pollution, which is the main reason for the continuous increase in the above components of groundwater in polluted irrigation areas [5, 6]. The corresponding original liquid substance content in the exudation is deducted, that is, the cumulative total amount of the above substances obtained by the sewage purely leached from the soil layer is obtained, as shown in Figures 3 and 4. It can be seen from this that in the sewage leaching process totaling 85400 mL, a total of $SO_4^{2-}13243.6$ mg, $CI^{-}2230.94$ mg, $HCO_3^{-}7315.33$ mg, $NO_3^{-}1976.61$ mg were washed out from the soil column.

Cation changes are different, as can be seen from Figure 2, in addition to the concentration of Ca^{2+} in the penetrating liquid is always higher than the original solution, the penetration concentration of K⁺, Na⁺, Mg²⁺ plasma is overwhelmingly lower than the concentration of the original liquid, indicating that a considerable part of these three ions are adsorbed by or attached to the soil layer, while Ca^{2+} is dissolved or desolated from the soil layer in large quantities, which is seen more clearly from the total cation wash out chart (Figure 4). Obviously, in addition to Ca^{2+} , the wash out of K⁺, Na⁺, mg²⁺ are negative, some of the cations contained in the sewage filtrate enter the soil layer are fixed, and Ca^{2+} is released from the soil layer (dissolved or desolated), and in the whole process of sewage leaching, K⁺ enters the soil layer 512.78 mg, accounting for 45.5% of the total input, Na⁺ enters the soil layer 1502.5 mg, accounting for 8.4% of the total input, mg²⁺ enters the soil layer 995.2 mg, accounting for 11.7% of the total input; Ca²⁺9861.4 mg was washed out of the soil column, which was the main reason for the increase in the total hardness of groundwater in the sewage irrigation area.

The different changes in the concentration of anion and cation of the penetration liquid indicate that a series of physical and chemical effects have occurred in the process of sewage leaching, and the concentration of the penetrating liquid is the result of the interaction between the sewage and the soil. Which chemical processes are the most influential in action is the key to grasping the migration and transformation of pollutants. Compared with the original solution, the concentration of all anions and Ca^{2+} increases, while the concentration of other cations decreases. Since this exchange process only occurs between the soil and the filtrate, the component of the increased concentration must be given by the soil, and the component of the reduced concentration must also remain in the soil.



Figure 3. The relationship between the volume of leachate and the total amount of main anions in soil column experiment.



Figure 4. The relationship between the volume of leachate and the total amount of main cation in soil column experiment.

The anions and Ca^{2+} washed out of the soil layer are the result of the dissolution of corresponding compounds such as $CaCl_2, CaSO_4, Ca(HCO_3)_2$, which are dissolved from the soil layer, the reason is the existence of a hydro chemical potential of dissolution in the solid-liquid phase equilibrium system. According to the theory of water chemistry, the ionic strength of an aqueous solution:

$$I=1/2 \quad (\sum m_i z_i^2) \tag{1}$$

where, m_i and z_i are the molar concentration (mol) and charge number of the ion, respectively. It suggests that the higher the concentration of ions, the greater the ionic strength of this aqueous solution. According to the Debye-Huckel equation, the activity coefficient of an ion can be calculated as follows:

$$logri = (-Azi^2 \sqrt{I}) / (1 + Bai \sqrt{I})$$
⁽²⁾

where: ri—the activity coefficient of the *i* ion; *A* and *B* are constants for expressing solvent characteristics at specific temperatures and pressures; ai—constant related to the effective diameter of the *i* ion; The meaning of the remaining symbols is the same as before.

The ionic strength (I) of the pit water used in the filtrate was calculated to be 0.065 mol, and it is clear that within this range, as the ion concentration increases, the activity coefficient of the ions decreases. Taking CaSO₄ (gypsum) as an example, there is a dissolution equilibrium equation:

$$CaSO_4 = Ca^{2+} + SO_4^{2-}$$
(3)

Its saturation index:

