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Investigations on different positions of electrodes and their effects on the distribution of Cr at the water sediment interface

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ABSTRACT: In most mining areas, significant concentrations of metals such as Pb, Cu, Cr, Zn, Cd, Fe, Mn, Co, Ni, Hg, Ar, halogenated organic compounds and radionuclides are found. Of those, Cr is one of the well-known heavy metals that forms toxic species. It is necessary to study the mobilization and accumulation of Cr at the sediment water interface in an electric field at varying different positions and conditions of the electrode arrangement. The tests were carried out with a natural sediment containing heavy metals from the river Weisse Elster (Germany). The electrokinetic experiments have been performed in columns filled with sediment using electrodes made of conductive polymers (polyethylene with carbon black) at a maximum current density of 0.5 mA/cm^2. The experimental results suggest that the mobilization and accumulation of Cr highly depends on chemical factors for e.g., pH value, redox potential, respectively redox status and the content of Fe, Al and organic matter in the soil or sediment. The sorption of Cr (III, VI) is very high in the pH range > 4.5. As expected, a high mobilization of Cr (III, VI) was seen in the case of the experiments with the anode at the sediment, because the pH value was lower than mentioned above. On the opposite, the best conditions for the Cr (III, VI) immobilization is high pH values (cathode at the sediment).

Key words: *Chromium, electrokinetic, pH-barrier, Eh-barrier, heavy metals, sediment, remediation*

INTRODUCTION

It has been found that the soils and sediments around old mining areas and former industrial sites are contaminated with heavy metals (EPA, 2000; Mulligan, *et al.*, 2001; Shrestha, *et al.*, 2003; Aliabadi, *et al.*, 2006). Cr is one of the common contaminants found there in surface waters, ground waters, soils, sediments, rocks, plants and animals. In addition Cr is widely used in the production of stainless steels, iron and nonferrous alloys as well as for plating wood preservations and leather tanning. It was also used as corrosion inhibitor in cooling towers and as component of fungicides. Cr exists in three oxidation states (II, III and VI). Especial attention is paid to Cr (VI) because of its potential to cause cancer in humans. It is highly soluble and mobile under neutral and higher pH conditions (Kortenkamp, *et al.*, 1996). Methods of cleaning contaminated soils and sediments by Cr are in high demand. Electrokinetic remediation is a clean and one of the most cost effective in situ technologies (Pamukcu, *et al.*, 1997; Puppala, *et al.*, 1997; Shrestha, *et al.*, 2003). A basic process of the electrokinetic remediation is the electromigration, where cations move to the cathode and anions towards anode in an electric field. Cr (VI) forms chromate (CrO_4^{2-}) and hydrogenchromate ($HCrO_4^-$) anions in aqueous solutions. Cr (III) is less toxic than Cr (VI), but large doses can also be on toxic. Former researchers had performed with the remediation rate or movement of these ions in the electric field with various surfactants, potentials and supplied current (Pamukcu, *et al.*, 1997; Puppala, *et al.*, 1997; Reddy, *et al.*, 1999; Manna, *et al.*, 2003; Sawada, *et al.*, 2003). It is still unknown, how the mobilization and immobilization occur with different electrode arrangements. The study pursues the aim to get a new fundamental knowledge about the mobilization and immobilization of Cr on the applications of different arrangements of electrodes in the remediation process.

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MATERIALS AND METHODS

Sediment sample was collected from the river Weisse Elster, near Kleindalzig, Germany, an old mining area on 01.03.2001. The most important parameters of the sediment were: the initial Cr (III, VI) concentration: 235.9 mg/kg, pore water pH of 5.85, organic content: (9.4 %), total sulphur: (14.9 g/kg) iron: (68.5 g/kg) and Mn: 600 mg/kg. Tap water from Dresden, Germany was taken for the experiment. It was almost free from Cr and had a pH value of 8.1. Electrodes were made from environmental friendly conductive polymer (polyethylene with carbon black) with a specific resistance of about 20 Ω/cm.

