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AQUEOUS GEOCHEMISTRY OF CHROMIUM: A REVIEW

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Abstract—The aqueous geochemistry of chromium is reviewed, especially with reference to the recent work of Rai *et al.* (Report EPRI EA-4544, 1986, Report EPRI EA-5741, 1988). The chromium content of natural waters is generally low whereas rocks exhibit a wide range of Cr concentrations. In natural environments, the most stable oxidation states of chromium are Cr(III) and Cr(VI). The following minerals can control the dissolved chromium content of natural waters: $Cr(OH)_3(s)$ and $(Fe, Cr)(OH)_3$ (ss) for Cr(III). Major Cr(III) disolved species are $CrOH^{2+}$ and $Cr(OH)_3^0$, as well as several organic and a few inorganic complexes, whereas $HCrO_4^-$ and CrO_4^{2-} are the main forms of Cr(VI) in natural waters. The chromium distribution is also controlled by redox processes. Oxidation of Cr(III) to Cr(VI), poor with dissolved oxygen, is very effective in the presence of solid MnO_2. Fe(II)- and organic matter-rich environments favour the reduction of Cr(VI) to Cr(III). Interaction with solid phases can also regulate the chromium content of water. Cr(III) exhibits a typical cationic sorption behaviour. Its adsorption increases with pH, but decreases when competing cations are present. Chromium (VI), on the other hand, exhibits a typical anionic sorption behaviour. Its adsorption decreases with increasing pH and when competing dissolved anions are present.

The migration of chromium is determined by the competition between complexation, dissolution/precipitation, redox processes and adsorption/desorption mechanisms. Cr(III) will migrate under acidic conditions and/or if present as dissolved organic matter complexes. Hexavalent chromium generally migrates rapidly but its mobility is inhibited when the Fe(II) and organic matter concentrations are high and when sorption processes are favoured (low pH).

Key words—chromium, geochemistry, natural waters, review, minerals, oxido–reduction, adsorption, migration

INTRODUCTION

Chromium is an essential nutrient for plant and animal metabolism (glucose metabolism, amino- and nucleic acid synthesis). However, when accumulated at high levels, it can generate serious trouble and diseases (nausea, skin ulcerations, lung cancer) and, as concentration reaches 0.1 mg/g body weight, it can ultimately become lethal (Mertz, 1974; Ajmal *et al.*, 1984). Chromium(VI) is the most toxic form for bacteria, plants and animals (Benoit, 1976; Mathur *et al.*, 1977; Ross *et al.*, 1981; Ajmal *et al.*, 1984).

Steelworks, chromium electroplating, leather tanning and chemical manufacturing produce high chromium wastes. Understanding the behaviour of chromium in natural aquatic systems is therefore of major concern. When confronted with the pollution of an aquatic system by chromium, it is important to know which are the major species involved, and what velocity and concentration of the migrating element can be expected.

The present paper reviews the basic reactions of the aqueous geochemistry of chromium and discusses the major parameters which control its migration in aquatic environments. Our objective is to provide, for geochemists and other professionals involved in Cr contamination problems, an up-to-date basis for the sound management of chromium water pollution or waste disposal.

OCCURRENCE OF CHROMIUM IN AQUATIC AND TERRESTRIAL ENVIRONMENTS

The chromium content of natural solids varies widely with the type and nature of rocks or sediments (Table 1). Granite, carbonates and sandy sediments present the lowest chromium content whereas shales, river suspended matter and soils typically exhibit highest levels. Highest chromium contents tend to be associated with finest grain size soils (Robertson, 1975) and sediments (Salomons and De Groot, 1978).

In natural waters, the range of chromium concentrations is quite large (Table 2). The median value in unpolluted fresh or seawater is usually low (less than 50 nmol/l). However, natural concentrations as high as 4 μmol/l have been observed. These high concentrations of dissolved chromium are usually associated with the very soluble chromate species (Robertson, 1975). For most natural waters, the Cr concentration is nevertheless below the 50 μg/l value (approx. 1 μmol/l) recommended for drinking water by the Commission of European Communities, the World

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Table 1. Chromium content of natural solids

Type of solid	Chromium content (μmol/g) Typical	Range	References
Lithosphere	2.4	1.5–3.8	a, b, c
Granite	0.4	0.02–0.5	d
Sandstone	0.7	0.2–1.9	e
Shale	1.7	1.7–7.7	d, e
Carbonate	0.2	0.02–0.3	e
Coastal suspended matter	—	0.01–0.21	f
Deep-sea clay	1.8	1.1–2.1	d, e
Marine sediment	—	0.2–0.7	h
River sediment	—	0–2	h
River suspended matter	3.6	—	i
Sandy sediment	0.5	0.3–0.7	d
Clayey sediment	1.2	0.7–1.6	i
Clay	2.3	0.6–11.3	c
Soil	1.9	0.02–58	a, e, j

(a) Jones and Jarvis (1981); (b) Mason (1958); (c) Vokal *et al.* (1975); (d) Matzat and Shiraki (1978); (e) Förstner and Wittmann (1979); (f) Jeandel and Minster (1984); (g) Elderfield (1970); (h) Robbe *et al.* (1984); (i) Turekian and Scott (1967); (j) Kick *et al.* (1971).

Health Organization or the U.S. Environmental Protection Agency.

MAIN CHROMIUM FORMS IN NATURAL AQUATIC SYSTEMS

Like all transition metals, chromium can exist under several oxidation states from Cr(0) (the metallic form) to Cr(VI). However, only the trivalent and hexavalent forms are important in the Eh–pH range of natural aquatic systems.