$$Bg = \left[Ca^{2+}\right] \left[SO^{2-}_{4}\right] / Kg \tag{4}$$

When Bg < 1, Gypsum dissolute: When Bg = 1, remain a state of dynamic equilibrium; When Bg > 1, the plaster precipitates. In equation (4), $[Ca^{2+}]$ and $[SO_4^{2-}]$ are the degree of activity of Ca^{2+} and SO_4^{2-} , the value of which is the product of the actual concentration mi multiplied by the activity coefficient ri, and Kg is the constant of the solubility product of CaSO₄. Due to the reduction of the activity coefficient, resulting in a decrease in the activity of the two, at the same time, because at a certain temperature, the Kg value remains unchanged, Bg becomes smaller, the reaction is carried out to the right, the dissolution of gypsum occurs, the $CaSO_4$ in the soil layer is continuously dissolved into the leachable filtrate, resulting in an increase in concentration, and this concentration change further accelerates the dissolution process, until most of the soluble CaSO₄ in the soil layer is dissolved, and the concentration of the leaching solution is gradually approaching the water concentration, which is the so-called salt dissolution (salt effect) [7-9]. The dissolution process of other compounds is also much the same. Since the dissolution of the above substances is totally dissolved, therefore, the dissolved quantity has a correspondence of the chemical formula, such as 1 mg equivalent (meq) CaCl₂ dissolution will produce 1 mg equivalent of Ca²⁺ and 2 mg equivalent cl⁻, both have a correspondence. According to this, the dissolved amount of different types of calcium salts can be calculated, namely CaSO₄275.9 meq, CaCl₂31.4 meq, Ca(HCO₃)260.0 meq. The dissolution of these substances generated a total of 367.3 meq Ca²⁺, and according to the measured data, a total of 493.1 meq Ca²⁺ was migrated from the soil layer, that is, the amount of Ca^{2+} dissolved by dissolution accounted for 74.5% of the total amount of Ca²⁺ moved out of the soil sample, so where did the remaining 125.8 meg Ca^{2+} come from?

Obviously, in addition to Ca^{2+} , the concentration of cations K⁺, Na⁺, Mg²⁺ is lower than that of the original liquid, indicating that the soil has absorbed them. Therefore, there must be an exchange adsorption effect of cations. Usually, the exchange adsorption capacity of Ca^{2+} is higher than that of Mg²⁺ and K⁺, Na⁺, but the changes in ion concentration, acidity and alkalinity of aqueous solutions, and ion exchange equilibrium can completely change this adsorption order. Although the high concentration of ions in the solution is low, it can also replace the low concentration ions with strong adsorption capacity, and the abnormal adsorption substance caused by the change of exchange equilibrium is also the result of the solution concentration and the adsorption concentration of the soil. Calculated according to the filtrate measured data and the Debye-Huckel equation, the activity of K⁺+ Na⁺ in the pit water is 7.57×10⁻³ mol, while the activity of Ca²⁺ is 4.23×10⁻³ mol, the former is 1.8 times that of the latter, and the high concentration of K⁺ and Na⁺ exchanges part of the Ca²⁺ in the soil, resulting in the elevation of Ca²⁺ in the solution. There are also exchange reactions for Ca²⁺, Mg²⁺ in soil and leaching fluid:

$$Mg^{2+}+Ca^{2+}_{(suction)} = Ca^{2+}+Mg^{2+}_{(suction)}$$
 (5)

In the equation, Mg^{2+} and Ca^{2+} , Ca^{2+} (suction) and Mg^{2+} (suction) are mg^{2+} and Ca^{2+} adsorbed by the soil in the leaching liquid respectively. Its selectivity constant is:

$$K_{Mg-Ca} = \frac{[Ca^{2+}]N_{Mg^{2+}}}{[Mg^{2+}]N_{Ca^{2+}}}$$
(6)

In the equation, $[Ca^{2+}]$ and $[Mg^{2+}]$ is the activity of Ca^{2+} and Ca^{2+} in the solution

phase (mol), $N_{Mg^{2+}}$ and $|N_{Ca^{2+}}$ is a mol percentage of solid phase adsorption of Mg²⁺ and Ca²⁺. In general, K_{Mg-Ca} is 0.6, $N_{Mg^{2+}}$ and $|N_{Ca^{2+}}$ can be estimated by the results of soil analysis. For Pit Water and test soil column, $[Ca^{2+}] = 4.23 \times 10^{-3}$ mol, $[Mg^{2+}] = 2 \times 10^{-3}$ mol, $N_{Mg^{2+}} = 0.16$, $N_{Ca^{2+}} = 0.84$, the reaction quantity value is obtained on the right side of the substitution equation (6):

$$Q_{Mg-Ca} = \frac{4.23 \times 10^{-3} \times 0.16}{2 \times 10^{-3} \times 0.84} = 0.4$$

In order to achieve the equilibrium of the reaction, the condition of Q=K, Q_{Mg-Ca} , must rise to 0.6, which leads to the release of Ca²⁺ and the adsorption of Mg²⁺. Since the adsorption of cations is equal to the exchange of electricity, a Ca²⁺ can replace 2 Na⁺ or K⁺, a Ca²⁺ can only replace a Mg²⁺, according to this calculation, the total amount of K⁺, Na⁺, Mg²⁺ lost in the leachable can be exchanged out of ca²⁺ of 121.1meq, and its amount is basically close to the increase of other Ca²⁺125.8 meq in addition to the dissolved source, which accounts for about 25.5% of the total increase of Ca²⁺. The dissolution of calcium salts and the exchange and adsorption of cations are only part of many complex water chemises in the leaching process, but this two-action basically controls the change of the macro components of the solid-liquid phase, which has very important theoretical significance for sewage irrigation and leakage groundwater pollution. The changes in soil soluble salts before and after sewage leaching are basically consistent with the above analysis, which further confirms the objective existence of the two effects (see Table 2).