Analytical reagent grade chemicals and double-distilled water were used for preparing all solutions. Stock solutions containing 1,000 mg/L of the analysts were prepared from metal nitrates in 1 % HNO_3 solution. Working standard solutions were prepared by appropriate dilutions of the stock solutions. Blank determinations were run by using the same reagents in equal quantities as described in the analysis procedure throughout the experiments.

Electrokinetic reactor

A schematic diagram of the experimental setup is shown in Fig. 1. The set up consists of PVC tubes (length: 0.6 m, diameter: 0.12 m). It was filled up at first with 1,700 g sediment, (covered 0.12 m of its depth) and then with water ratio of 4:1 by volume with sediment in the column. After filling the columns, the two electrodes were installed in different position according to the requirements of the experiments. The middle coverage of the electrode in relation to sediment surface was 20 %. The distance apart of two electrodes was 8 cm and used voltage 3 V (electric field strength: 37.5 V/m) (Shrestha, *et al.*, 2003). The voltage could be adjusted by external control devices. Two sampling pipes for taking the water sample for analysis and Pt-wires for measuring redox potential were fixed near to the anode and to the cathode. Besides a small fermenting tube for balancing the inside pressure was installed.

The sequential extraction after (Förster and Calmano 1982) was applied to determine the initial binding forms of Cr and total concentration in the sediment.

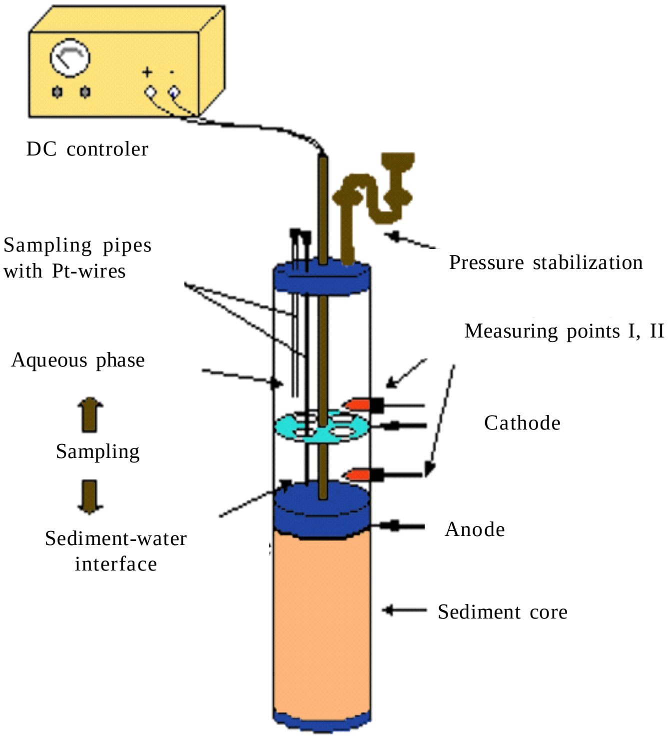

Fig. 1: Experimental assembly (Shrestha, *et al.*, 2003)

All experiments were carried out at room temperature without light to prevent from unnecessary development of oxygen by autotrophic organisms and biomass. The water samples were taken from water sediment interface periodically for long time to observe the trend of accumulation and mobilization with respect to time and pH. Water samples were taken in a day gap initially and at 15 days gap in the later stage. Every time, 10 mL of water sample was taken without affecting the system of the column. The taken volume was refilled with tap water after sampling. The metal concentrations were measured by using an atomic absorption spectrometer with induced couple plasma (ASS-ICP, ZEISS, Jena).

RESULTS

Binding form of original Cr in sediment

The sequential extraction procedures give an idea of the distribution of the different chemical forms of Cr in the sediment matrix. Fig. 2 illustrates the results of this procedure. It is clearly to be seen that nearly 50 % of the total Cr existed in form of oxides or hydroxides and more than 40 % as organometals or sulphides or thioorganometals. From analysis of the redox status follows that in the sediment had more Cr (III) than Cr (VI).