Main dissolved species of chromium

In low Eh environments, the main aqueous Cr(III) species are Cr^{3+}, $Cr(OH)^{2+}$, $Cr(OH)_3^0$ and $Cr(OH)_4^-$ (Rai *et al.*, 1986, 1987). The Cr^{3+} species is prevalent only at pH lower than 3.6 (Fig. 1). Polymeric species such as $Cr_2(OH)_2^{4+}$, $Cr_3(OH)_4^{5+}$ and $Cr_4(OH)_6^{6+}$ are never significant in natural systems (Rai *et al.*, 1986, 1987). Trivalent chromium behaves as a typical "hard" Lewis acid and readily forms complexes with a variety of ligands: hydroxyl, sulphate, ammonium, cyanide and sulphocyanide, fluoride and chloride (to a lesser extent), and natural and synthetic organic ligands (Deltombe *et al.*, 1966; Bartlett and Kimble, 1976; Nakayama *et al.*, 1981b; Morel, 1983; Payà Pérez *et al.*, 1988).

Table 2. Dissolved chromium in natural and man-made waters

Type of water	Chromium concentration (nmol/l) Typical	Range	References
Seawater	3	0.1–16	a–j
Interstitial water (marine sediments)	—	1.0–6.6	k
River	10	0–2200	l, m, n
Lake	—	<2 – 33	o, p, q
Groundwater	<20	10 – 4000	r–u
Polluted water	—	960–27,000	v
Tap water	8	0–700	w

(a) Grimaud and Michard (1974); (b) Cranston and Murray (1978); (c) Nakayama *et al.* (1981a); (d) Nakayama *et al.* (1981c); (e) Campbell and Yeats (1981); (f) Murray *et al.* (1983); (g) Cranston (1983); (h) Jeandel and Minster (1984); (i) Jeandel and Minster (1987); (j) Sherrell and Boyle (1988); (k) Gaillard *et al.* (1986); (l) Kopp and Kroner (1968); (m) Trefry and Presley (1976); (n) Cranston and Murray (1980); (o) Copeland and Ayers (1975); (p) Borg (1987); (q) Johnson and Sigg (1989); (r) Matthess (1974); (s) Brinckman (1974); (t) Robertson (1975); (u) Deverel and Millard (1988); (v) Permutter *et al.* (1963); (w) Vokal *et al.* (1975).

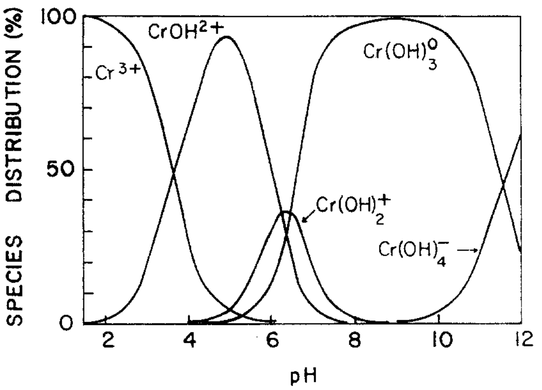

Fig. 1. Calculated inorganic chromium (III) speciation as a function of pH (solution in equilibrium with $Cr(OH)_3(s)$; equilibrium data from Rai *et al.*, 1986, 1987).

Under oxidizing conditions, aqueous chromium is present in a Cr(VI) anionic form, $HCrO_4^-$ or CrO_4^{2-}, depending on the pH (see Fig. 3).

Prevalent chromium minerals

Because of their high solubility and their requirement for oxidizing conditions, natural chromium(VI) minerals are very scarce in nature. Therefore, minerals such as $CrO_3(s)$ will not control the solubility of chromate ions under typical conditions. However, in environments rich in Ba or Pb, hydrated minerals $XCrO_4 \cdot nH_2O$ can maintain low CrO_4^{2-} concentrations (James and Bartlett, 1983; Rai *et al.*, 1984).

Under moderately oxidizing to reducing conditions, Cr(III) minerals are significant controls for dissolved chromium. Eskolaite $Cr_2O_3(s)$, even if scarce, is a possible solubility control and could maintain low concentrations of aqueous Cr at pe + pH values lower than 16 (Deltombe *et al.*, 1966; Rai *et al.*, 1984). Direct precipitation of chromite [$FeCr_2O_4(s)$] from aqueous solution is not expected at low temperature in natural systems (Hem, 1977). However, chromites are known to form readily under laboratory conditions (Rai *et al.*, 1984). $FeCr_2O_4$ (s) is not likely to be a Cr solubility controlling phase unless for acidic and reducing conditions ($pe + pH \leq 14$). Amorphous [Fe(III), Cr(III)] hydroxide is probably the main Cr solubility-controlling phase in natural environments (Fig. 2). This mixed hydroxide readily forms at room temperature and behaves as a solid solution (Fe_{1-x}, Cr_x) $(OH)_3$ (ss). For typical natural conditions, the mole fraction (x) of chromium will be low (around 1%). When the solution is free of dissolved iron, as in most laboratory experiments, $Cr(OH)_3(s)$ is considered to be the solubility-controlling phase.

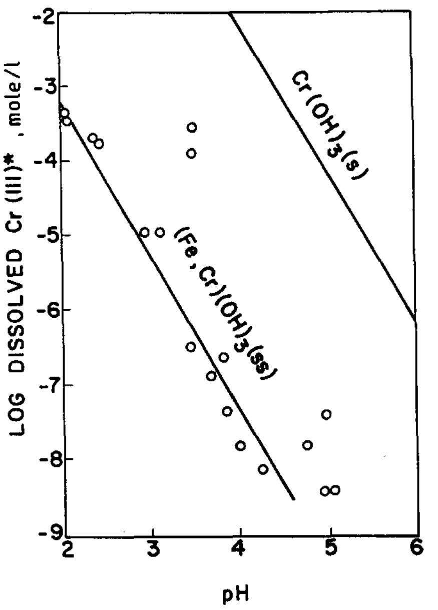

Fig. 2. Chromium activity from suspension of ($Fe_{0.99}$, $Cr_{0.01}$) $(OH)_3$ (ss) (from Rai *et al.*, 1986; in pH adjusted 0.01 M NH_4ClO_4 or $NaClO_4$ maintained under N_2 atmosphere); dissolved Cr(III) as $CrOH^{2+}$.