Composition	\mathbf{K}^{+}	Na ⁺	Ca ²⁺	Mg^{2+}	Cŀ	SO4 ²⁻	HCO ₃ -	NO ₃ -
Native soil (front)	0.8	12.5	67.1	7.7	26.0	137.4	45.9	8.7
Leached soil (back)	1.3	22.5	34.1	5.2	14.1	84.3	54.5	< 0.40
Up (+) down (-)	+0.05	+10.0	-33.0	-2.5	-11.9	-53.1	+8.6	-8.7

Table 2. Analysis of soil soluble salt before and after sewage leaching (unit: mg/100g dry soil).

The abnormal change of Mg^{2+} in the table is the result of networking, while the anomaly of HCO_3^{-} is caused by the shift of carbolic acid equilibrium.

4.2. Clean Water Leaching Process

Three intensities of leaching simulation were performed in the clear water leaching test stage. At the first time, 2600 mL of clean water was poured into the water, its intensity was equivalent to a heavy precipitation process. At the second time, it was poured into 19,500 mL of clean water, which was equivalent to one year of precipitation in the area's abundant water year; The third time, 28300 mL of clean water was poured in, which is equivalent to the precipitation of two dry years in the area. The changes in the content of each component of the penetration solution are shown in Figures 1 and 2.

Obviously, all the cations and Cl⁻, SO_4^{2-} concentrations in the effluent are in a sharp decline state, and the early rate reduction is significantly greater than that in the later stage, a high-intensity precipitation can reduce the leaching concentration of these components by 13.3% to 30.6%, one year of precipitation can reduce the leaching concentration by 60% to 84.3%, and two years of precipitation can be further reduced

by 70.7 to 90.6%. The reason for the rapid decline in the concentration of clean water leaching liquid is that the soil layer of the gas-clad belt has undergone long-term sewage leaching, in which the soluble salt has been consumed in large quantities, and the entry of clean water is only a piston to promote the sewage residue in the soil layer, so the leaching liquid concentration will drop sharply and soon approach the clear water concentration. Therefore, clean water irrigation has the role of rapid purification of the gas belt or aquifer, and the cleaning wheel irrigation cannot fundamentally solve the problem of groundwater pollution, but the irrigation of clean water dredges the pollution channel, which will accelerate the downward migration speed of pollutants.

Significant shifts in carbolic acid equilibrium occurred during the clean water leaching process, in which the HCO_3 ⁻ concentration increased in contrast to the above components, and by the end of the test, it had increased by 68.6%. Correspondingly, the water chemistry type of the leaching fluid is also rapidly transformed from the initial SO_4 type to the SO_4 ·HCO₃ type, and then to the HCO_3 ·SO₄ type, and the entire conversion process takes only 26.5 hours, and the water chemical field has undergone such a significant evolution in such a short period of time, which shows that the cleaning effect of clear water irrigation or rainfall on the soil layer is very obvious [10].

5. Conclusions

(1) The soil layer of the gas-bearing belt in the polluted irrigation area has almost no interception capacity for pollutants such as SO_4^{2-} , Cl^- , NO_3^- etc., on the contrary, due to the influence of salt dissolution and adsorption alternation, some pollutants in the soil layer are dissolved (released), making the soil layer of the gas-bearing belt a potential second source of groundwater pollution, thus further aggravating groundwater pollution.

(2) In the process of sewage leaching, the water-rock (soil) interaction is mainly based on the total dissolution of CaSO₄, CaCl₂ and Ca (HCO₃)₂, supplemented by K⁺, Na⁺, Mg²⁺ adsorption exchange Ca²⁺, which together lead to an increase in the content of groundwater SO₄²⁻ and total hardness.

(3) Whether it is sewage leaching or clear water leaching, the movement of carbonic acid balance occurs, accompanied by the complexation of some ions.

(4) Clean water irrigation can wash out a large number of pollutants trapped in the soil layer, and at the same time, dredge the pollution channel. Therefore, the sewage washing wheel irrigation cannot fundamentally solve the problem of groundwater pollution, however, clean water can be used for irrigation to gradually remove the pollution of the gas belt and the underground aquifer.

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