

Progress of Chromium Migration and Transformation in Groundwater-Rock Interface

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Abstract. Chromium migration and transformation is a complex process in groundwater-rock interface, including a series of physical and chemical reactions, such as adsorption-desorption, redox, dissolution-precipitation, complexation-dissociation etc. It was affected by groundwater pH, Eh, the type and the content of dissolved substances, the velocity of groundwater, the lithology of aquifer medium and other factors. This paper reviews the chromium migration and transformation in groundwater-rock interface, migration models and simulation softwares involved in this process.

Instructions

Water-rock interaction is a geochemistry process between water and rock (rock and mineral), it attracts the attention of researchers in earth science, environmental chemistry, hydrogeology, engineering geology, etc. Since 1970s, water rock interaction began to involve in the pollution and remediation of groundwater. Domestic and foreign scholars carried out lots of research on migration and transformation of the organic pollutants, variable valence heavy metals and nitrogen, phosphorus in water-rock interface, and provides an important theoretical basis for the prevention and control of pollution.

In recent years, with the rapid development of the industry involved in chromium and chromium chemicals widely used, unsaturated zone and groundwater pollution have become increasingly serious caused by chromium compounds into the groundwater system. Chromium disposition and distribution in groundwater-rock interface is a complex process, influenced by many factors, such as forms of chromium, types and quality of groundwater, physical and chemical properties of aquifer, etc. The study on migration and transformation of chromium in groundwater-rock interface has an important guiding significance for repairing and controlling the chromium pollution of groundwater.

Migration and Transformation of Chromium in Groundwater-rock Interface

Existing forms of chromium in groundwater determine the chromium migration and transformation capabilities, and its distribution between solid phase and liquid phase. In the natural groundwater and unsaturated zone, chromium usually exists as two forms: Cr (VI) and Cr (III). Main Existing Forms of Cr (VI) are $\text{Cr}_2\text{O}_7^{2-}$ 、 CrO_4^{2-} 、 HCrO_4^- ，with the negatively charged(Sun, 2011). Small portion of Cr (VI) can be adsorbed to soil colloids and formed insoluble substance with soil component, while most are free in groundwater. Cr (III) mainly exists as Cr^{3+} and CrO^{2-} ，which easily occurred adsorption and complexation with soil colloids and organic matter, or generate oxygen and hydroxide precipitate, with poor mobility. Cr (VI) and Cr (III) can be transformed into each other by redox in appropriate circumstances. Therefore, chromium reaches equilibrium by adsorption-desorption, oxidation-reduction, precipitation-dissolution, complexation-dissociation process in groundwater-rock system.

Adsorption-Desorption.In the Eh-pH range of the natural groundwater-rock system, Cr (VI) mainly exists in the form of oxyacid anion. The adsorption of Cr (VI) by soil colloid is the primary way that it migrates from liquid into solid. There are mainly two types of adsorption: physical adsorption and physicochemical adsorption. In acidic soil of $\text{pH}<6$, Cr (VI) is absorbed as the form of HCrO_4^- ，which belongs to the electrostatic adsorption (Liu,2000). Clay minerals with inorganic

hydroxide groups including iron oxide, alumina, montmorillonite, kaolinite and fewer, as the main adsorption of anions, control the adsorption quantity of anions(Lu,2007), accompanying by hydroxyl releasing. Soil colloids can also produce specific adsorption by exchanging with OH^- and HCrO_4^- , which has the stronger adsorption force. The adsorption of Cr (VI) is mostly physicochemical adsorption.

The soil pH has some significant effect on the adsorption of Cr (VI). One is the soil pH can change the chemical form of Cr (VI) so that effect on the content of HCrO_4^- . Li Hangbin(Li,2011)found that, the content of HCrO_4^- decreased as pH increased, while the content of CrO_4^{2-} increased as pH increased. When the pH is larger than 8, there only CrO_4^{2-} exists in the system. The adsorption has almost come to a halt. On the other side, the soil pH can change the surface charge of soil minerals (Yan, 2010). Lower pH is helpful to the apparent adsorption of Cr (VI).The positive charge on the hydrated metal oxides surface decreased and negative charge increased with the rise in pH, so that the adsorption of Cr (VI) decreased.