Redox behaviour of chromium in aquatic environments

The distribution between Cr(III) and Cr(VI) will be regulated by oxido–reduction reactions. A new Eh–pH diagram (Fig. 3) is presented here for solutions in equilibrium with $Cr(OH)_3$(s).

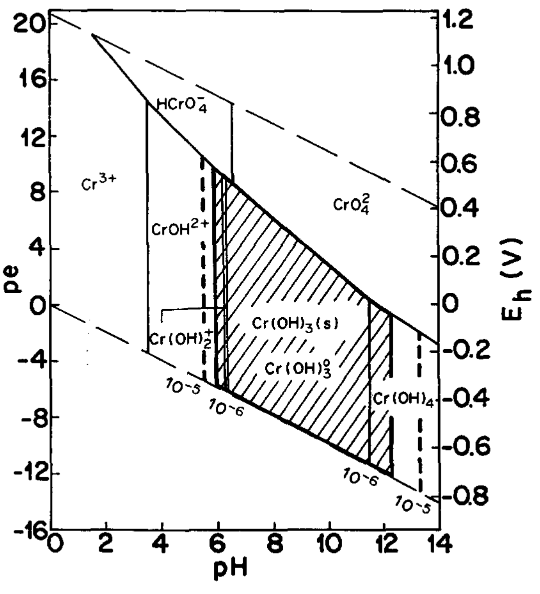

Fig. 3. pe–pH relationships for dissolved aqueous chromium species in presence of $Cr(OH)_3$(s). Equilibrium data from Rai *et al.* (1987). The hatched zone represents the domain of stability of $Cr(OH)_3$(s) for 10^{-6} M of total dissolved Cr, which can be extended to the dashed lines for 10^{-5} M of total dissolved Cr. At total concentrations of chromium lower than $10^{-6.84}$ M (7.5 μg/l), all chromium will be in dissolved form.

The redox transformation of Cr(III) into Cr(VI) or vice versa can only take place in the presence of another redox couple which accepts or gives the three necessary electrons. In natural aquatic environments, the main significant redox couples are: H_2O/O_2 (aq), Mn(II)/Mn(IV), NO_2/NO_3, Fe(II)/Fe(III), S^{2-}/SO_4^{2-} and CH_4/CO_2.

Cr oxidation. Dissolved oxygen was found to oxidize Cr(III) into Cr(VI) (Schroeder and Lee, 1975; Nakayama *et al.*, 1981b; Rai *et al.*, 1986; Eary and Rai, 1987). But the rate of oxidation at room temperature is very slow and enables trivalent Cr to be involved in faster concurrent reactions (sorption or precipitation). Therefore, the oxidation of Cr(III) by dissolved oxygen is unlikely in soils.

Manganese oxides are likely to be responsible for most Cr(III) oxidation in aquatic environments. They are present as grain coatings, crack deposits or finely disseminated grains, in relation with bacterial activities or not. The oxidation reaction would occur in three steps (Schroeder and Lee, 1975; Bartlett and James, 1979; Amacher and Baker, 1982; Rai *et al.*, 1986; Eary and Rai, 1987):

(1) adsorption of Cr(III) onto MnO_2 surface sites,
(2) oxidation of Cr(III) to Cr(VI) by surface Mn(IV),
(3) desorption of the reaction products, Cr(VI) and Mn(II).

Theoretical stoichiometries have been suggested:

$$Cr^{3+} + 1.5\delta \cdot MnO_2(s) + H_2O = HCrO_4^- + 1.5\,Mn^{2+} + H^+ \quad (1)$$

and

$$Cr(OH)^{2+} + 3\beta \cdot MnO_2(s) + 3H_2O = HCrO_4^- + 3MnOOH(s) + 3H^+ \quad (2)$$

[(1) Amacher and Baker, 1982; (2) Eary and Rai, 1987].

The solid MnOOH(s) would decay into aqueous Mn^{2+} afterwards. The Cr(III) oxidation rate, related to the amount and the surface area of Mn oxides (Schroeder and Lee, 1975; Eary and Rai, 1987) is initially rapid and slows down significantly after 20–60 min. This reaction does not reach completion. All the Mn(IV) reaction sites are probably not accessible to Cr(III) (Amacher and Baker, 1982; Rai *et al.*, 1986).

Cr reduction. Discharge of industrial wastes, decomposition of organic matter and sulfate reduction provide dissolved sulfides which can be involved in Cr(VI) reduction. This reaction, initially rapid, slows down after 5 min but reaches completion after one day (Schroeder and Lee, 1975).