Arrangement of electrodes

Results of the measurement at the water sediment interface

The concentration at the interface increased gradually from 0.7 µg/L to 9.12 µg/L in the reference column during the experimental time of 181 days (Fig. 3). The pH value was almost in steady state condition at 6.5. At pH 6.5, most Cr(VI) is present as CrO_4^{2-} ions. It was noted that Cr (III) (if available) could be oxidised to Cr (VI) by reaction with Mn ions (Moore and Ramamoorthy, 1986), although the reaction rate was not appreciable affected by dissolved oxygen, slightly acidic or basic conditions limited the oxidation rate. Probably, this is the cause that Cr was released from sediment to interface. The most of Cr was Cr (III). The released Cr is the exchangeable Cr at the soil surface. In the case of anode at the sediment-water interface and cathode in the aqueous phase, at the phase II, the pH decreased from pH = 6.5 to 2-3.0 (Fig. 3a). The observed Cr concentration increase at the interface from 2 µg/L to maximal 250 µg/L. The Cr-mobilization rate was high at phase II. From the sequential extraction it was already proved that there was the most Cr in Cr (III). This attachment decreases with increasing pH. Fig. 3c shows similar trend as Fig. 3a. When the anode is 8 cm below the sediment-water interface and cathode at the sediment-water interface, at the phase II (Fig. 3b), the pH increased from 6.0 to 12.0. Fig. 3d shows similar tend as Fig. 3b.

Results of the measurement in the sediment

Fig. 4 shows the pH profile of the experimental columns at various conditions in the sediment. In Fig. 4 a, due to formation of hydrogen ions at the anode, pH was lowered from 6.7 to 5.0 after 180 days of voltage supply at the interface. It shows that once the sediment is acidified, it takes long time to neutralize it under currentless conditions. The pH-profile of the interstitial water showed clearly that the acidic front reached the sediment horizon (0 to -6 cm depth) after 180 days. In this depth, the sediment buffered the acidification and became neutral.

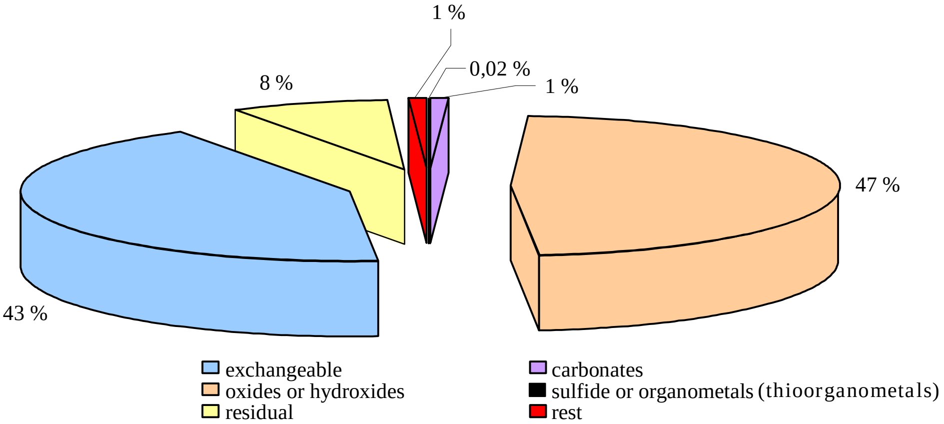

Fig. 2: Percentage of Cr in different binding forms in sediment after sequential extraction (Shrestha, *et al.*, 2001)