Compared with other anions, such as chloride ions, nitrate ions and sulfate ions, Cr (VI) is absorbed to oxides and clay particles more tightly, which was slightly inhibited when the Cr (VI) concentration was higher. The results of competitive adsorption of anions show that, competing oxyanions promoted Cr (VI) desorption, directly participating in competition of adsorption site, while when the concentration of SO_4^{2-} , F^- and H_2PO_4^- reached 10^{-4}mol/L , there has a significant inhibitory effect (Zhang,1990). Many scholars' research (Zhu,1985) showed that different minerals have different Cr (VI) adsorption capacity. Its order is kaolinite> illite> montmorillonite. Red soil dominated by kaolinite, containing a large number of iron and aluminum oxide colloids with positive charge, with weak negative and low pH, has strong adsorption of Cr (VI) (Xiong,1975). While the yellow brown soil mainly illite and the chernozem mainly montmorillonite on Cr (VI) adsorption is relatively weak, the order of Cr (VI) adsorption capacity of three kinds of soil is red soil > yellow brown soil > chernozems.

Soil clay minerals in Cr (III) adsorption ability is 30~300 times larger than Cr (VI). Cr (III) adsorption process and capacity depends on the water-rock system pH, and increases with the rise of pH. When the groundwater pH is relatively low, Cr (III) exists as complex cation, such as CrOH_2^+ , $\text{Cr}(\text{OH})_2^+$; while at high pH, exists as complex anion, such as $\text{Cr}(\text{OH})_4^-$ (Li, 2005). In the range of pH 2 ~ 6, Cr (III) cation was mainly nonspecifically adsorbed by soil colloid with the negative charge. Cr (III) cations may also be nonspecifically adsorbed by desorption or association of H^+ with hydroxyl in the colloid group (i.e., physicochemical adsorption). In pH 4~6, Cr (III) is easily adsorbed and co-precipitated with Fe^{3+} and Al^{3+} (Liu,2000;Li,2005).Research (Luan,1990) shows that changes of water oxidation reduction potential have a great impact on the release of heavy metals from sediments. The order is the oxidation state> weak oxidation> reduction state. If the state is relatively stable, the lower oxidation reduction potential is, the more easily the heavy metal released. The reason is that manganese oxides be reduced easily make oxide colloid partial dissolved, thus reducing the amount of adsorption of heavy metals. At the same time, the exchange adsorption of Cr (III) of active components in the soil can transfer Cr (III) from water to soil. Haiyan Sheng (Sheng,2005) proved that there are many functional groups on the humus, such as -COOH, $-\text{NH}_2$, which can generate a complex chelate reaction with Cr (III), so that the Cr (III) is strongly adsorbed. The order of Cr (III) adsorption capacity of different kinds of minerals is: montmorillonite > illite > kaolinite (He,2001) The research of Chen Yingxu(Chen,1994) showed that at pH 4, Qingzini predominated montmorillonite has strong electronegativity, the Cr (III) adsorption amount is large; dry red soil and veins mud field dominated with kaolinite and iron and aluminum oxides has weak electronegative, thus has relatively small adsorption capacity. Liu Yunhui(Liu,2000) shows that in the same condition of pH, Cr (III) adsorption ability of brown soil is larger than fluvo aquatic soil and cinnamon soil.

Oxidation-Reduction.Because the toxicity and mobility of Cr (VI) are far larger than Cr (III), it is expected that Cr (VI) can be directly transformed into Cr (III) that reduce its harm under reducing conditions. Therefore, the study of the oxidation-reduction reaction of chromium in the soil mainly focusses on two aspects in recent years. One is how Cr (VI) be reduced to Cr (III) when it gets into

the soil, and if the Cr (III) in the reaction product can be reduced again; the other is the reaction behavior of these reactions in different conditions. At the same time, another focus is the addition of reducing substances to promote the reduction of Cr (VI).

Cr (VI) can transform into Cr (III) in four ways: the reduction reaction with H_2S , SO_2 and Fe^{2+} , electron-transfer reactions occurs on the mineral surface, the reaction with non humic organic matter (such as carbohydrates and protein) and the reduction reaction with soil humus(Wang,2007). In the general range of pH and Eh, Cr (VI) will be reduced by organic compounds with hydroxyl, ferrous ions and the soluble sulfide soon. The lower the pH, the faster the reduction reaction(Li,2005 ;Eary,2007).