Weathering of Fe(II)-containing minerals (biotite, hematite, some clays, etc.) and some industrial wastes generate dissolved Fe(II) ions. These ions can be

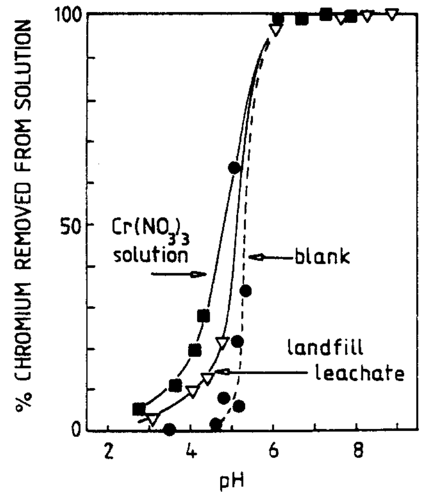

Fig. 4. Chromium (III) adsorption as a function of pH and of solution composition, at 25°C (from Griffin *et al.*, 1977). [Initial chromium concentration 1.5×10^{-3} mol/l; 2 g kaolinite/l; the curve labelled "blank" represents a $Cr(NO_3)_3$ solution without kaolinite.]

involved in Cr(VI) reduction as follows (Rai *et al.*, 1988).

$$\underset{\text{from hematite or biotite}}{[3FeO]} + 6H^+ + Cr(VI)(aq) = Cr(III)(aq) + 3Fe(III)(aq) + 3H_2O. \quad (3)$$

Chromium reduction by Fe(II) is complete within 2 min. End products of this reaction are Fe(III)/Cr(III) co-precipitates in acidic solution (Stollenwerk and Grove, 1985) and probably $Cr(OH)_3(s)$ in neutral to alkaline conditions because of the very low solubility of $Fe(OH)_3(s)$ (Rai *et al.*, 1988).

Hexavalent chromium can also be reduced by organic matter such as simple amino-acids (Schroeder and Lee, 1975) or humic or fulvic acids (Goodgame *et al.*, 1984; Boyko and Goodgame, 1986). Intermediate Cr(V) species are produced and decay into Cr(III) in a few days. This reduction is favoured by acidic conditions (Cary *et al.*, 1977; Bloomfield and Pruden, 1980; Grove and Ellis, 1980; Stollenwerk and Grove, 1985). Even if rapid in the first few minutes, the reaction is slower than Cr(III) oxidation.

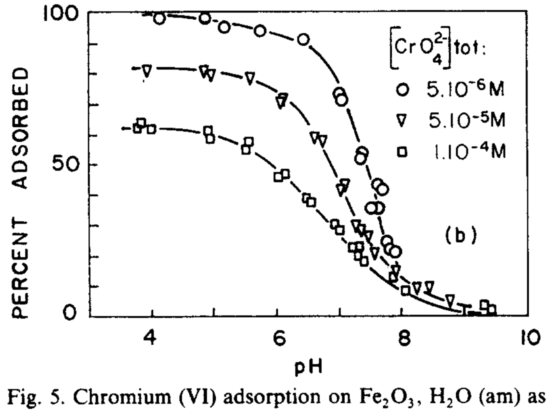

Fig. 5. Chromium (VI) adsorption on Fe_2O_3, H_2O (am) as a function of total dissolved chromium (Rai *et al.*, 1986).

ADSORPTION OF CHROMIUM ON NATURAL SOLIDS

Processes involving chromium (III)

As other cationic metals, Cr(III) is rapidly, strongly and specifically adsorbed by soil Fe and Mn oxides, clay minerals and sand (Schroeder and Lee, 1975; Korte *et al.*, 1976; Bartlett and Kimble, 1976; Griffin *et al.*, 1977; Rai *et al.*, 1984; Dreiss, 1986). This process is rapid, about 90% of the added chromium is sorbed by clay minerals and iron oxides in 24 h. The adsorption of Cr(III) increases with pH (Fig. 4) (Griffin *et al.*, 1977; Rai *et al.*, 1984) and the organic matter content of soils (Payà Pérez *et al.*, 1988). It decreases when other inorganic cations or dissolved organic ligands are present in the solution (Fig. 4).

Processes involving chromium (VI)

Chromate ions can be adsorbed by Mn, Al and Fe oxides, clay minerals and natural soils and colloids (MacNaughton, 1975; Griffin *et al.*, 1977; Davis and Leckie, 1980; James and Bartlett, 1983; Stollenwerk and Grove, 1985; Music *et al.*, 1986; Rai *et al.*, 1986, 1988; Zachara *et al.*, 1987). Adsorption of hexavalent chromium is a surface complexation reaction between aqueous chromates and hydroxyl-specific surface sites. Davis and Leckie (1980) and Benjamin and Bloom (1981) found that each Cr(VI) surface complex covers 3–4 hydroxyl surface sites. This co-ordination reaction is pH dependent (Fig. 5). At dilute concentrations, adsorption of Cr(VI) increases as pH decreases whatever the adsorbent (Griffin *et al.*, 1977; Bartlett and James, 1979; Davis and Leckie, 1980; Rai *et al.*, 1984, 1986, 1988; Zachara *et al.*, 1987). This result suggests that Cr(VI) adsorption is favoured on adsorbents which are positively charged at low to neutral pH (i.e. which have high pH_{ZPC} values).

As aqueous CrO_4^{2-} concentrations increases, the fractional adsorption decreases (Fig. 5) (Benjamin and Bloom, 1981; Rai *et al.*, 1986) but the adsorption density increases (Rai *et al.*, 1986). A larger ionic strength decreases the adsorption of chromate (Davis and Leckie, 1980; Mayer and Schick, 1981; Stollenwerk and Grove, 1985; Rai *et al.*, 1984, 1986). This is due to a lowering in CrO_4^{2-} activity, a reduction in coulombic attraction for chromate species on solid surfaces and/or to the presence of competing anions (Fig. 6).