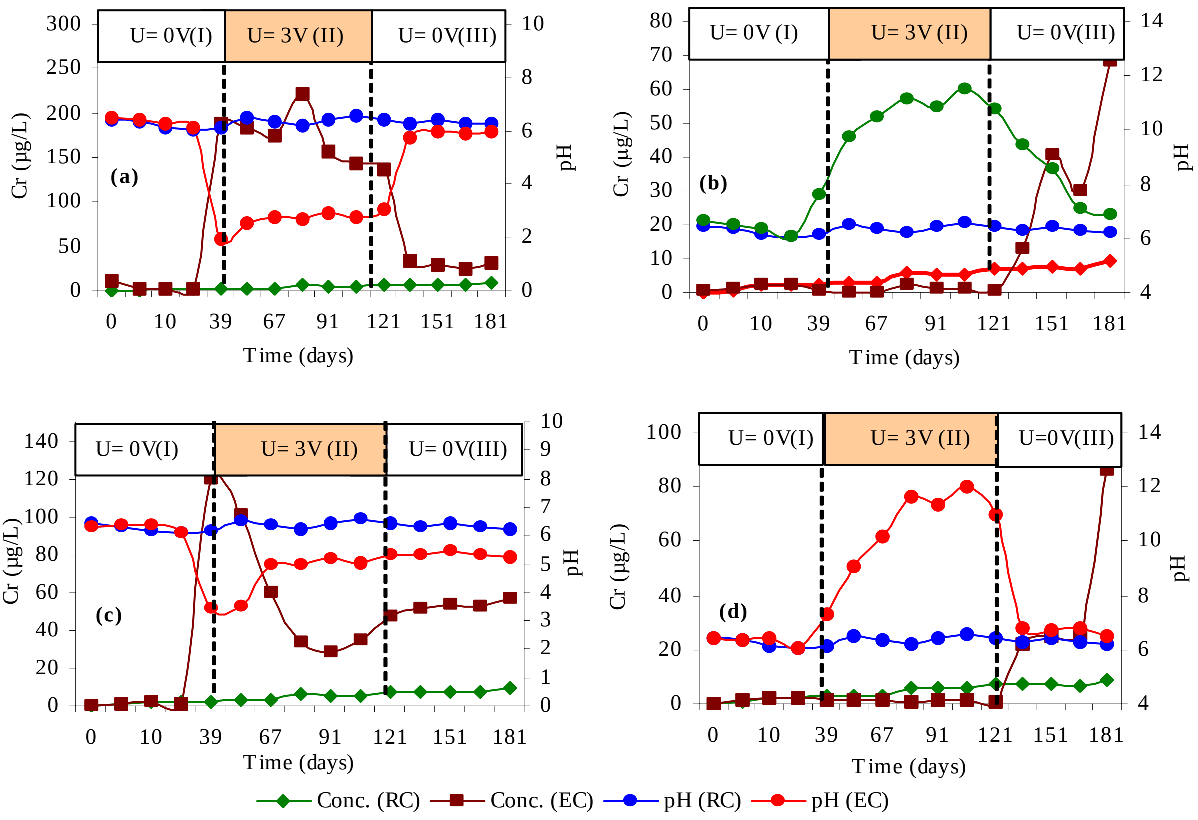

Fig. 3: Temporal changes in total Cr concentration and pH values at the sediment water interface in the experimental column (EC) (with U = 3 V/without voltage) and in the reference column (RC) (Fig.: 3a) anode at the sediment water interface and cathode in aqueous phase, Fig.: 3b) cathode at and anode 8 cm below the sediment water interface, Fig. 3c) anode 4 cm above and cathode 4 cm below the interface and Fig. 3d) cathode 4 cm above and anode 4 cm below the sediment water interface]

In Fig. 4b, the pH-profile of the interstitial water show that the alkaline front reached the first sediment horizon (0 to -2 cm) after 180 days.

In this area, pH was in the range of 8-9. In deeper sediment horizons the anode influence becomes always greater. The anodically produced protons are neutralized and in sediment depth of about 6 cm the pH is about 6. It is know that hydrogen ions can move twice time faster than that of hydroxide ions. Therefore, at a sediment depth of 4 cm, the pH value is lower than 7.0. In Fig. 4c, the pH-profile of the interstitial waters showed the alkaline front reached in the first sediment horizon (0 to -2 cm) after 180 days as in Fig. 4b. But, the pH was not so high as in Fig. 4b or it came near to neutral pH value of ~ 7.5. With the pH profile in the sediment, the distribution of the metals in the sediment also changes. Following explanations (Fig. 5) shows the distribution of Cr in the sediment phase. In contrast to Cr (VI), Cr (III) is relatively immobile in soil. Regardless of pH and redox conditions, most Cr (VI) in soil is reduced to Cr (III) under anaerobic conditions. pH of 5at the first sediment horizon (0 to -2 cm depth) went to 4.56; may be this was the preferable condition to migrate chromate to the anode. Very little Cr (VI) and Cr (III) might migrate to the interface as Cr (III) has stopped transport after pH 5.5. In case of the results of the experiment in Fig. 5b, the trend of Cr was just similar to the case of Fig. 5a because only chromate started to migrate towards the anode. In case of Fig. 5c, the anode might attract the anions. From the experiments, it can be shown that the best arrangements where Cr can accumulate in the sediment to make water free from the contaminants are the conditions as to be seen in Fig. 4 and Fig. 5. If decontamination of sediment is needed, anode should be kept at or 4 cm above the sediment-water interface (Table 1).