Inseong Hwang(Hwang,2002) demonstrated that the reduction capability of Fe^{2+} in the solution can be partly transferred to solid medium that the solid phase medium can continue to remove Cr (VI) through the research of the influence of Fe^{2+} on the reduction kinetics of Cr(VI) in aquifer, and proved that it is feasible method by injecting Fe^{2+} in the aquifer to remedy Cr (VI) contaminated aquifer and groundwater. Kh rici-Bousnoubra (Kh, 2009) discovered that the H_2S released by industrial site get into the shallow layer, reducing the Cr (VI) to insoluble Cr (III). Lirong Chen (Chen,2011) demonstrated that when the organic matter content is greater than 2% in the soil,Cr (VI) will almost all be reduced to Cr (III), generating insoluble hydroxide precipitation so that be adsorbed and fixed. In the acid condition, purifying effect of humic acid on Cr (VI) can be attributed to: firstly $\text{Cr}_2\text{O}_7^{2-}$ diffuse to humic acid in the solution, and be adsorbed and redoxed, Cr (III) in reduction product partly be adsorbed, and part of it get into the water again.

More than 90% of Cr (III) compounds in soil can be quickly fixed, however, Cr (III) adsorbed by clay minerals in soil continuous desorb affected by soil pH and the oxidant, due to the role of ligand such as Cl^- , SO_4^{2-} , HCO_3^- returns to the water (Gao,2005)and small part of Cr (III) can be oxidized to Cr (VI). Cr (III) oxidation is prone to occur in the soil with rich organic matter and poor MnO_2 (Garman,2004), therefore, it is necessary to consider the content of manganese oxide in soil or sediments when predicting the formation and harm of chrome material, but Cr (III) in the water can hardly be oxidized by the oxygen in the air(Lai,2006). Yingxu Chen(Chen,1993) consider that Cr (III) diffuse from the solution to the surface of MnO_2 particles so that occur complexation reaction, and transfer electron with MnO_2 , as a result, Cr (III) is reduced to Cr (VI) anionic and entre the water. Hongmin Yang(Yang,2009) found that in the acidic environment, $\bullet\text{OH}$ can be oxidant of Cr (III), Cr (VI) increased with increasing concentration of $\bullet\text{OH}$.

Cr (VI) reduction process is influenced by pH. Junxiang Yang's (Yang,2005) research on the impact of pH on the Cr (VI) reduction by S^{2-} indicates that the higher the pH, the smaller the reaction rate. It is probably due to in neutral and alkaline conditions, S^{2-} can be oxidized by dissolved oxygen. Jiaquan Xu(Xu,1994) believes that the general trend of the effect of pH on reaction rate constant K is that K increases with the rise of pH. In Fe^{2+} system, Cr (VI) reduction reaction will stop at $\text{pH}>8.0$, which is because Fe^{2+} occurs precipitation. Xue Liu's(Liu,2010) experiments indicate that the electromotive force of Cr (VI) reduction ($E^0=1.23$) in the acidic condition is larger than that in the alkaline conditions. Therefore, it can be concluded that Cr (VI) reduction reaction is easier in low pH. Hellerich(Hellerich,2005) also confirmed that when pH is less than 4, about 50% of Cr (VI) are reduced to Cr (III); but in neutral water, Cr (VI) concentration and total chromium are similar. Therefore, Cr (VI) compounds are only existing in neutral or weak alkaline environment (Sun, 2007).

Soil redox potential determines the form and concentration of chromium and the main mineral elements in system (Su,2010). The higher the redox potential, the stronger the oxidation ability, the more easily the Cr (III) oxidation reaction occurs, and the more stable the Cr (VI) exist. When the redox potential is relatively low, Cr (III) forms insoluble compounds with sulfide easily, being fixed by clay minerals or closed by iron and aluminum oxides.

Precipitation- Dissolution.Cr (VI) compound solubility is large in general, but it can precipitate with barium, lead, silver and other heavy metal ions (Zhao,2006).However, Due to low concentrations of these metal, Cr (VI) in water has strong ability.