Competitive adsorption of hexavalent chromium with cations and anions was also investigated (Benjamin and Bloom, 1987; Stollenwerk and Grove, 1985; Rai *et al.*, 1984, 1986, 1988; Music *et al.*, 1986; Zachara *et al.*, 1987). Millimolar concentrations of major cations such as K^+, Ca^{2+}, Mg^{2+} (Rai *et al.*, 1986) have only a slight influence on

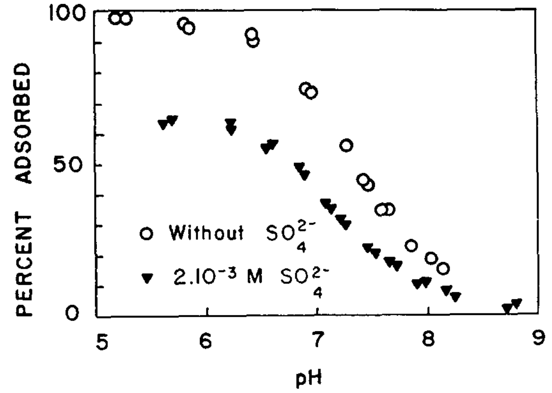

Fig. 6. Influence of dissolved anion (SO_4^{2-}) on fractional adsorption of CrO_4^{2-} by $Fe_2O_3 \cdot H_2O$ (am) (from Rai *et al.*, 1986). $SO_4^{2-} = 2.5 \times 10^{-3}$ M; $CrO_4^{2-} = 5 \times 10^{-6}$ M; $Fe_T = 0.87\ 10^{-3}$ M.

Cr(VI) adsorption. The pH adsorption edge is slightly shifted to higher pH. Cation sorption enhances the positive surface charge and favours electrostatic adsorption of anions. On the other hand, chromates either increase or have no effect on heavy metal adsorption (Cd^{2+}, Co^{2+}, Zn^{2+}) but competition for surface sites is relatively minor (Benjamin and Bloom, 1981). In systems where metal binding is enhanced, a secondary surface phase must have formed: an iron-chromate solid (Benjamin and Bloom, 1981).

Competing anions have a drastic effect on Cr(VI) adsorption. The competing effect will vary, depending on dissolved concentrations of the competing anion and CrO_4^{2-}, on their relative affinities for the solid surface and on surface site concentration (Rai *et al.*, 1986). A shift of the pH adsorption edge towards lower pH values (Fig. 6) was generally observed (Stollenwerk and Grove, 1985; Music *et al.*, 1986; Rai *et al.*, 1986, 1988; Zachara *et al.*, 1987) for competing anions such as Cl^-, NO_3^-, SO_4^{2-}, HCO_3^-, $H_2SiO_4^{2-}$, phosphate mixtures ($HPO_4^{2-}/H_2PO_4^-$, 1:1) and MoO_4^{2-}.

Adsorption of chromates in the presence of a mixture of ions is lower than in two-solution systems, particularly when $H_2SiO_4^{2-}$ is present. The effect appears to be qualitatively additive (Rai *et al.*, 1986; Zachara *et al.*, 1987).

The kinetics of Cr(VI) adsorption are not well documented. However, Amacher *et al.* (1988) recently showed that the adsorption of chromates on soils follows a two-step reaction rate. They assumed that faster reversible reactions reach equilibrium within 24 h but the overall Cr retention reaction does not reach complete equilibrium even after 2 weeks. These authors suggested irreversible or slow reversible reactions such as coprecipitation or internal diffusion as an explanation for this behaviour.

Adsorption of Cr(VI) does not seem totally reversible. Stollenwerk and Grove (1985) and Amacher *et al.* (1986) observed a slight irreversibility but the reason for this phenomenon is not fully elucidated. The former suggested a specific adsorption of hexavalent chromium (i.e. chemically bound) on alluvium, whereas the latter attributed this lack of reversibility to reduction of Cr(VI) to Cr(III), possibly by organic matter from the soil studied, which in turn leads to strong retention.

In natural environments, chromate sorption will be highly influenced by the electrostatic conditions imposed by the common major anions which bind to the solid surfaces. Adsorption of Cr(VI) can therefore be expected to be minimal in groundwater and soil (Rai *et al.*, 1986).

MIGRATION OF CHROMIUM IN AQUATIC ENVIRONMENTS

As seen in the preceding sections, the solubility of chromium is strongly dependent upon its oxidation state (Fig. 7). In addition to redox conditions, the effect of water chemistry (pH, competing ions, complexing agents) and of natural solids (adsorbents) can also be quite significant. As a result, hydrogeochemical cycles of chromium should be mainly controlled by the local environmental conditions, without forgetting, as we will see later, that the establishement of equilibrium between Cr(III) and Cr(VI) is not rapid.

General trends (see Fig. 8)

Trivalent chromium is generally expected not to significantly migrate in natural systems because Cr(III) minerals [$Cr(OH)_3(s)$, $FeCr_2O_4(s)$, $(Fe_{1-x}, Cr_x)(OH)_3(ss)$, etc.] readily precipitate in neutral to alkaline pH range and maintain low Cr(III) dissolved concentrations. In neutral to slightly acidic waters Cr(III) is removed from solution by adsorption. Under acidic conditions ($pH < 5$), the dissolved Cr(III) concentration can be higher than the drinking water limit (1 μmol/l) and it can easily migrate. Precipitation and adsorption can be inhibited by complexation with dissolved ligands such as natural organic matter (Gerritsee *et al.*, 1982) causing severe pollution. Cr(III) can be solubilized following surface oxidation in the presence of solid MnO_2 (Schroeder and Lee, 1975; Nakayama *et al.*, 1981c).