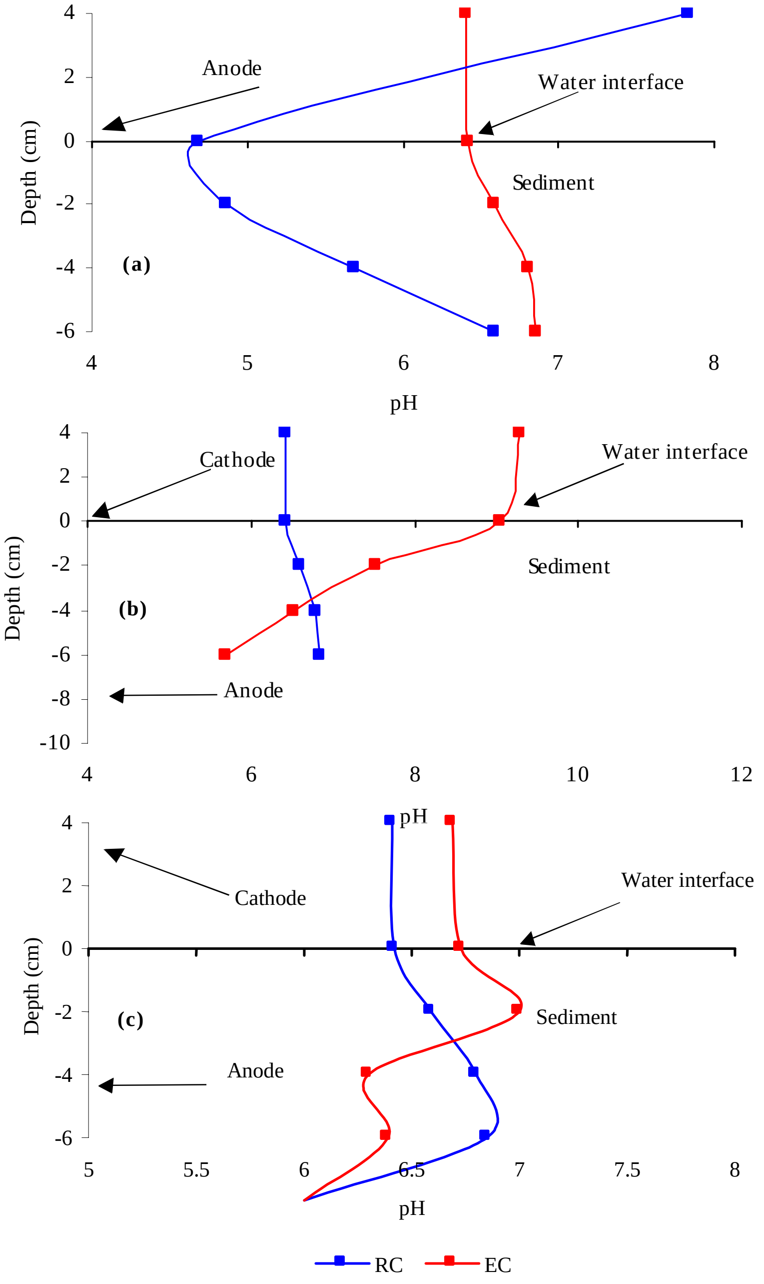

Fig. 4: pH profiles at the sediment water interface after 180 days of voltage supply, U = 3 V
[4a: Anode at the sediment water interface and cathode in aqueous phase; 4b: Cathode at and anode 8 cm below the sediment water interface and 4c: Anode 4 cm below and cathode 4 cm above the sediment water interface]

DISCUSION AND CONCLUSION

The batch experiments were conducted at maximum current density of about 0.5 mA/cm^2 in the columns fitted with electrodes made from conductive polymers at room temperature in absence of direct daylight. The mobilization or accumulation of Cr at the sediment water interface at different electrode positions s were studied by measuring pH and heavy metal concentrations in water and sediment.