Cr(III) precipitation include oxide, hydroxide and chromium dihydrogen phosphate. Due to the

presence of alkaline substances, carbonate and other pH buffer substances in the soil and groundwater, and the solubility product of $\text{Cr}(\text{OH})_3$ is small ($K_{\text{SP}}=5.4 \times 10^{-31}$), which make most of the Cr (III) transfer from groundwater to soil as $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ (Dong,2006). In the water-rock system, Cr (III) began to precipitate at $\text{pH} > 4$, at the range of $\text{pH} 4\sim 6$, Cr (III) precipitation increased with pH , and at $\text{pH} 5.5$, Cr (III) almost all precipitated. (Sun,2010; Yang,2011). This precipitation is ligand molecules of Cr (III) and water or hydroxyl. In the strong alkaline water of $\text{pH} > 10.5$, Cr (III) hydrolysis occurs, generating $\text{Cr}(\text{OH})_4^-$ ion, precipitated Cr (III) partly transfer into water again, at this time, the soil colloid is also with strong negative charged and $\text{Cr}(\text{OH})_4^-$ is free (Chen,1994) in liquid phase. In the range of $\text{pH} 3\sim 7$, phosphate anions which mainly dominated by H_2PO_3^- can precipitate with Cr (III) to generate $\text{Cr}(\text{H}_2\text{PO}_4)_3$ precipitation in the water so that Cr (III) concentration decreased rapidly, the existence of phosphate to Cr (III) pH rapidly decreased critical precipitation. But the presence of phosphate has little effect on Cr(III) hydrolysis.

pH has a significant effect on the solubility of Cr (III). Changxun Dong (Dong,2006) considered that the rise of pH leads to Cr (III) hydrolysis degree enhanced that form $\text{Cr}(\text{OH})_3$ precipitate, which can improve the stability of Cr (III). Bin Yang (Yang,2006) believed that, at low pH , Cr (III) can form organic complexes, so that the migration ability is improved; at $\text{pH} > 4$, Cr (III) solubility reduced, and completely precipitated at $\text{pH} 5.5$. Cr (III) could form polycyclic compounds of chromium, and ultimately precipitated as chromium hydroxide in alkaline water. Kun Zhao (Zhao,2006) found Cr (III) can be adsorbed by hydrated iron, aluminum oxide on the surface to be the component of the crystal in weak acidic or alkaline conditions, thus forming the co-precipitation.

Other ions in the water-rock system can be co-precipitated with Cr (III). Huifang Sun (Sun,2010) found that in the presence of organic matter, the existence of AlCl_3 and FeCl_3 makes a contribution to the removal of Cr (III) from the water, and in most cases, the co-precipitation of AlCl_3 is better than FeCl_3 . Xiuli Yang (Yang,2011) proved that the hydrolysis of calcite in Ma Lan loess (i.e. carbonate) can cause the Cr (III) co-precipitation reaction by simulation and experiment of water-rock interaction.

Complexation-Dissociation. Complexation is a complicated process of metal ions and inorganic or organic ligands (Ding,1998). Complex and free ion are in a balanceable and dynamic state, which has significant influence on the adsorption. In natural water, Cr (VI) generally will not generate coordination compounds, while inorganic ligands and organic with negative charged form stable complexes with Cr (III).

Cr (III) can form complexes with hydroxyl, ammonia, fluoride, cyanide, thiocyanate, bromide ion, sulfate and other inorganic ligands. Guo Wang (Wang, 1994) argues that these inorganic ligands affect adsorption by complexing with Cr(III). Jingsheng Chen (Chen,1975) believes that the complexation of hydroxyl on heavy metal is actually the hydrolysis reaction of heavy metal ions, improving the solubility of heavy metal hydroxides greatly. In recent years, the complexation of organic matter and Cr (III) become the focus of research, including the complexation ability of different kinds of organic matter, the mechanism of complexation reaction, the stability of complex, influencing factors of complexation, etc. There are hydroxyl, carboxyl, enolate, sulfonic acid, amino and many other important complexing functional groups and chelating groups in the organic matter of the soil. Complexing functional groups can provide electronic, generating metal-organic complexes with metal ion, while chelating groups have more than two electronic ligands that forming chelating. Yajun Wang (Wang,2007) believes that the humic acid containing many functional groups, with large amount of negative charge, so that the adsorption of heavy metal cations is high, but considering that the surface of soil colloids are also negatively charged, the humic acid only combined with chromium ion to change the valence of the chromium ions, in order to enhance the interaction between chromium ion and soil particles. Jiang Jiang (Jiang,2001) holds that the complexation of the dissolved organic matter and heavy metal is prone to form soluble complexes, enhancing the solubility of heavy metals. Huifang Sun (Sun,2010) proved that EDTA is a ligand with six teeth that has the strongest chromium complexing ability by studying on the

removal of Cr (III) from water under the existence of a variety of organic compounds respectively; in addition, citric acid easily form complexes with chromium due to providing 3 matching site.