Two main mechanisms are thought to control the mobility of hexavalent chromium (Rai *et al.*, 1988): Cr(VI) reduction into Cr(III), which is afterwards rapidly precipitated or adsorbed, and adsorption. In Fe(II)- and dissolved organic matter-rich environments, reduction of Cr(VI) is more likely to occur and the resulting aqueous trivalent chromium concentration will be controlled by the solubility of a Cr(III) mineral. In such cases, Cr(VI) should not migrate significantly and the total chromium content of water should fall below the drinking water limit. In soils or sediments with high content of Fe and Mn oxides or clay minerals and under acidic and oxidizing conditions, Cr(VI) should be removed by sorption processes (Cary *et al.*, 1977; Stollenwerk and Grove,

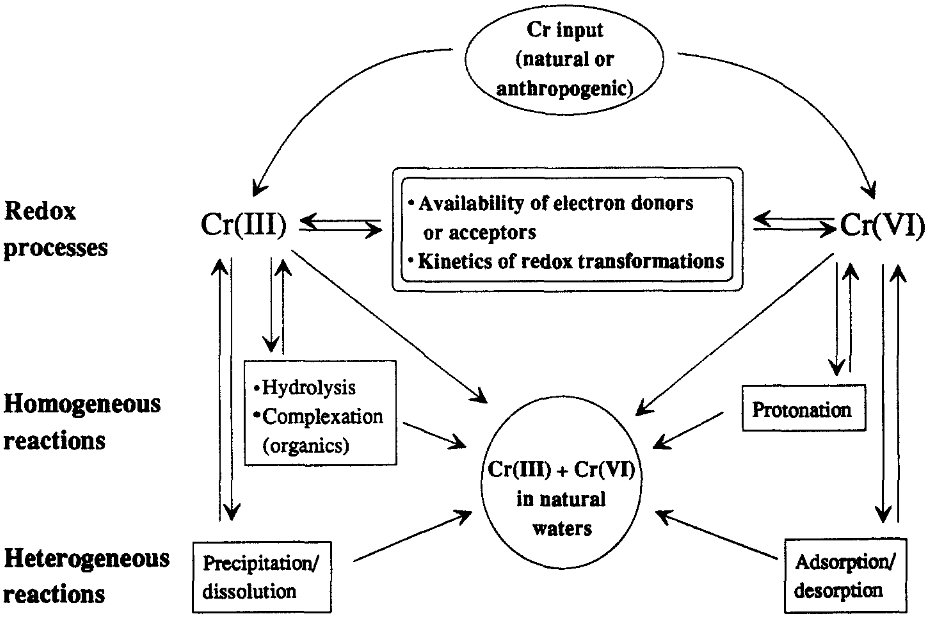

Fig. 7. Aqueous geochemistry of chromium.

1985; Rai *et al.*, 1986, 1988; Eary and Rai, 1987). But adsorption is significantly depressed by competing background anions (Rai *et al.*, 1988) so that Cr(VI) is expected to be highly mobile. In alkaline environments, sorption is not strong enough to keep Cr(VI) from moving through soil or sediments.

Chromium and manganese

Chromium and manganese form a pair of chemical elements with contrasting tendencies (Murray *et al.*, 1983). Under oxidizing conditions, Cr(VI) is soluble as CrO_4^{2-} while Mn(IV) is scavenged as $MnO_2(s)$.

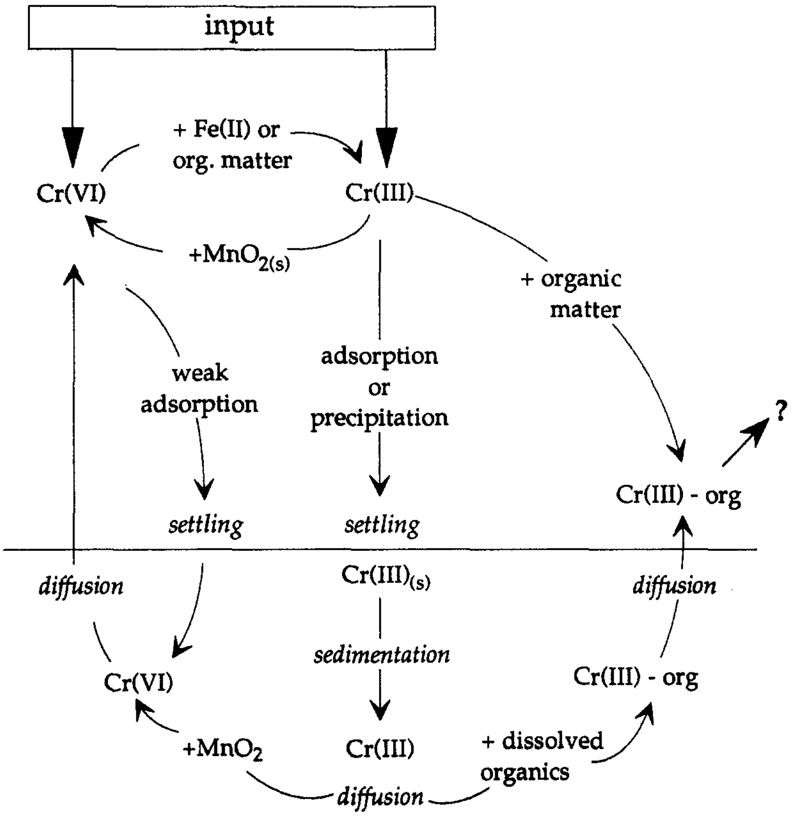

Fig. 8. Chromium cycling in the aquatic environment.

Under reducing conditions, Cr(III) is removed from solution as $Cr(OH)_3(s)$ while Mn(II) is soluble as Mn^{2+}. These chemical transformations were demonstrated using data from the low oxygen water of the Eastern Tropical Pacific (Murray *et al.*, 1983). The chromium profiles exhibited a pronounced minimum in Cr(VI) and a maximum in Cr(III) while dissolved manganese (mostly Mn(II)) showed a maximum in the same region.