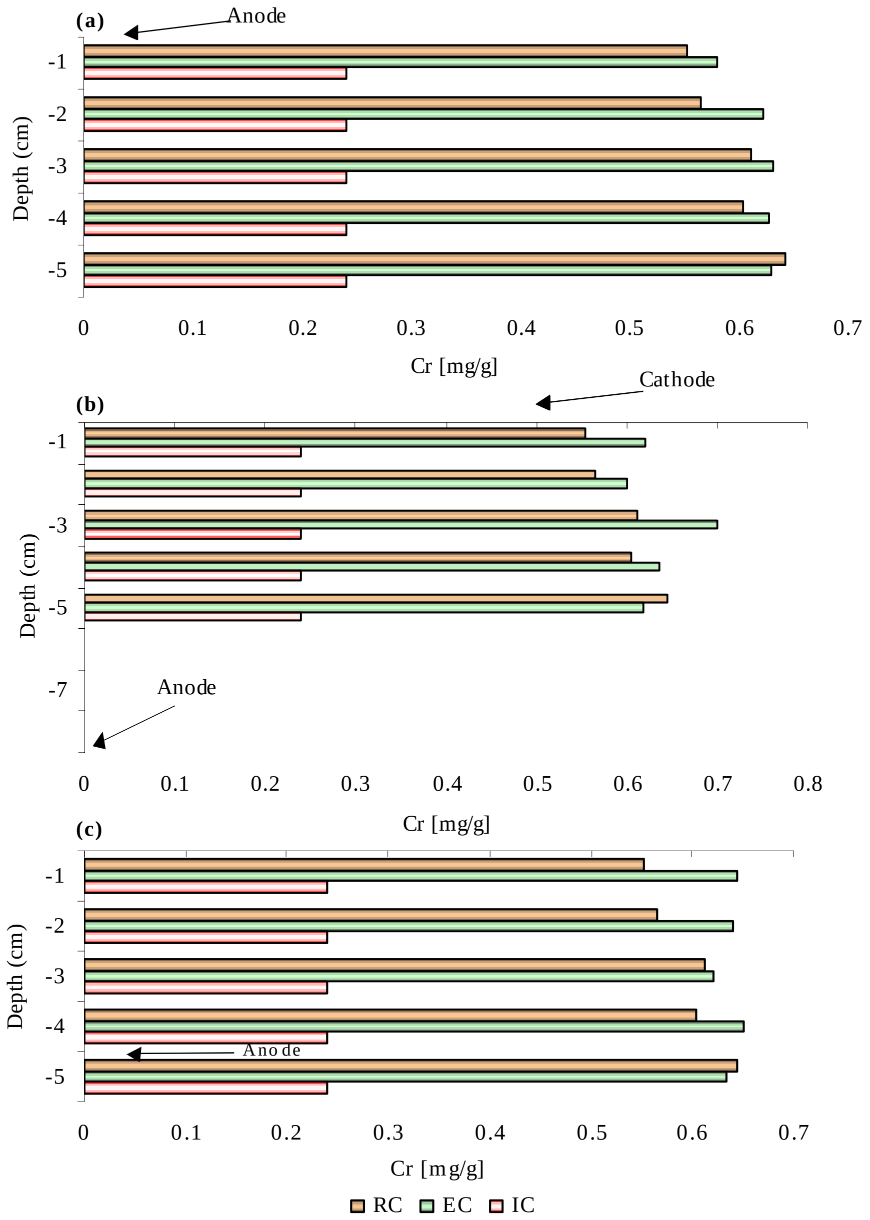

Fig. 5: Cr distribution profile after 180 days of voltage supply, U = 3; V= constant (5a: Anode at the sediment-water interface and cathode in aqueous phase; 5b: Cathode at and anode 8 cm below the sediment water interface and 5c: Anode 4 cm below and cathode 4 cm above the sediment water interface)

Table 1: Increment percentage of chromium at water sediment interface after supplying voltage