The Simulation

The mathematical models used to describe the dynamic characteristics of chromium migration and transformation are usually Langmuir equation, the Temkin model, Henry model, the first order dynamic model, the second-order kinetic equation, the Elovich equation etc. At present, much research carried by domestic and foreign scholars show that the Freundlich equation, Langmuir equation can simulate chromium adsorption process more properly in the soil.

Yan Feng(Yan,2008) believes that the soil pH of Cr (VI) have a greater impact on apparent adsorption dynamics. The first order kinetic equation and parabolic model can better characterize the Cr (VI) characteristics of the adsorption kinetics in acidic soil, correlation coefficient was 0.99, while these equations cannot extend to alkaline soil. Ailing Ren (Ren,2000) and UweBuczko(UweBuczko,2004) preliminarily analyze the mechanism and adsorption dynamic of chromium migration and transformation in unsaturated zone through the soil column leaching experiment and numerical simulation, found that the isothermal adsorption process of Cr (III), Cr (VI) both accorded with Langmuir equation. About the chromium reduction and precipitation reaction, most studies have demonstrated that the reduction between Cr (VI) and sulfide is the first order reaction. But the research of Junxiang Yang(Yang,2005) on the reaction kinetics and the factors of Cr (VI) and S^{2-} in solution at constant temperature and anaerobic conditions showed that the initial reaction stage is the first order reaction in the constant solution pH (7~9) and excessive sulfide, the reaction rate was significantly increased at the late reaction.

In recent years, research on simulation has been paid more attention to. The software applied widely are numerical simulation software Visual-Modflow and geochemical simulation software Phreeqc. Visual Modelflow is applied to simulate the migration process of pollutants in the groundwater, widely used in the actual field, but rarely used in chromium migration research in domestic and abroad. While Phreeqc can choose some equations describing the corresponding chemical reactions, calculating the composition of multiphase equilibrium solution. Jeanine (Jeanine,2002) applied the Phreeqc software to simulate chemical equilibrium to predict the concentrations of various ions in chromium slag leachate and the variation of pH, which showed that Cr (VI) in chromium slag exist in chromium calcium aluminate (sandwiched layered double hydroxides with chromium) and hydrogarnet containing Cr (VI) , solid phase dissolved lead to the dissolution of Cr (VI) , calcium, aluminum, silicon and magnesium in the range of pH8~12. Under natural conditions pH is unlikely to change much in the landfill due to high pH buffer capacity of chromium slag. Xiuli Yang (Yang,2011) analyze the component, surface structure, surface site concentrations and cation exchange capacity and other characteristics of Malan loess, according to the result of analysis, Phreeqc was utilized to establish the water-rock interaction model of Malan Loess and Cr (III), and carried out the variable initial concentration experiment, removal of carbonate experiment and extraction experiment, which illustrate that the removal of Cr (III) by Malan loess in aqueous solution are mainly chromium precipitation and co-precipitation caused by the hydrolysis of calcite and surface chromium complexation of manganese oxide, supplemented by chromium cation exchange of silicate minerals.

Conclusions

Cr transfers in the groundwater-rock interface through adsorption and desorption, oxidation and reduction, precipitation and dissolution and complex and dissociation,which influenced by groundwater pH, Eh, organic matters, other coexisting ions and the properties of the aquifer,etc. Due to the complexity of several reactions, existing at the same time and difficulty in distinguishing, and different features of migration and transformation in different soil and water, it's an extremely difficult assignment to determine the chromium behavior of migration and transformation., It is necessary to Improve the knowledge of chromium behavior in water-rock interface to accurately determine the potential crisis, and also can improve the method to reducing

the danger of pollution area to the lowest level, adopt effective methods to repair and governance unsaturated zone and underground water contaminated by chromium.

At present, most research on chromium contaminating in groundwater-rock interface stay in the stage of laboratory simulation, lack of combination of aquifer of actual contaminated sites and groundwater characteristics, and the research of a plurality of effect factors is not enough, that is urgent to carry out the simulation research of the actual site . Revealing the mechanism of chromium pollution in water-rock interface with a number of interactions, establishing pollution model of the actual sites is conducive to predict chromium contaminated site pollution more accurately, so that the control of chromium pollution in groundwater has much more pertinence.

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