These contrasting tendencies for the solubility of Cr and Mn were also observed in shallow groundwater of the Western San Joaquin Valley in California (Deverel and Millard, 1988). In the alluvial–fan geologic zone, dissolved Cr is high while dissolved Mn is low. In the basin–trough zone Cr is low and Mn is high.

Chromium in oceans

The general picture of total dissolved chromium in oceans is a slight depletion at the surface (Cr = 2.0 nmol/l compared to 2.6 nmol/l below 1000 m) and bottom excess possibly due to the release of Cr(III) from sediments (up to 15.8 nmol/l) (Jeandel and Minster, 1984; Grimaud and Michard, 1974). Surface depletion and correlations between Cr and nutrients (P, Si) indicate biogeochemical cycling of Cr, even though Cr has no reported marine biochemical function (Campbell and Yeats, 1981; Cranston, 1983; Jeandel and Minster, 1987).

The observed Cr(III)/Cr(VI) ratio in seawater is often in excess of the thermodynamic equilibrium value. This is explained by a slow oxidation reaction (Elderfield, 1970; Jeandel and Minster, 1984).

The sources of Cr to the oceans are diverse. No budget has ever been established. Removal of chromate under simulated estuarine conditions shows a peak in the 0.1–1.0‰ salinity range (Mayer and Schick, 1989). This behaviour was attributed to reductive adsorption by the estuarine sediments. No significant input of Cr in dissolved form is thus likely through estuaries. Mineral dusts deposited on the sea surface by the Atlantic north east winds are a significant source of Cr for the underlying deep-sea sediments (Chester, 1986). Comparing surface concentrations in the central Mediterranean and similarly nutrient-depleted Atlantic surface waters (Sargasso Sea) indicates that the Mediterranean is enriched by about 40% in chromium, most of this enrichment being due to sources within the Mediterranean basin itself (Sherrell and Boyle, 1988). The chromium content of metalliferous sediments is mainly due to scavenging from the water column. The input of Cr into the oceans by hydrothermalism is negligible (Jeandel and Minster, 1984).

In interstitial water of coastal marine sediments, enrichment of Cr near the sea-bottom sediments interface was interpreted as the decomposition of labile organics with subsequent regeneration of organically complexed Cr(III) or biologically incorporated Cr(VI) (Gaillard *et al.*, 1986). Right below the sea–sediment interface, the interstitial water is depleted in Mn which indicates the presence of Mn-oxides. This in turn most likely leads to the oxidation of Cr(III) into Cr(VI) followed by diffusion into the bottom sea water of chromate-rich waters (Gaillard *et al.*, 1986). The release of Cr from bottom sediments is also apparent further out at sea up to the outer edge of the continental margin (Cranston, 1983).

It can thus be proposed that Cr sources to the oceans are mostly in particulate form (suspended solids from river and aerosols). Chromium cycling in the water column occurs in response to nutrient biogeochemistry. When Cr scavenged by particles is deposited on the ocean floor, diagenetic processes can lead to remobilization of Cr either as chromate or as organic Cr(III) complexes (Fig. 8).

Chromium in lakes

A new Cr(III)/Cr(VI) speciation method, based on ion exchange, was developed by Johnson and Sigg (1989) and tested on the strongly eutrophic lake, Greifensee (Switzerland). When the lake is well mixed (dissolved oxygen = 6 mg/l), there is no Mn dissolved in water and all the chromium (*c.* 2.5–3.5 nmol/l) is present as chromate. During the stagnation period, Mn and Cr behave as above (no Mn, Cr = 2.5 nmol/l) for the surface waters but for the hypolimnion, in the absence of dissolved oxygen, Mn and Fe are solubilized (up to 10 and 1 μmol/l, respectively) and Cr is slightly depleted (about 1.5 nmol/l). It is only at the bottom of the lake that Cr(III) accounts for a significant fraction of total Cr (about 50% at a depth of 28 m). Johnson and Sigg (1989) concluded that Cr(VI) will not be reduced before sulfide is available. Even when reduction occurs, under these extreme conditions, Cr(III) should not be found to any large extent because it is removed from solution by precipitation and/or by interaction with mineral or organic materials. Such a decrease in total Cr is observed in the hypolimnion of the Greifensee. The question is raised about the fate of Cr(III) in the water column. Is it oxidized to Cr(VI) and recycled (when the lake is well mixed) to the lake water or is it definitively trapped in the sediments, scavenged by solid particles falling to the lake bottom sediments?

Chromium in groundwater

Migration of hexavalent chromium through aquifers has frequently been observed (Perlmutter *et al.*, 1963; Ku *et al.*, 1978; Stollenwerk and Grove, 1985; Rai *et al.*, 1984, 1986, 1988). A 15 m per year progression was observed for a contaminated groundwater plume (Perlmutter *et al.*, 1963; Ku *et al.*, 1978). Breakthrough curves obtained by column experiments (Stollenwerk and Grove, 1985) show that Cr(VI) is weakly delayed in alluvium at pH 6.8 and that the higher the flow rate, the faster the Cr(VI) migration.

The impact of water chemistry was demonstrated in field experiments involving injections in various zones of a gravel aquifer of 100 μmol/l of Cr(VI) (Kent *et al.*, 1989). Some chromium disappeared from the aqueous phase in the anoxic part of the aquifer due to the reduction to less soluble Cr(III) species. Chromate moved with the water except in the sites with low pH and low concentrations of anions where it was retarded due to competition with these species for adsorption sites.