Type of column	Average Cr concentration at the interface (µg/L)	Increment with respect to RC (%)
reference column (RC)	4.3	+ 0
column with anode at interface	150	+ 35
column with cathode at interface	0.94	- 0.74
column with anode 4cm above and cathode 4cm below the interface	68.5	+ 15
column with cathode 4cm above and anode 4cm below the interface	1.2	-0.72

The highest mobilization of Cr was found when the anode was placed at or above the interface where an acidic front was clearly observed. The pH effect on uptake and distribution of Cr may be attributed to presence of different Cr species in the exposure solutions. Stum and Morgan (1981) reported that at higher pH, the molar ratio of CrO_4^{2-} to $HCrO_4^-$ was 1: 0.05, while at lower pH, this ratio was 1:1 indicating that the $HCrO_4^-$ concentration increased at same total Cr concentration. Adsorbed Cr (III) and Cr (VI) at iron oxides, aluminium oxide are mobilized at acidic pH and oxic conditions. The existence of $Cr_2O_7^{2-}$ is not possible because extremely low pH values and strong oxidizing conditions are necessary for it. Chromate in the sediment can only be reduced to Cr (III) by accepting electrons e. g. from Fe (II) under anaerobic condition regardless of pH and Eh (eq. 1). The reaction rate is very slow in presence of organic matter under environmental pH and temperature conditions, but the reaction rate increases with decreasing in pH value.

$$CrO_4^{2-} + 3Fe^{2+} + 8H^+ \Rightarrow Cr^{3+} + 3Fe^{3+} + 4H_2O \qquad (1)$$

At pH values; less than pH 4.5, Cr (III) is the dominant Cr species according to species distribution in aqueous phase. $[Cr^{3+}] > [CrO_4^{2-}]$. At very low pH values and oxidizing conditions $[Cr_2O_7^{2-}]$ and $[CrO_4^{2-}]$ are the dominant species. They have high affinity to sediment surfaces at positively charged sites.

$$(=SOH_2^+)_2\,CrO_4^{2-} \Rightarrow 2\,(=SOH_2^+) + CrO_4^{2-} \qquad (2)$$

$$2\,(=SOH_2^+) + 2OH^- \Rightarrow 2(=SOH) + 2\,H_2O \qquad (3)$$

The mobilized ions may be moved towards the anode and Cr^{3+} which mobilized at the phase II, completely precipitated as Cr $(OH)_3$ at higher pH value at the phase III (eqs. 4-7).

$$Cr^{3+} + OH^- \Rightarrow Cr(OH)^{2+} \qquad (4)$$

$$Cr(OH)^{2+} + OH^- \Rightarrow Cr(OH)_2^+ \qquad (5)$$

$$Cr(OH)_2^+ + OH^- \Rightarrow Cr(OH)_3^0 \qquad (6)$$

$$Cr(OH)_3^0 \Rightarrow Cr(OH)_3(s) \qquad (7)$$

The best immobilization condition for Cr is in the case where the cathode was at or above and anode below the interface. Under alkaline conditions Cr (III) will be precipitated as hydroxide (eq. 7,8),

$$Cr^{3+} + 3CO_3^{2-} + 3H_2O \Rightarrow Cr\,(OH)_3\,(s) + 3\,CO_2 \times H_2O \qquad (8)$$

CrO_4^{2-} got left from the sediment surface, moved to the aqueous phase. If there is Cr (VI) as the chromate in the water, there is an adsorption at the interface at low pH - value or a mobilization at weak acid, neutral and especially high pH value. It is the important point to take in account of the distribution of metals in the sediment with pH profile in the sediment. After 180 days of current supply, it was found that pH of the interstitial water decrease when anode is at or a few centimetres below the interface and cathode inside the sediment. There the Cr concentration was found to be low near the interface. pH values were in the range of 6.5-8.5, when the is positioned anode 8 cm or 4 cm below and cathode 4 cm above the interface. Under this condition Cr were accumulated at the interface. Electrochemical method is a good method to influence the migration, immobilization and mobilization of Cr but before using this method, one must study the chemistry and the interaction processes of the metal or metal complex and the solid matrix. It is beneficial to gain knowledge of the contaminant type.

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