CONCLUSIONS

The aqueous geochemistry of Cr is discussed in Fig. 7. Present knowledge of chromium cycling is summarized in Fig. 8. It is far from clear yet what are the rates of oxidation and reduction under various environmental conditions. Moreover, new speciation techniques (e.g. Jeandel and Minster, 1984; Johnson and Sigg, 1989) should be cross-validated and some of the marine data may then need to be reevaluated. Another part of the chromium cycling (Fig. 8) which is very weak is the complexation/dissociation of Cr and natural organics. These processes are often postulated to explain data (e.g. Gaillard *et al.*, 1986) but there is a lack of direct evidence of its significance (such an example is given in Kent *et al.*, 1989).

Further studies of Cr(III) and Cr(VI) in natural systems are indeed essential for the understanding of chromium hydrogeochemical cycles. These studies should always relate the redox conditions of the environment studied by a variety of indicators (Eh, dissolved oxygen, dissolved Fe and Mn, nitrate/nitrite, sulphate/sulphur).

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APPENDIX

Reaction	Log *K*	Reference
$4Cr(OH)_3(s) + 6H^+ = Cr_4(OH)_6^{6+} + 6H_2O$	20.8	a
$4Cr(OH)_3(s) + 5H^+ = Cr_3(OH)_4^{5+} + 5H_2O$	17.3	a
$2Cr(OH)_3(s) + 4H^+ = Cr_2(OH)_2^{4+} + 4H_2O$	13.7	a
$Cr(OH)_3(s) + 3H^+ = Cr^{3+} + 3H_2O$	9.35	a
$Cr(OH)_3(s) + 2H^+ = CrOH^{2+} + 2H_2O$	5.78	a
$Cr(OH)_3(s) + H^+ = Cr(OH)_2^+ + H_2O$	−0.49	a
$Cr(OH)_3(s) = Cr(OH)_3^0$	−6.84	a
$Cr(OH)_3(s) + H_2O = Cr(OH)_4^- + H^+$	−18.3	a
$H^+ + CrO_4^{2-} = HCrO_4^-$	6.51	b
$2H^+ + CrO_4^{2-} = H_2CrO_4^0$	5.65	c
$2H^+ + 2CrO_4^{2-} = Cr_2O_7^{2-} + H_2O$	14.56	d
$2HCrO_4^- = Cr_2O_7^{2-} + H_2O$	1.52	d
$Na^+ + CrO_4^{2-} = NaCrO_4^-$	0.70	e
$BaCrO_4(s) + H^+ = Ba^{2+} + HCrO_4^-$	−3.43	f
$BaCrO_4(s) = Ba^{2+} + CrO_4^{2-}$	−9.76	f

(a) Rai *et al.* (1987); (b) O'Hare and Boerio (1975); (c) Schmidt (1984); (d) Linge and Jones (1968); (e) Turner *et al.* (1981); (f) Rai *et al.* (1988).

Reaction	Log *K*	Reference
$1/3Cr^{3+} + 4/3H_2O = 1/3HCrO_4^- + 7/3H^+ + e^-$	−22.8	a
$1/3CrOH^{2+} + H_2O = 1/3HCrO_4^- + 2H^+ + e^-$	−21.6	b
$1/3Cr(OH)_2^+ + 2/3H_2O = 1/3HCrO_4^- + 5/3H^+ + e^-$	−19.5	b
$1/3Cr(OH)_3^0 + 1/3H_2O = 1/3HCrO_4^- + 4/3H^+ + e^-$	−17.4	b
$1/3Cr(OH)_3^0 + 1/3H_2O = 1/3CrO_4^{2-} + 5/3H^+ + e^-$	−19.6	b
$1/3Cr(OH)_4^- = 1/3CrO_4^{2-} + 4/3H^+ + e^-$	−15.8	b

(a) Amacher and Baker (1982), derived from Garrels and Christ (1965); (b) recalculated from Garrels and Christ (1965) and Rai *et al.* (1987).

Reaction	Sorbent	Log *K*	Reference
$SOH + CrO_4^{2-} + H^+ = (SOH_2^+ - CrO_4^{2-})^-$	$Fe_2O_3 \cdot H_2O$ (am)	10.1	a
$SOH_2^+ + CrO_4^{2-} = (SOH_2^+ - CrO_4^{2-})^-$	$Fe_2O_3 \cdot H_2O$ (am)	4.7	a
	$Fe_2O_3 \cdot H_2O$ (am)	5.5	b
	Fe_2O_3 (22 sites/nm^2)	6.11	c
	Fe_2O_3 (10 sites/nm^2)	6.74	c
	α-FeOOH	5.6	c
	α-Al_2O_3	5.84	d
	Kaolinite (6 sites/nm^2)	3.68	c
$SOH + CrO_4^{2-} + 2H^+ = (SOH_2^+ - HCrO_4^-)^0$	$Fe_2O_3 \cdot H_2O$ (am)	19.3	a
$SOH_2^+ + HCrO_4^- = (SOH_2^+ - HCrO_4^-)^0$	$Fe_2O_3 \cdot H_2O$ (am)	7.5	a
	$Fe_2O_3 \cdot H_2O$ (am)	6.5	b
	Fe_2O_3 (22 sites/nm^2)	7.79	c
	Fe_2O_3 (10 sites/nm^2)	8.15	c
	α-FeOOH	8.7	c
	α-Al_2O_3	5.7	d
	Kaolinite (6 sites/nm^2)	4.42	c

(a) Zachara *et al.* (1987); (b) Davis and Leckie (1980); (c) Rai *et al.* (1988); (d) Rai *et al.* (1988), calculated from Honeyman (1984).